**Clicking Polymers Together:**
**Assembly of Complex, Controlled Polymer Structures from Efficient Chemistries**

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A new paradigm encompassing several distinct chemical reactions and, more importantly, a generalized approach to molecular design and synthesis has been rapidly adopted in the fields of chemical synthesis, biotechnology, materials science, drug discovery, surface science, and polymer synthesis and modification. The *Click Chemistry* paradigm focuses on implementation of highly efficient reactions that achieve quantitative conversion under mild conditions. As such, these reactions represent ideal candidates for further development, understanding and implementation. In particular, the synergistic combination of these click chemistries with photochemical initiation and polymer formation has been used to afford 4D control of polymer formation, structure and patterned assembly. Here, we will focus on three distinct vignettes related to our implementation of photoclickable polymer systems. The first of these focuses on the development of covalent adaptable networks (CANs) where the ability to controllably alter the network structure is used to alter topography and other material properties by forming materials which can be switched revesibly from elastic to plastic simply by exposure to light. Secondly, we will focus on the development of approaches to photoinitiate the Cu(I) catalyzed azide-alkyne cycloaddition (CuAAC) click reaction. Here, implementation of this reaction in surface modification, hydrogel formation, and lithography as well as in the development of a new class of photopolymerization reactions will be presented. Finally, the development and implementation of click nucleic acids (CNAs) based on the thiol-ene click reaction will be presented. This distinct class of oligonucelotides combines the vast advantages of synthetic oligonucleotides such as peptide nucleic acids with the power of click reaction chemistry to form materials that hybridize with both natural and synthetic olignonucleoitides via Watson-Crick base pairing while being simple to produce in large scales appropriate for directed assembly and other high value materials applications.