

## **POLYMER REACTION ENGINEERING IN THE ORIGINS OF LIFE: HOW TO GET FROM SYNTHETIC RUBBER TO CHEMICAL EVOLUTION**

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How does a chemical engineer go from synthetic rubber production to origins of life research and still be in polymer reaction engineering? The answer is simple: There are significant problems in chemical evolution (and likely in many other fields of research) where the tools of polymer reaction materials can be applied very effectively. This talk documents two of them.

In the study of chemical evolution, there are two schools of thought. The first, often called *the RNA world*, RNA developed before proteins, and hence before enzyme catalysts. There is evidence for this in the fact that some polynucleic acids (RNA or RNA-like) function even today in an enzymatic capacity. If RNA was formed in the *RNA world*, then it must have been capable of replicating, not as it currently does by the use of polymerase enzymes, but without enzyme function, essentially by self-assembly. In the first part of this talk, methods of polymer reaction engineering were used to develop a mechanistic model of nonenzymatic polynucleotide replication. The model is made possible by the rate constants developed by Harvard researchers. This model treats the ideas of stalling proposed by the Harvard team in a direct kinetic mechanism. When one assumes that multiple incorrect insertions in a row are unlikely, the model returns estimates of the error threshold very much in agreement with the modified Eigen model (based on probability arguments) proposed by the Harvard team. In addition, the current model gives average lengths of polynucleotides, categorized by ultimate nucleoside (type and correct/incorrect) as well as the average lengths of interior and terminal sequences of correct and incorrect insertions in a row.

In the second view of chemical evolution, proteins were formed first, and eventually developed the enzymatic capability that enables essentially all of the chemistry of modern life. Although it is generally accepted that amino acids were present on the prebiotic Earth, the mechanism to form long chain polypeptides is still unclear. The second part of the talk, will discuss work in the noncatalytic formation of long chain polypeptides. We have found a simple system capable of forming peptide bonds under mild conditions. Hydroxy acids form metastable oligoesters in the oscillating (hot dry/cool wet) system and are converted into mixed copolymers via the ester-amide exchange reaction. Here, we use HPLC coupled with UV/MASS SPEC to track the growth of oligomers from valine/ lactic acid mixtures. The copolymerization is simulated by our kinetic (population balance) model to validate the proposed mechanism and optimize feed policies that result in longer oligomers. Finally, we evaluate feed policies that result in longer oligomers containing only one hydroxy acid residue at the N-terminus of a polypeptide. Peptide polymerization by this route follows kinetics similar to those of living polymerization. These results suggest a prebiotically-plausible route to the synthesis of longer depsipeptides that might lead to the formation of secondary structures, and ultimately, enzyme catalysts.