

Chapter 14

Thesis Summary and Future Work

This thesis describes the use of non-covalent interactions between complementary crown ethers and alkyl ammonium ions/paraquats to create well-defined large aggregates, *e.g.*, dendrimers, linear arrays, and modified side-chain polymers, all with pseudorotaxane linkages. The reversibility of non-covalent interactions warrants the thermodynamic stability of these supramolecular aggregates. First, dibenzo-24-crown-8 and bis-*m*-phenylene-32-crown-10 with monofunctionality were prepared in large scale. These crown ethers were incorporated into small building blocks, which were later self-assembled with other building blocks containing complementary recognition units to generate large aggregates. A novel 1:3 pseudorotaxane complex between a triply charged ammonium ion and dibenzo-24-crown-8 was formed in both solution and the gas phase. Similarly, defect free non-covalent dendrimers were prepared by simply mixing the triply charged ammonium ion and a series of dendrons bearing the dibenzo-24-crown-8 moiety in noncompetitive solvents such as chloroform and acetone. As a result of the poor solubility of the triply charged ammonium ion and steric hindrance experienced by neighboring dendron units in the 1:3 complexes, the formation of these dendrimers were time dependent in chloroform. The wholly complexed self-assembling dendrimers were also evidenced by mass spectrometry. Linear non-covalent pseudorotaxane polymers were constructed in solution by self-assembly of two complementary homoditopic molecules containing secondary ammonium ions and dibenzo-24-crown-8 moieties and a heteroditopic molecule containing a paraquat and bis-*m*-phenylene-32-crown-10 moiety. Viscosity measurements of the non-covalent polymers supported the presence of large hydrodynamic volume aggregates. The formation of fibers and films from high concentration solutions indicated the polymeric nature of the aggregates. Thermal analysis (DSC) on the solid state samples, prepared by freeze-drying technique, indicated that these polymers were amorphous. Finally, side-chain polypseudorotaxanes were spontaneously assembled in solution by simple recognition of side-chain crown ether polymethacrylates with dibenzylammonium ion. Polymethacrylate with a greater

fraction of the crown ether repeat unit showed a lower apparent " K_a " and % loading when complexed with the ammonium ion. The thermal properties and morphology of the side-chain polypseudorotaxanes were distinct from the individual components.

This concept of non-covalent interactions may be extended by incorporating oligomeric PS and/or acrylates or liquid crystalline linker segments in complementary homoditopic and heteroditopic molecules to generate a variety of non-covalent polymers. Use of higher K_a systems such as cryptand-paraquat system is expected to improve the efficiency of the construction of non-covalent polymers. The knowledge gained from the syntheses of linear non-covalent polymers and side-chain polypseudorotaxanes will be applied to the synthesis of non-covalent network systems. As illustrated in Figure 14.1, cross-linked polypseudorotaxanes (**3**) should be generated with reversible network formation by self-assembly of side-chain dibenzo-24-crown-8 polymethacrylates (**1**) and homoditopic molecules containing secondary ammonium ion (**2**). Such non-covalent network systems may be advantageous over the conventional network systems due to the reversibility of the non-covalent interactions thermally or by use of competitive solvent such as DMSO. For example, the equilibrium in Figure 14.1 will be shifted to the left to give the individual building blocks **1** and **2** at higher temperatures where these systems may be processed. At lower temperatures the equilibrium is shifted back to regain the cross-linked structure of **3**.

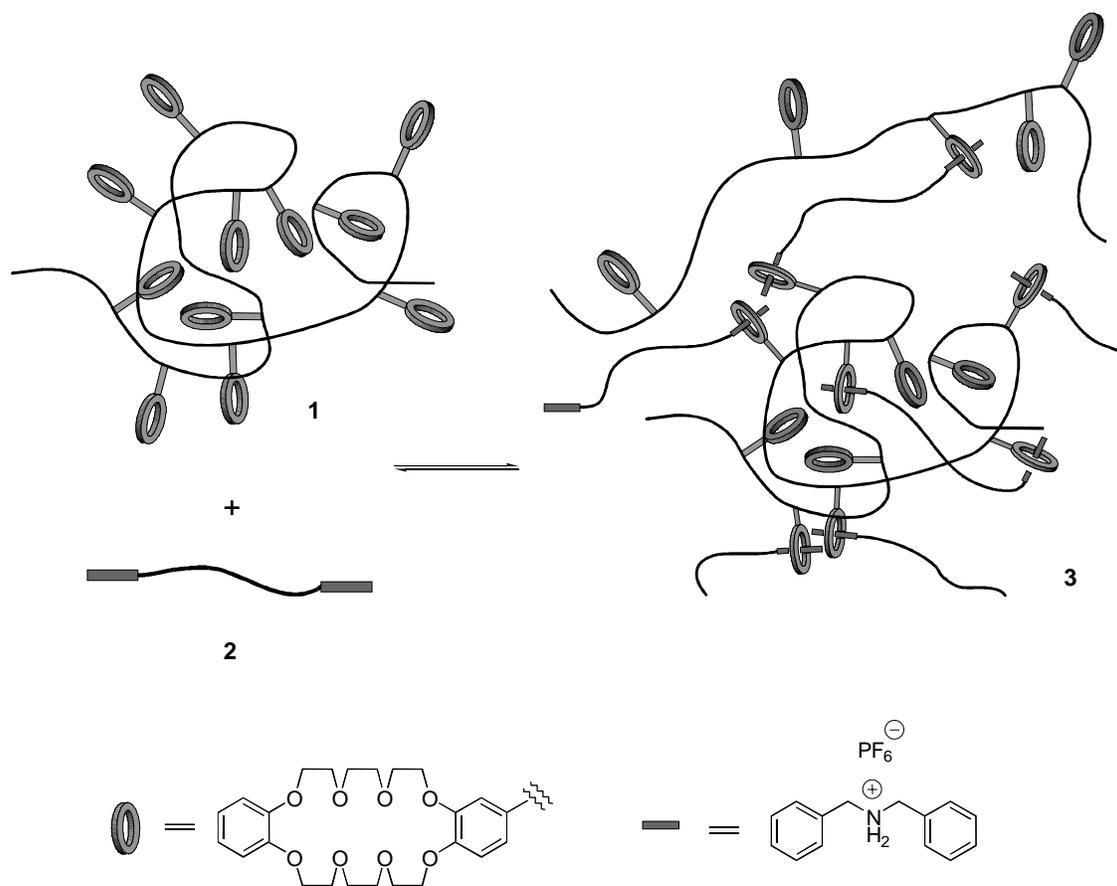


Figure 14.1. Synthesis of non-covalent network system.