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Synthesis of New Water-Soluble Metal-Binding Polymers: Combinatorial Chemistry Approach

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Research Objective

(1) Develop rapid discovery and optimization approaches to new water-soluble chelating polymers for use in Polymer Filtration (PF) systems, and (2) evaluate the concept of using water and organic soluble polymers as new “solid” supports for combinatorial synthesis.

Research Progress and Implications

Polymer Filtration (PF), which uses water-soluble metal-binding polymers to sequester metal ions in dilute solution with ultrafiltration (UF) to separate the polymers, is a new technology to selectively remove or recover hazardous and valuable metal ions. Future directions in PF must include rapid development, testing, and characterization of new metal-binding polymers. Thus, we are building upon and adapting the combinatorial chemistry approach developed for rapid molecule generation for the drug industry to the rapid development of new chelating polymers.

We have focused on four areas including the development of: (1) synthetic procedures, (2) small ultrafiltration equipment compatible with organic- and aqueous-based combinatorial synthesis, (3) rapid assay techniques, and (4) polymer characterization techniques.

- (1) **Synthetic Methods Development:** Three classes of ligands are being addressed: (1) acylpyrazolones, (2) polyisoxazoles, and (3) 1,2-aminoalcohols. We are synthesizing representative examples of these three classes of ligands by solution-phase chemistry in order to master the chemistry of these compounds. In the acylpyrazolones, we have prepared over 40 derivatives having variation mainly in the side chain at C-4. One significant finding is that Mitsunobu chemistry allows good regiochemical control for synthesis of O-alkylated systems. Two types of polyisoxazoles have been prepared; one ready for attachment to a water-soluble polymer and another as a monomer for polymerization into a polyacrylamide system. 1,2-Aminoalcohols have been prepared, but this chemistry does not promise to be adaptable to solid phase organic synthesis (SPOS) and therefore we are incorporating this motif as a monomer structural feature into other polymer systems. However, the acylpyrazolones and polyisoxazoles will be studied for use in SPOS and eventual combinatorial application.
- (2) **Small Ultrafiltration Equipment:** To develop a homogeneous synthesis approach a robust, parallel synthesis apparatus which incorporates UF as the mode of separation for ready recovery of polymer/product and removal of excess reagents is under construction. An early prototype was built of Teflon[®] that incorporated UF membranes at the bottom of cylindrical holes and incorporated vacuum filtration. This unit gave undesirable cross-talk between the individual cylindrical reactors. A second design is in progress that uses centrifugal force for filtration and has individual vessels that can not cross-contaminate.
- (3) **Rapid Polymer Assaying Techniques:** Dried Spot X-Ray Fluorescence: Spotting was on a variety of substrates including polypropylene, Moxtek's AP1 and AP2 films. The AP2 films, which could be heated, exhibited the best spot formation, while a silicone film (Rain-X) helped with spot formation on the polypropylene. Experiments with four surrogate water-

soluble polymers at a concentration of 0.5% and 0.1 M NaNO₃ resulted in large backgrounds, which obscured analyte signal for the 100 ppb test solution. Further experiments with polymer at 0.1% and no NaNO₃ resulted in improved sensitivity. All elements in the test solution were observed in the starting solution, the retentate and filtrate solutions. Qualitatively, the retentate showed greater elemental intensities than the starting solution or the filtrate, indicating a concentration effect by the polymer. The observation of the metals in the filtrate, demonstrated sensitivity approaching 10's of ppb. Increasing counting time increased analyte peak intensities as well as the background. These results indicate the feasibility of using MXRF as a means for screening water-soluble polymer for metal ion binding effectiveness. The next step is to develop a calibration to quantify the metal distribution among the different solutions. Lower polymer concentrations will be studied to further reduce the background and increase sensitivity. Preliminary design plans indicate a good potential for matching the combinatorial reaction vessel with the Moxtek sample holder to maximize sample throughput and minimize confusion during sampling.

Auto-Radiography: Radionuclides (Am, Pu) are prime candidates for radiochemical assay techniques. The polymer/metal ion solutions are placed in a small vessel containing a UF membrane and filtered to near dryness. The sample spot is analyzed using a photographic film, which is placed in close proximity to the radiation source for a time sufficient to expose the film. In this way a whole series of vessels will be spotted simultaneously using multiple syringe techniques, filtered simultaneously, and exposed to the photographic film simultaneously such that the density of the exposed film will allow determination of the best metal binders. Preliminary tests have involved the use of fixed-sources of radiation, "check" source. These are being used to optimize film types, distance, and exposure times.

- (4) **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. 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.

Planned Activities

Some planned activities have been indicated under each individual task. Overall activities will include completion of the synthetic methods development, performing the combinatorial synthesis, testing the polymers on a suite of metals, and characterizing the best candidates