Supramolecular Macromolecules

Polymeric materials have been used as essential components in the synthesis of supramolecular materials rarely, despite their many advantages. Success in this area will deliver multifunctional properties for the next generation of materials. Most importantly, they increase organizational length scales compared to small molecules, opening a range extending from the atomic (0.1 nm) to the mesoscopic (2,000 nm). These properties could be as simple as controlled viscosity, allowing lower cost manufacturing, to complex multiscale organization and specific placement of chemical groups throughout the material, leading to new properties. Many applications exist, and we are specifically interested in targeted drug delivery, electronic, self-healing, and responsive materials. We focus on metal-ligand interactions since these are discrete, well defined, geometrically constrained, and competitive under a variety of environmental conditions. In addition, the interaction strength is widely tunable based on the choice of metal ion and organic ligand. We were the first laboratory to demonstrate successfully the impact these groups have on solution viscosity. In addition, the synthesis of block copolymers in which metal ligands are confined to one or more segments, as shown in the figure, had never been reported until our recent Macromolecules paper. To prepared block copolymers and narrow polydispersity materials we use 'living' or controlled radical polymerization techniques including atom transfer radical polymerization (ATRP), reversible addition fragmentation chain transfer (RAFT), and nitroxide mediated polymerization (NMP).

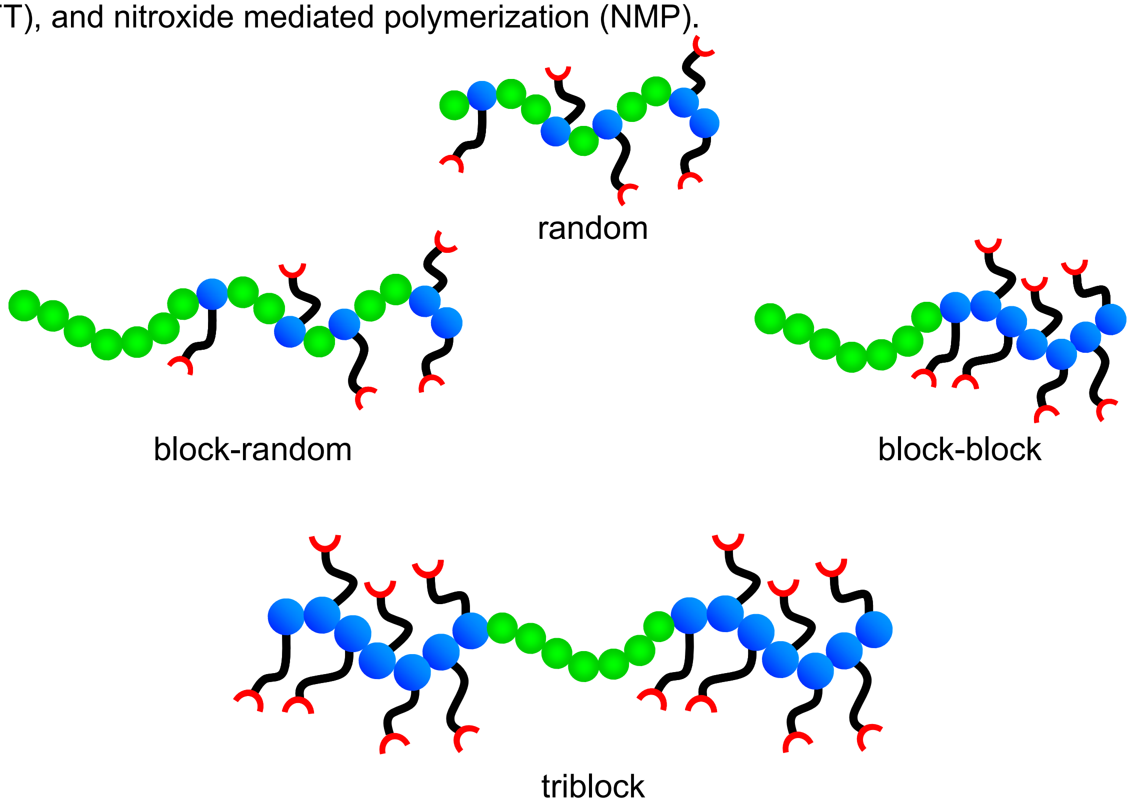

Figure 1. An array of copolymer architectures prepared for generating novel supramolecular materials.

An example of the copolymers we prepare is shown in Figure 2. The key styrene based monomer (Sty_{Terpy}) was synthesized in high yield (80%). This monomer allows a number of copolymers to be synthesized including random and block copolymers. A GPC trace of a macroinitiator and the resulting block copolymer is shown in Figure 3.

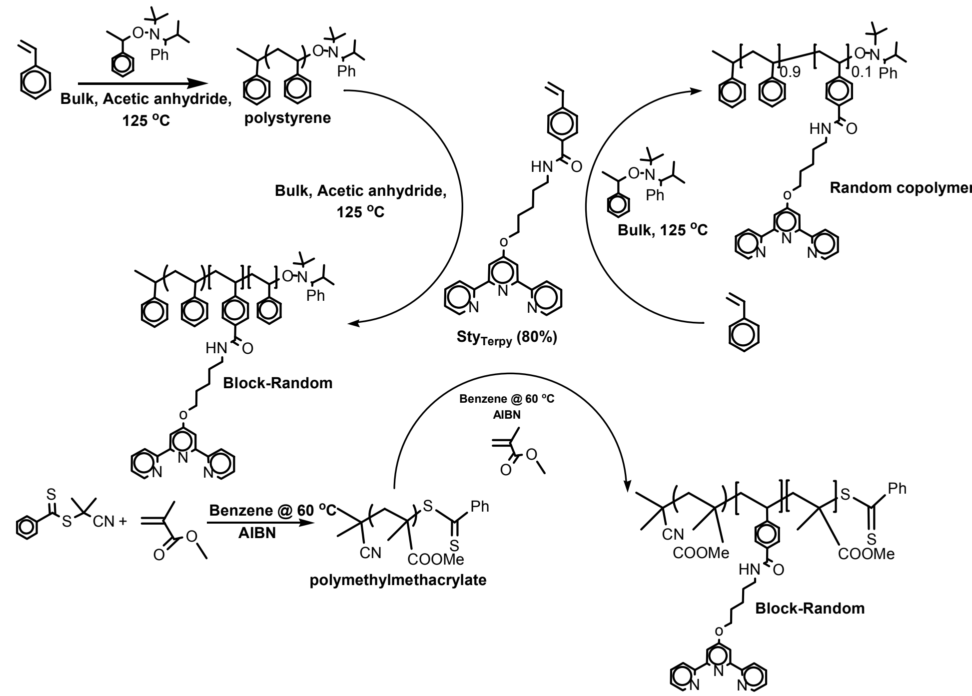

Figure 2. Synthetic outline for the preparation of several copolymers.

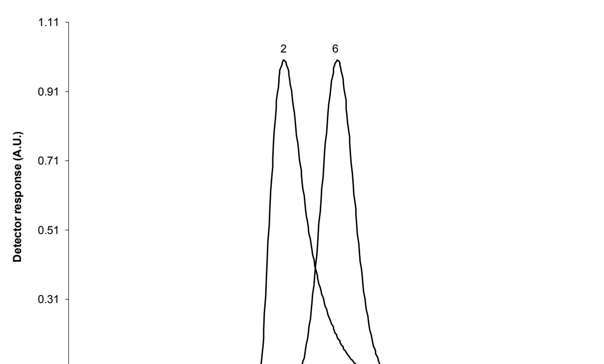

Figure 3. GPC chromatograms for a macroinitiator and block copolymer prepared by nitroxide mediated polymerization.

These copolymers have led to a number of interesting properties we are currently exploring. They include nanoparticle formation, novel luminescence and electroluminescence, heavy metal and solvent sensors, magnetic materials, thermochromic films, reversible cross-links, and solvochromism.

An illustration of the nanoparticles we have discovered is shown in Figure 4. These nanoparticles are only formed upon the addition of metal ions and create novel objects with an amazing density of metal centers.

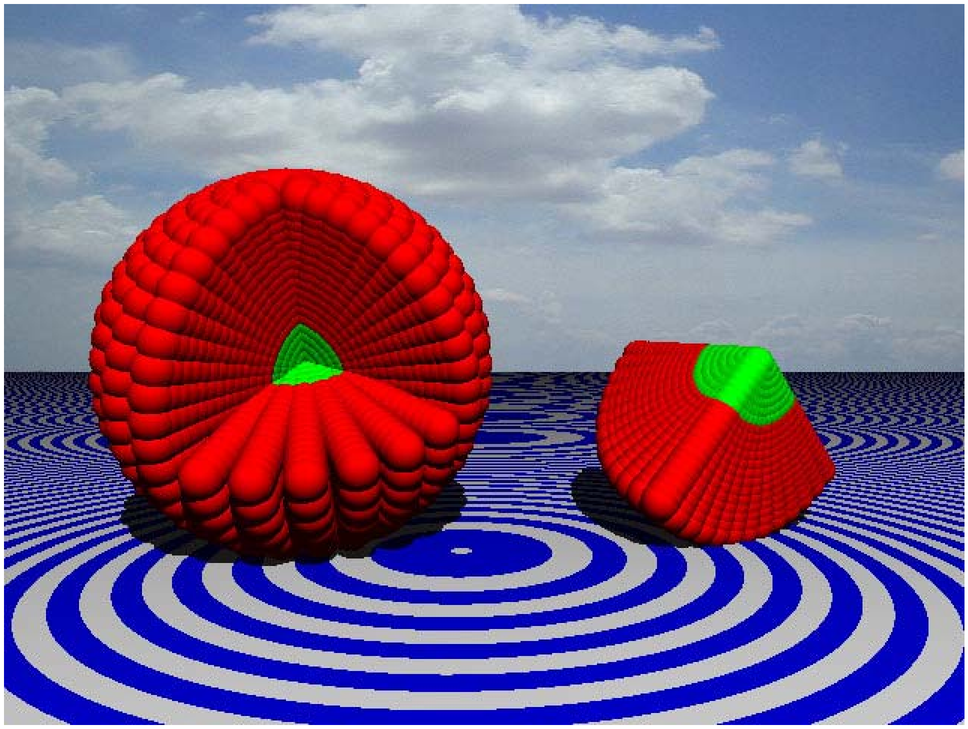

Figure 4. Nanoparticles created by the addition of metal ions to a block copolymer architecture. The particles are roughly 50 nm in diameter and have a density of over 600 metal centers.