



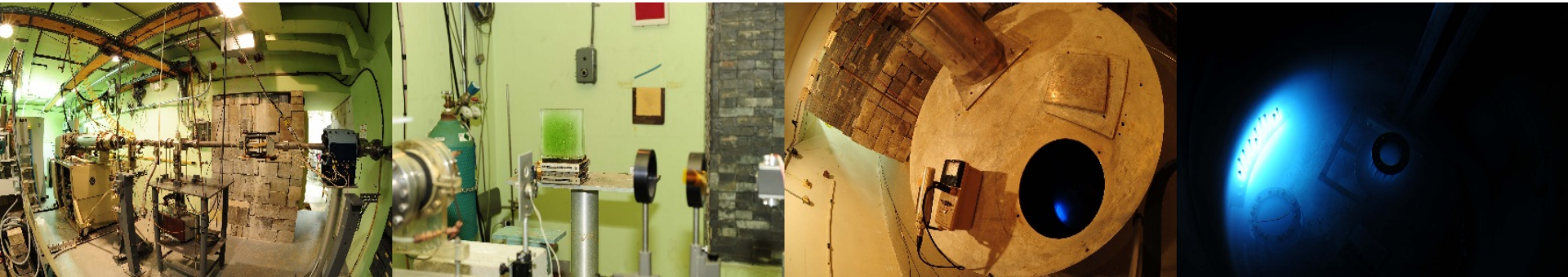
ELECTRON BEAM SYNTHESIS OF NANOCOMPOSITES AND NANOGEELS

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**The Council on Ionizing Radiation Measurements and
Standards-Conference-2017**

National Institute of Standards and Technology

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Global Applications of Ionizing Radiation

- Polymer crosslinking
- Graft polymerization
- Enzyme immobilization
- Controlled drug release
- Hydrogels and gel-filled membranes
- Used to create 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**

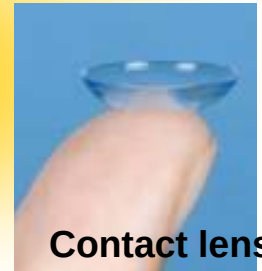


Wound dressing



**Crosslinking of
electrical cable surface**

Sterilization process



Contact lens



Magnetic Nanocomposites

- Magnetic nanocomposites, in which magnetic nanoparticles are encapsulated in polymeric matrices have important applications in medicine, imaging, electronics and mechanical devices.
- However, the development of processes leading to magnetic nanocomposites with desirable, predictable and reproducible properties has turned out to be a difficult challenge.



Challenges

- Attempts to produce magnetic nanocomposites encapsulated in polymeric matrices have often yielded products with large variations in structure and in magnetic properties.
- The difficulties in controlling the product are greatly magnified when the particle size is in the nanometer range.
- Agglomeration;



Challenges-Continued

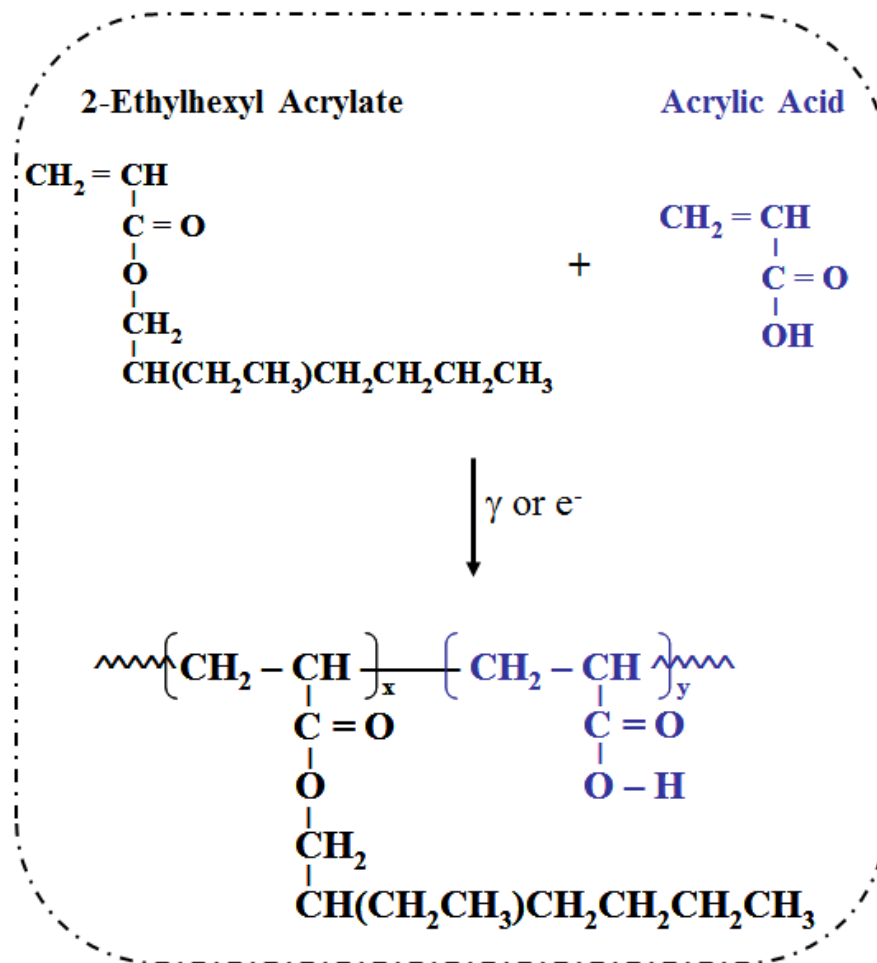
- Superparamagnetic ionomers
 - Ionomers have many useful properties but little work has been done on iron-based ionomers
- Superparamagnetic nanocomposites
 - A ferromagnetic species (e.g. magnetite Fe_3O_4) which shows paramagnetic behavior when the grain size is smaller than the size of a domain, which is about 100nm.



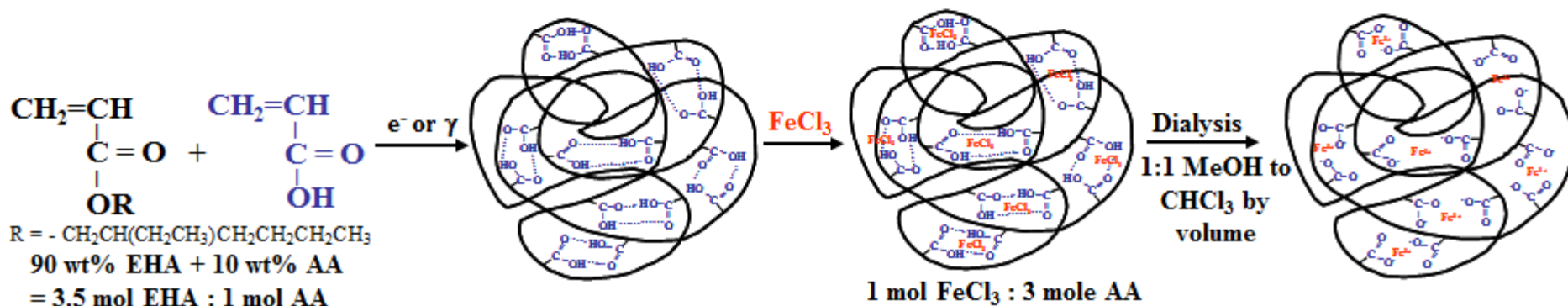
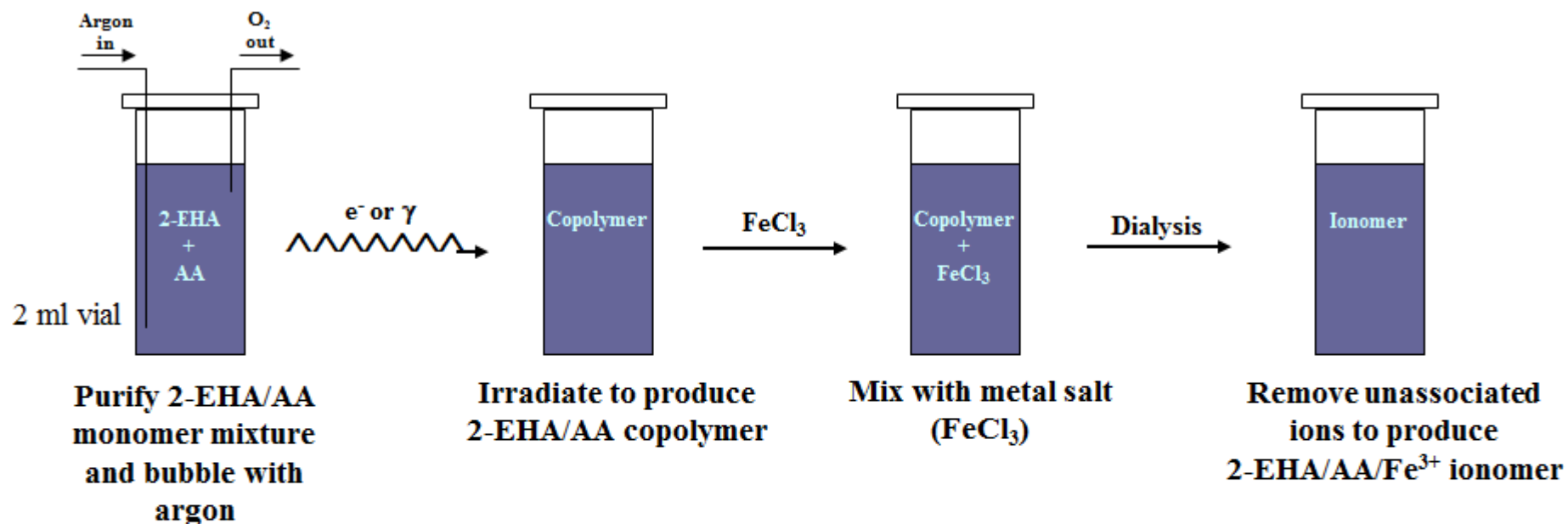
Our Approach

- Our approach to the synthesis of magnetic nanocomposites is to aim for incorporation of magnetically active ions or oxide nanoparticles into acrylate copolymers.
- The magnetic properties of such structures are expected to be predictable and controllable since they are controlled by the **distance between adjacent magnetically active groups along the backbone of the polymeric molecules.**
- Various compounds of iron or other transition metals are considered for inclusion in a polymeric matrix.

Radiation-Induced Copolymerization of 2-EHA and AA

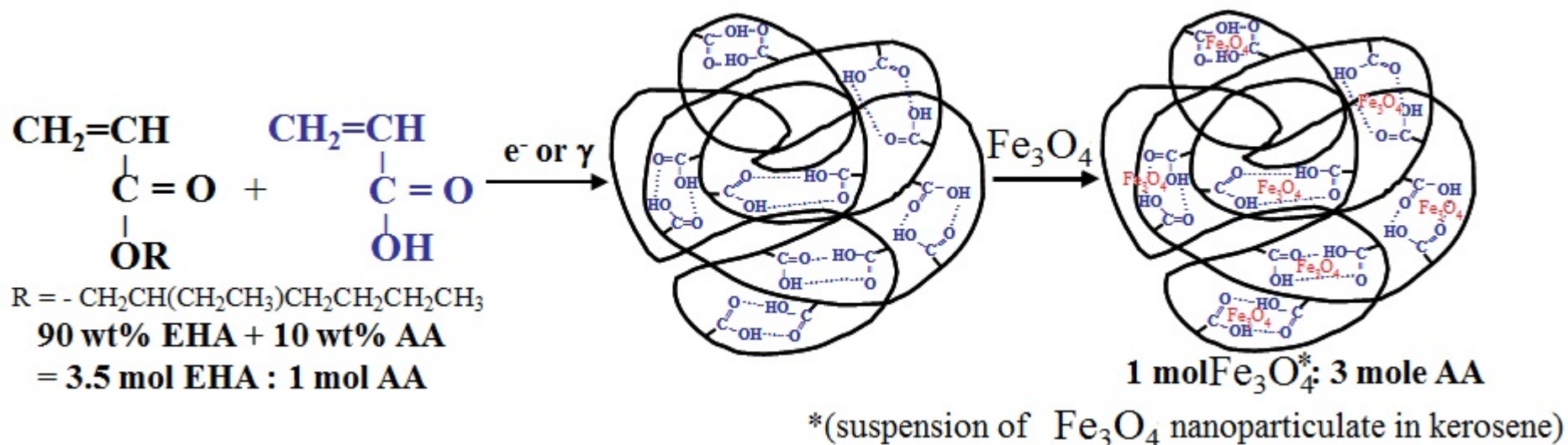


Experimental Procedure for Ionomer Synthesis-FeCl₃



Magnetite Nanocomposite Synthesis (Fe_3O_4)

- Another type of samples are made by reacting the copolymer (2-EHA/AA) with a suspension of nanoparticulate Fe_3O_4 in kerosene.

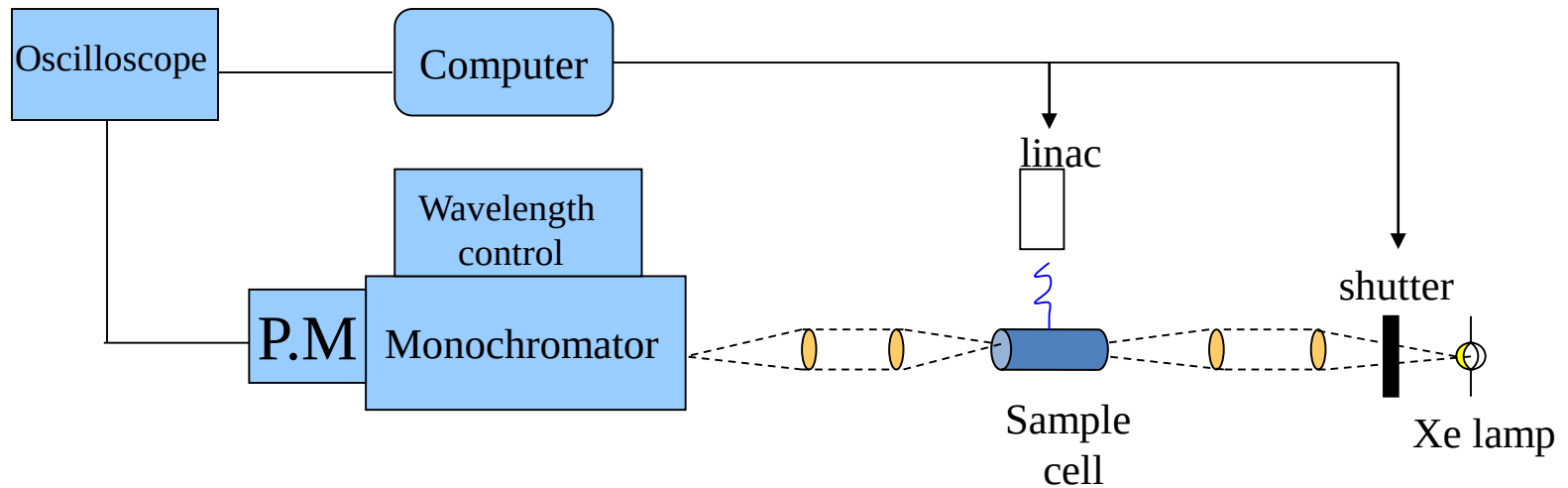




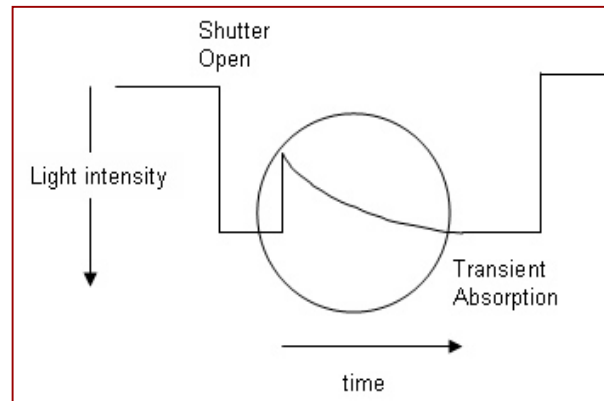
Pulse Radiolysis

- **Objective:**
 - Study the effect of acrylic acid on the radiation-induced polymerization of 2-ethylhexyl acrylate
- **Method:** Pulse electron beam radiolysis – optical detection
 - direct measurement of transient species produced in the early stages of the polymerization reaction
- **Significance:**
 - Study the role of chemical intermediates on the mechanism of acrylate polymerization reactions (radical ions, initiating radicals, oligomer radicals)

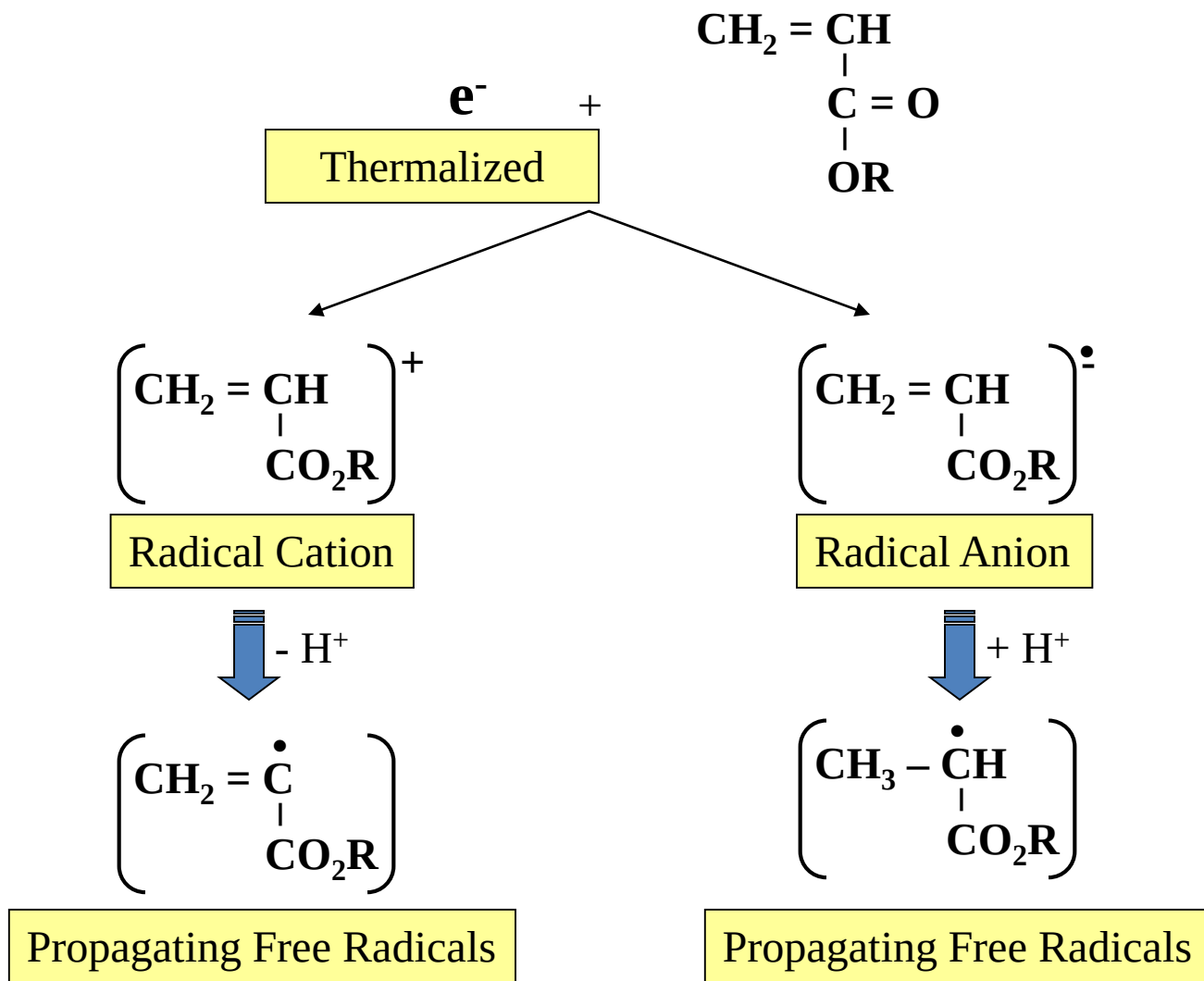
Pulse Radiolysis



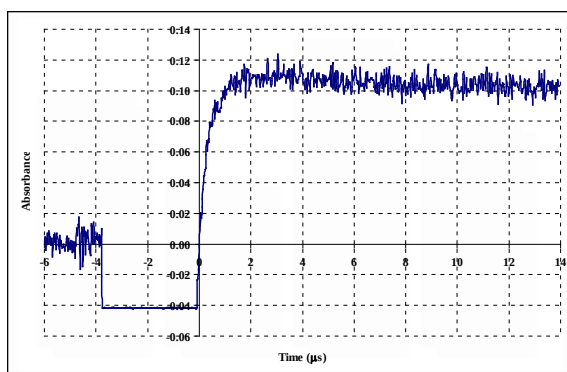
Transients generated is detected by optical absorption changes.



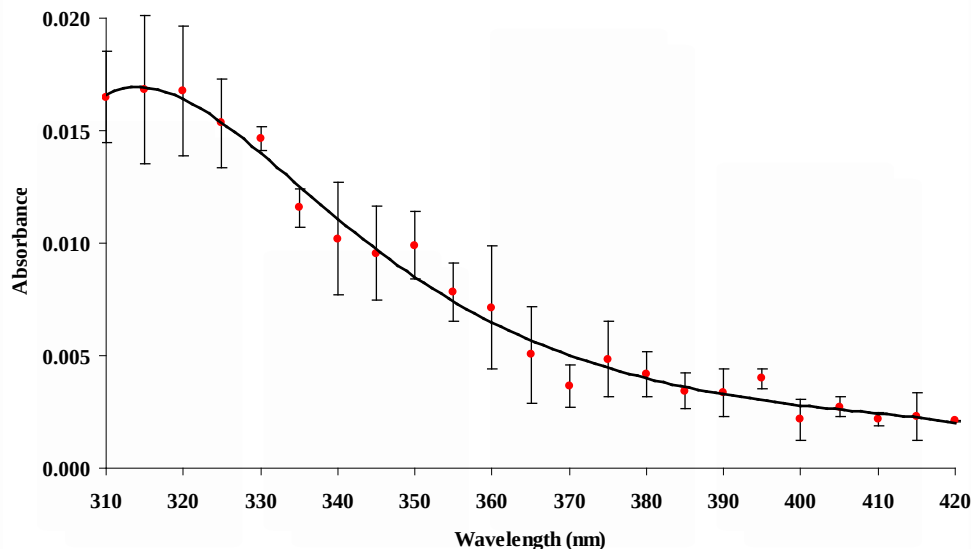
2-Ethylhexyl Acrylate Transient Species



Build-up Corresponds to: Initiation (formation of 2-EHA•)



Objective: determine the absorption maximum for transients in pure 2-EHA based on absorbance 2 ms (build-up) after the pulse



University of Maryland Linac

$[2\text{-EHA}]_0 = 4.80 \text{ mol dm}^{-3}$

Linac energy: 7 MeV

Dose: 85 Gy/pulse

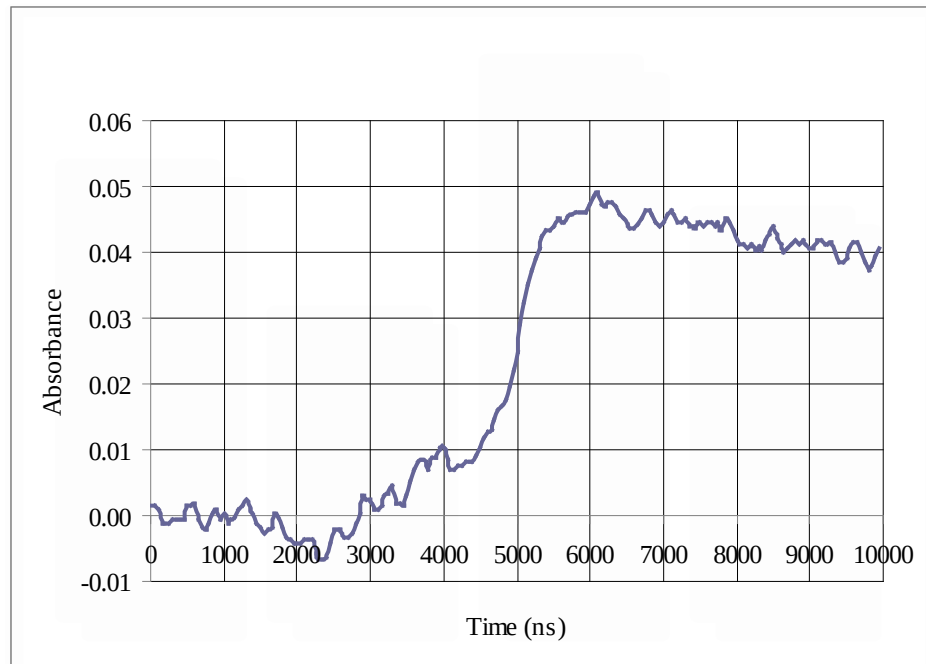
Pulse length: 3 μs

Argon saturated

Measure absorbance build-up 2 ms after the pulse

Build-up Corresponds to: Initiation (formation of 2-EHA•)

University of Notre Dame Linac



University of Notre Dame Linac

$[2\text{-EHA}]_0 = 4.80 \text{ mol dm}^{-3}$

Linac energy: 8 MeV

Dose: 5 - 10 Gy/pulse

Pulse length: 20 – 40 ns

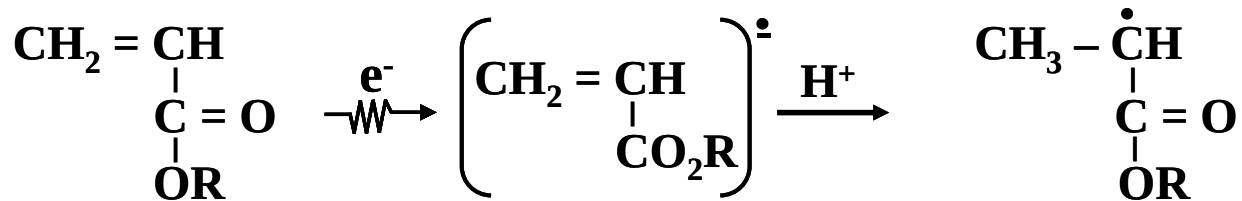
Argon saturated

Build-up of Transients in Pure 2-EHA

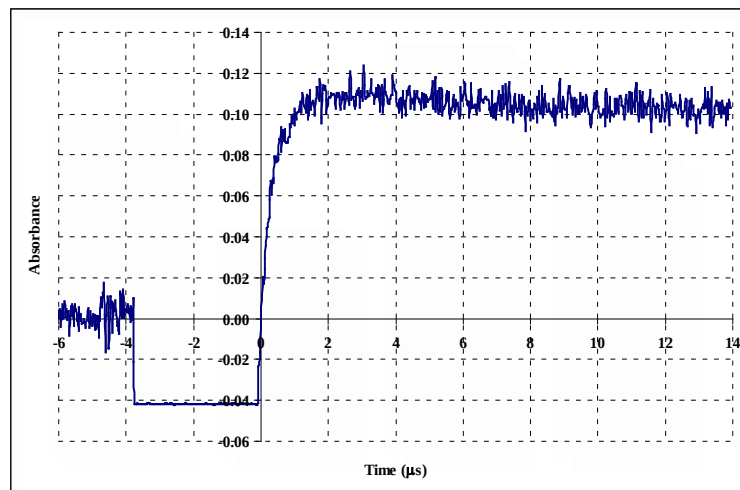
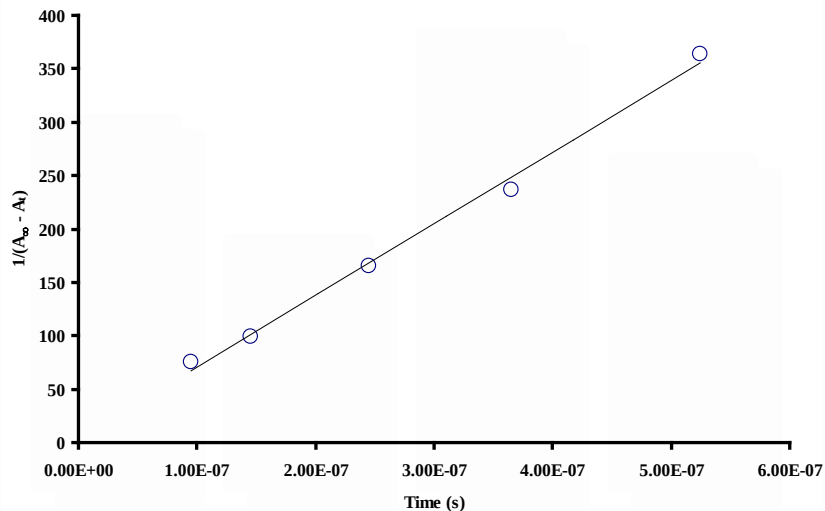
Proposed Mechanism for the Build-up of Transients in Pure 2-EHA:

- Initiation (formation of 2-EHA neutral carbon-centered free radical)

⇒ 2nd order reaction (since $[EHA^{\bullet}] \approx [H^+]$)



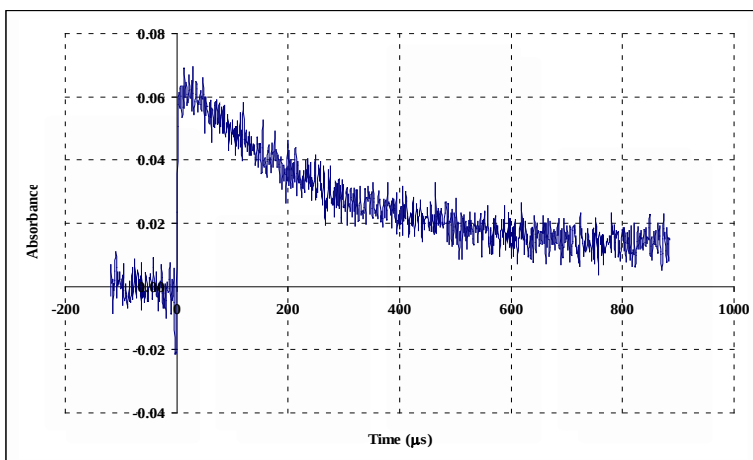
R = - CH₂CH(CH₂CH₃)CH₂CH₂CH₂CH₃



Observed rate coefficient for build-up of transients in pure 2-EHA:

$$k_{\text{obs}} = ((7 \pm 3) \times 10^8) \epsilon_{\text{EHA}}.$$

Transient Absorption Spectrum of Pure 2-EHA (based on decay)



Objective: determine the absorption maximum for transients in pure 2-EHA based on absorbance 800 ms (decay) after the pulse;

Decay corresponds to:

- propagation reaction
- termination reaction

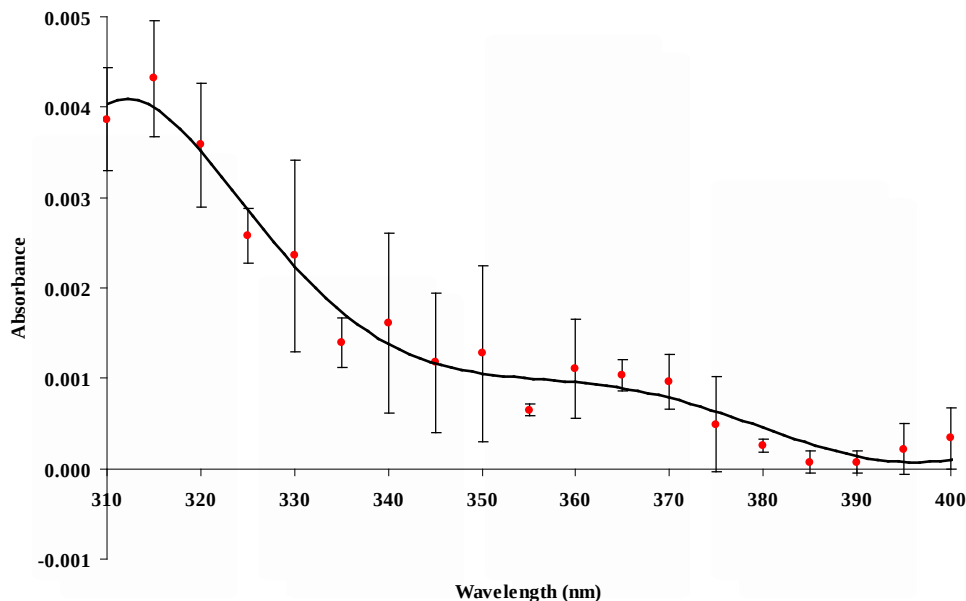
Absorbance maxima for pure 2-EHA*:

(i) **320 – 330 nm**

monomer radicals

(ii) **360 – 370 nm:**

oligomer & polymer radicals



University of Maryland Linac

$[2\text{-EHA}]_0 = 4.80 \text{ mol dm}^{-3}$

Linac energy: 7 MeV

Dose: 80 Gy/pulse

Pulse length: 3 μs

Argon saturated

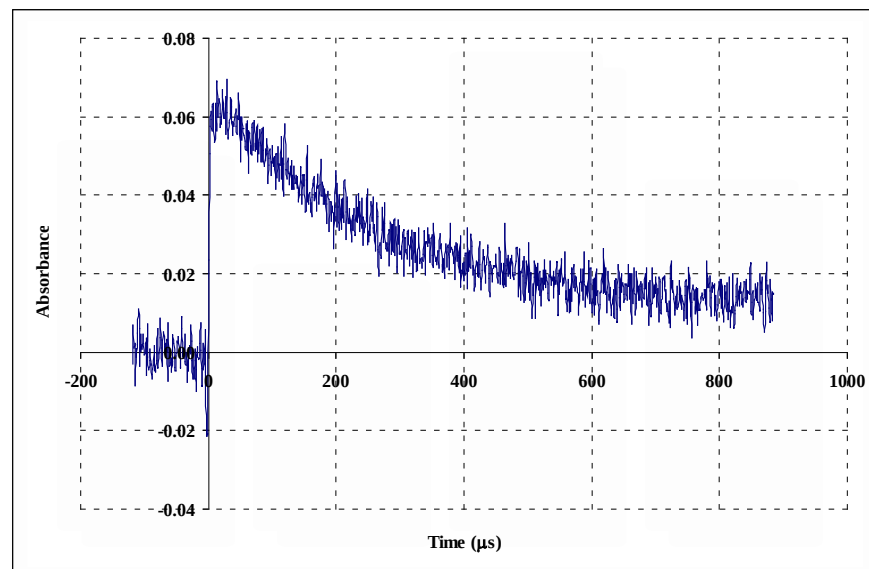
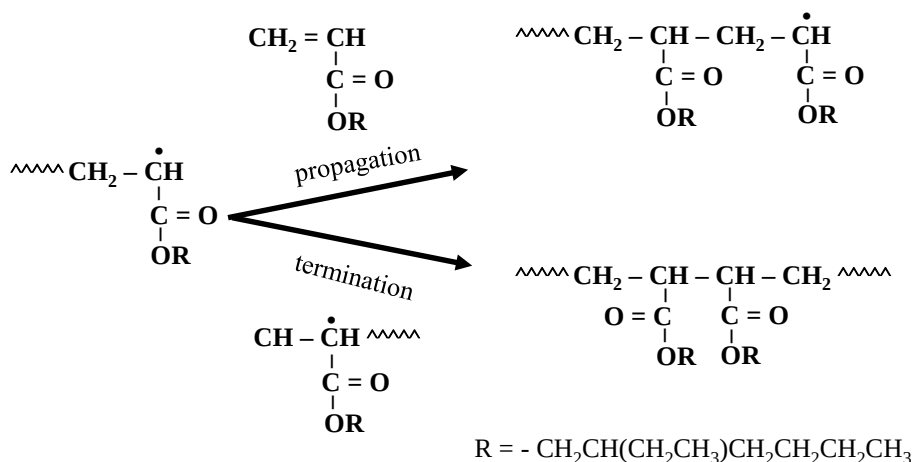
Time scale: 100 $\mu\text{s/div}$

Measure absorbance build-up 800 ms after the pulse

Decay of Transients in Pure 2-EHA

Proposed Mechanism: Pseudo-1st order decay of transients:

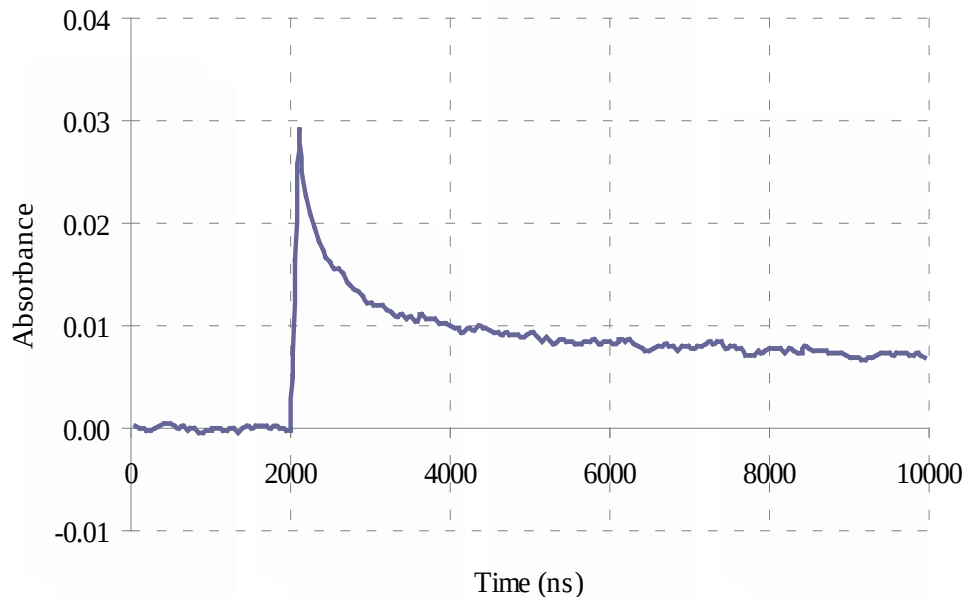
- Propagation $\Rightarrow$ pseudo-1st order reaction (since $[EHA]_0 \gg [EHA^\bullet]$)



Observed rate coefficient for decay of transients in pure 2-EHA:

$$k_p = (5 \pm 1) \times 10^2 \text{ s}^{-1}$$

Decay of Transients in Pure 2-EHA



University of Notre Dame Linac

$[2\text{-EHA}]_0 = 4.80 \text{ mol dm}^{-3}$

Linac energy: 8 MeV

Dose: 5 - 10 Gy/pulse

Pulse length: 20 – 40 ns

Argon saturated

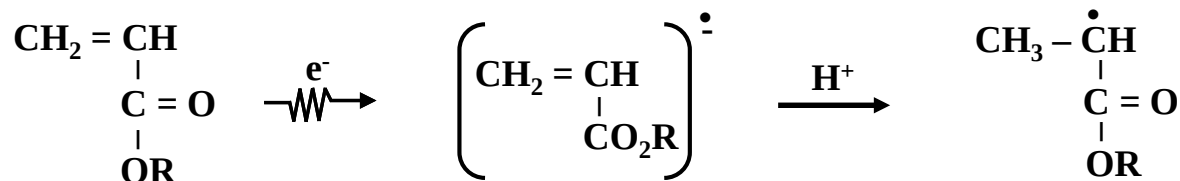
Observed rate coefficient for decay of transients in neat 2-EHA:

$$k_p = (5 \pm 1) \times 10^2 \text{ s}^{-1}$$

Summary: Homopolymerization of Pure 2-EHA

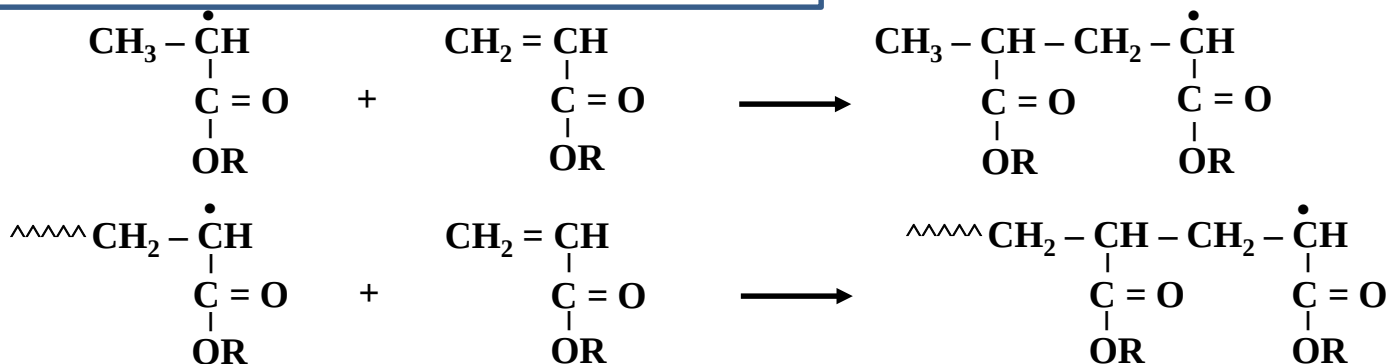
1. Initiation:

- 2-EHA scavenges electron to form radical anion
- 2-EHA radical anion transforms into a neutral free radical

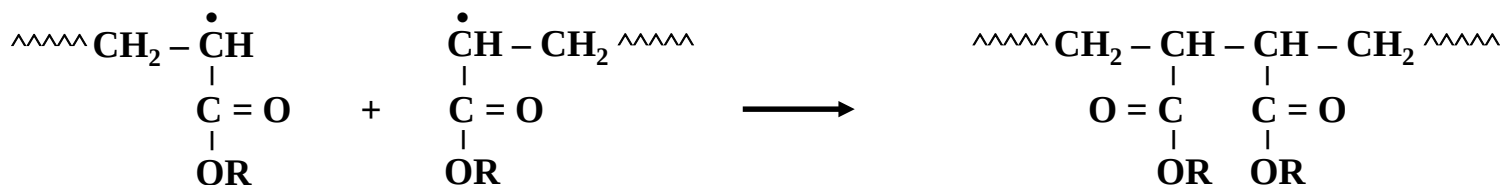


2. Propagation:

- Homopropagation (addition of 2-EHA to 2-EHA radical)



3. Termination: radical recombination

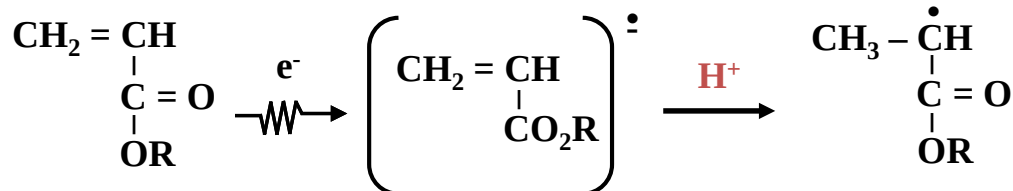


Build-up of Transients in 2-EHA/AA

Proposed Mechanism for the Build-up of Transients in 2-EHA/AA:

- Initiation (formation of 2-EHA neutral carbon-centered free radical)

⇒ pseudo-1st order reaction (since $[EHA^\bullet] \ll [H^+]$)



University of Maryland Linac

$[2\text{-EHA}]_0 = 4.32 \text{ mol dm}^{-3}$

$[\text{AA}]_0 = 1.46 \text{ mol dm}^{-3}$

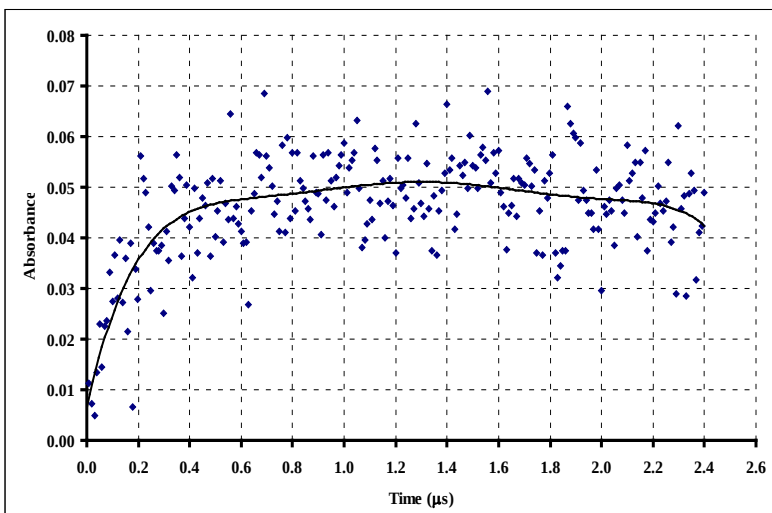
$[\text{H}^+]_0 = 10^{-3} \text{ mol dm}^{-3}$

Linac energy: 7 MeV

Dose: 80 Gy/pulse

Pulse length: 3 μs

Argon saturated



$$A = \log\left(\frac{V_0}{V}\right) = \varepsilon_{EHA^\bullet} [EHA^\bullet] l$$

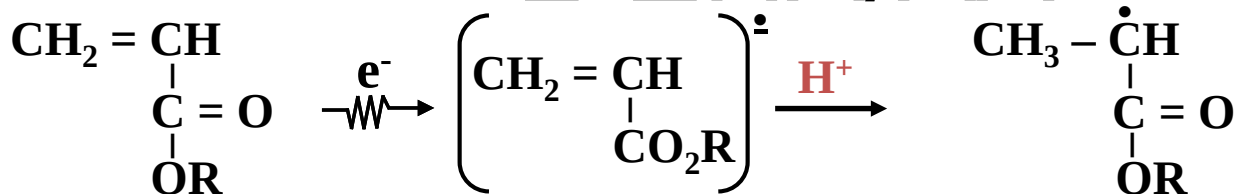
$$\text{1st order rate law: } \ln(A_t) - \ln(A_0) = k[H^+]_0 t$$

Observed rate coefficient for build-up of transients in neat 2-EHA:

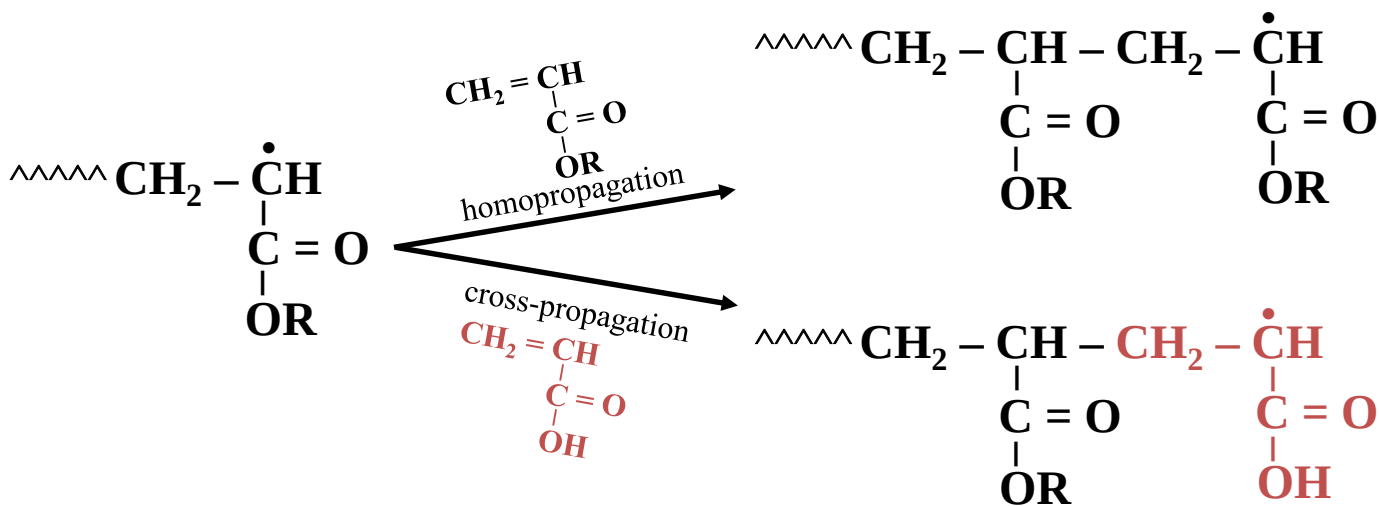
$$k_{\text{obs}} = (1.5 \pm 0.3) \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

Summary: Copolymerization of 2-EHA/AA

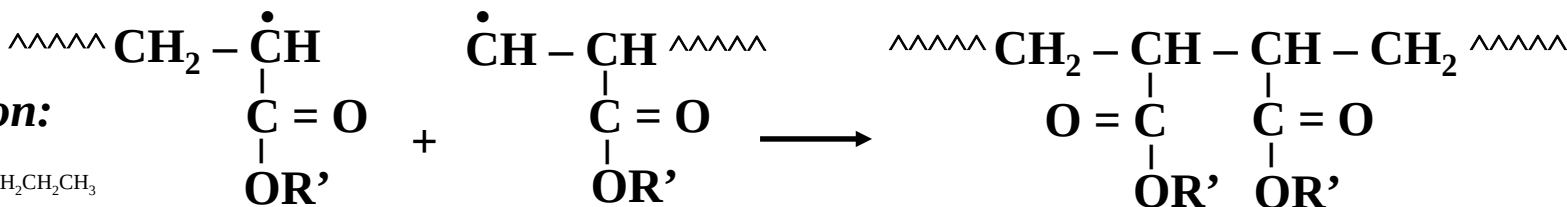
1. Initiation:



2. Propagation:



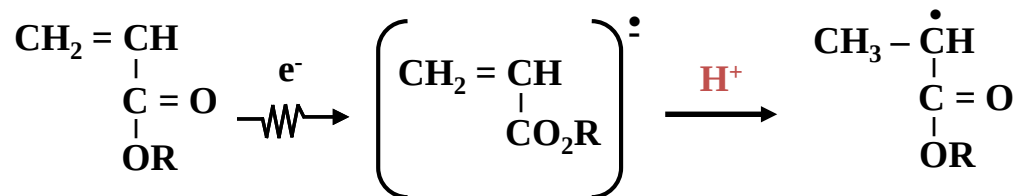
3. Termination:



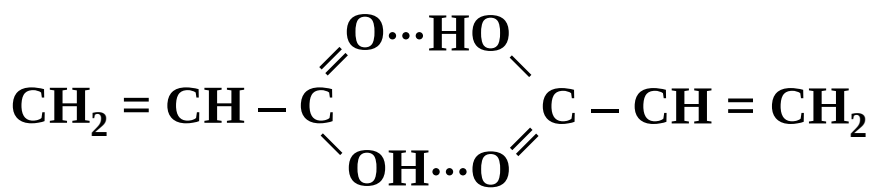
Role of Acrylic Acid

Functions of Acrylic Acid:

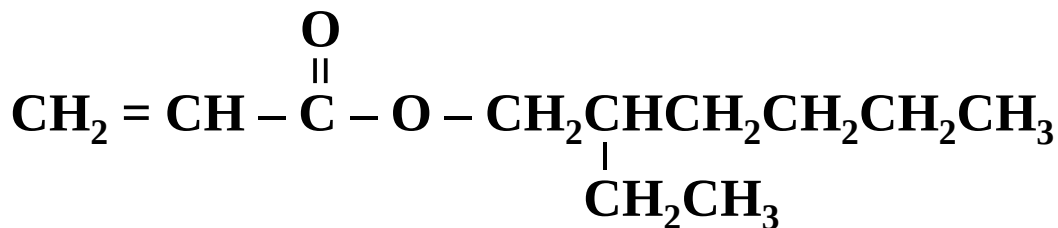
1. Co-monomer
2. Crosslinking sensitizer
3. Metal salt incorporation
4. Protonation reaction



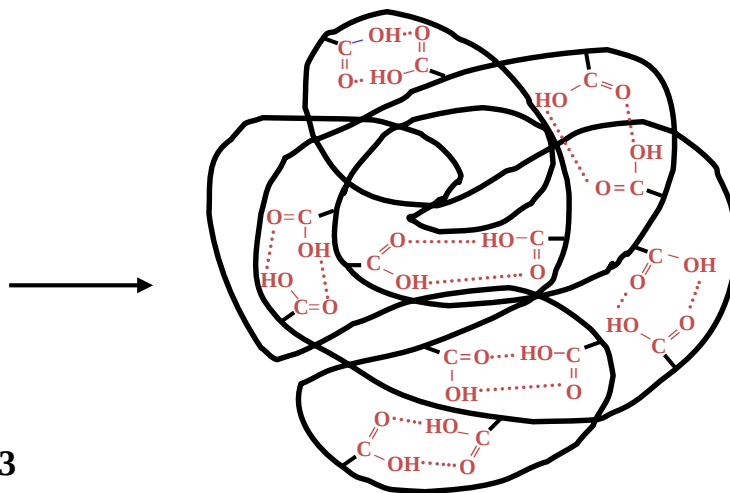
Acrylic acid hydrogen-bonded bridged dimer:



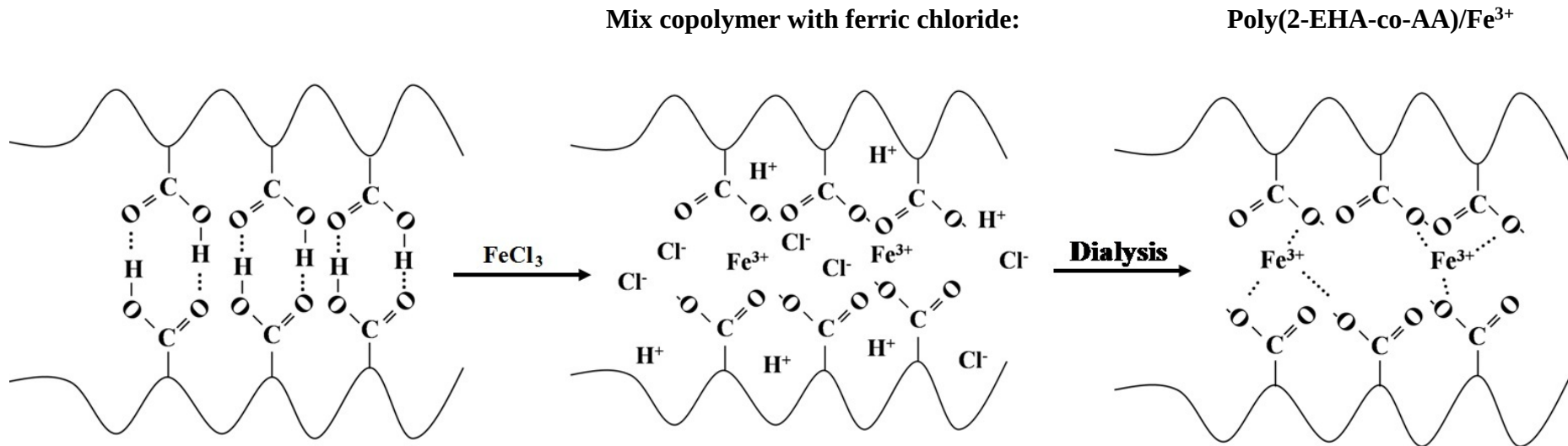
+



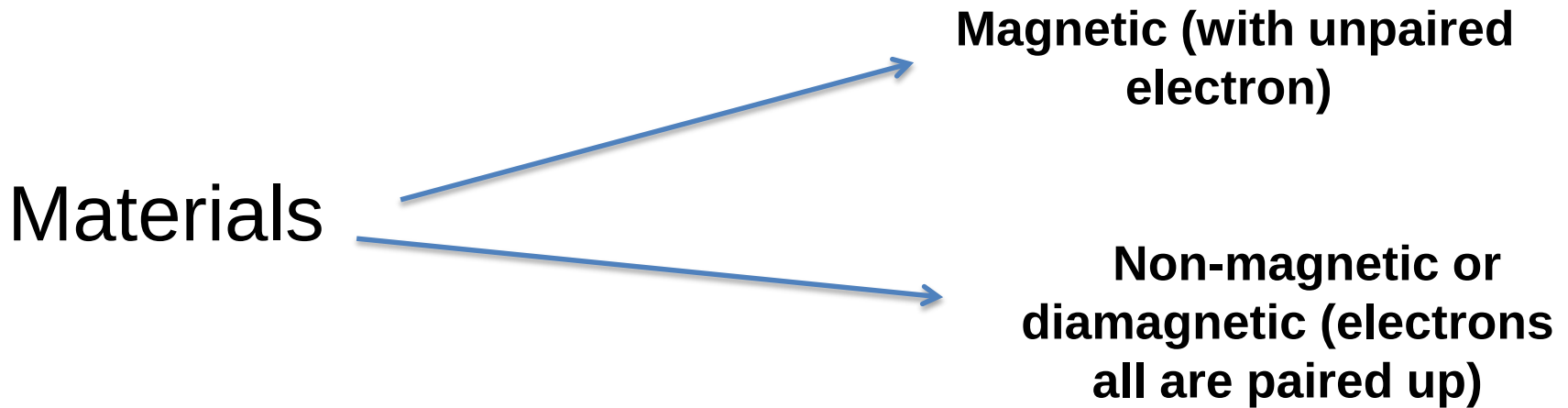
Acrylic acid hydrogen-bonded bridges in copolymer:



Poly(2-EHA-co-AA) Ionomer Synthesis



Magnetic Properties



A:  -----> **Paramagnetic**

B:  -----> **Ferromagnetic**



Magnetic Properties

- Paramagnetism
 - Individual spins can be oriented in the direction of an external magnetic field
 - Magnetization proportional to field and disappears when field is removed
 - Curie's Law of temperature dependence

Where:

Magnetic susceptibility in $\text{emu cm}^{-3} \text{ Oersted}^{-1}$

C: Curie constant

T: Temperature in Kelvin

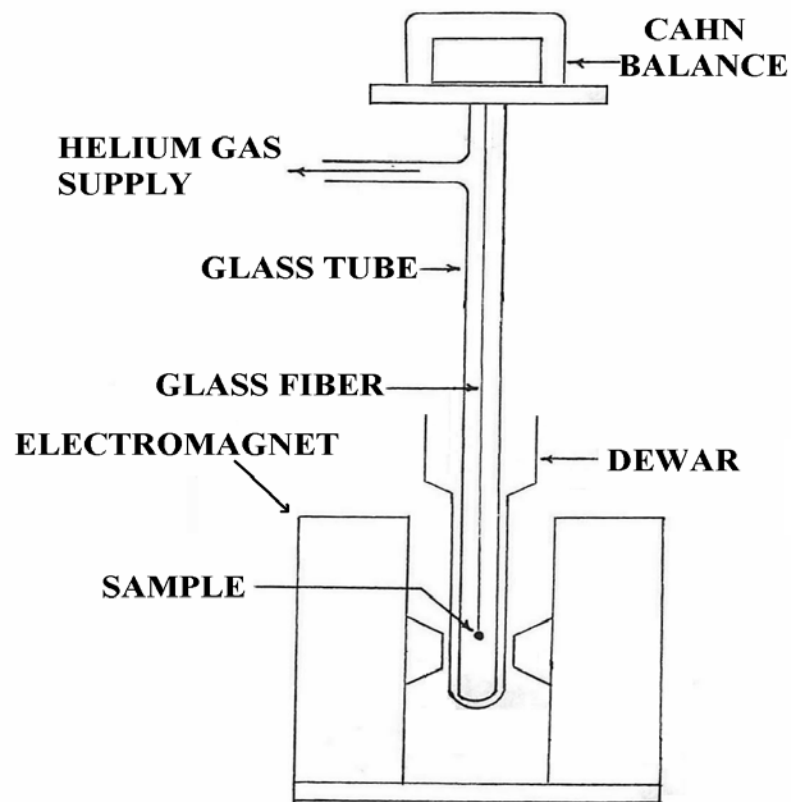


Magnetic Properties: Continued

- Ferromagnetism
 - Cooperative behavior of spins within domains of about 100nm
 - Magnetization much stronger, exhibits hysteresis, and saturates at high fields with all spins aligned in direction of fields
- Superparamagnetism
 - Phenomenologically similar to ordinary paramagnetics
 - Observed when grains of ferromagnetic material become smaller than domain size – small number of spins per grain weakens cooperative behavior

Magnetic Susceptibility Measurements:

Vibrating Sample Magnetometry (VSM) and Magnetic Cluster Characterization



(Magnetization in emu cm^{-3}) $M = \chi H$

Langevin function:

$$M_T = M_S + N_{sp} \mu \left[\frac{\cosh(\mu H / kT)}{\sinh(\mu H / kT)} - \frac{kT}{\mu H} \right]$$

Coercivity:
$$H_c = \frac{2KV}{\mu} \left[1 - 5 \left(\frac{kT}{KV} \right)^{1/2} \right]$$



Use of Nanodispersed Fe_3O_4 for nanocomposite formation

- In order to incorporate magnetic nanoparticles into the 2-EHA/AA copolymer, we start from nanoparticle suspensions in a hydrophobic medium (kerosene).
- Homogenous samples produced
- Magnetic properties determined using Vibrating Sample Magnetometry (VSM)
- Varying percentages of nanodispersed Fe_3O_4 added to samples (0.1-20%)



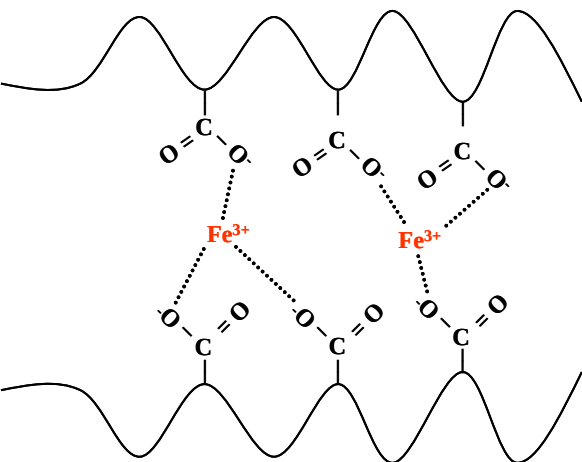
Experimental Methods

- Fourier Transform Infrared (FTIR) Spectroscopy
 - Used to characterize nature of bonds in acrylic copolymer ionomers
- X-ray Photoelectron Spectroscopy (XPS)
 - Used to characterize the chemical environment of Fe^{3+} in ionomers
- Energy Dispersive X-ray Spectroscopy (SEM/EDS)
 - Used to study microstructure and perform quantitative elemental analysis (in particular, Fe) in ionomers and nanocomposites
- Transmission Electron Microscopy (TEM)
 - Used to study nanomorphology of ionomers
- Vibrating Sample Magnetometry (VSM)
 - Magnetic properties



Results

FTIR: Poly(2-EHA-co-AA)/Fe³⁺ Ionomer (effect of FeCl₃ concentration)



$[2\text{-EHA}]_0 = 4.32 \text{ mol dm}^{-3}$ (74.7 mol%)

$[\text{AA}]_0 = 1.46 \text{ mol dm}^{-3}$ (25.3 mol%)

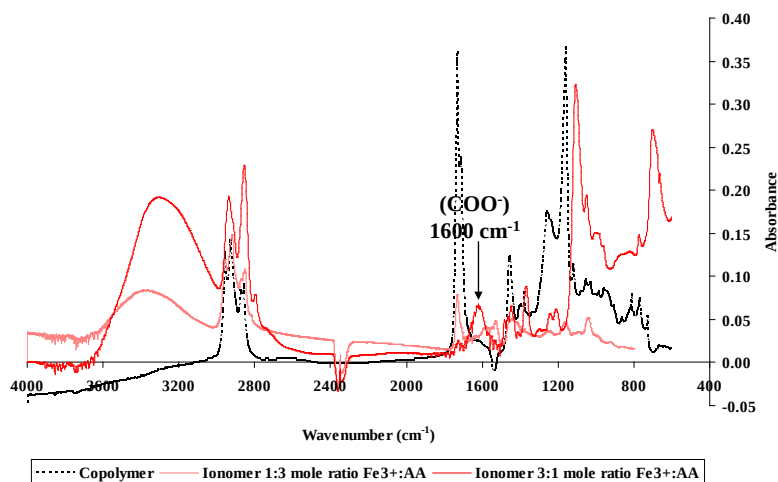
Gamma irradiation

- Dose: 100 Gy
- Dose rate: 0.83 Gy s⁻¹

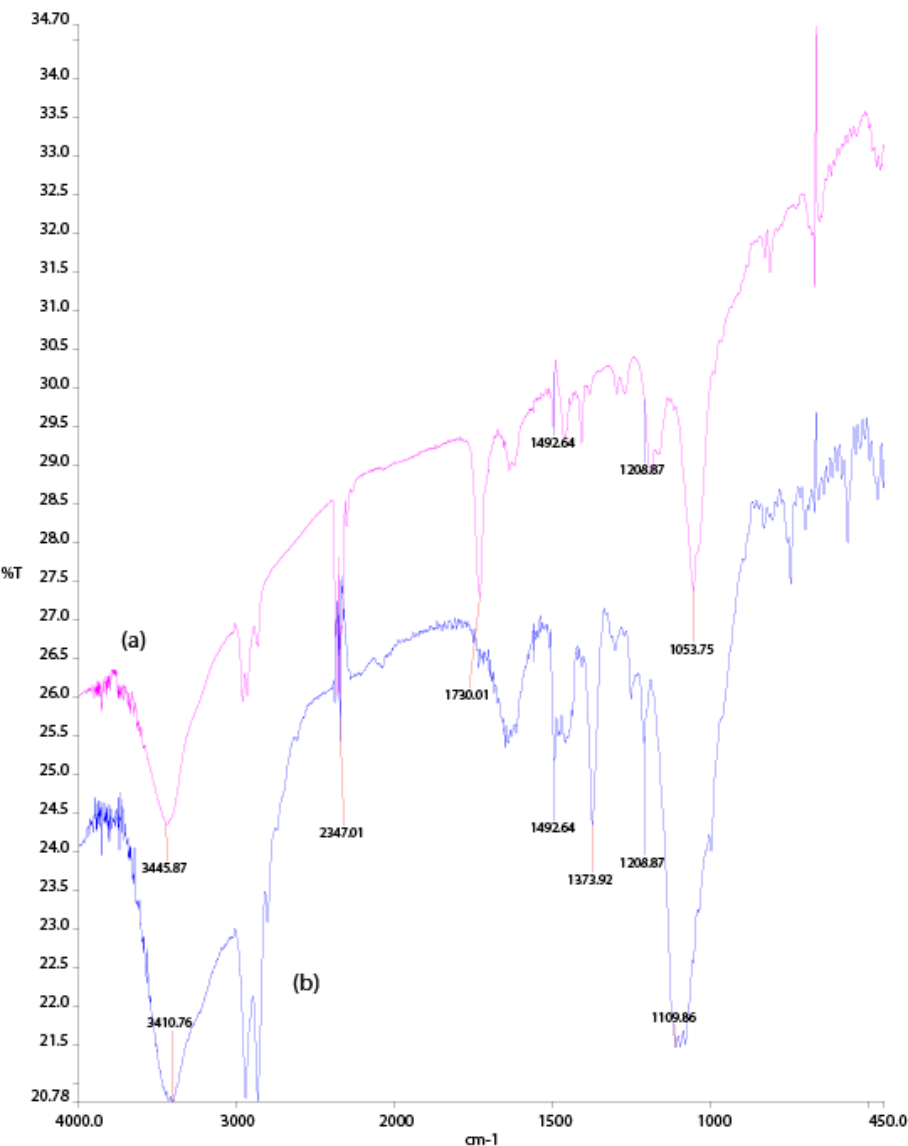
After dialysis, a new absorbance band appears:

1600 cm⁻¹: asymmetric carboxylate
(COO⁻) stretch

This indicates formation of the ionomer.



FTIR of FeCl_3 (1% Fe) in 2-EHA-co-AA

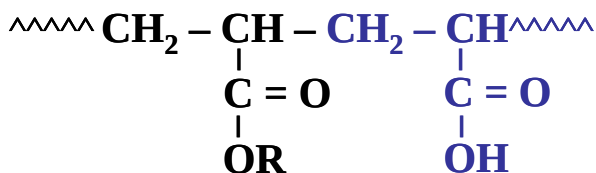
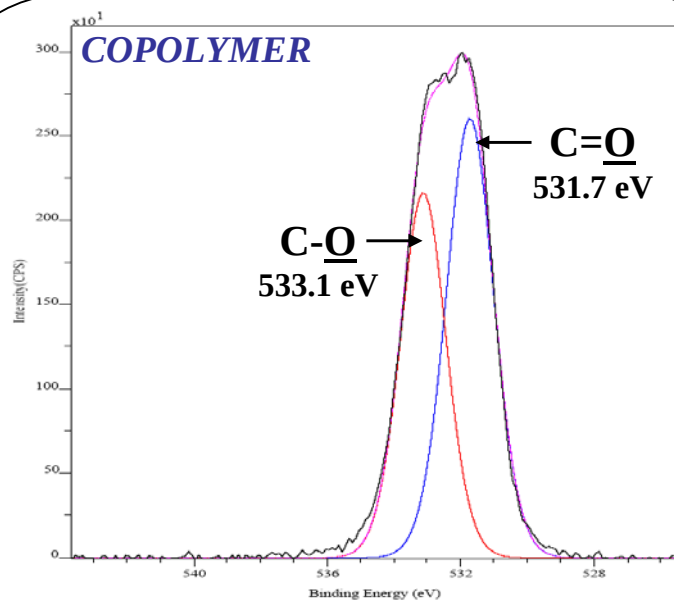


FTIR spectra of 2-EHA-co-AA co-polymers:

- Pure co-polymer mole fraction of 2.7% Fe ionomer in a mole fraction of 75% 2-EHA/25% AA, produced by exposure of monomer mix to 100 Gy of Co-60 gamma radiation at a dose rate of 0.22 Gy/s;
- Same co-polymer after reaction with FeCl_3 to produce a mole fraction of 73.0% 2-EHA/24.3% AA/2.7% Fe^{3+} ionomer.

X-ray Photoelectron Spectroscopy:

1s Analysis of Poly(2-EHA-co-AA)/Fe³⁺ Ionomer



O 1s Spectrum of 2-EHA/AA Copolymer

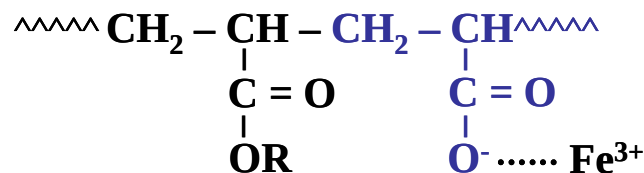
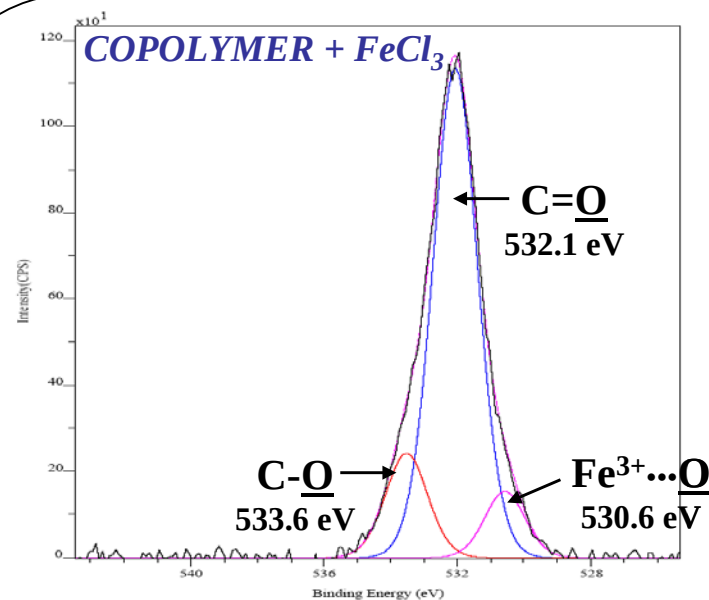
[2-EHA]₀ = 4.32 mol dm⁻³ (74.7 mol%)

[AA]₀ = 1.46 mol dm⁻³ (25.3 mol%)

Gamma irradiation

- Dose: 100 Gy

- Dose rate: 0.83 Gy s⁻¹

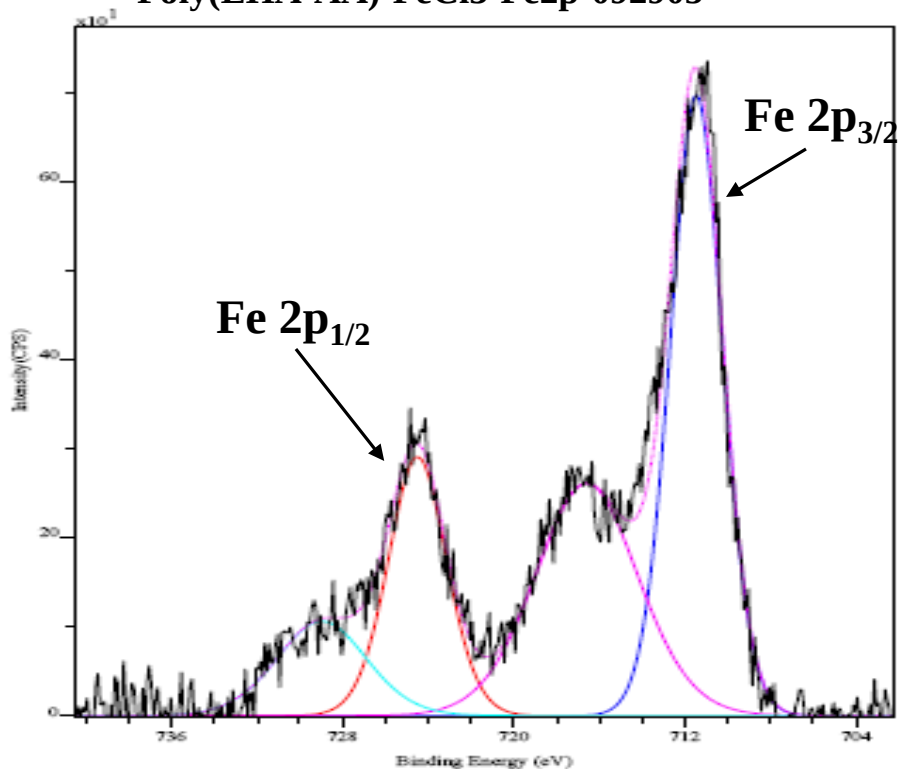


O 1s Spectrum of Copolymer/FeCl₃ Mixture

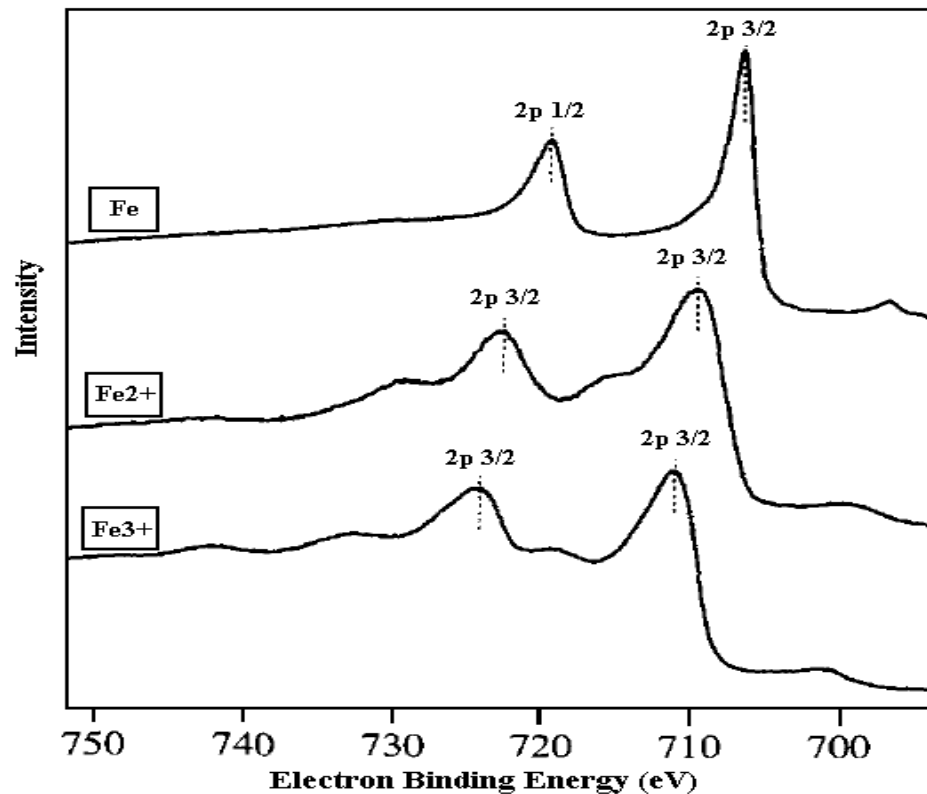
Formulated composition based on 1:3 mole ratio of FeCl₃ to AA

Fe 2p XPS of Poly(EHA-co-AA)+FeCl₃

Poly(EHA-AA)-FeCl₃-Fe2p-092905



	Fe 2p _{3/2}	Fe 2p _{1/2}
Exp	711.5	724.5
Fe⁰ (Fe)	706.8	719.8
Fe²⁺ (FeO)	709.8	722.8
Fe³⁺ (Fe₂O₃)	711.2	724.3





Summary of Spectroscopic Results

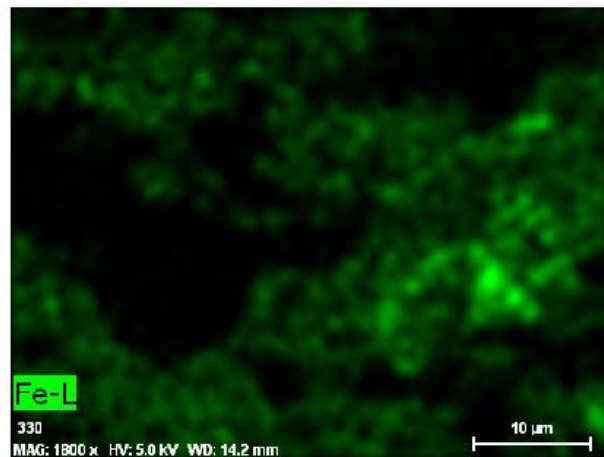
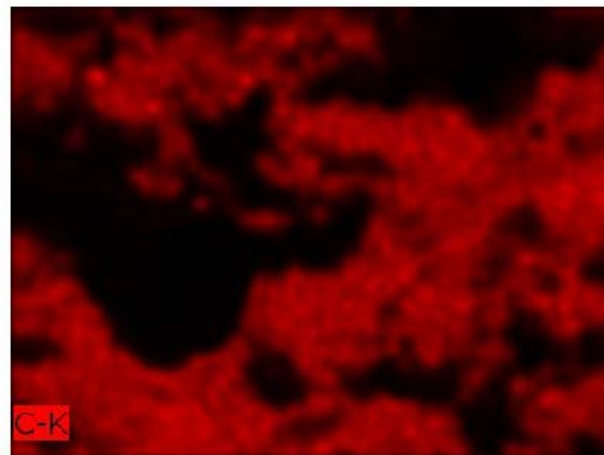
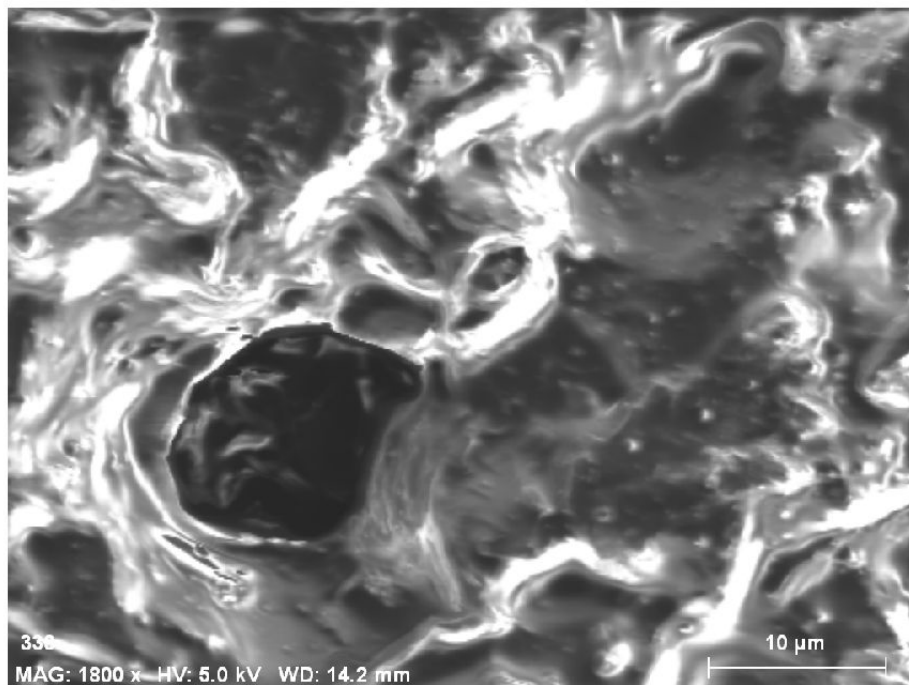
- FTIR

- The appearance of a peak at 1374 cm^{-1} indicates the incorporation of Fe^{3+} into the copolymer.

- XPS

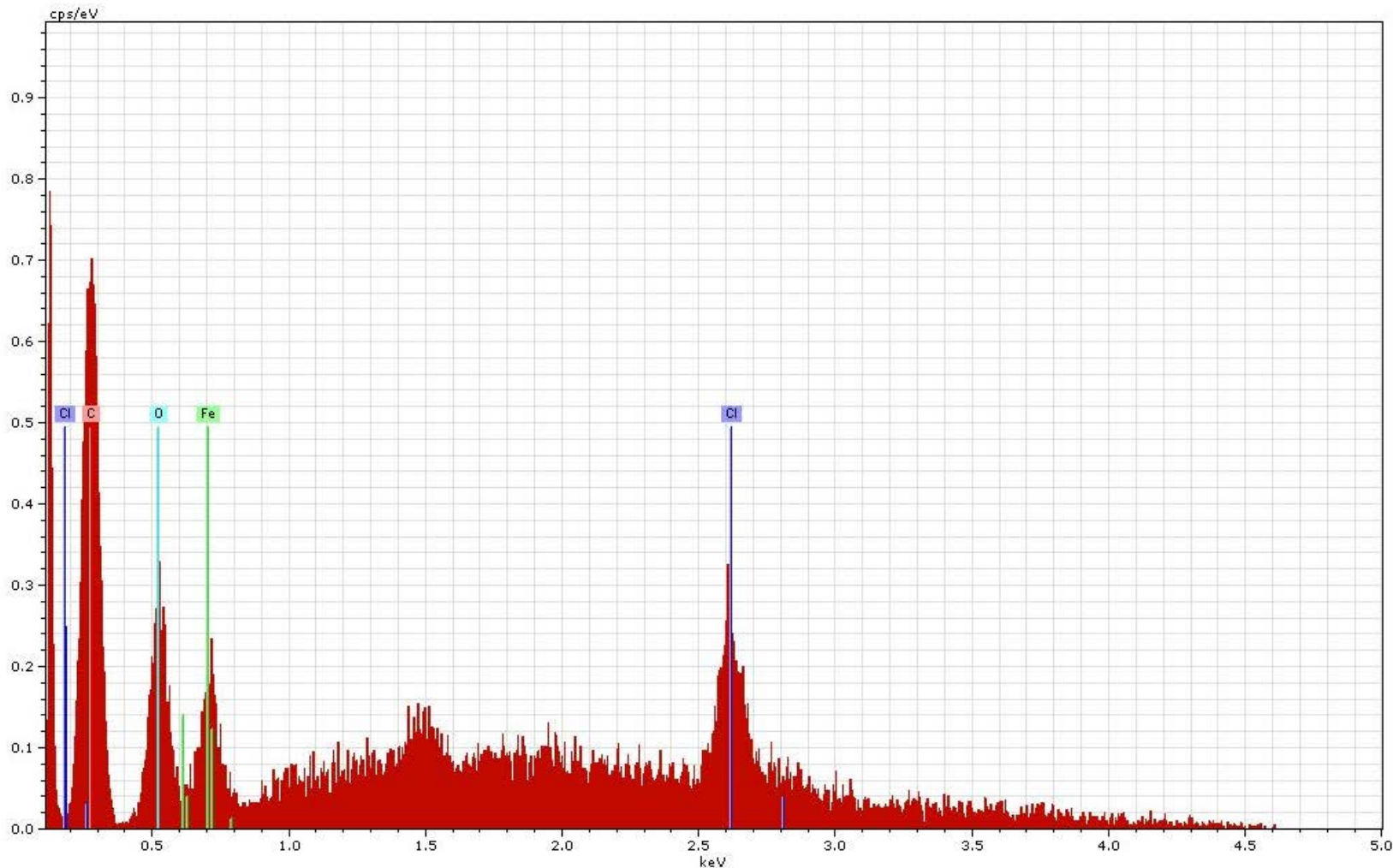
- The observation of the 530.6-eV peak in the XPS spectrum results from interaction between ferric ions and the oxygen atoms of acrylic acid in the copolymer.

Scanning Electron Microscopy and Elemental Mapping for C and Fe: FeCl_3 (1% Fe) Ionomer





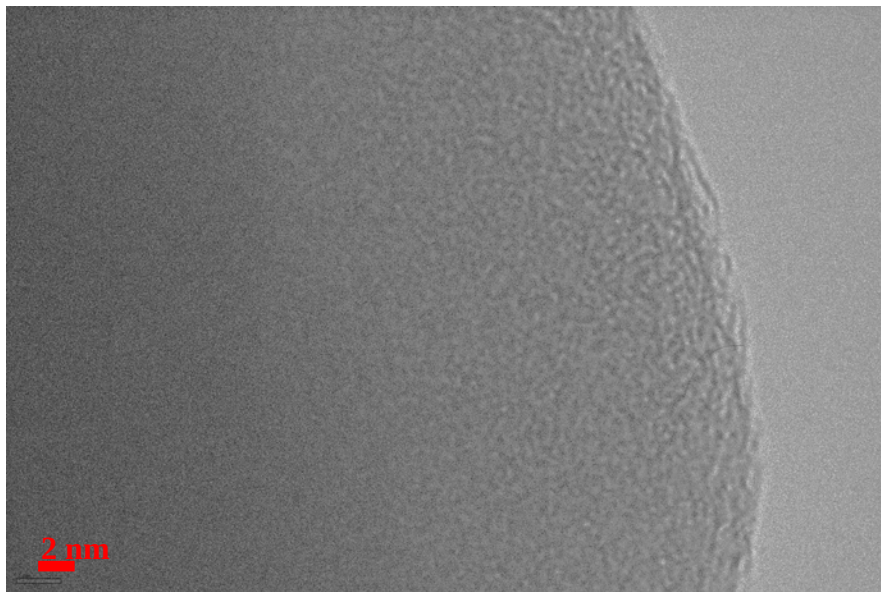
Energy Dispersive X-ray Analysis: FeCl_3 (1% Fe) Ionomer





TEM: Poly(2-EHA-co-AA) Ionomer

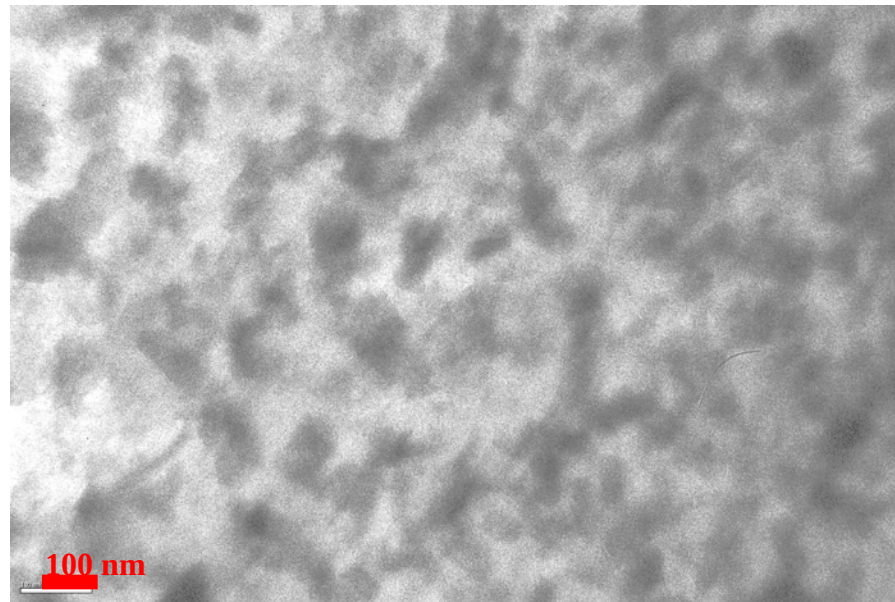
Low Concentration



Iron cation clusters ≤ 1 nm
 $\Rightarrow$ average 3.50 cations per cluster

Poly(2-EHA-co-AA)/Fe³⁺ (1:3 mole ratio Fe³⁺:AA)

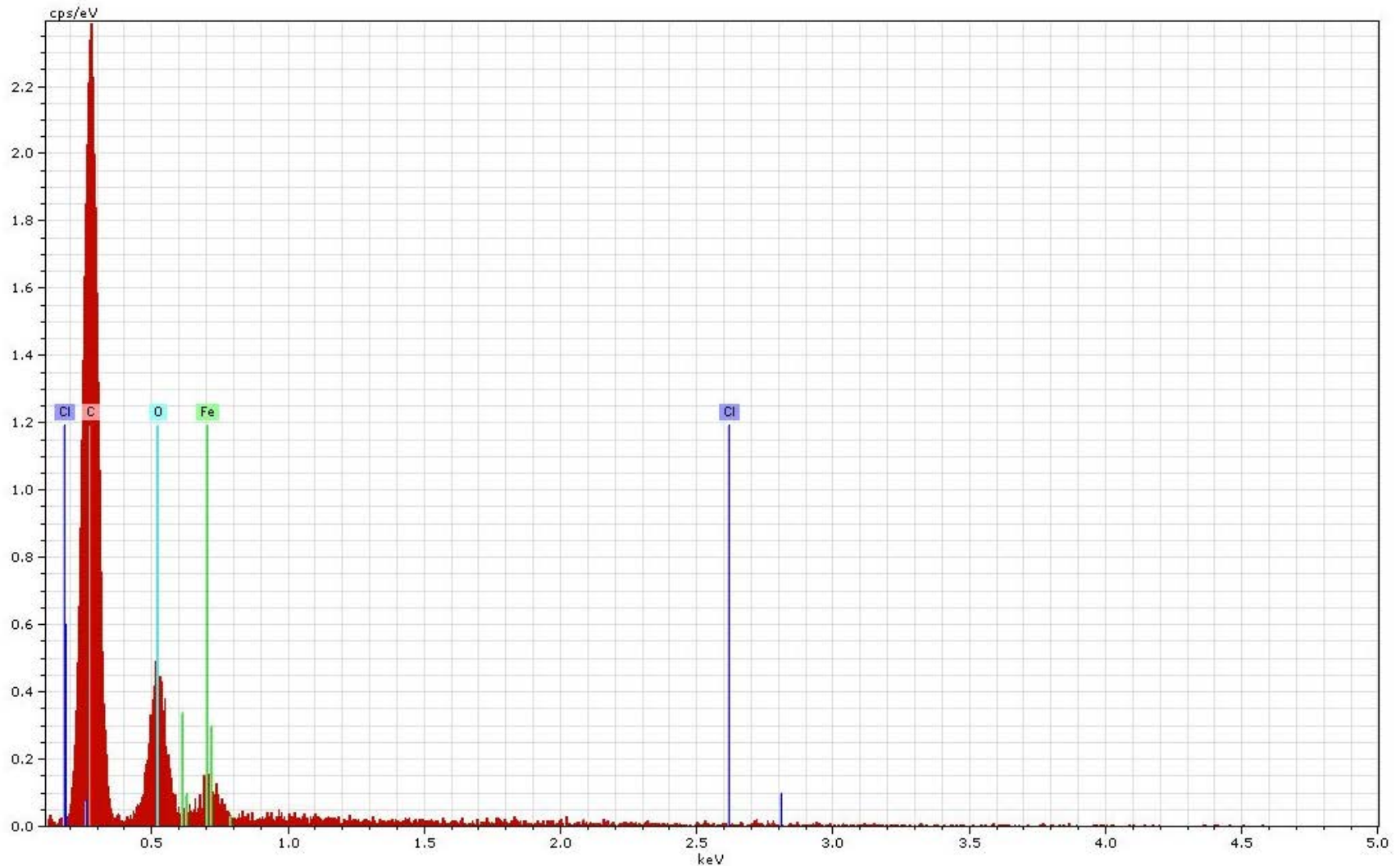
High Concentration



Iron cation clusters ≤ 100 nm
 $\Rightarrow$ average 350 cations per cluster

Poly(2-EHA-co-AA)/Fe³⁺ (3:1 mole ratio Fe³⁺:AA)

Energy Dispersive X-ray Analysis: Fe_3O_4 (1% Fe) Nanocomposite





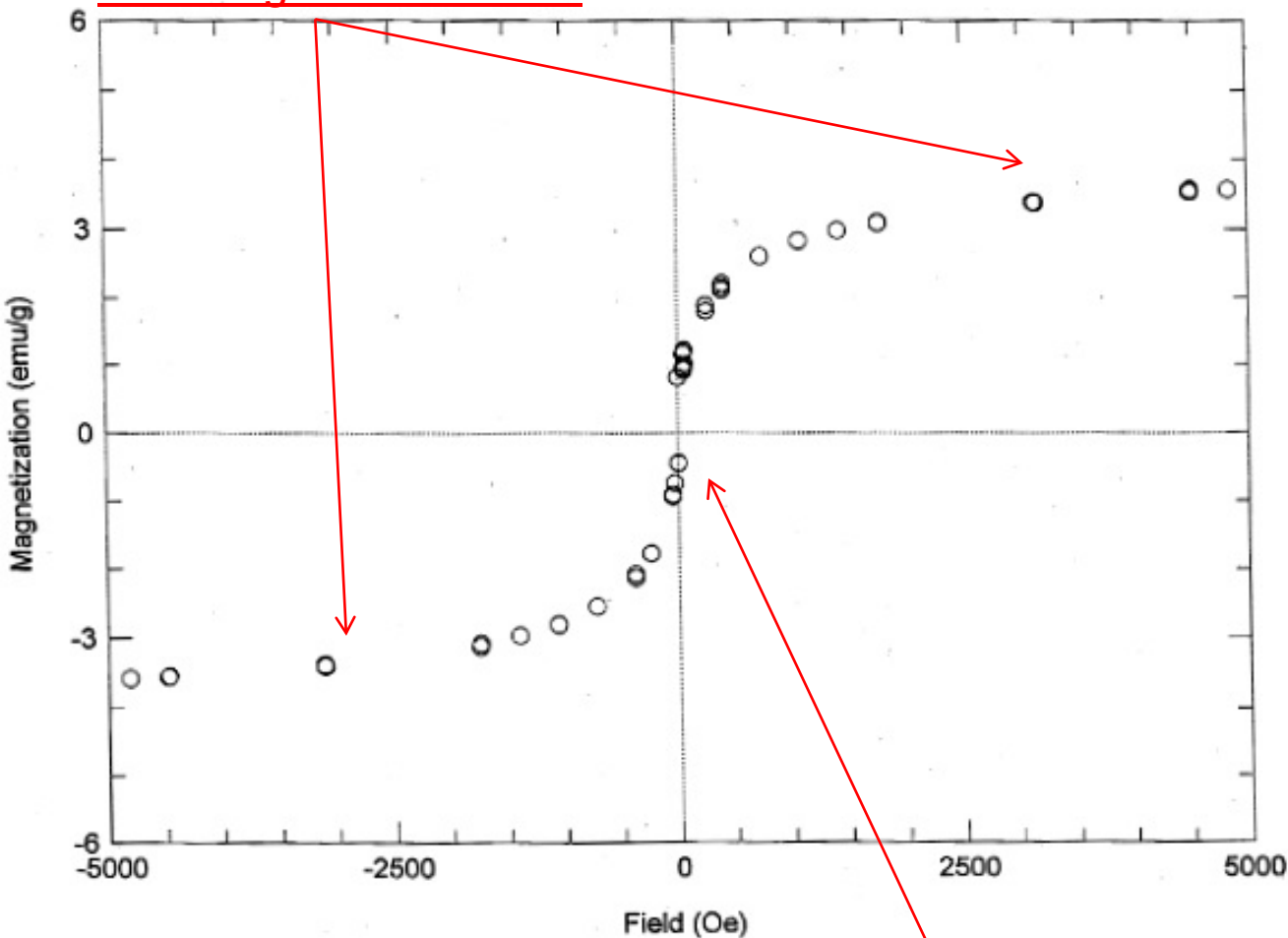
Summary of Spectroscopic Results

- SEM/EDS
 - The EDS of both ionomers and nanocomposites shows incorporation of Fe into the copolymer.
 - Based on the similarity between the C and Fe maps, as well as the SEM image, it is concluded that the distribution of Fe throughout the ionomer microstructure is uniform.
- TEM
 - The micrographs of FeCl_3 based ionomers show the presence of Fe-rich regions with a linear dimension of the order of 100 nm. These regions may consist of clustered ionomers.

Magnetization Measurements:

Magnetite Nanocomposite (1%) – 15nm

Paramagnetic behavior

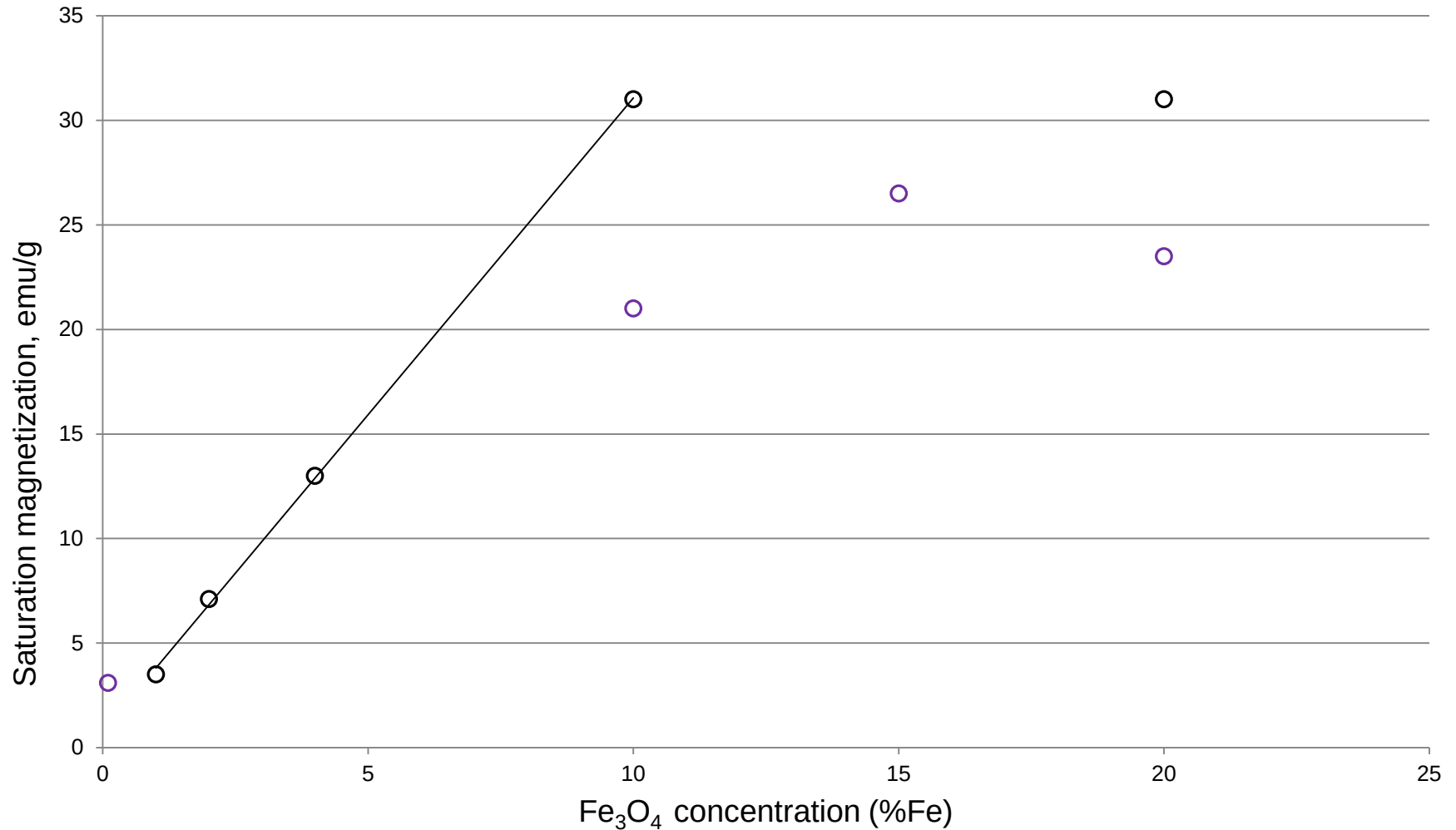


In nanoparticles which are smaller than the domain size but not extremely small, there is a mixed ferromagnetic/ superparamagnetic behavior as reflected in the Langevin equation;

Ferromagnetic behavior



Magnetization of Fe_3O_4 samples in 2-EHA/AA copolymer: Various Nanocomposite Concentrations



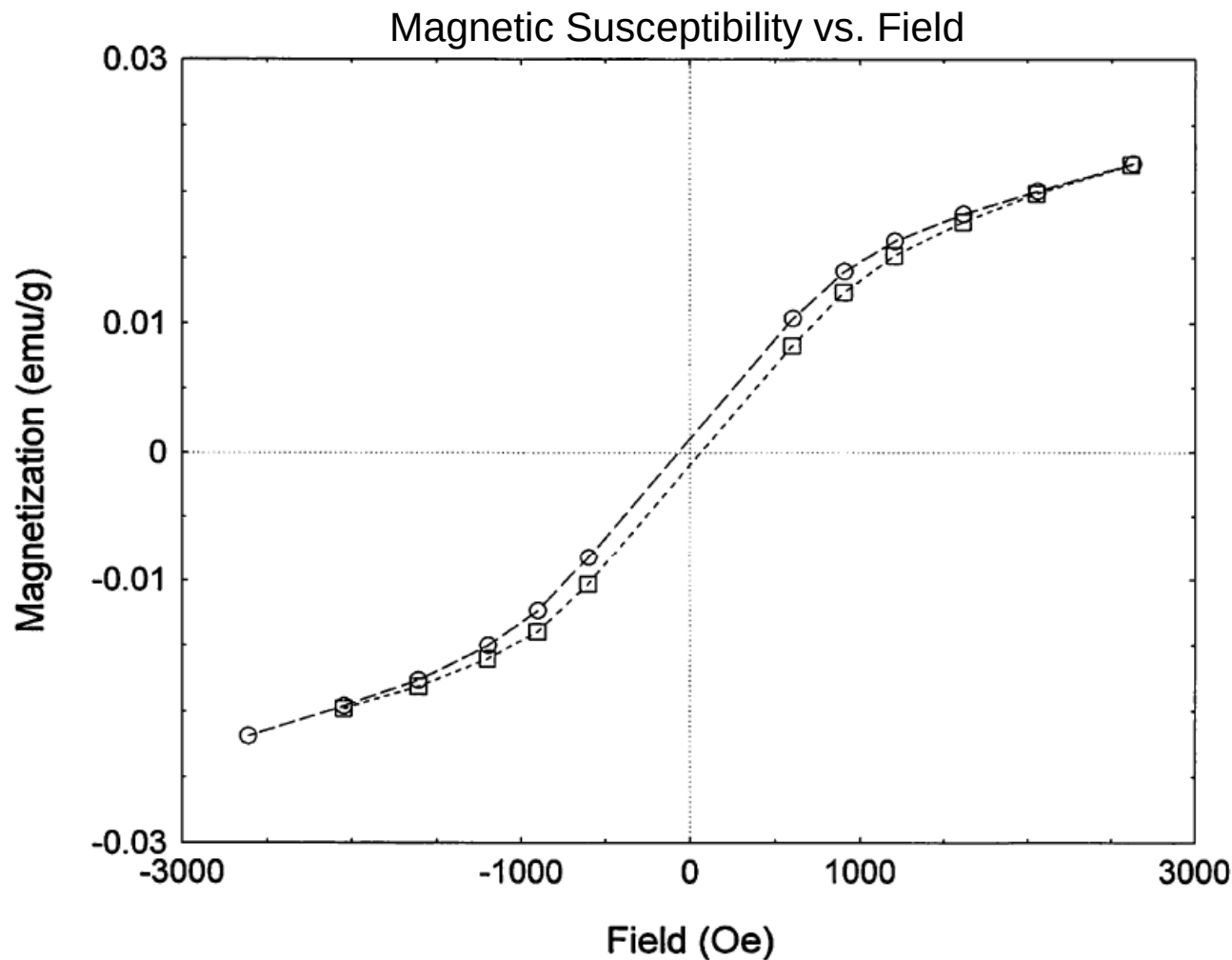


Implications of Magnetization Results for Magnetite Nanocomposites

- The magnetization results show a combination of ferromagnetic behavior (hysteresis) at relatively small magnetic fields with superparamagnetic behavior at large fields.
- The ferromagnetic behavior can be attributed to the presence of larger nanoparticles and the superparamagnetic behavior to smaller nanoparticles.
- As expected, the magnetization increases with magnetite concentration up to about 10% Fe (in the form of Fe_3O_4). Above this concentration, the magnetite apparently no longer forms a uniform suspension in the 2-EHA/AA copolymer.



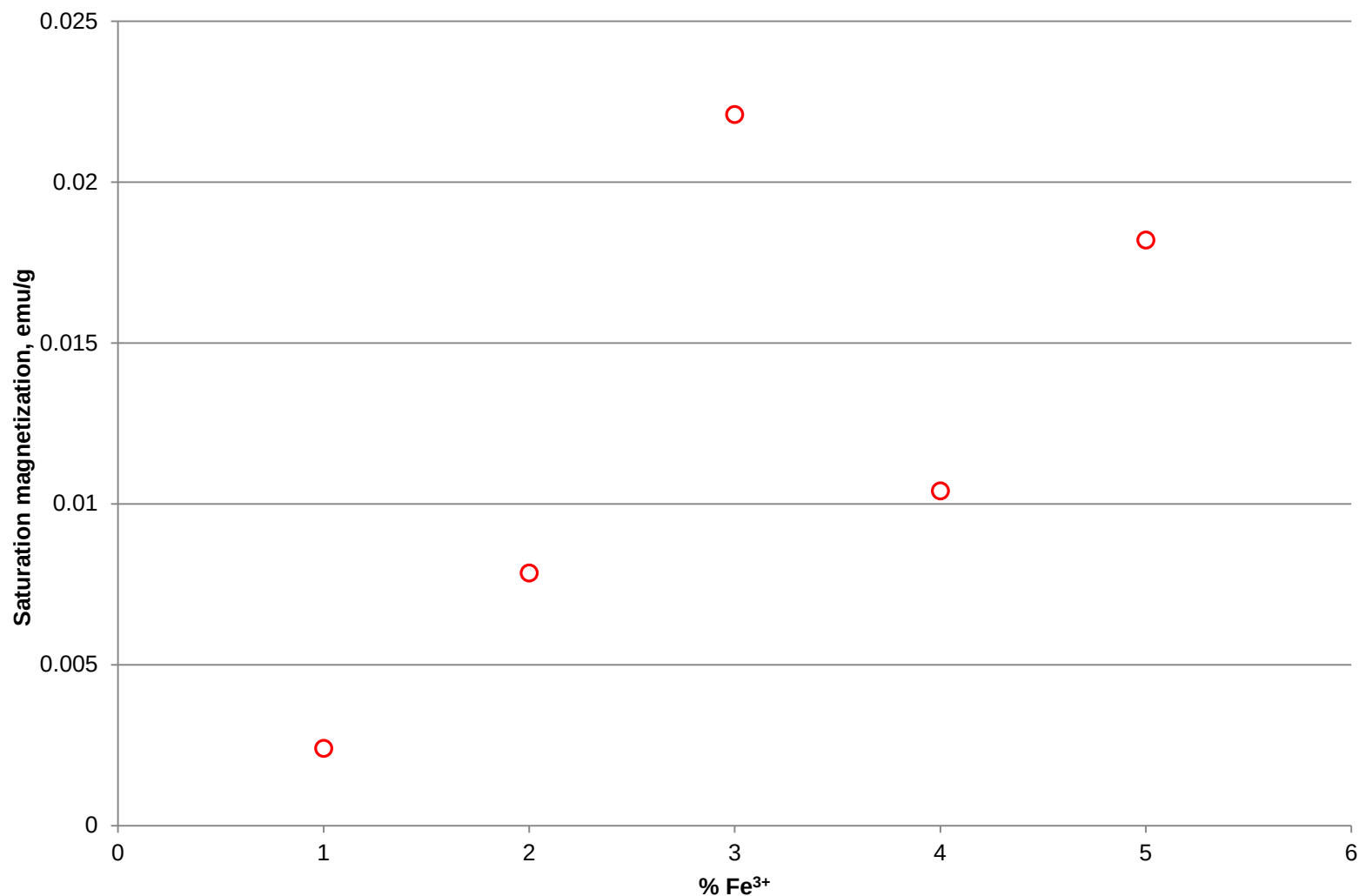
Magnetic Susceptibility Measurements: Ferric Chloride Ionomer



2-EHA-co-AA co-polymers produced by irradiation, and of co-polymers reacted with FeCl_3 to produce a 2.7 mol% Fe ionomer in a 73 mol% 2-EHA/24 mol% AA mixture;



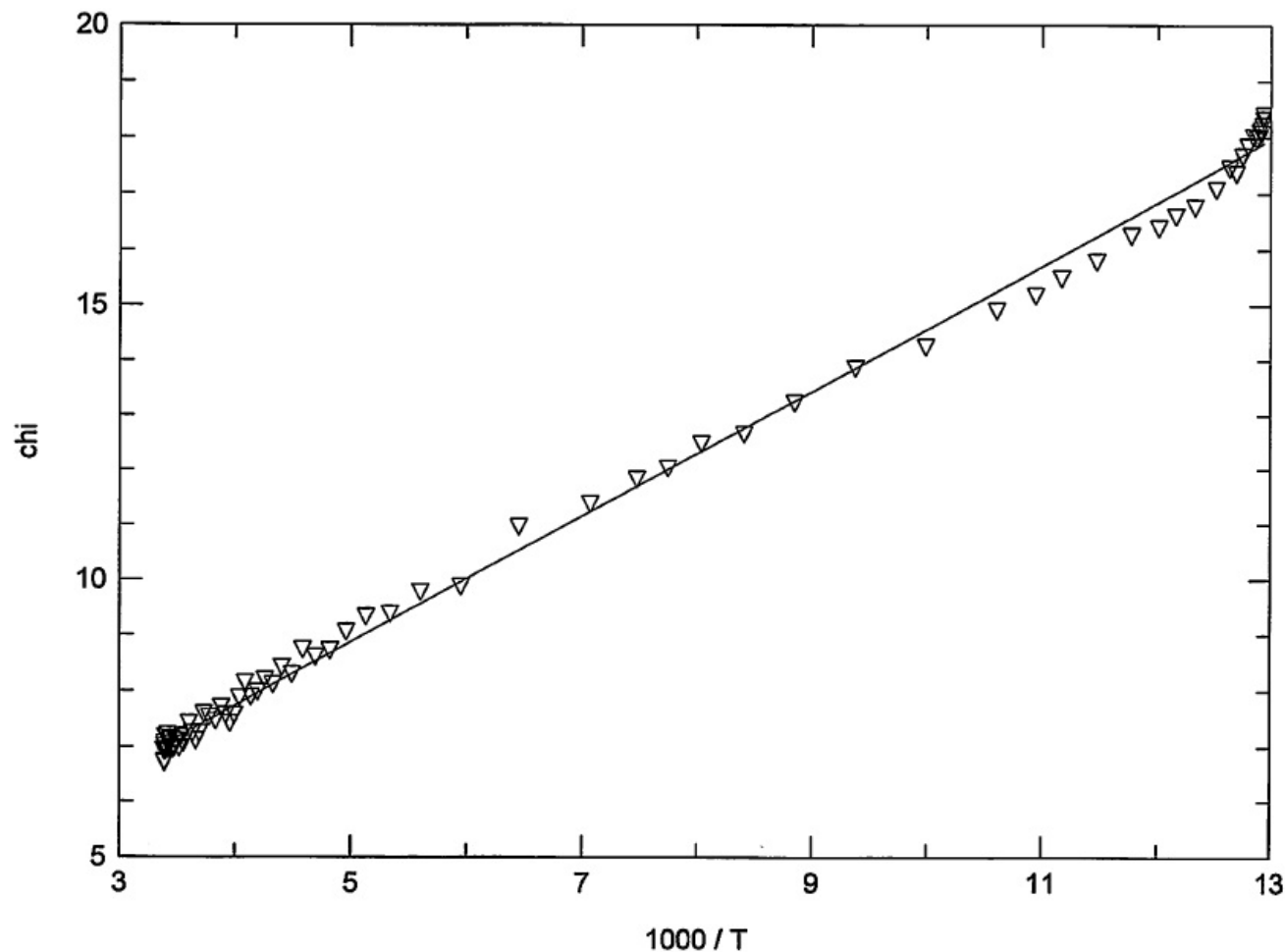
Magnetization of FeCl_3 samples in 2-EHA/AA copolymer: Various Ionomer Concentrations





Magnetic Susceptibility Measurements: Ferric Chloride Ionomer

Magnetic Susceptibility vs. Temperature



2-EHA-co-AA co-polymers
produced by irradiation, and
of co-polymers reacted with
 FeCl_3 to produce a 2.7 mol%
Fe ionomer in a 73 mol% 2-
EHA/24 mol% AA mixture;



Implications of Magnetization Results for FeCl_3 Ionomers

- According to Curie's Law for paramagnetic materials, $\chi = C/T$
Our results show a positive deviation from the Curie's Law dependence at low temperature.
- This deviation can be attributed to a mutual spin alignment contribution to the magnetization.
- In nanoparticulate materials both a superparamagnetic behavior (due to very small particles) and cooperative behavior (due to larger particles) contribute to the total magnetization; such combined effect is indeed clearly visible in our results.
- The ferromagnetic behavior is expected to be more noticeable at lower temperatures, where thermal motion is least likely to disrupt mutual spin orientation. This is indeed reflected in our results.
- Note that specific magnetization of the FeCl_3 ionomers is much lower than the one observed with the magnetite nanoparticles. This is to be expected in view of the strong tendency of magnetite to exhibit ferromagnetic behavior. However, it is remarkable that some mutual spin alignment takes place within the FeCl_3 ionomers.



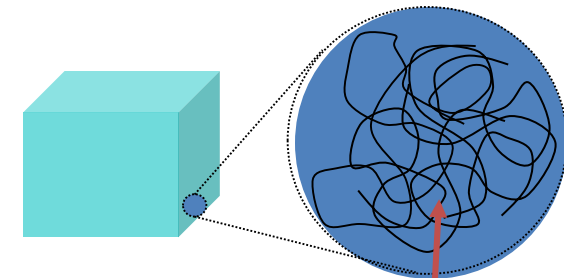
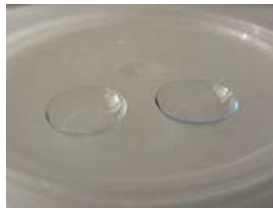
Summary of Results

- Spectroscopic evidence and magnetic measurements confirm the formation of magnetic nanocomposites.
- Depending on the chemical nature and size of the nanoparticle composites, it is possible to obtain different types of magnetic behavior for different applications.

• Hydrogel

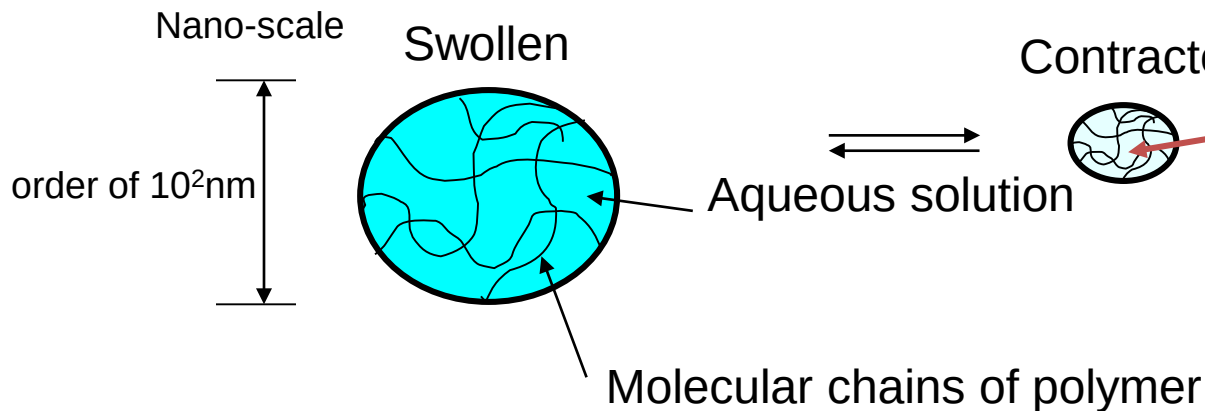
Structure: 3D polymer network & filling liquid (water)

- Common applications -



Conventional Macroscopic hydrogel

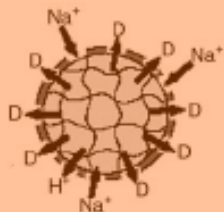
Nanohydrogel



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

Hydrogels in nanotechnology

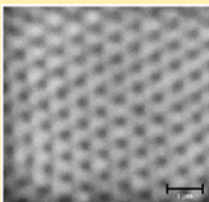
Drug Delivery



P. F. Kiser, G. Wilson, D. Needham, *Nature* 1998, 394, 459.

Self-Assembly

S. B. Debord, L. A. Lyon, *J. Phys. Chem. B* 2003, 107, 2927.

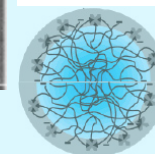


Chemical / Biological Sensors



▲ - Biotin

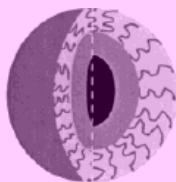
✕ - Avidin



J. Kim, S. Nayak, L. A. Lyon, *J. Am. Chem. Soc.* 2005, 127, 9588.

Nano-Reactors

S. Liu, J. V. M. Weaver, M. Save, S. P. Armes, *Langmuir* 2002, 18, 8350.



Inorganic nanoparticles in hydrogel

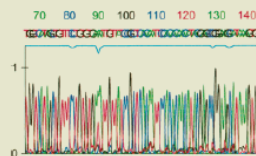
Biomaterials



T. Shiroya et al., *Colloids Surfaces B: Biointerfaces* 4 (1995) 267-274

Enzymes immobilized in the hydrogel microspheres.

Chemical / Biological Separations

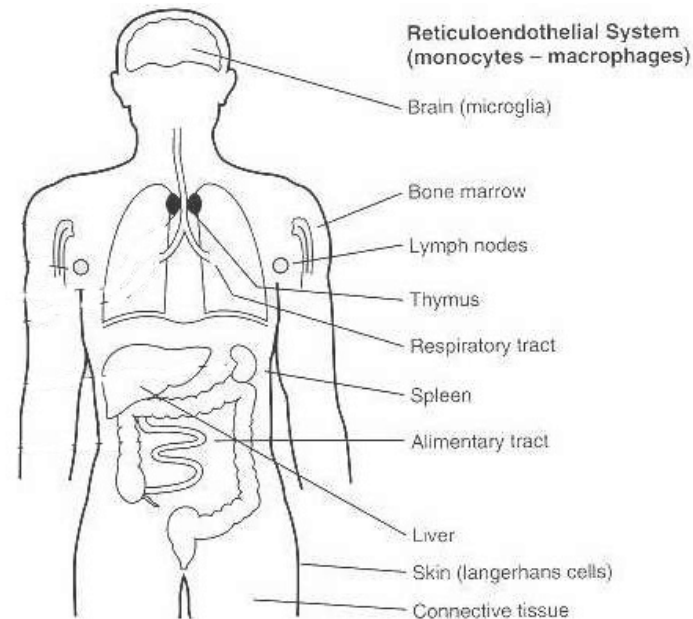


E. A. S. Doherty et al., *Anal. Chem.* 2004, 76, 5249.

Particle size and bioavailability

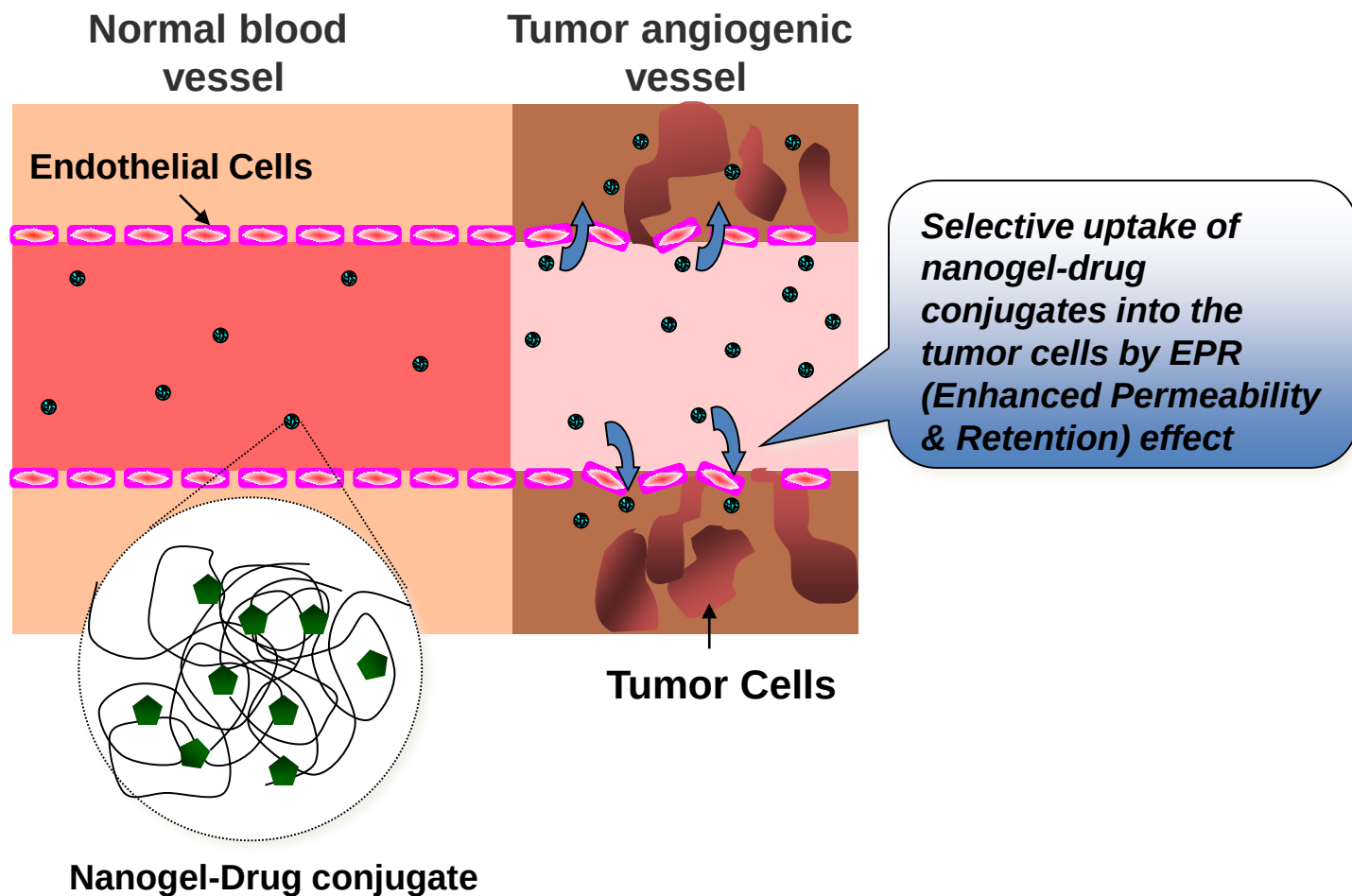
Size (within nanoscale) strongly affects *circulation time in blood & bioavailability* of the particles within the body by evading RES (Reticulo endothelial system).

Particle diameter (nm)	Effects
5-10	Removal through extravasation & renal clearance
10 - 70	Penetrate very small capillaries within body tissues → most effective distribution in certain tissue
70 - 200	Longest circulation times
> 200	Filtration by spleen → removal by phagocyte system → decreased circulation times



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).





Goal of research

Synthesis & characterization of polymer nanohydrogels.

a. Physical parameters in synthesis.

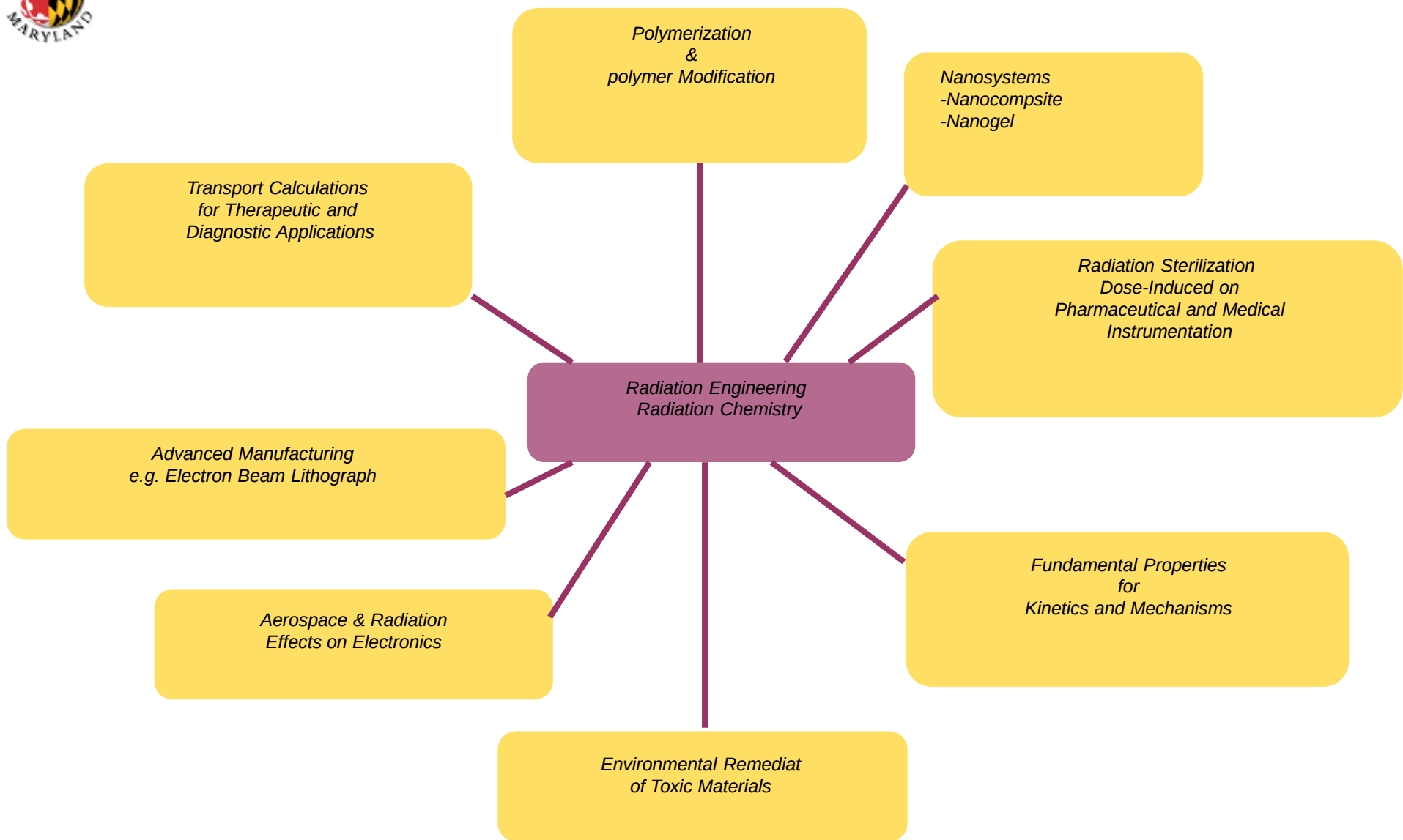
; concentration, temperature, physical confinement, dose, and dose rate effects.

b. Characterization of nanohydrogels.

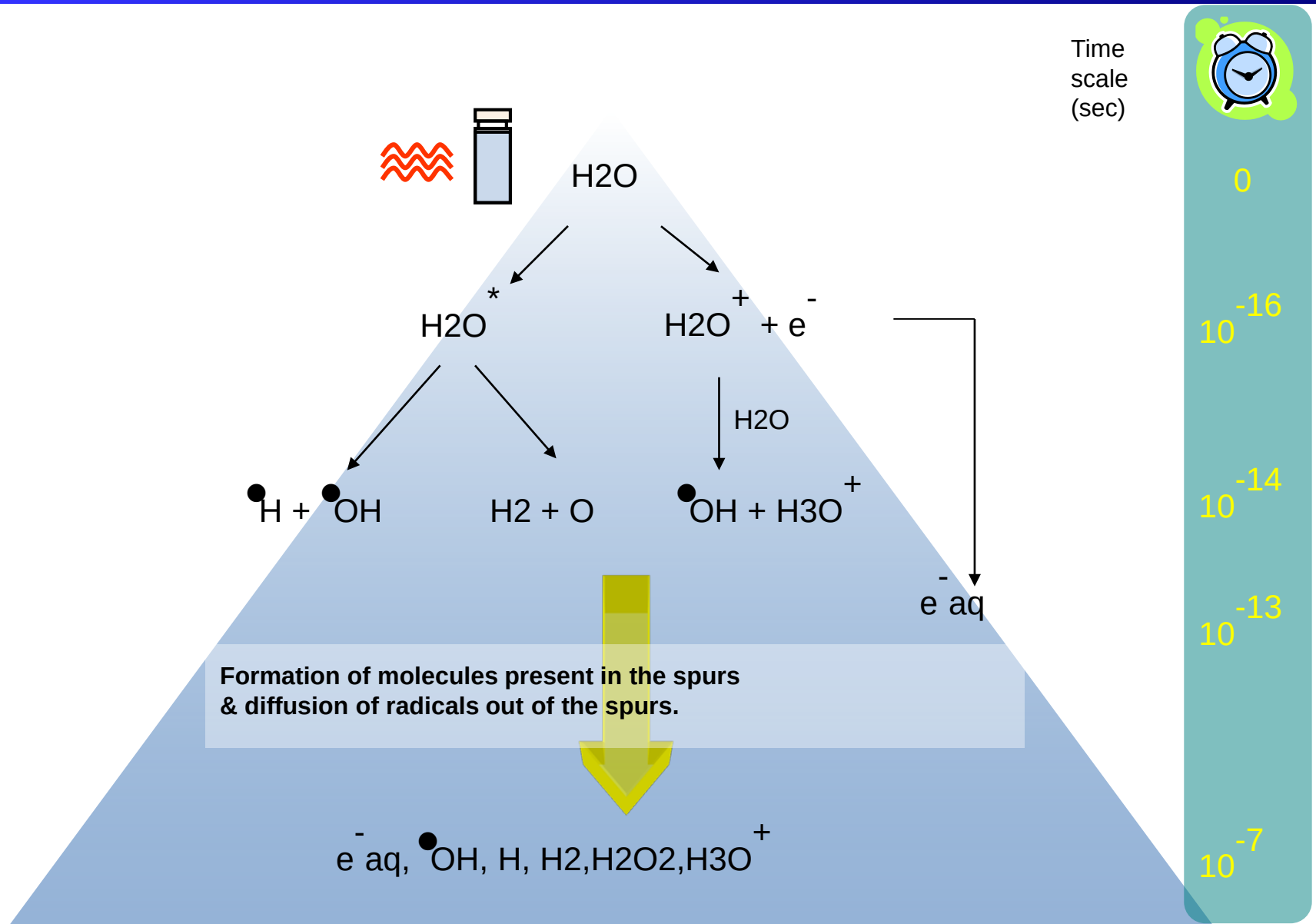
; Molecular weight, size, and conformation.

c. Free radical kinetics in nanohydrogel synthesis.

; Reaction rate constant ($2k_2$) of polymer radical reaction, Activation energy (E_a) of polymer radical decay.



Radiolysis of water



Radiation chemistry in aqueous solutions

Radiation chemical yields ($\mu\text{mol/J}$) for water irradiated by electron & gamma-ray radiation.

$$G(e_{\text{aq}}^-) = G(\bullet\text{OH}) = G(\text{H}_3\text{O}^+) = 0.28; G(\text{H}) = 0.062; \\ G(\text{H}_2) = 0.047; G(\text{H}_2\text{O}_2) = 0.072$$

Hydroxyl radical ($\bullet\text{OH}$)

Most efficient in abstraction of H from polymer chain producing C-centered free radicals.

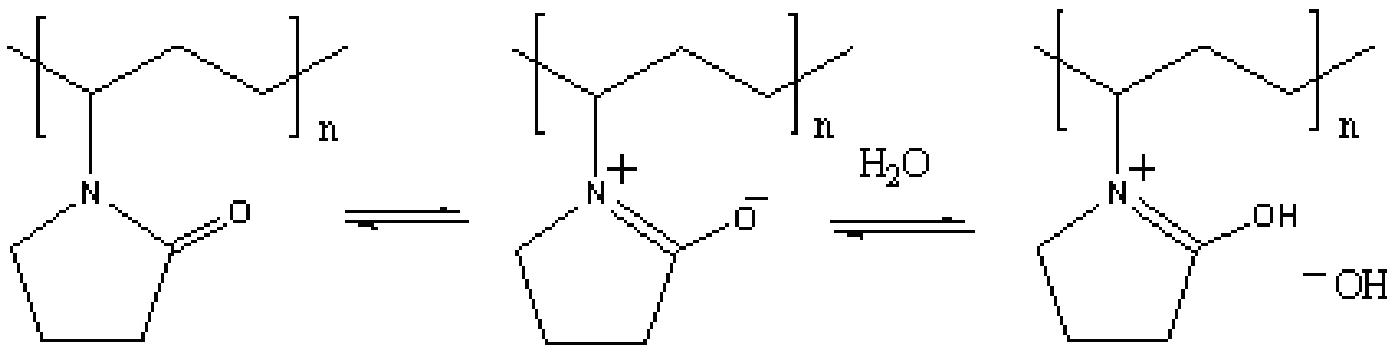
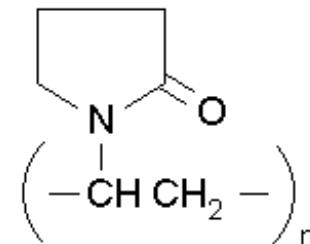
N₂O enhances the generation of $\bullet\text{OH}$ by converting e_{aq}^- into $\bullet\text{OH}$
 $\text{N}_2\text{O} + e_{\text{aq}}^- \rightarrow \bullet\text{OH} + \text{OH}^- + \text{N}_2$ ($k = 8.7 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$)

Radiation Chemistry-Continued

- **Hydroxyl radical ($\cdot\text{OH}$)**
 - Powerful oxidant
 - Highly reactive (through addition, abstraction or electron transfer)
- **Solvated electrons (e_{aq}^-)**
 - Strong reducing agent
 - Requires a suitable vacant orbital
 - Reactivity is greatly enhanced by electron withdrawing substituents, such as Cl
 - e_{aq}^- can be effective in dechlorinating PCBs even when other organic species are present in much higher concentrations

Poly(vinyl pyrrolidone), PVP

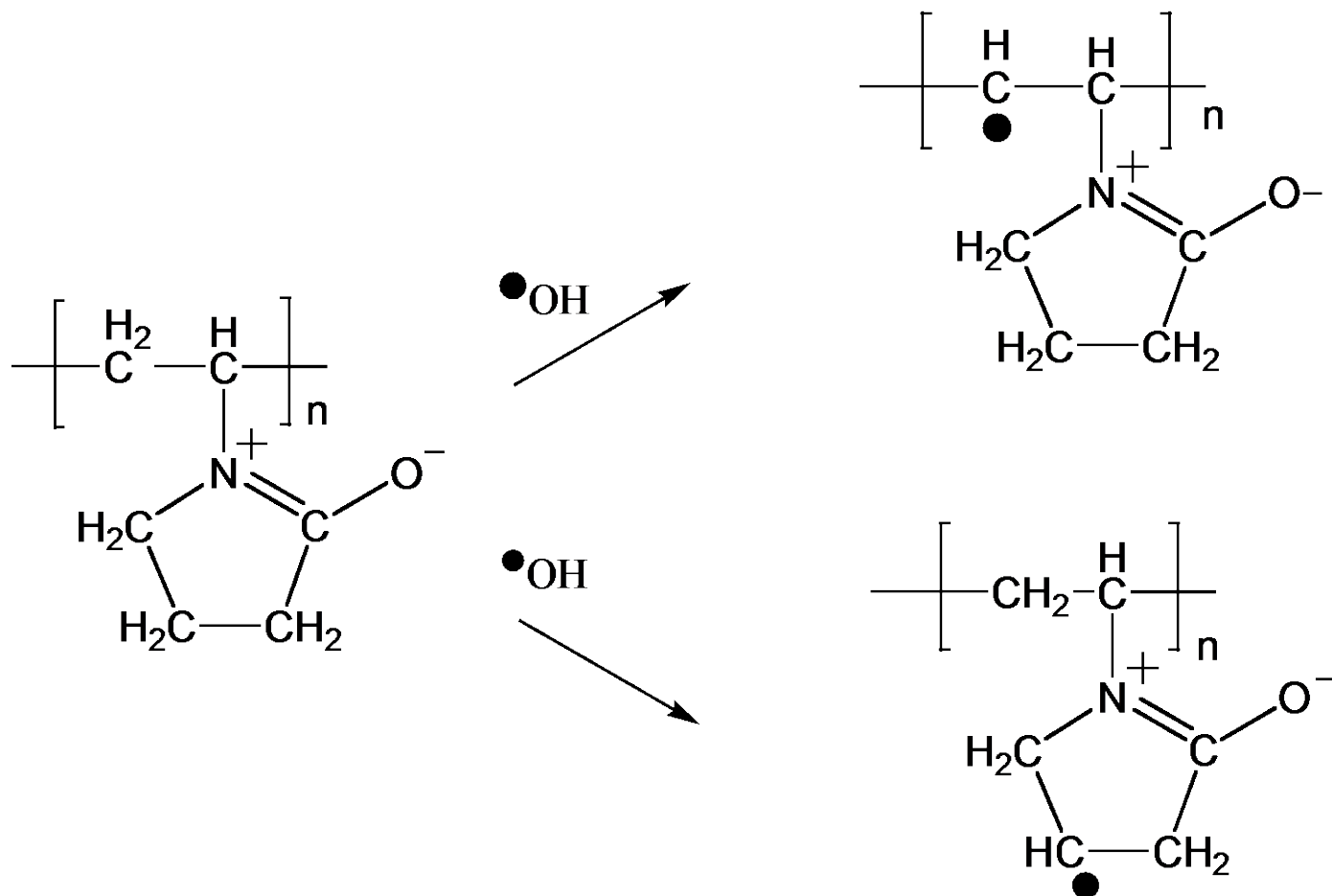
- $pK_a = 5 - 8$
- Non-antigenic, biologically compatible.
- Low toxicity.
- Extensive applications in pharmaceuticals, biomedical sciences, food and beverage, cosmetics etc.
- Zwitterion structure $\rightarrow$ Interaction between polar groups through electrostatic forces.



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

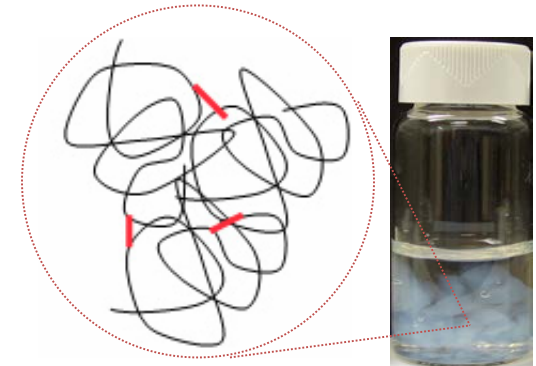
Reactions of $\cdot\text{OH}$ with PVP

H abstractions of carbon in PVP

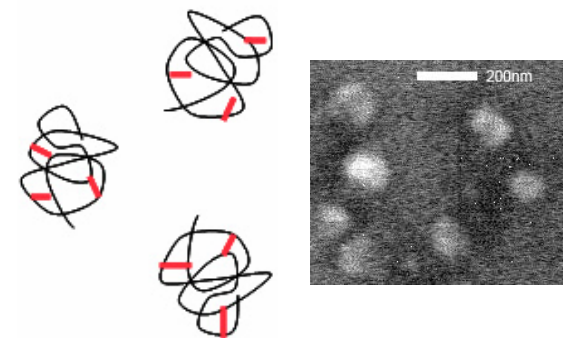


Inter- vs. Intra-crosslinking

Macroscopic gel



Nanogel



- Polymer radical
- Crosslinked bond

**Ionizing
Radiation**

**Inter-molecular
Crosslinking**

**Intra-molecular
Crosslinking**

**Polymer chain
in water**

Strategies to maximize intra-crosslinking reaction yield

1. Increase # of C-centered free radicals on the backbone of the polymer

; High dose rate = pulse repetition rate (Number of Pulses per second

2. Prevent inter-molecular reaction

- Thermally collapsed polymer chains in aqueous solution by disruption of water-polymer H-bonds at high temperature.**
- Low concentration of polymer solution.**
- Physical isolation by nano-template.**



Novel approaches in this work

1. Polymer conformation effects.

; Temperature-dependent chain conformations

→ Kinetics & Activation energy of gel-forming reactions.

2. Solution & irradiation parameters effects.

; Temperature, Concentration, Pulse repetition rate,

Pulsed vs. Steady-state radiolysis.

3. Nano-confinement effects

; Polymer chains entrapped in the Nanoporous membrane pores for spatial isolation.

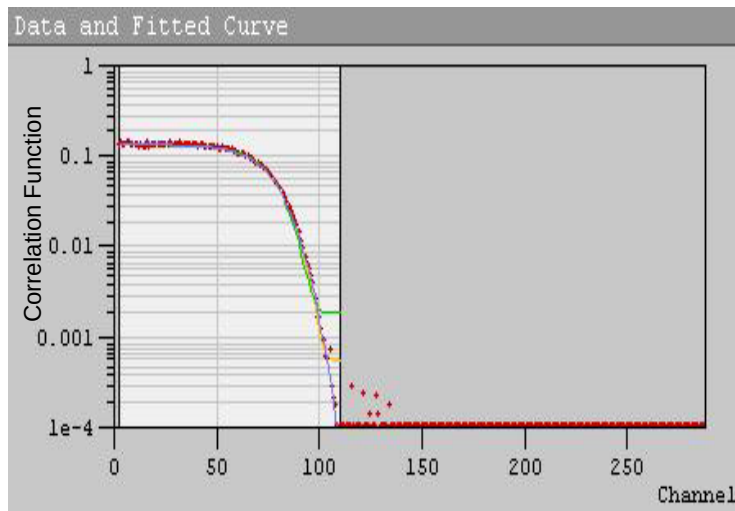
4. Characterizations

; Size exclusion chromatography for R_h , M_w distributions.

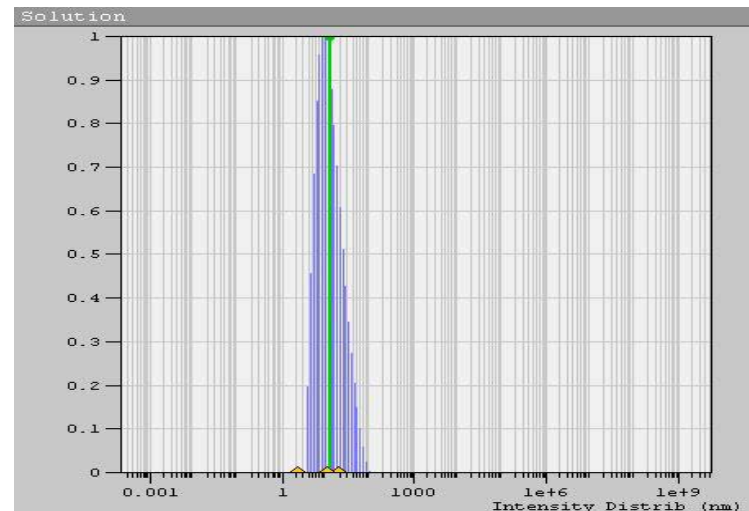
Characterization

Temperature-controlled dynamic light scattering (DLS) for R_h

1. Probe structural relaxations & dynamics.
2. Translational diffusion coefficient (D) & subsequent hydrodynamic radius (R_h) by using the time dependent fluctuations of scattering intensity at certain angle θ .



Correlation function

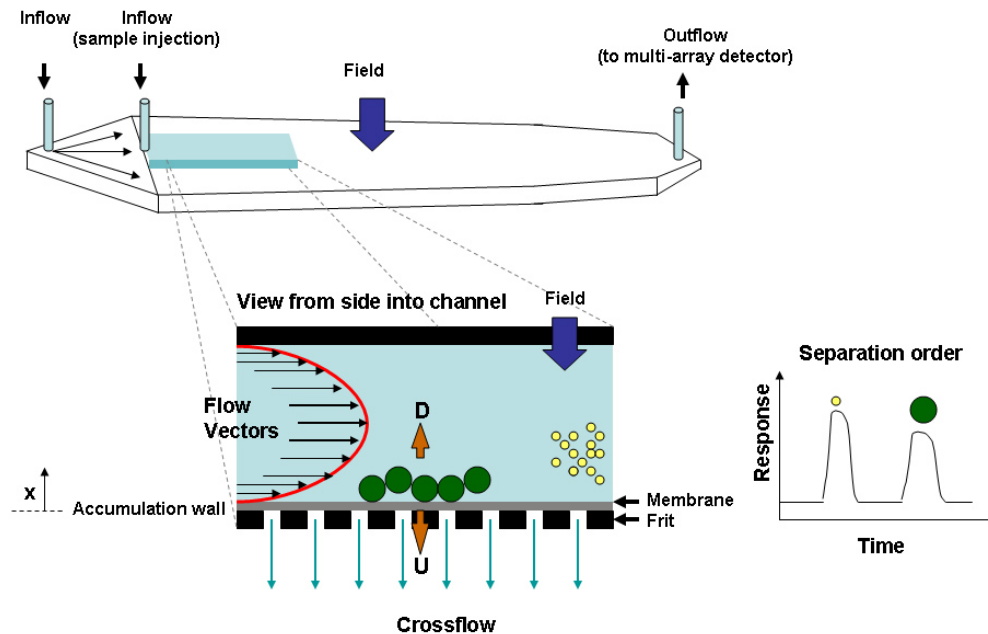


R_h distribution

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 I_s at certain angle $\theta \rightarrow R_h$.
3. Measure the angle dependent I_s and corresponding concentration from UV spectroscopy $\rightarrow M_w$.





DLS

If the scattering species is a dilute monodisperse spherical particle, then the electric-field correlation function forms a single exponential decay of time (τ), which is given by:

$$g_1(\tau) = \exp(-Dq^2\tau)$$

where D is the translational diffusion coefficient of the particle and q is the wave vector.

The hydrodynamic radius (R_h) can then be calculated using the **Stokes-Einstein relationship**:

$$R_h = \frac{k_B T}{6\pi\eta D}$$

where k is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the solvent.



Outline

I. Introduction.

II. Backgrounds.

III. Nanohydrogels synthesized by ionizing radiations.

III-a. Thermal & radiation parameter effects in e-beam radiation.

III-b. Thermal & radiation parameter effects in steady-state radiolysis.

IV. Kinetics studies of PVP radical-radical reactions.

V. Nano-template assisted ionizing radiation for nanohydrogel synthesis.

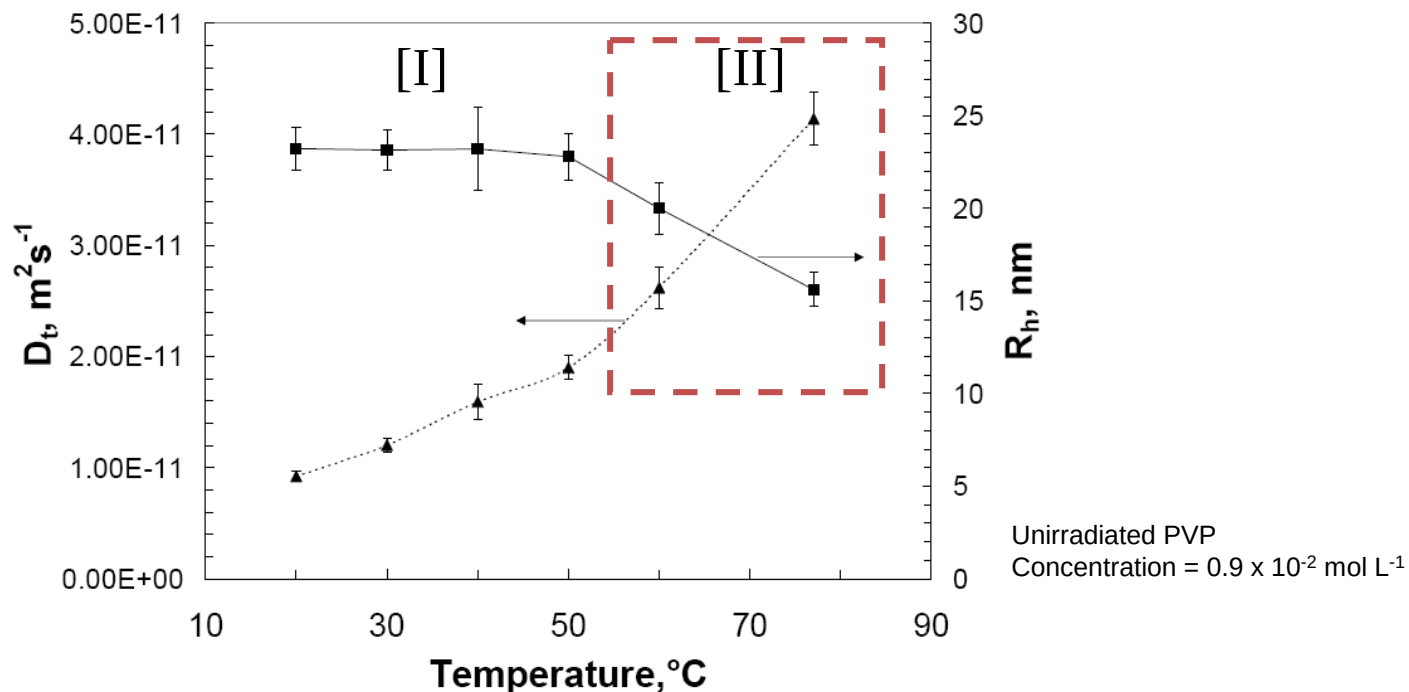
VI. Conclusions.

Conditions in pulsed e-beam 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 N₂O prior to irradiations

Rh & D vs. Temperature



[I] 20 - 50 °C; R_h is almost constant

[II] 50 - 77 °C; R_h decreases as temperature increases.

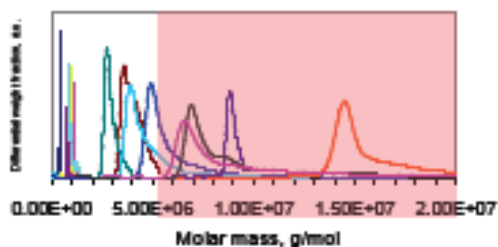
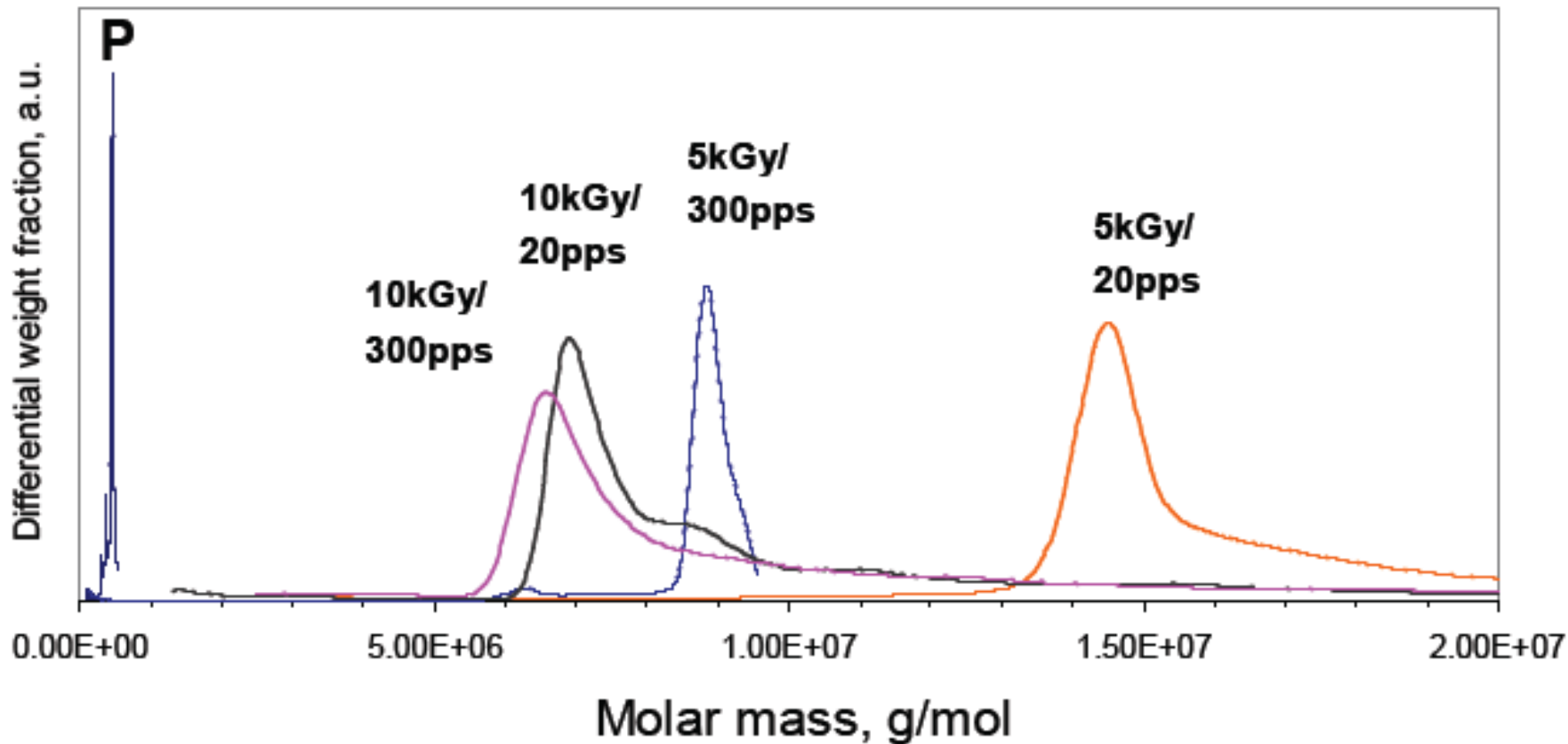
At higher temperatures, interactions of monomers within a polymer chain become more favored due to the disruption of water-polymer hydrogen bonds.

→ Collapsed polymer molecule.

Pulse repetition rate effect on Mw

$c = 0.9 \times 10^{-2} \text{ mol L}^{-1}$

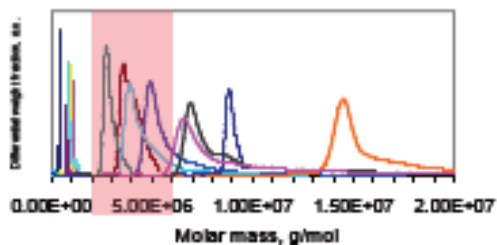
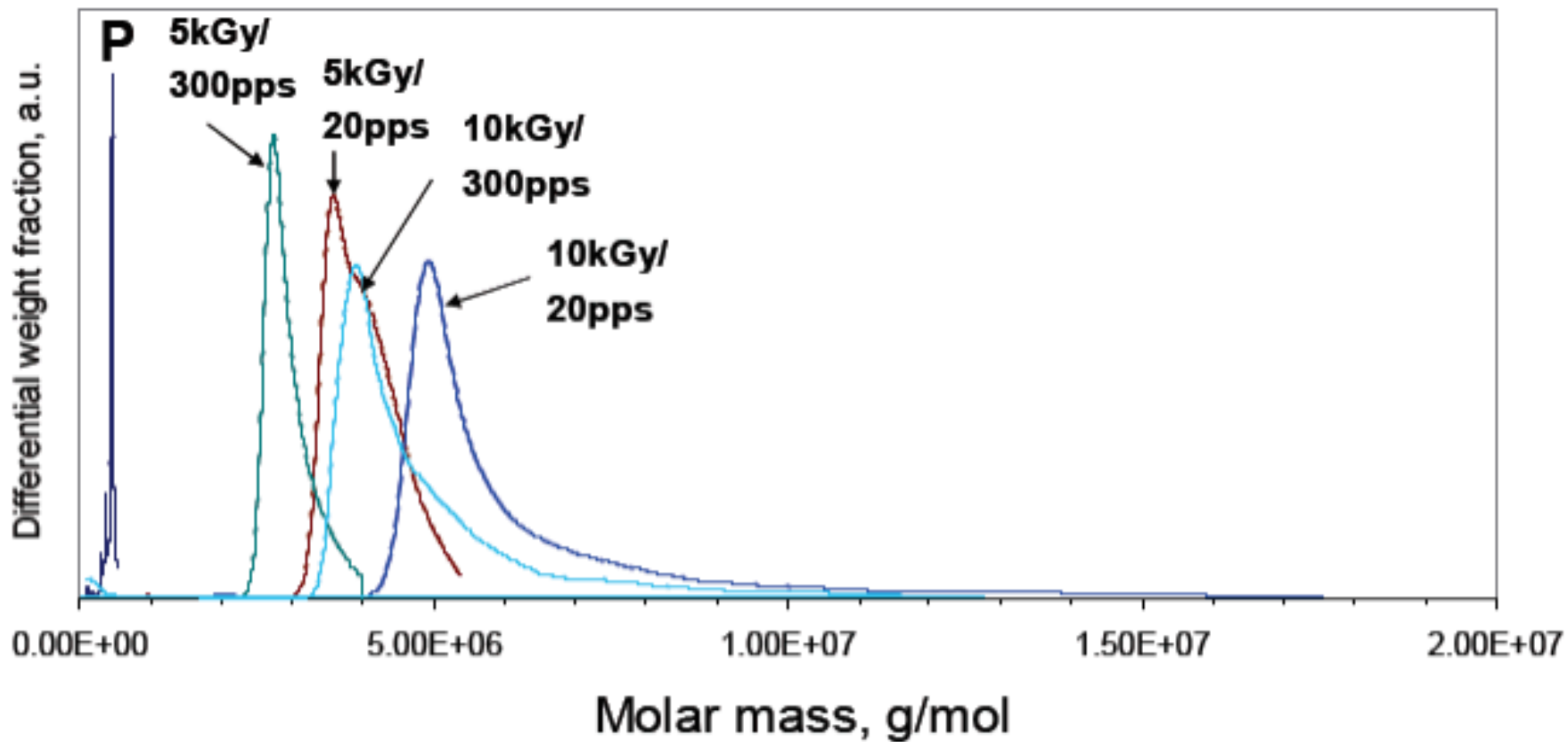
20 °C



Pulse repetition rate effect on Mw

$$c = 0.9 \times 10^{-2} \text{ mol L}^{-1}$$

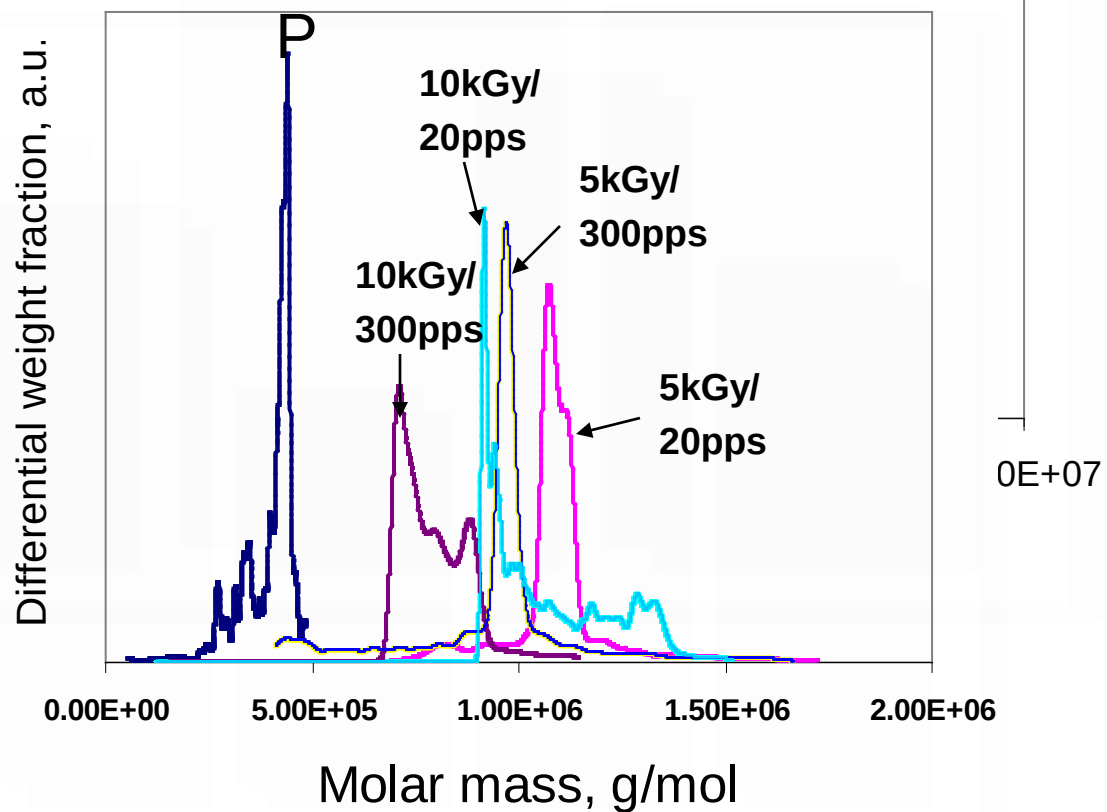
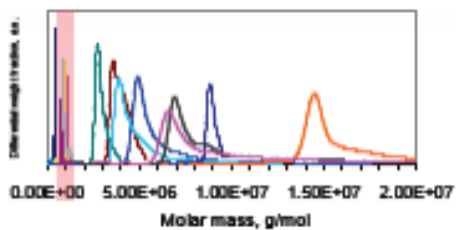
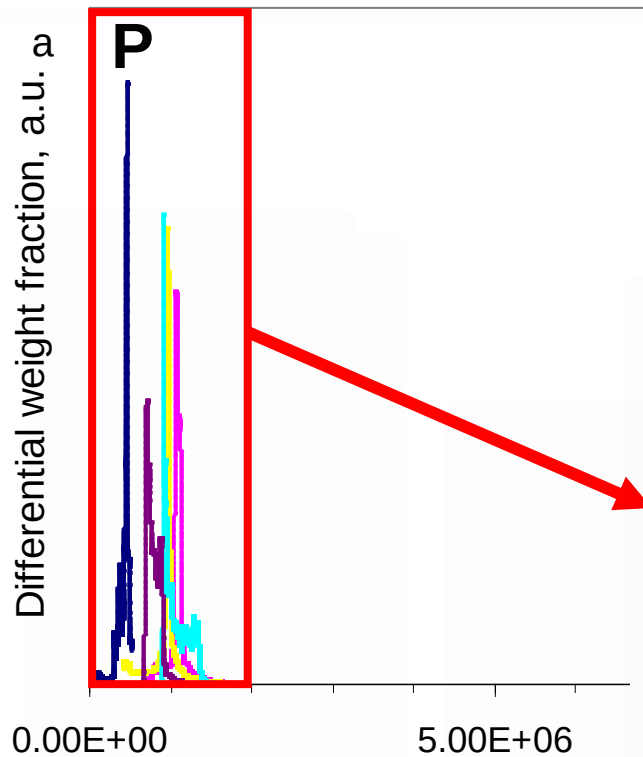
60 °C



Pulse repetition rate effect on Mw

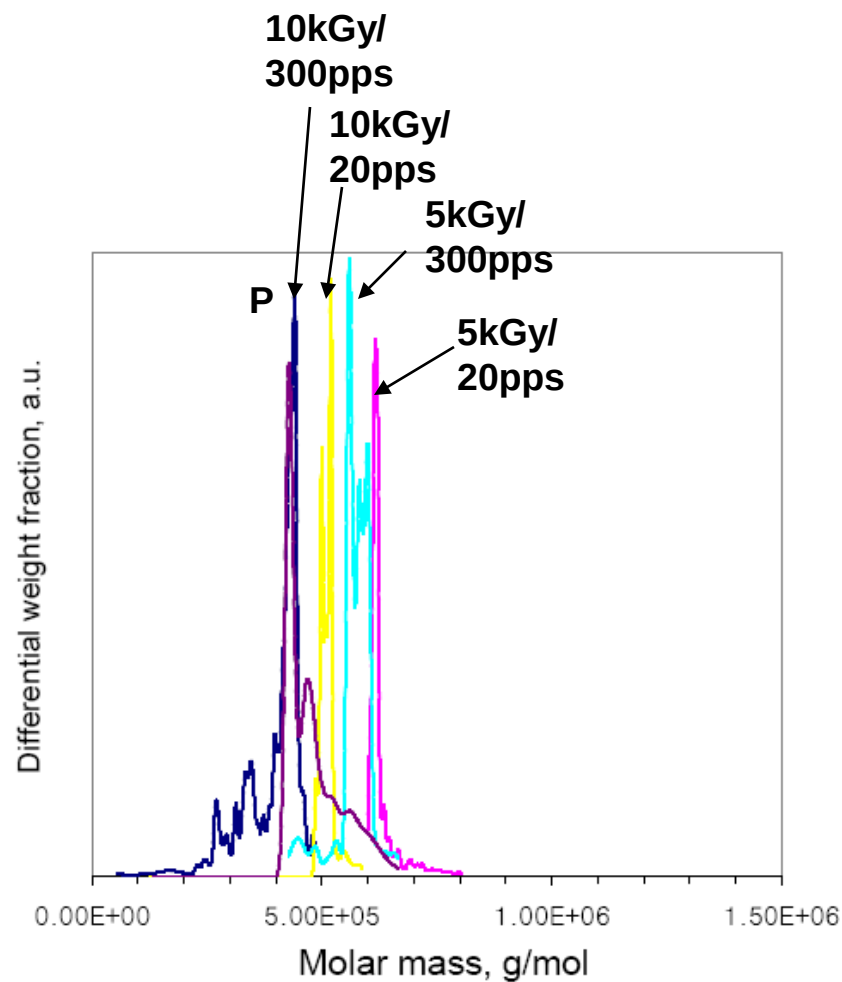
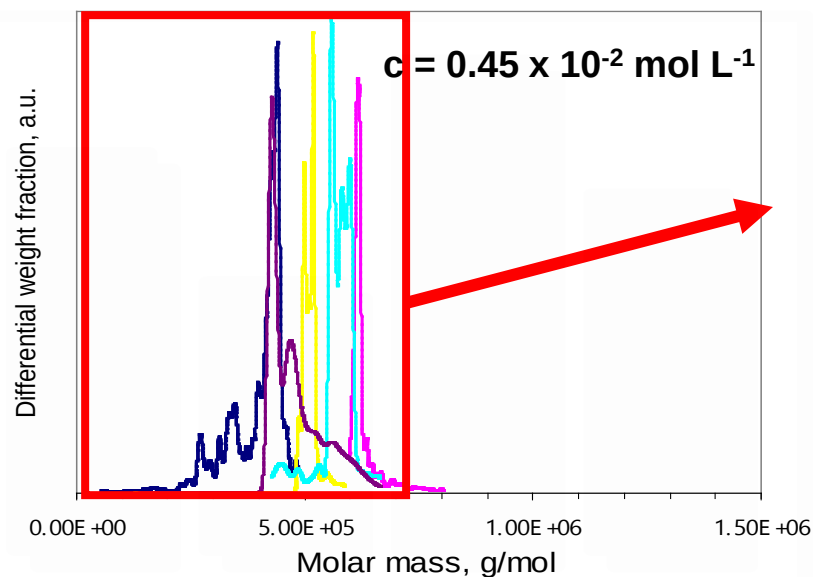
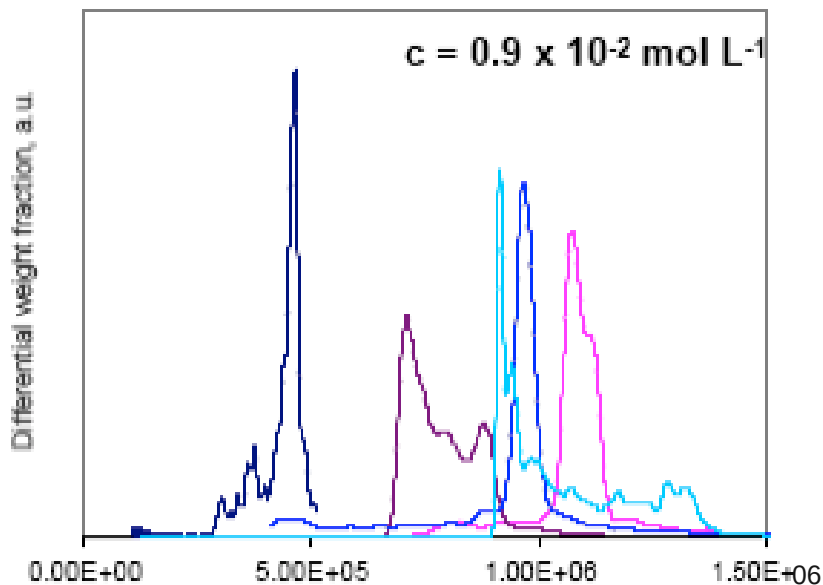
$c = 0.9 \times 10^{-2} \text{ mol L}^{-1}$

77 °C



Concentration effects on Mw

77 °C



The number of inter-molecular crosslinks, c_x (mol L⁻¹)

$$4c_x - c_s = 2c \left(\frac{1}{M_{w,0}} - \frac{1}{M_w} \right) \xrightarrow{\text{if } c_s \approx 0} c_x = \frac{c}{2} \left(\frac{1}{M_{w,0}} - \frac{1}{M_w} \right)$$

Charlesby, A., Atomic Radiation and Polymers, 1960, Oxford: Pergamon Press.

The radiation yield of inter-molecular crosslinking, G_x (mol J⁻¹)

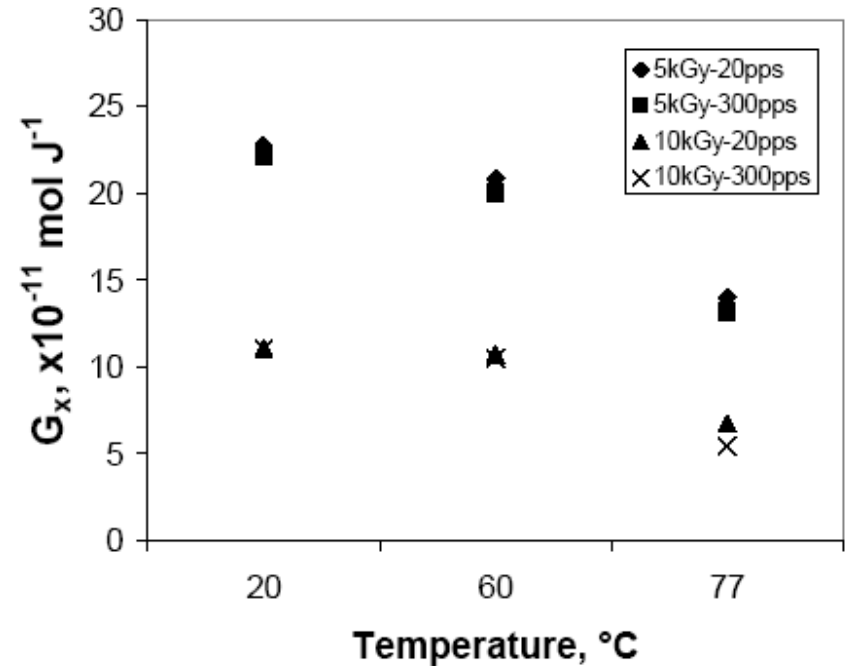
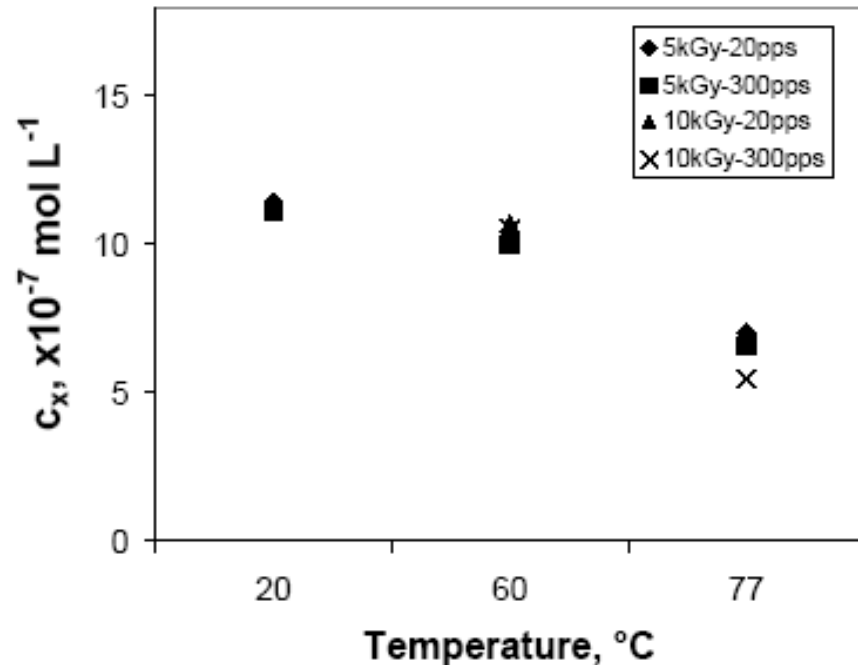
$$G_x = \frac{c}{2Dd} \left(\frac{1}{M_{w,0}} - \frac{1}{M_w} \right)$$

Table Crosslinking parameters (c_x , G_x) of the synthesized PVP product at different concentrations; irradiation temperature = 77 °C.

		c_x ($\times 10^{-7}$ mol L $^{-1}$)		G_x ($\times 10^{-11}$ mol J $^{-1}$)	
Concentration (mol L $^{-1}$)		0.0045	0.009	0.0045	0.009
Dose (kGy) / Pulse repetition rate (pps)	5 / 20	1.96	7.00	3.92	14.00
	5 / 300	1.48	6.58	2.96	13.15

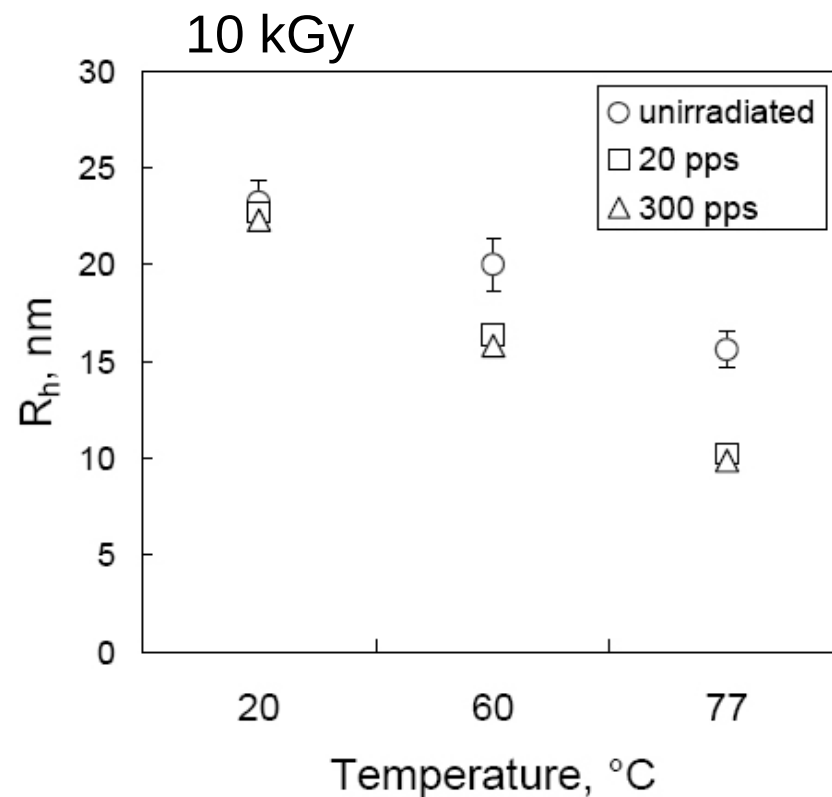
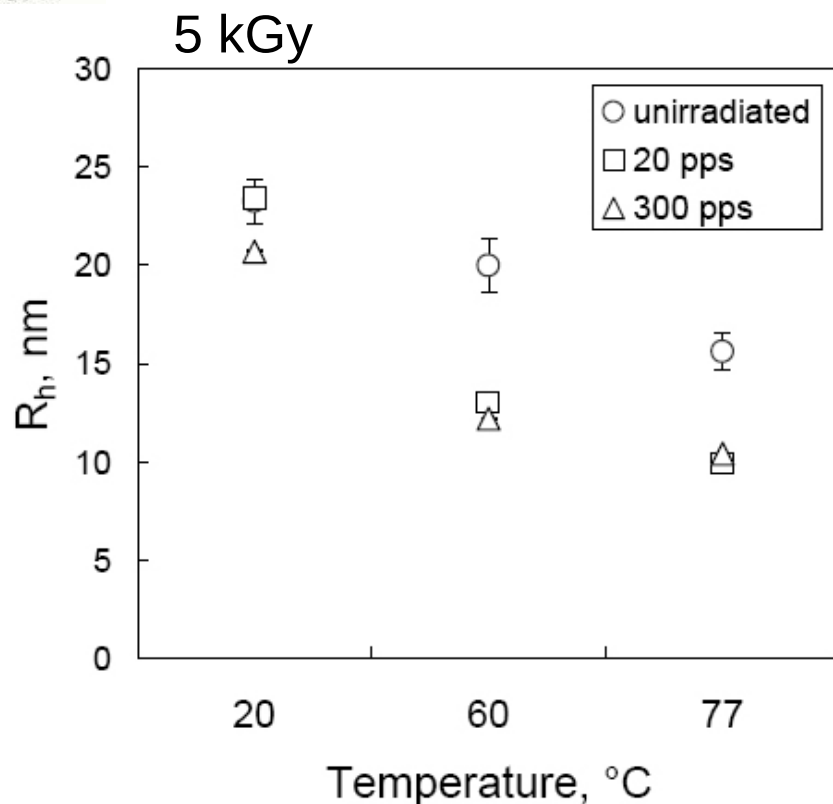
The number of inter-molecular crosslinking bonds in a unit volume of sample is much less at 0.45×10^{-2} than that at 0.9×10^{-2} mol L $^{-1}$ thereby yielding lower molecular weight. (lower radiation yield of inter-molecular crosslinking, G_x)

Crosslinking parameters (c_x , G_x)



1. The c_x & G_x values decrease as temperature increases
 $\rightarrow$ promoted intra-molecular crosslinking reactions.
2. High pulse repetition rate (300 pps)
 $\rightarrow$ Reduced inter-molecular crosslinking reactions.

Parameter (T, pps) effects on Rh



1. High temperature irradiation → smaller Rh.

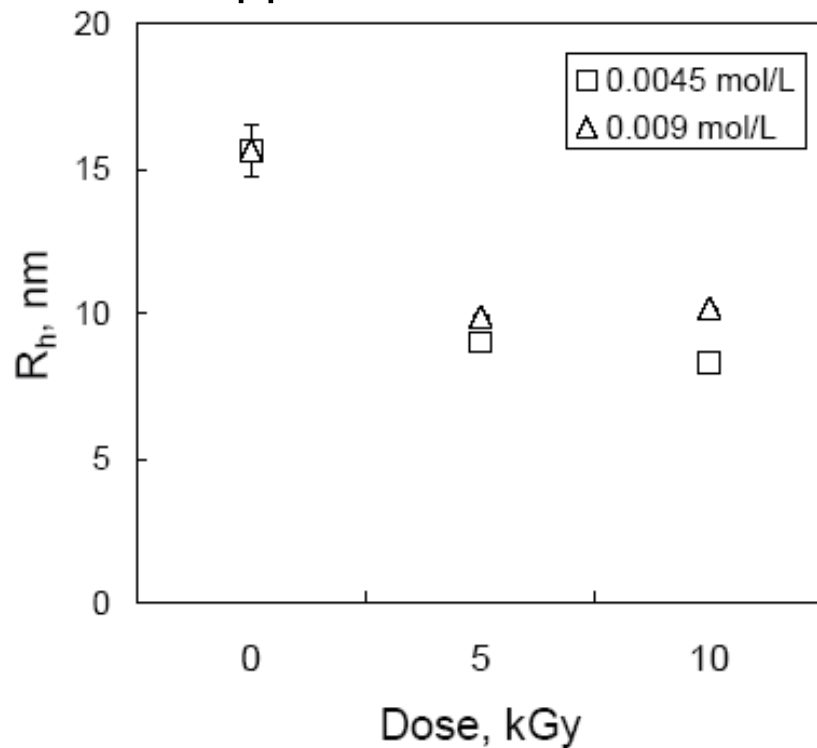
2. High PPS → smaller Rh.

; More # coexisting C-centered free radicals in the same chain per unit time.

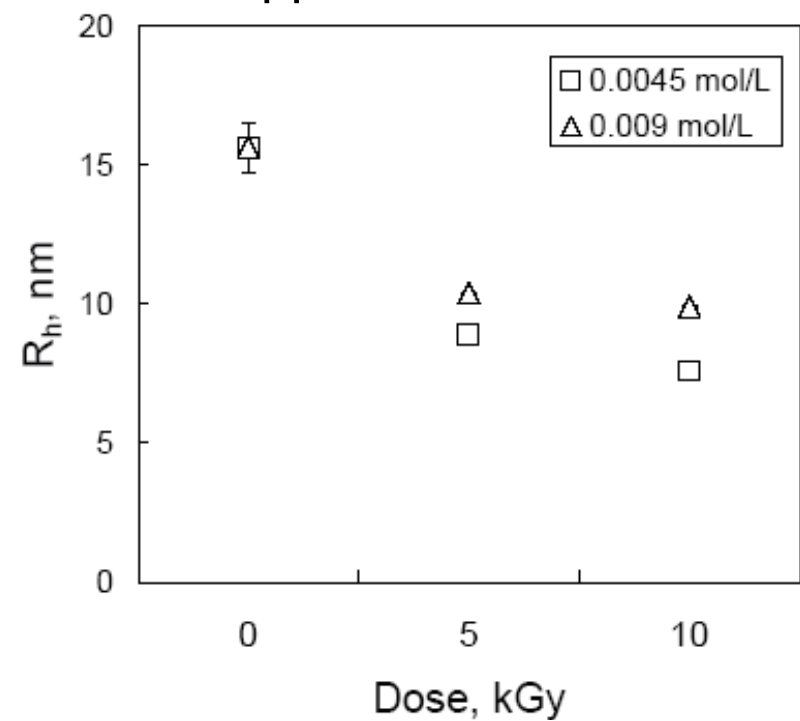
→ Promoted intra-molecular radical-radical recombination rather than diffusion-driven inter-molecular radical reaction.

Concentration effect on Rh

20 pps



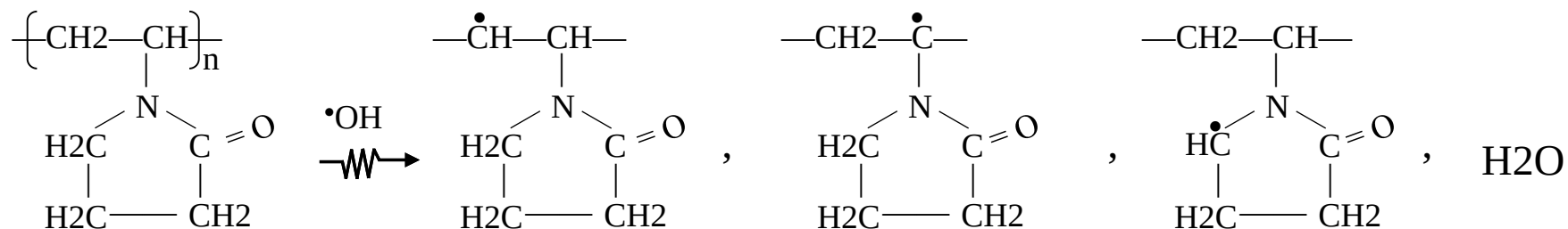
300 pps



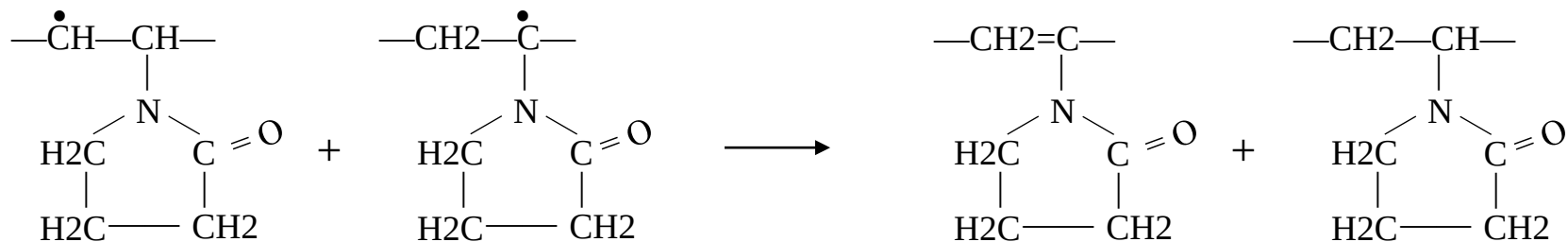
Lower conc. ($0.45 \times 10^{-2} \text{ mol L}^{-1}$) $\rightarrow$ smaller Rh
 ; Promoted intra-crosslinking reactions at lower solution concentration.

Proposed Mechanism for Enol Formation

Hydrogen abstraction from PVP by hydroxyl radical:

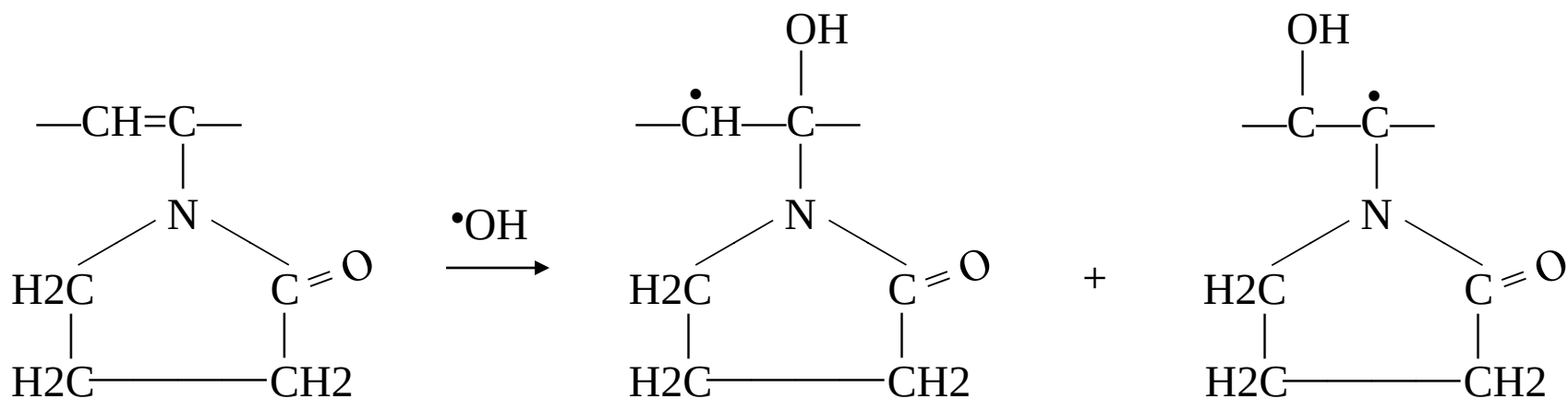


Disproportionation termination of PVP backbone radical:

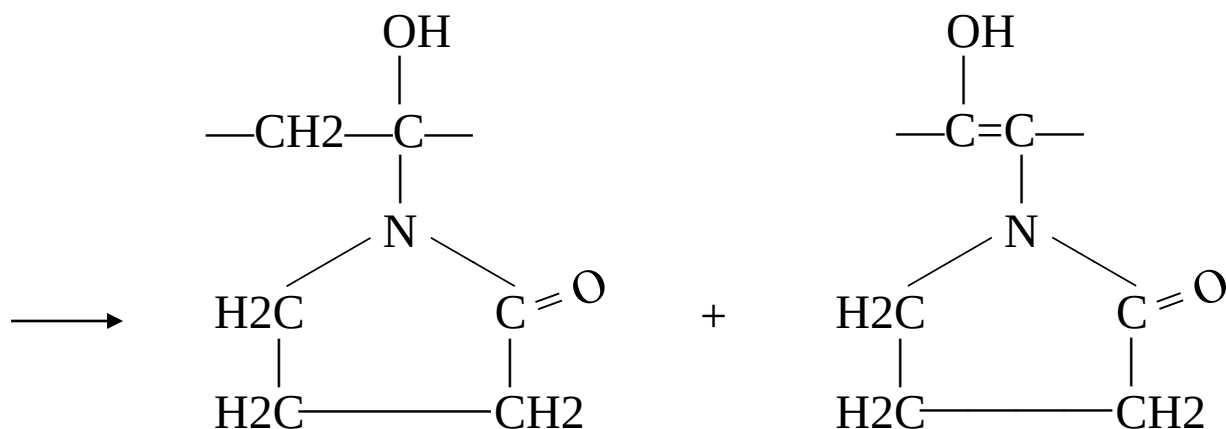


Proposed Mechanism for Enol Formation

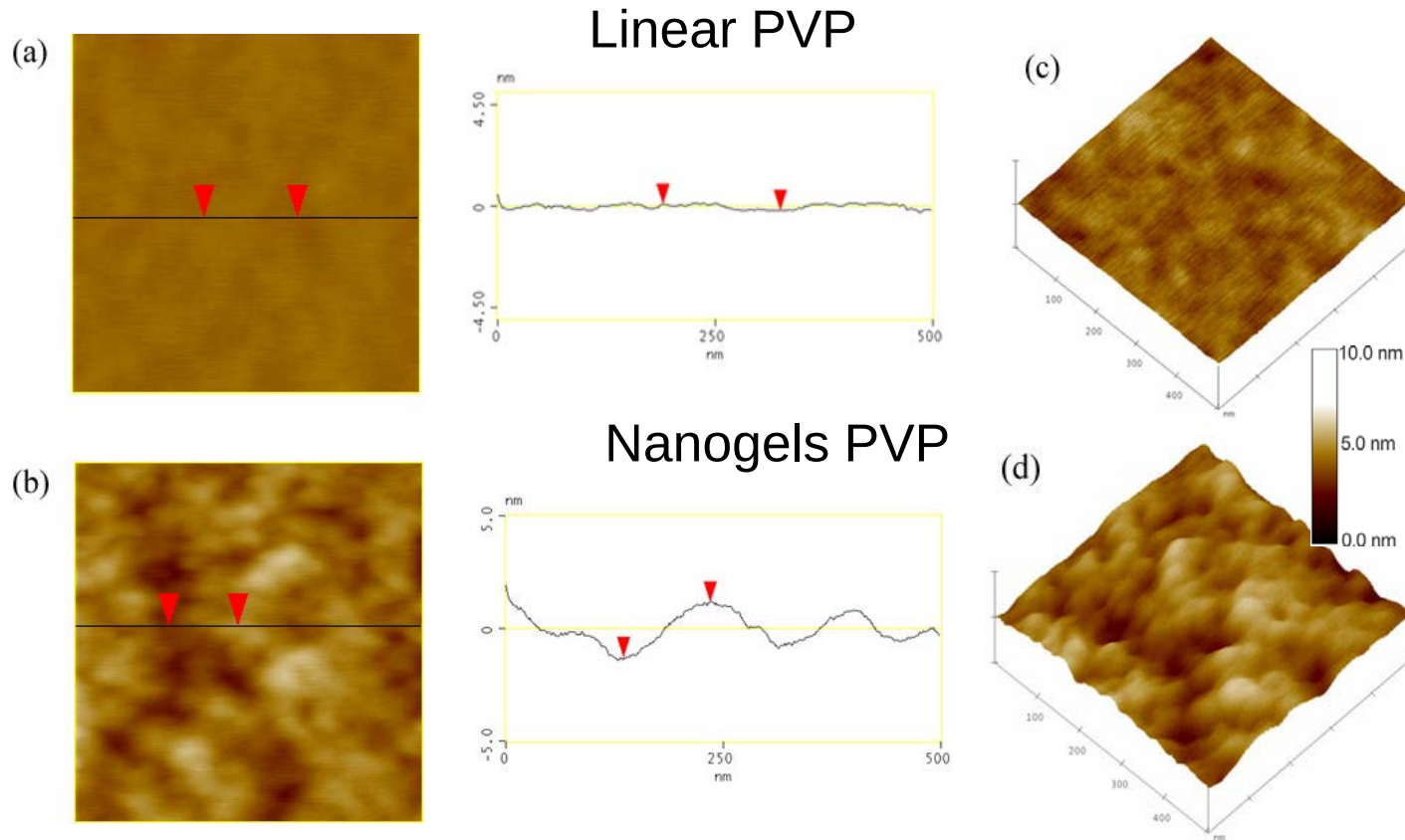
Formation of PVP-OH radical adduct:



Formation of enol:



Topographical observations of nanohydrogels by AFM



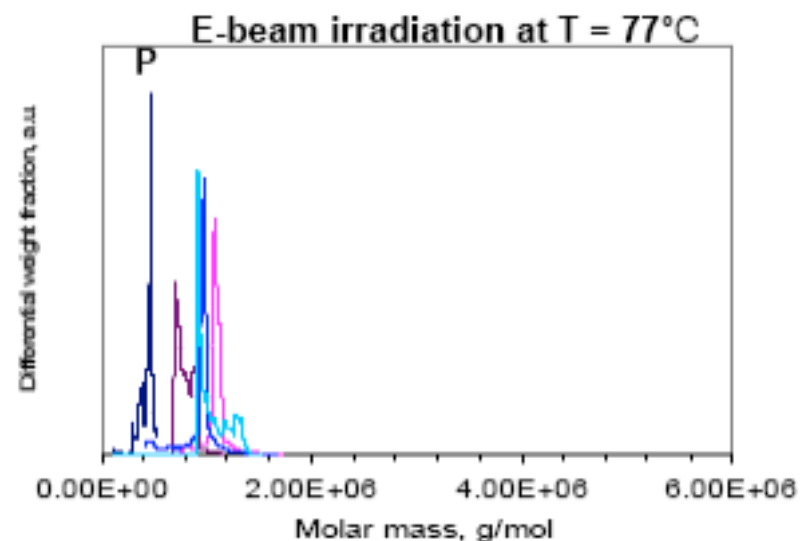
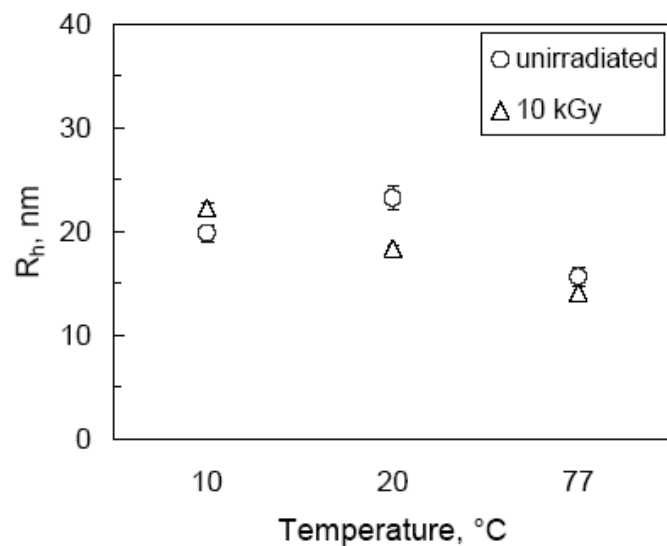
PVP aqueous solutions (unirradiated & nanohydrogel) cast on mica. Unirradiated sample (linear chain) shows flat surface morphology. **Nanohydrogels show spherical contour of surface.**

Conditions in steady-state gamma radiolysis

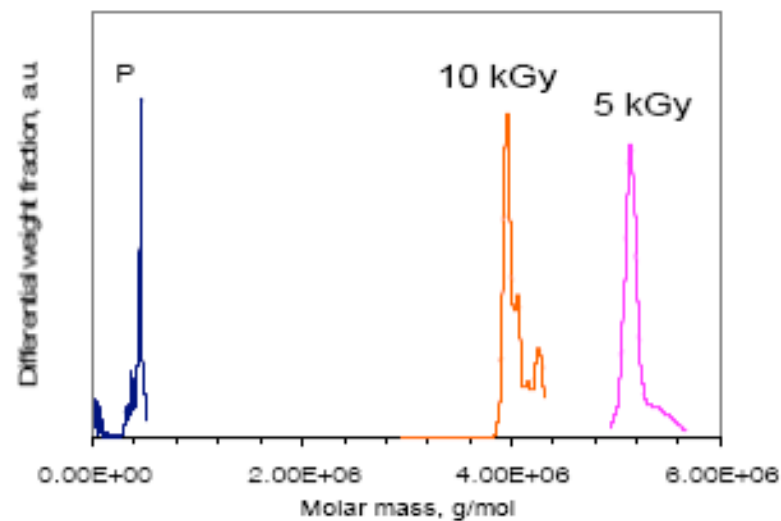
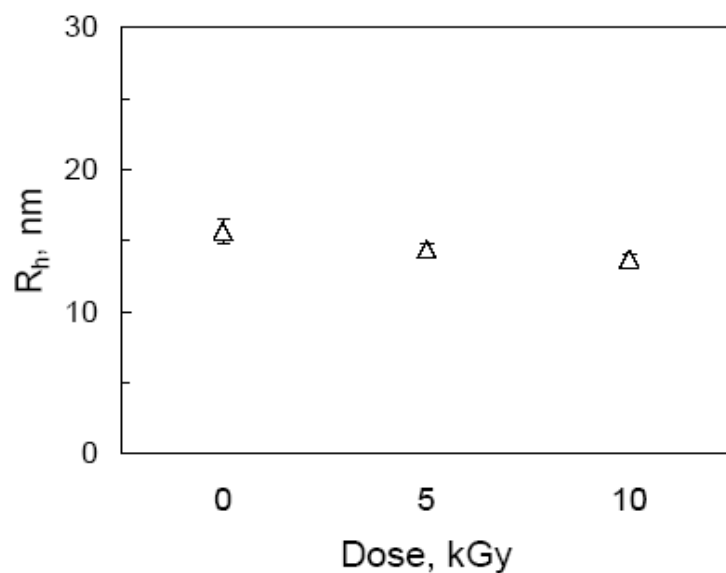
Temperature of PVP aqueous solution, °C	10, 20, 77
Total irradiation dose, kGy	5, 10
Solution concentration, mol L ⁻¹	0.9 x 10 ⁻²
Average dose rate, Gy s ⁻¹	0.97
Solution pH	7 – 7.5

All solutions are saturated with N₂O prior to irradiations

Parameter (T, dose) effects on Rh, Mw

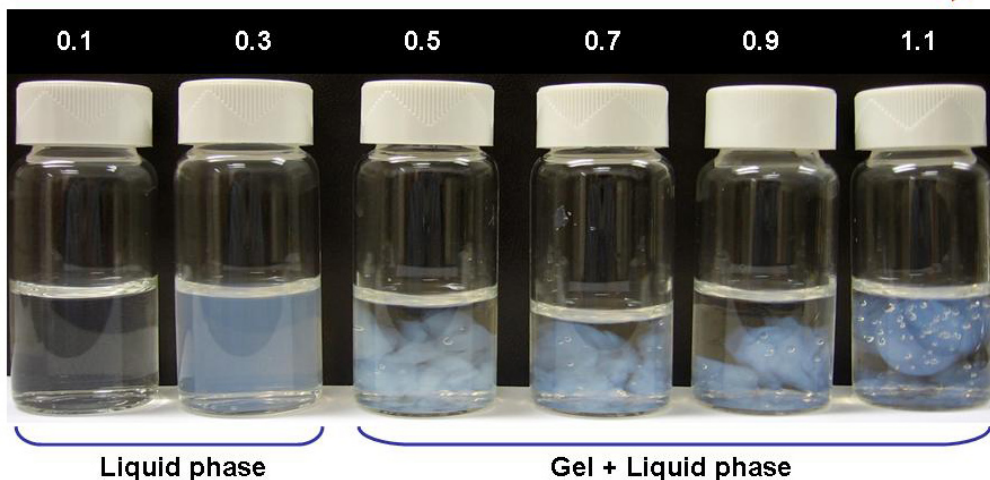


Irradiation $T = 77^\circ\text{C}$



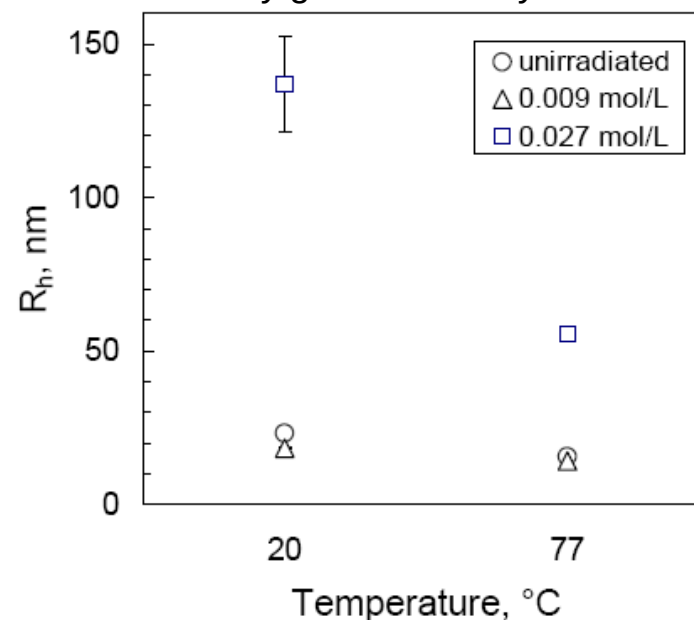
Concentration effect on Rh

PVP concentration (wt%)



10 kGy gamma-radiolysis at 20 °C

10 kGy gamma-radiolysis



- 0.3 wt% (2.7×10^{-2} mol L⁻¹) sample transformed into an opaque liquid after irradiation.
; Greater amount of inter-molecularly crosslinked PVP particles with larger Rh.
- 0.3 wt% sample irradiated at high temperature (77 °C) yielded a smaller R_h (55.4 ± 0.7 nm) than those prepared at 20 °C ($R_h = 136.8 \pm 15.6$ nm).
; Collapsed conformation at high T → more densely crosslinked structure with smaller Rh.



Outline

I. Introduction.

II. Backgrounds.

III. Nanohydrogels synthesized by ionizing radiations.

IV. Kinetic studies of PVP radical-radical reaction.

IV-a. Absorption spectra of transient species.

IV-b. Reaction rate constant for polymer radical reactions.

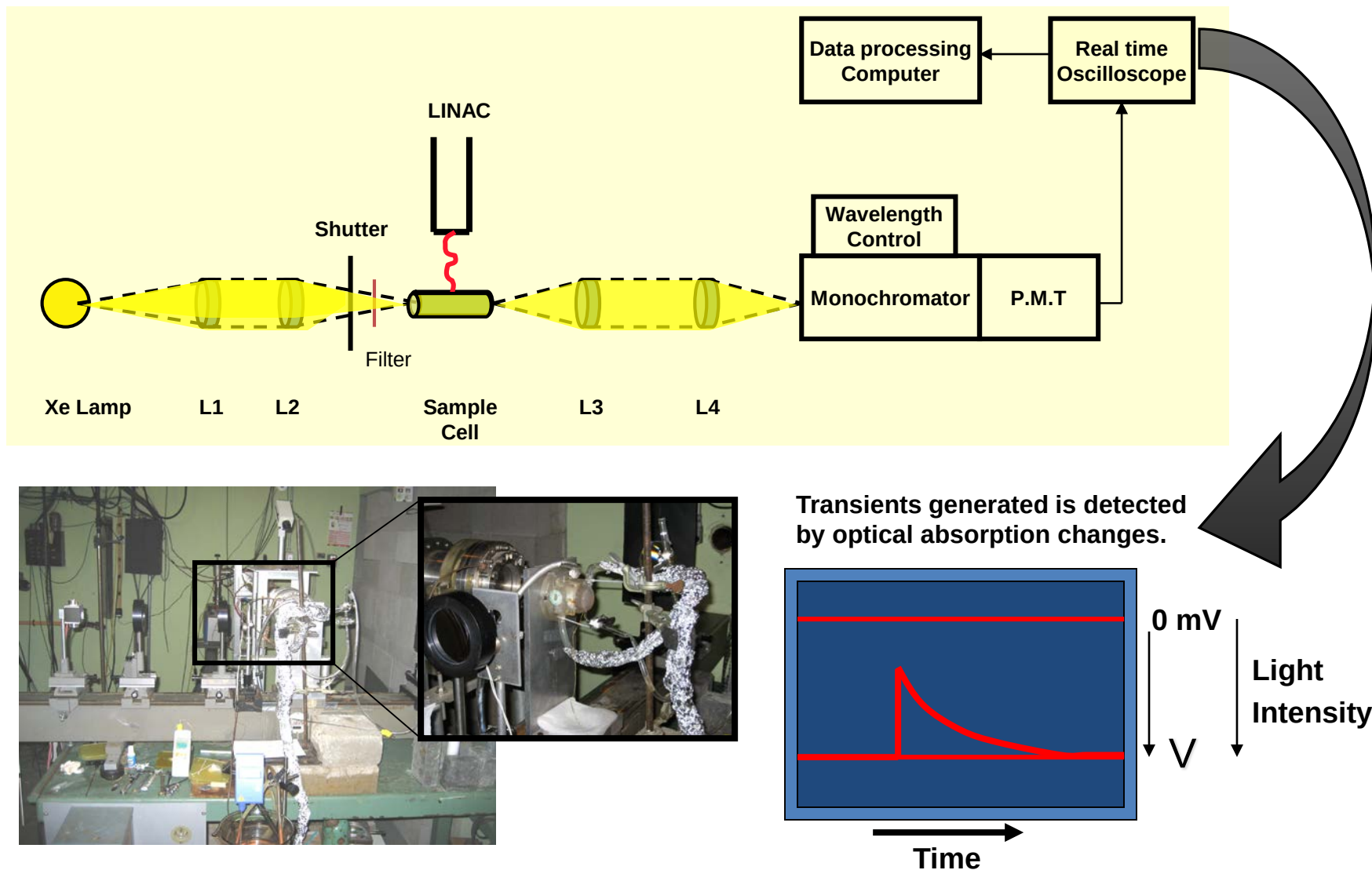
IV-c. Activation Energy of radicals decay.

**V. Nano-template assisted ionizing radiation for
nanohydrogel synthesis.**

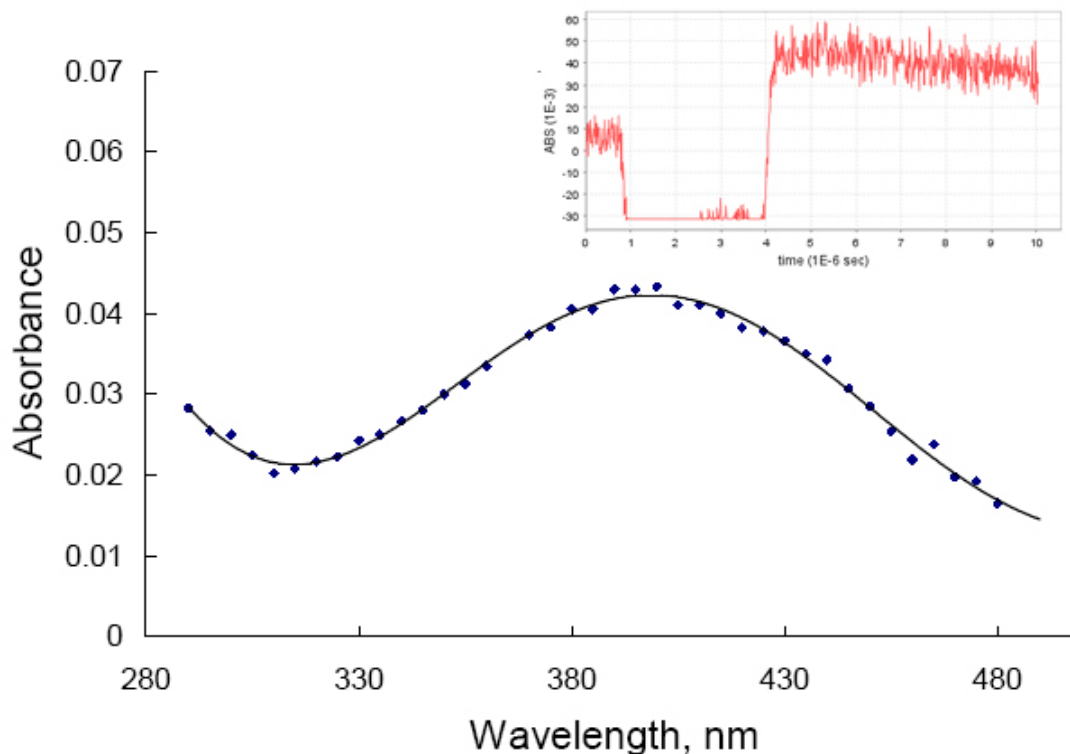
VI. Conclusions.

Pulse radiolysis analysis

Fast chemical reaction kinetics (rate constant, k) & radiation yield (G-value) can be studied in micro to nano second range.



Absorption spectra of transient species of PVP

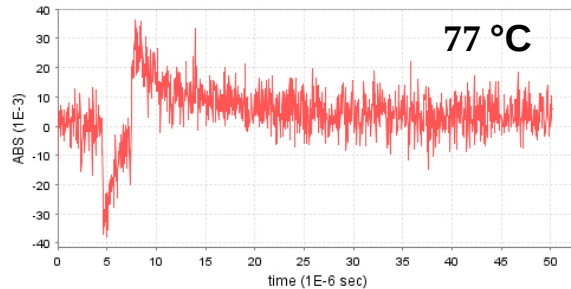
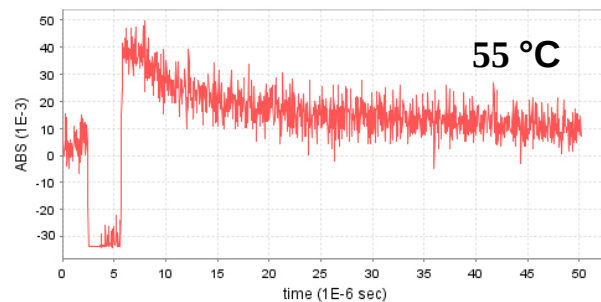
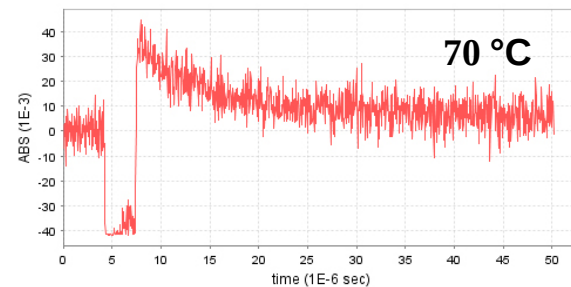
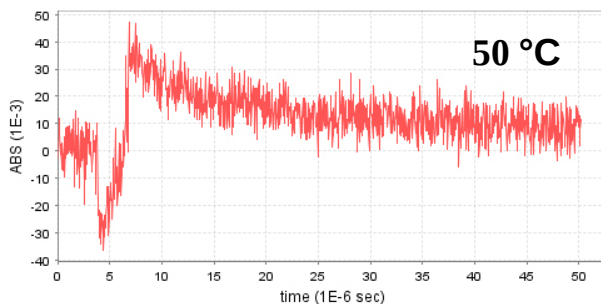
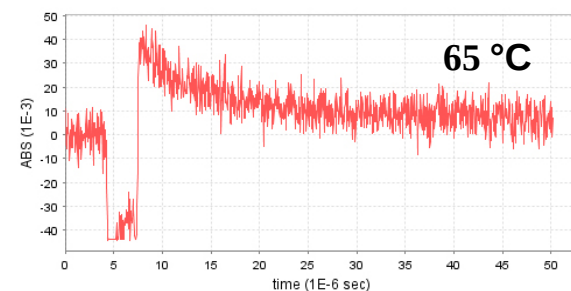
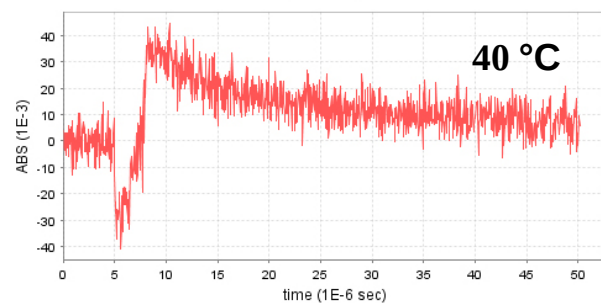
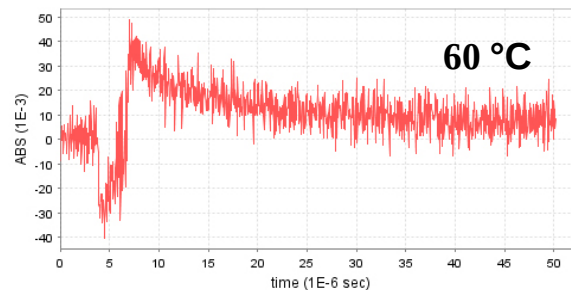
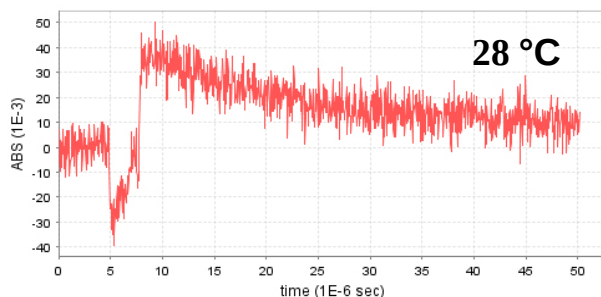


The molar absorption coefficient at 390 nm ($\epsilon_{390 \text{ nm}}$) at 25 °C

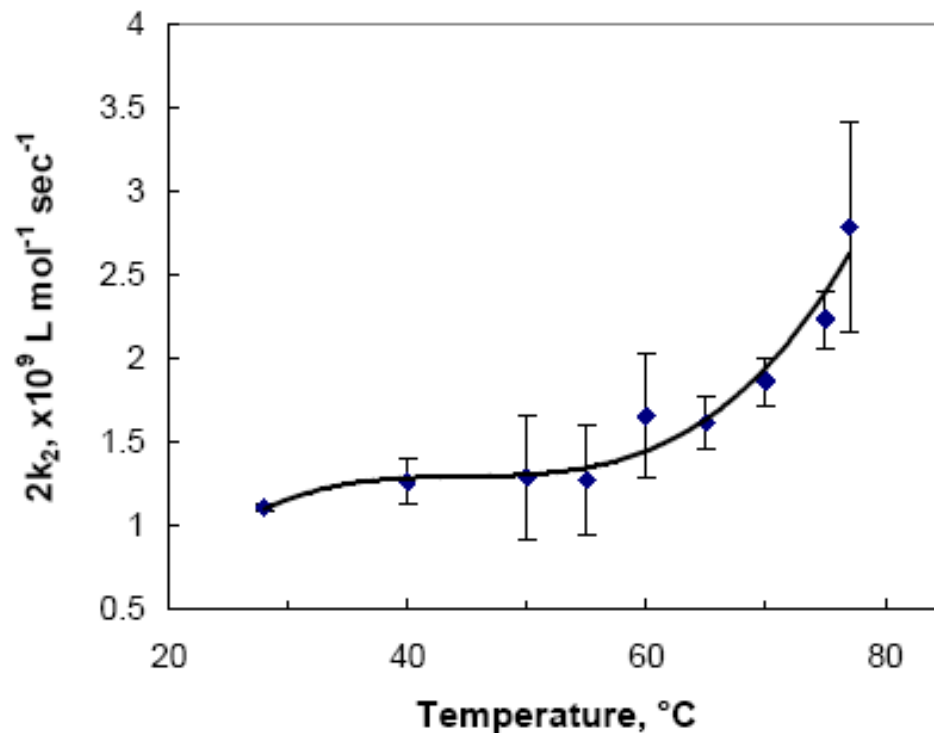
$$\epsilon_{390 \text{ nm}} = \frac{\Delta A \times N_A}{D \times G \times l} \quad \longrightarrow \quad \epsilon_{390 \text{ nm}} = 510 \pm 30 \text{ L mol}^{-1} \text{ cm}^{-1}$$

where D is dose (Gy), ΔA is absorbance difference, N_A is Avogadro's number, G is G-value of (PVP-H) $\bullet$ formed during pulse radiolysis (i.e., 0.62 $\mu\text{mol J}^{-1}$) and l is optical path length of the cell (1 cm)

Bimolecular decays of (PVP-H) $\cdot$ radicals at various T



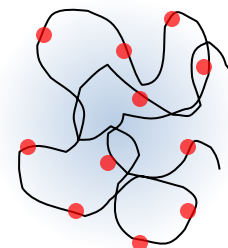
Change of $2k_2$ as a function of temperature



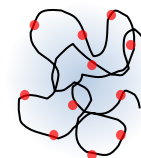
At high temperatures (55 – 77 °C), inter-distances of the radiolytically generated carbon-centered radicals on a same chain is expected to decrease than those at low temperatures (28 - 55 °C) because of the collapsed chain conformation.

→ Faster $2k_2$ in the high T region.

Low T (28 – 55 °C)

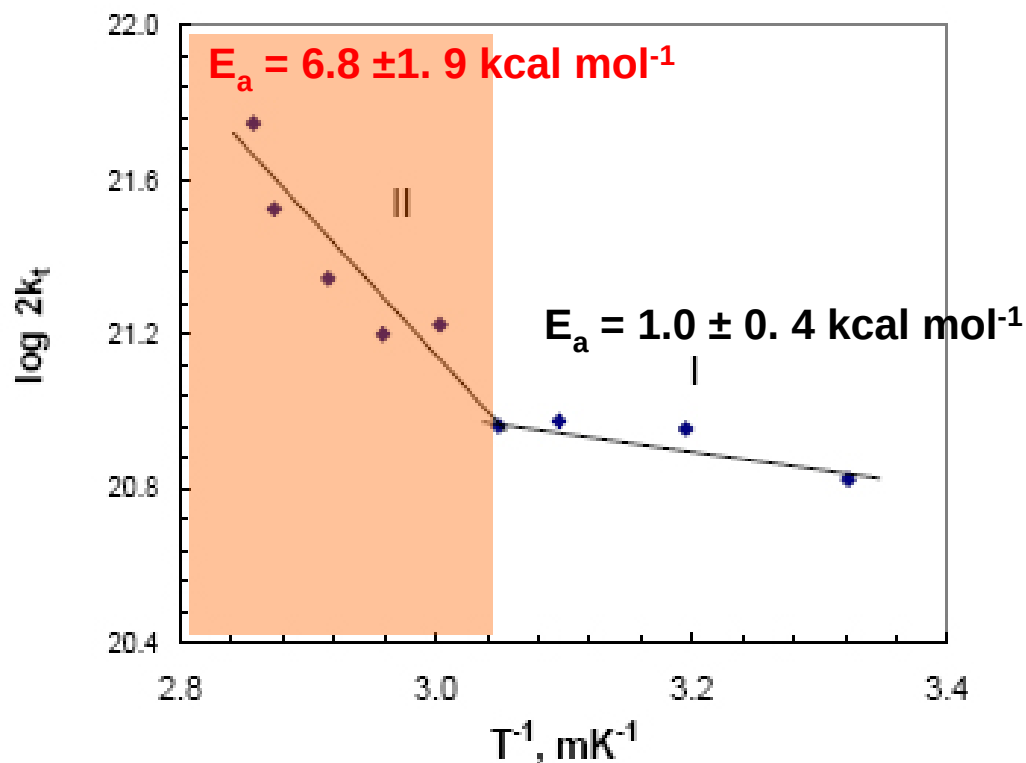
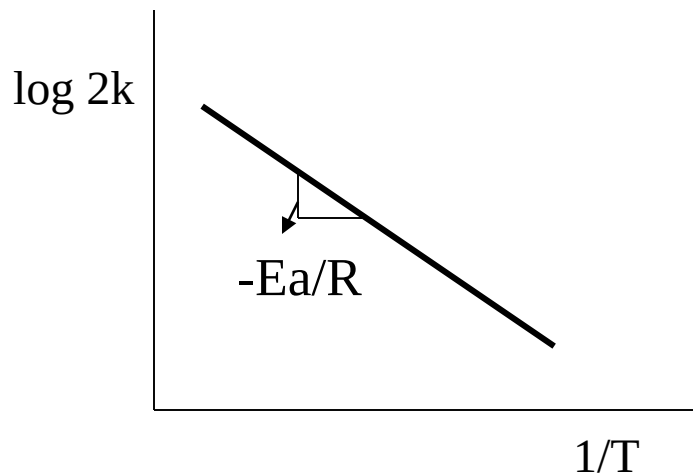


High T (55 – 77 °C)



Activation energy of radical decay

$$k = k_0 e^{-E_a/RT}$$



At the higher temperature range of 55 - 77 °C, the mobility of polymer segments having less hydrogen bond with water is expected to reduce
 → E_a for polymer radical-radical recombination reactions is increased.



Outline

I. Introduction.

II. Backgrounds.

III. Nanohydrogels synthesized by ionizing radiations.

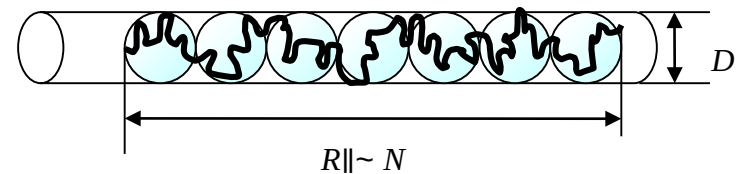
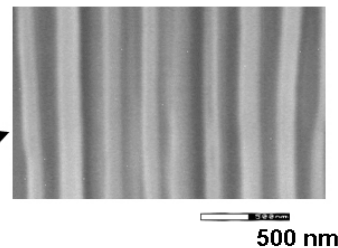
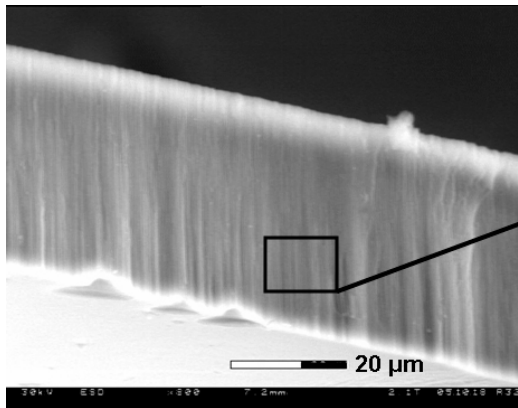
IV. Kinetics studies of PVP radical-radical reaction.

**V. Nano-template assisted ionizing radiation for
nanohydrogel synthesis.**

VI. Conclusions.

Nanoporous membrane as nano-template

1. Efficient and convenient in production of 1D structured nanomaterials.
2. Shape and dimension of nanoscopic polymer materials is easily controlled by treated time, surface chemistry of membrane, temperature, etc.
3. Alumina nanoporous membrane possesses the uniform and straight cylindrical holes with controlled aspect ratio.
4. The behavior of confined polymer chains in a cylindrical pore is generally explained by the biaxial compression model.

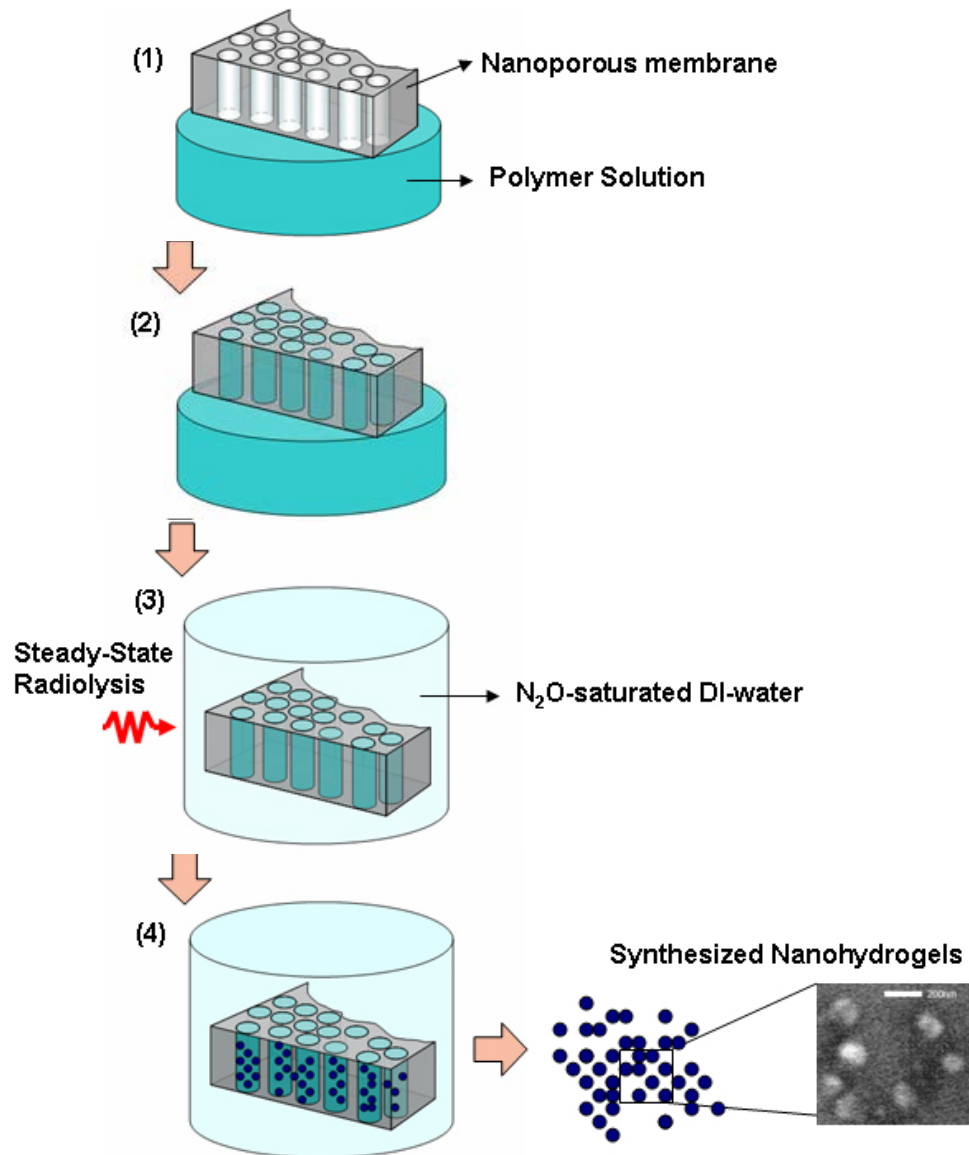


$$R_{||} \approx D \left(\frac{N}{g} \right) \approx \left(\frac{b}{D} \right)^{2/3} Nb$$

ESEM image of the cross section of alumina nanoporous membrane used in this experiment: the average diameter of 200 nm and the height of 60 μm.

Schematic of a real chain confined in a cylinder diameter D .
 N = Number of monomers, b = length of monomer

Procedure of the template-assisted nanohydrogel synthesis

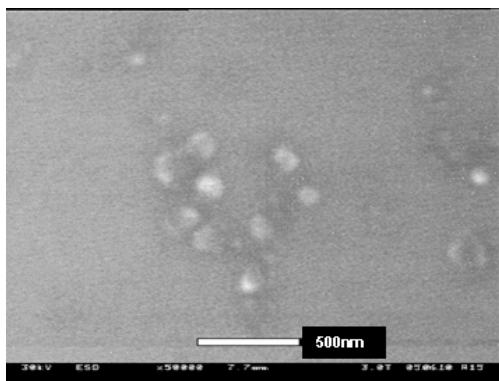
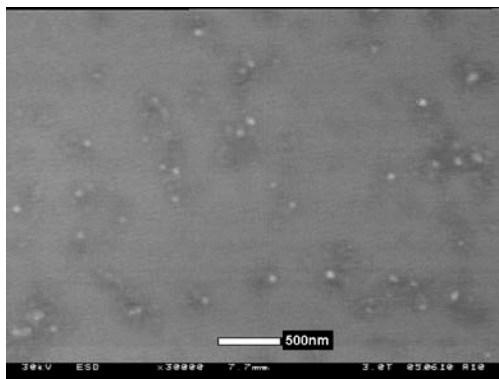


Schematic procedure of the template assisted γ -ray irradiation:

- (1) Contact the nanoporous membrane on PVP aqueous solution.
- (2) Introduce solution into capillaries of the membrane.
- (3) Steady-state ionizing radiation (γ -ray) to produce the crosslinked gel structure in trapped PVP within the capillaries of membrane.
- (4) Separate PVP nanohydrogels from membrane by dissolving in sodium hydroxide solution.

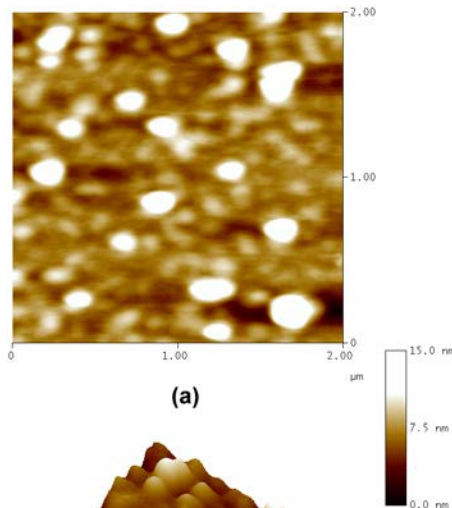
ESEM, AFM, FTIR results

ESEM

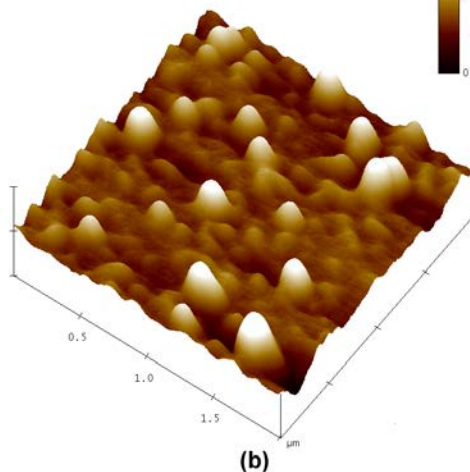


Diameters = 90 – 190 nm

AFM



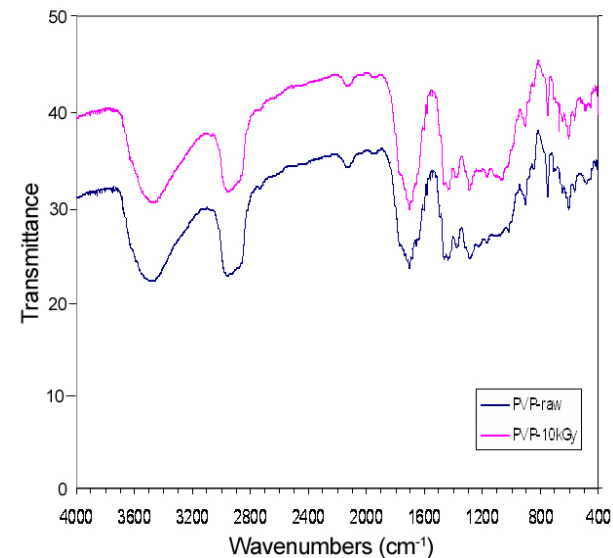
(a)



(b)

Diameters = 95 – 180 nm

FTIR



Unirradiated and irradiated PVP are chemically identical.

wave number, cm ⁻¹	Functional group
1690 3020-2820	Carbonyl at >C(=O)-N- Symmetrical & asymmetrical stretching of C-H in -CH ₂ -
3690-3090 2200-1900	Bound water



Conclusions

1. Combined inter- and intra-molecular crosslinking bonds were observed in the synthesis of PVP nanohydrogels even in dilute system ($c = 0.9 \times 10^{-2} \text{ mol L}^{-1}$) by the influence of chain diffusive motion and PVP chemical structure.
2. Thermally collapsed conformation of chains at high temperature is favorable for intra-molecular crosslinking due to shorter inter-radical distances on the same PVP backbone.
3. High pulse repetition rates of electron beam irradiation preferentially yields smaller intra-molecularly crosslinked nanohydrogel.



Conclusions

4. Faster $2k_2$ were observed in the high temperatures (50 – 77 °C), due to the reduced inter-distances of the radiolytically generated carbon-centered radicals on a same chain (by collapsed chain conformation) than those at low temperatures (28 - 50 °C).
5. High E_a of decay at high temperature is found and can be explained by the motion of individual polymer segment (monomer) requires more energy to overcome the increased friction.
6. Highly ordered cylindrical capillary pore structure in the nanoporous membrane gives the spatial isolation of polymer chains and promotes PVP radical-radical reactions only within the molecules in a same capillary pore.



Acknowledgments

**National Institute of Standards
and Technology (NIST)**



A. JAMES CLARK
SCHOOL OF ENGINEERING

Thank you

