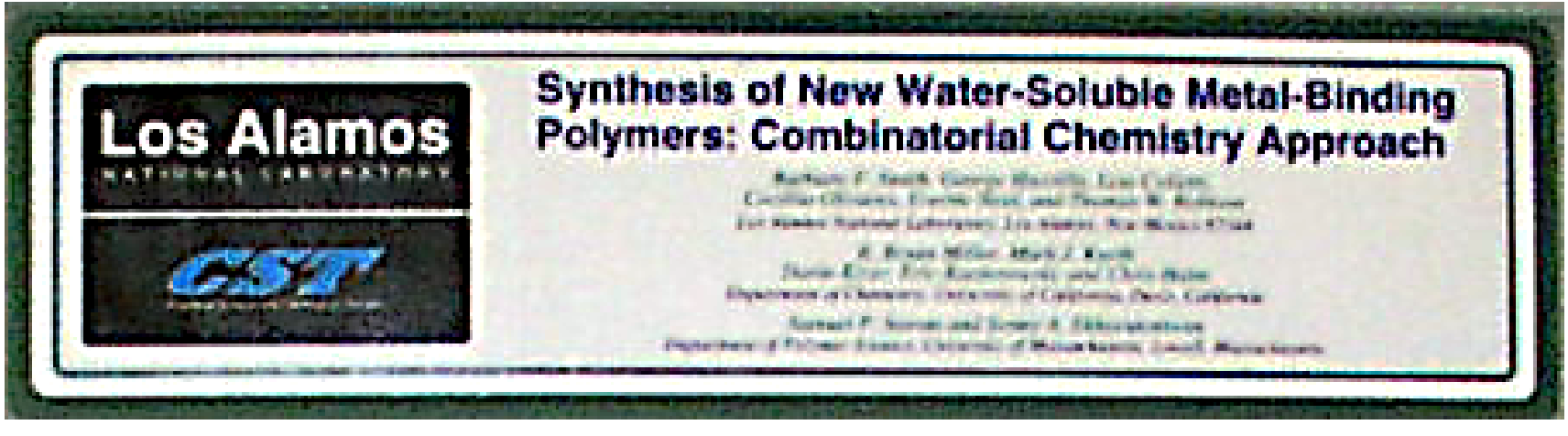

Los Alamos
NATIONAL LABORATORY
CST
Synthesis of New Water-Soluble Metal-Binding Polymers: Combinatorial Chemistry Approach

Background

(1) Synthetic Methods Development

Cartoon of Polymer Filtration™

Pyrazolone Synthetic Studies

Advantages of Polymer Filtration™

- Metal-ion binding in homogeneous solution
- High metal-ion capacities and metal-ion selectivity
- Can blend polymers to bind suites of metal ions
- No requirements on mechanical stability of polymer
- No hazardous organic solvents
- No sludge formation/Colloids do not interfere
- Low energy requirements/low pressure and temperature
- Small footprint/mobile
- Readily scales from bench top to process scale
- Easily meets metal discharge limits

Derivatives of Acylpyrazolones

Research Needs

Research Objective

Mitsunobu and Claisen Reactions of Pyrazolones

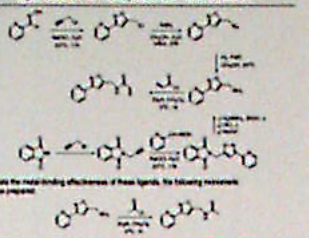
Research Approach

Combinatorial Chemistry

Combinatorial Strategy

Polyisoxazole Synthesis

Synthesis of Acrylamide Monomers



To evaluate the metal-binding effectiveness of these ligands, the following monomeric ligand was prepared:

(2) Rapid Polymer Assaying Techniques

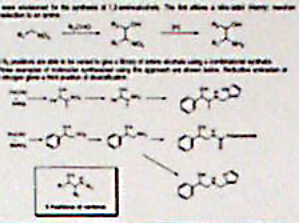
X-ray Microfluorescence spectroscopy (XRF)

- Dried spot methodology:
  - Allows the direct analysis of radioactive and nonradioactive samples using energy dispersive x-ray microfluorescence.
  - Sensitivity increases when liquid is removed.
  - Detection limits approach less than 1 ng in the dried spot.
  - Permits direct analysis of multiple radioactive samples.
  - Metal ions can be measured in the presence of soluble polymers.

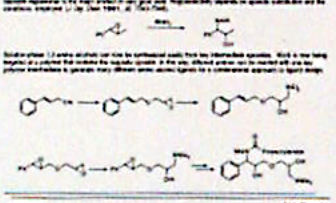
Auto-Radiography/Radiochemistry

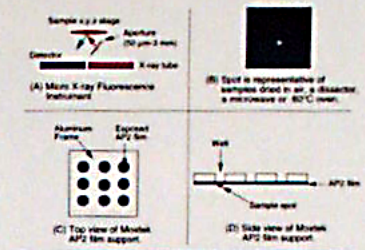
- The target metal ions are radionuclides (particularly Pu and Am).
- Multiple samples will be ultrafiltered on membranes.
- The sample spot is analyzed using a photographic film.
- The density of the exposed film will show the best metal binders.
- Or Ultrafiltration units can be directly counted.

1,2-Aminoalcohols – Synthetic Studies



1,2-Aminoalcohols – Synthetic Studies (cont.)



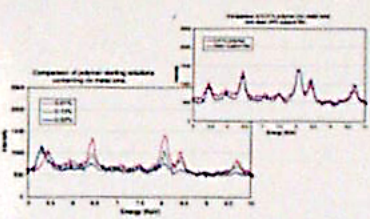


(A) Micro X-ray Fluorescence Instrument

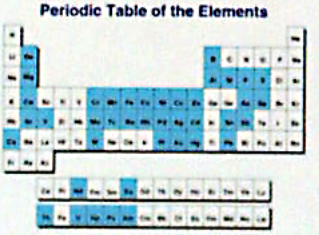
(B) Spot is representative of samples dried in air, a dissector, a microwave or 60°C oven.

(C) Top view of Mostek AP2 film support.

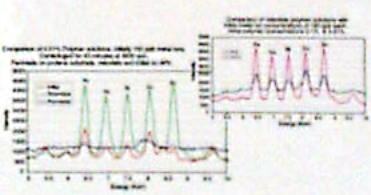
(D) Side view of Mostek AP2 film support.



Periodic Table of the Elements



Metal ions under investigation for recovery/removal using Polymer Filtration™



(3) Polymer Characterization

- Aqueous polymer behavior is in many respects much more difficult to characterize, predict, and evaluate than are organic soluble materials. This is in large part due to the complex nature of water itself, where ionic strength, added ions, pH and temperature all combine to form a very complex environment. Coupling this with the nature of polymeric chelating agents, which are oftentimes ionic, the chemical and physical behavior of such systems can span a wide range. We are employing laser light scattering photometry to evaluate:
  - The change in hydrodynamic volume,
  - Association of polymers,
  - Weight-average molecular weight, and
  - Radius of gyration under conditions of varying pH, temperature, ion strength, and added ions to understand the complex conformational aspects of these systems.

  Basic Principles of light scattering
  - The amount of light scattered is directly proportional to the product of molecular weight and solute concentration.
  - The angular variation of scattered light is directly related to the size of the molecule.
- We are using cadmium NMR to evaluate the metal binding sites on the polymers. We are evaluating the polyamine backbone polymers to baseline the techniques along with some previously functionalized polymers to determine the changes that occur upon functionalization and to develop a database. These capabilities will be transferred to the new polymers as they are discovered in the combinatorial process.

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General Conclusions on Light Scattering Experiments on Modified Polyamine Polymers

General conclusions:

- Light scattering studies provide absolute size and molecular weight characterization of modified polyamine polymers under a variety of conditions that may be employed in "real world" use of these materials.
- Modified polymers behave sufficiently differently under various conditions of pH, ionic salt concentration and concentration that detailed studies of their solution behavior will allow for process optimization under a variety of use conditions.
- Modified polymers do show aggregation under certain conditions leading to higher effective molecular weights and particle sizes. Such insight may allow for better optimization of the retention of polymer under use conditions.

Specific conclusions:

- The character of the aqueous solution in which the polymer is dissolved is very important in the measurement of the weight-average molecular weight of the polymer, e.g. an ionic polymer dissolved in a non-ionic solvent leads to polymer aggregation, increasing the salt concentration effectively increases the amount of single polymer chains.
- For the functionalized polyamines (PEIC and PEIP), the observed molecular weight decreases as the % functionalization increases. This suggests that more highly modified polymers do not form aggregates as may occur more readily with lesser modified polymers.
- Increasing the polymer concentration allows for more polymer aggregation, effectively raising the observed molecular weight of the polymer.
- Better solvents, as indicated by the second viral coefficient, correlate with decreased polymer aggregation.
- pH effects solution properties in a complex manner consistent with the ionic nature of the polymers.

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Basic Light Scattering Equation

$$K^*C/R(\theta) = 1/MP(\theta) + 2A_2C$$

Where:

$K^* = 4\pi^2(dn/dc)^2 n_0^2/(N_A \lambda_0^4)$

C is the concentration of the solute molecules (g/ml).

R(θ) is the fraction of light scattered, relative to the incident beam.

N_A is Avogadro's number.

λ_0 is the wavelength of light.

Dn/dc is the refractive index increment, which tells how much the refractive index of the solution varies with solute concentration.

M is the weight-average molecular weight.

A_2 is the second viral coefficient (a measure of solvent-solute interaction), not used for chromatographic calculations due to typically low values of z.

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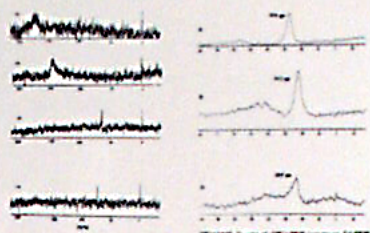

The ^{13}C-PEIC complex NMR spectra of different levels of functionalization of PEIC (Carboxyl-modified PEI), where (1) 20% (2) 50% (3) 75% and (4) 100% functionalized.

^{13}C-NMR spectra of ^{13}C-PEIP complexes. Cd-PEIP complexes have chemical shifts of (1) 139.88 ppm for Cd-PEIP (1.25 complex), (2) 114.12 ppm for Cd-PEIP (5.25 complex) and 118.87 ppm for Cd-PEIP (5.75 complex).

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Zimm Plot

Plot K^*C/R_0 vs $\sin^2(\theta/2) + kc$,
where k is chosen for scaling the data

$\theta = 0$, line gives A_2
$C = 0$, line gives $\langle rg^2 \rangle$
$\theta = 0$, $C = 0$, point gives Mw

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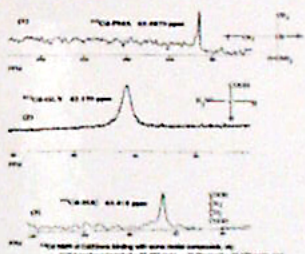

^{13}C-NMR of Cadmium binding with some metal complexes, (A) 1) Polyethylenimine (MW = 95.497 ppm), 2) Diaminoethane (MW = 60.175 ppm), and 3) Sulfonic acid (MW = 65.418 ppm).

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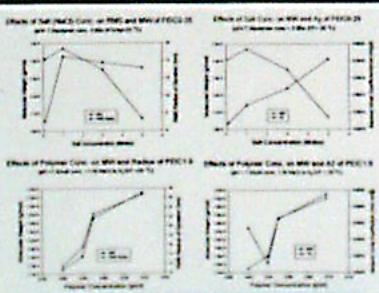

Effects of Salt (NaCl) Conc. on RMS and MW of PEIC(1.25 ppm Chemical conc. 1.0 Mw of PEIC (1.75)

Effects of Salt Conc. on MW and Ag of PEIC(1.25 ppm Chemical conc. 1.0 Mw of PEIC (1.75)

Effects of Polymer Conc. on MW and Radius of PEIC(1.5 ppm Chemical conc. 1.0 Mw of PEIC (1.75)

Effects of Polymer Conc. on MW and A2 of PEIC(1.5 ppm Chemical conc. 1.0 Mw of PEIC (1.75)

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^{13}C-NMR spectra of Cadmium bound to EDTA (B = 85.89 ppm) and PANAM-3.5E dendrimer (B = 116.89 ppm).

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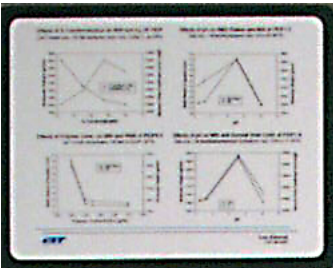
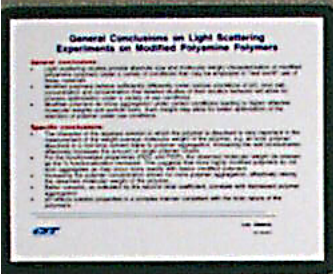


(4) Small Ultrafiltration Equipment

Solid Supports for Synthesis

- Solid phase synthesis is a marriage to both peptide and split synthesis
- The solid phases can be resin beads, solid polymeric films, or ceramics
- Some phase synthesis is necessary for rapid purification of intermediates (ability to use excess reagents to force reactions to completion)
- Drawback of solid phase synthesis:
  - Of the thousands of organic synthetic reactions developed, only ca. 100 have been adapted to work under solid phase conditions
  - Solid / solid / solid interfacial
  - Two phase reactions are difficult with resin-based synthesis



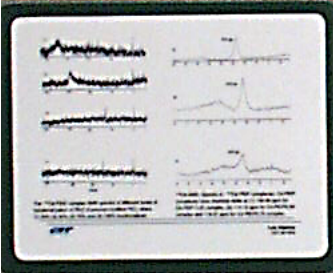
General Conclusions on Light Scattering Experiments on Modified Polyamine Polymers

General conclusions:

- Light scattering studies provide absolute size and molecular weight characterization of modified polyamine polymers under a variety of conditions that may be employed in "real world" use of these materials
- Light scattering studies successfully differentiate between various chemistries of ionic and nonionic polymers and concentrations that maximize the effect of their solution behavior and allow for optimization of their performance in a variety of real world applications
- Light scattering studies can be applied to a variety of solution conditions (pH, ionic strength, temperature, etc.) to optimize polymer performance. Such studies may allow for better optimization of the polymer for its application under real conditions

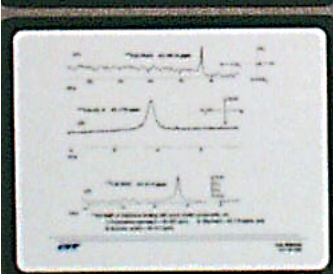
Specific conclusions:

- The chemistry of the epichlorohydrin/ammonia which the polymer is described is very important to the molecular weight and size of the polymer. Molecular weight of the polymer may be more polymer dependent on the ammonia content relative to epichlorohydrin
- Polymers with high ammonia content (polymer A) have a high molecular weight and are highly branched. Increasing the ammonia content further (polymer B) does not significantly increase the molecular weight of the polymer, but does increase the amount of large aggregates
- Polymers with low ammonia content (polymer C) have a low molecular weight and are highly linear. Increasing the polymer concentration shows no more polymer aggregation, effectively ideal, non-interacting polymer solution behavior
- Polymer solutions at the isoelectric point (pH 4) are unstable, correlated with decreased polymer performance
- Polymer solutions are unstable in a complex manner consistent with the ionic nature of the polymers

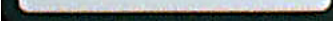


New "Solid" Supports

- We have prepared using soluble polymers as new "solid" supports with LiP to separate from excess reagents
- Advantages include:
  - Homogenous synthesis conditions
  - Byproduct acids are not a problem
  - Ease of removing excess reagents
  - Handle automatable as liquid transfers are easier than solids
  - Specific when the target exists soluble metal-binding ligands
- We are using water and organic soluble polyamine; the fabrications impart excellent aqueous solubility to the polymers, and they are also soluble in a number of organic solvents useful in organic synthesis
- Have grafted reagents from the MACROMOLECULAR polymer used previously, as polyamines have multiple attachment points as opposed to one per strand, and
- Separation is accomplished with ultrafiltration instead of precipitation



Schematic of Diversomer™ Unit Used for Resin-Based Synthesis



Some Potential Applications of Polymer Filtration™

- Analytical preconcentration
- Nuclear power/nuclear facility waste streams
- Electroplating rinse waters
- Photofinishing waste streams
- Acid Mine drainage/advanced mining technologies
- Treatment of ground water/drinking water
- Precious metals industry
- Catalyst waste streams
- Electronics waste streams
- Cooling tower water
- Textile industry
- Municipal waste streams
- Soil remediation/surface decontamination