NC STATE UNIVERSITY
Department of Chemistry

Amine-Based Polymer Synthesis for Phosphorus Capture

STEPS
Science and Technologies for Phosphorus Sustainability

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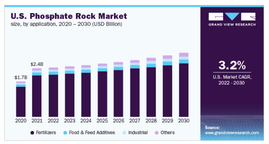
Introduction

Phosphorus as a material is very useful for nutrient enrichment and has enjoyed widespread popularity as a major contributor to fertilizer. However, much of the organic phosphorus used today comes from the mining of phosphate rock, a non-renewable energy source.



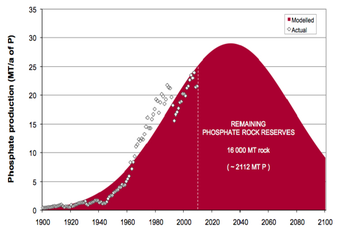


Figure 1,2. Graph contrasting available phosphate rock and global usage AND graph detailing phosphate rock market and utility

In an effort towards promoting renewable phosphorus and alleviating the harmful effects of its excess, there are many commercially available products designed to recapture it from the environment. However, these products are inadequate, largely due to their inability to release the trapped phosphorus.

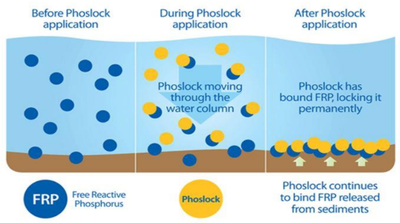


Figure 2. Visual depiction of Phoslock capturing Free Reactive Phosphorus for a given body of water

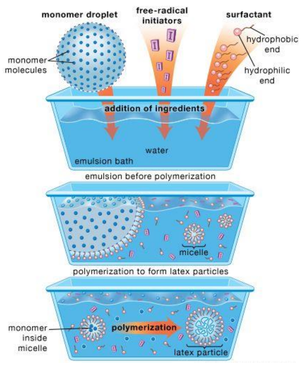


Figure 3. Diagram of emulsion polymerization with emphasis on micelle suspension

To remedy this, a latex polymer is proposed. This molecule will be acrylamide-based because of its amenability with radical polymerization. Ideally, the emulsion will trap phosphorus and moreover release it with minimal time, energy, or resource expenditure. The crosslinker Bis-Acrylamide might prove useful in forming more discreet micro and nano-particles if the polymerized monomer chains become entangled and will be kept in reserve until necessary.

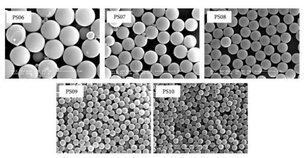


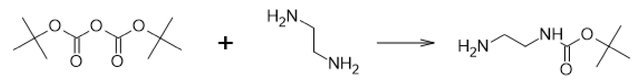
Figure 4. Microscopic images of polymer bead suspension

Project Goals

- Advance systematic structure-property relationships concerning phosphorus capture and release
- Synthesize latex linked and crosslinked acrylamide polymers
- Test aforementioned polymers for phosphorus catch-and-release efficacy

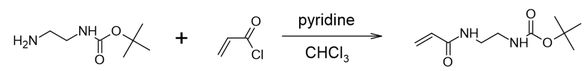
Monomer/Polymer Synthesis

To begin, the Boc protecting group was attached to ethylenediamine in preparation for reaction with the acrylamide.



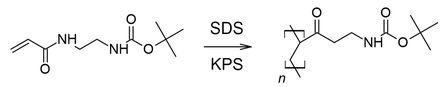
Trial 1: 40% yield
Trial 2: 63% yield
Trial 3: 75% yield
Trial 4: 78% yield

The mono-boc-EDA was reacted with acrylamide to produce the first base monomer for use in polymerization. Boc was chosen as a protecting group because its bonds break when exposed to a strong acid, and EDA was added to bypass acrylamide's water solubility.

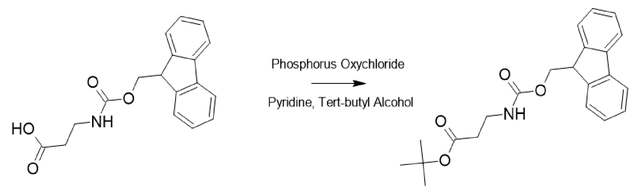


Trial 1: 31% yield
Trial 2: 41% yield
Trial 3: 53% yield

Once the monomer synthesis was confirmed, emulsion polymerization was attempted using potassium persulfate as the free radical initiator and sodium dodecyl sulfate a surfactant.



After synthesis of the first monomer, work was begun on the second monomer. For this trial, a tert-butyl group was attached to the below ester using phosphorus oxychloride and tert butyl alcohol.

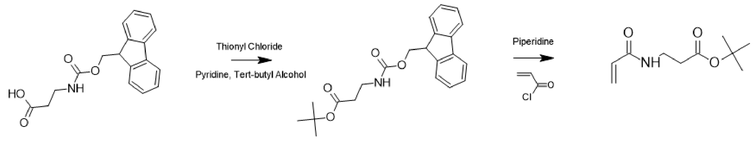


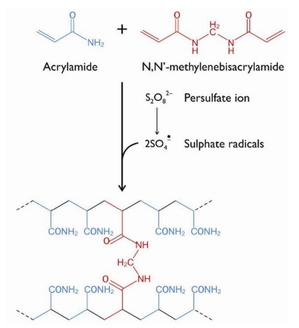
Trial 1: 10% yield
Trial 2: 7% yield
Trial 3: 8% yield

Although this process was able to produce the desired ester, it yielded too little final product to be feasibly used. Reasons for this might include the inability of the chloride to properly replace the alcohol, interfering with the Fmoc and tert-butyl reaction, or differing environmental conditions from the referenced literature.

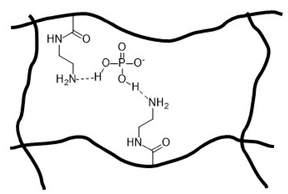
Future Work

The next step in terms of synthesizing the second monomer is to re-react the Fmoc and tert-butyl alcohol using a different chloride. To this end, the same reaction substituting thionyl chloride is proposed. After this, usage of piperidine and the acid chloride will remove the protecting group, exposing the amine and acid groups with the potential to bind phosphorus. Finally, a similar emulsion polymerization process might be attempted.





Time did not allow for crosslinked polymer trials however the predicted reaction is shown to the left. The crosslinker acts as a bridge between the acrylamide polymer chains, preventing the strands from getting jumbled. Below, a different representation of the chemical structure is depicted, showing a "zoomed in" portion of the larger chain.



To the right is a basic setup for Dynamic Light Scattering, a way to measure macroparticle size using photons and the principle of Brownian motion.

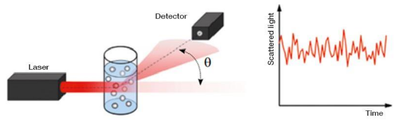
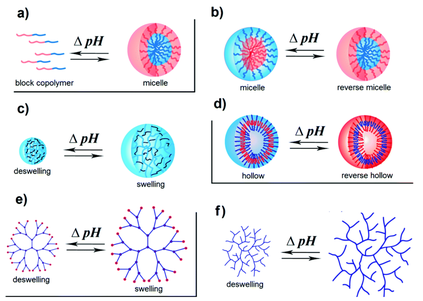


Figure 5. A simplified model of Dynamic Light Scattering



Once an adequate number of polymers are created, they will then be tested and categorized in accordance with phosphorus and phosphate retention ability. They will then be subjected to numerous conditions (including but not limited to changes of ph and temperature) with hopes that the phosphorus and phosphates are released.

Figure 6. A chart showing the multiple shape changes a polymer can undergo when exposed to ph changes

References

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