

## Chapter VII

### Conclusions and Future Work

The research discussed in this thesis focused on designing receptors and substrates that contain complementary functional groups that form supramolecular assemblies, or supermolecules, by way of molecular recognition. A rotaxane conformation was also the desired complexation conformation. Therefore, large (greater than 22 atoms) bis(phenylene) crown ethers and secondary ammonium salts were chosen as the receptors and substrates, respectively. The host-guest systems were analyzed primarily by NMR spectroscopy, mass spectroscopy, and X-ray crystallography. The determination of the stoichiometry and association constants in solution was of great importance to develop a strategy for designing a suitable system for the synthesis of rotaxanes and polyrotaxanes.

It was determined that the bis-(*meta*-phenylene) crown ethers were not suitable candidates for use in rotaxanes and polyrotaxanes due to the low association constants for the complexes formed in solution. The dibenzo-24-crown-8 (**DB24C8**) moiety appeared; however, to have association constants of reasonable value to be used to produce rotaxanes and polyrotaxanes using the secondary ammonium ions as receptors. The synthesis of difunctional monomers of **DB24C8** would be complicated by the resulting isomers, but it may not be necessary to isolate the isomers for main-chain polymers. Polymers having **DB24C8** side-chain groups could be made easily by reacting pre-made polymers with reactive backbone groups with several of the mono-functional **DB24C8** monomers discussed in this **Chapter II**. 30-crown-10 might also be used for threading polymer chains containing secondary ammonium ions (both side- and main-chain).

From the model compound study that N,N'-dibenzyl-*p*-xylylenediammonium bishexafluorophosphate had a higher overall association constant than the *meta*-analog when complexed with **DB24C8**. However, the synthesis of main-chain polymers having benzylic secondary ammonium ion moieties would be complicated for *para*-substituted monomers due to the insolubility of the polyimine precursors. It is suggested that both

*meta*- and *para*-substituted monomers be used instead. It also may not be necessary for every repeat unit to contain a complexation site.

More work must be done to understand the complexation of bis-1,3,5-phenylene-[5.5.5]-cryptand with secondary ammonium ions. Also, the 26-membered analog must be synthesized as well. It is believed that it will form stronger complexes with secondary ammonium ions. Due to the difficulty in synthesizing the cryptand receptors the system may not be reasonable for creating larger supramolecular assemblies. However, the cyclization of the dialcohol of bis-(*meta*-phenylene)-32-crown-10 and **DB24C8** maybe an easier route to other bicyclic receptors and may result in higher association constants as well.

The complexation between the crown ethers and cryptands with secondary ammonium ions discussed in this thesis show promise for creating supramolecular assemblies. The functionalization of both the receptors and substrates needs to be investigated more to create more freedom in designing larger systems with reasonable association constants. Also, a suitable synthetic pathway for the blocking of the crown ethers onto the secondary ammonium ions to form rotaxanes and polyrotaxanes must be investigated.