

**Enhanced Architectural and Structural Regulation Using
Controlled Free Radical Polymerization Techniques;**

Supramolecular Assemblies: Pseudorotaxanes and Polypseudorotaxanes

Jason William Jones

Professor Harry W. Gibson, Committee Chair
Department of Chemistry

(ABSTRACT)

Due in large part to the growth and development of reliable surface characterization techniques, as well as to advances in the physical and chemical techniques used to modify surfaces, the technology of surface modification has seen rapid expansion over the past two decades. A major thrust of this research is the growth of controlled/"living" polymeric brushes from the surface of various substrates, an advance that promises to be a facile and reproducible way of altering surface properties. A unique initiator bearing ATRP (atom transfer radical polymerization), cleavage, and condensation functionalities was prepared and attached to the hydrolyzed surface of silica gel. Preliminary results indicate that control of reversibly terminated grafts of varying degrees of polymerization with polydispersity indices approaching 1.5 can be readily achieved—significant findings in the quest to design desired surface characteristics.

Important physical characteristics may also be altered by way of varying molecular topologies. In the second major research thrust, the use of self-assembly to construct such topologies in the form of pseudorotaxanes fashioned from diverse macrocycles with multifarious guest ions is discussed. While the underlying goal was to investigate and understand the mode of complexation based on such environmental factors as substituent affects and neighboring group influences, new insight was gained on the synthetic manipulation of cooperative events—events that freely occur in nature. The complexation behavior of several functionalized bis-(*meta*-phenylene)-32-crown-10 macrocycles with various paraquat guest moieties was. As expected, studies indicated

that electron-donating substituents on the crown ether drive association, a likely result of increased π - π interactions among host and guest species. The association between a bicyclic macrocycle and dimethyl paraquat was also investigated. Not surprisingly, binding of paraquat by the bicyclic was much stronger than the binding found in analogous macrocycles. Lastly, the endgroup functionalization of poly(propyleneimine) dendrimers with two crown ether macrocycles was performed and the complexation with host-specific guests studied. Curiously, two extreme binding regimes were found: the larger 32-membered crown ether assembly displayed anti-cooperative behavior upon complexation with paraquat, while the smaller 24-membered macrocyclic system exhibited cooperative effects with 2° ammonium ions. These cooperative results are among the very first described for non-biological systems and hint at their potential use in developing highly efficient, synthetically designed supramolecular systems.