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Polymer Chemistry, Surface Chemistry, Materials Chemistry

Our research involves the synthesis and study of responsive polymers that undergo spontaneous structure reorganization in response to external stimuli. Three classes of environmentally responsive polymers, mixed homopolymer brushes, thermosensitive watersoluble polymers, and multi-responsive nanocages, are being developed and studied in our laboratory. In general, we use “living”/controlled polymerization techniques (atom transfer radical polymerization (ATRP), nitroxide-mediated radical polymerization (NMRP), ring-opening polymerization, and reversible addition-fragmentation chain transfer process) to synthesize polymers and polymer brushes with controlled molecular weights and well-defined architectures. These soft materials have potential applications in smart coatings/adhesives (surface-responsive materials), controlled encapsulation and triggered release of substances, catalysis, biotechnology, and nanotechnology.

Environmentally Responsive Mixed Homopolymer Brushes

Mixed homopolymer brushes, composed of two chemically distinct homopolymers randomly or alternately immobilized via covalent bonds on a solid surface with high grafting densities, represent a new class of stimuli-responsive materials. In addition to the stretched conformations assumed by surface-tethered polymer chains, phase separation between two immiscible polymers and/or between polymers and solvents occurs, enriching their phase behavior. Theoretical studies have discussed whether symmetric mixed homopolymer brushes on a flat substrate phase separate laterally forming a "ripped" state or vertically producing a "layered" state under equilibrium melt conditions (Scheme 1), and have predicted that the "ripped" state is the one to appear. In selective solvents, micellar structures with solvophobic chains associating into a dense core and the solvophilic chains forming an outer shell have been predicted. By tuning parameters including grafting density, molecular weights, chemical compositions, solvents, and temperature, a variety of surface structures and properties could be achieved by mixed brushes. Moreover, different structures formed from the same brushes under different conditions are reversible because of the covalent bond between the polymer and the substrate, making mixed brushes robust surface-responsive materials.

We have developed a unique strategy to synthesize well-defined mixed brushes with controlled molecular weights and narrow polydispersities by a “grafting from” approach (Scheme 2). Two different living radical polymerization techniques, ATRP and NMRP, were used to grow two different polymers from asymmetric difunctional
initiator-terminated self-assembled monolayers (Y-SAMs) on flat substrates and nanoparticles. These brushes have been shown to respond to environmental changes, exhibiting different surface morphologies and surface properties (Figure 1). The ongoing projects include the study of self-assembly of mixed brushes by combinatorial methods, well-ordered nanoscale patterns via self-assembly, phase morphologies of mixed brushes in polymer matrices, multi-responsive organic/inorganic hybrid particles, asymmetrically modified silica nanoparticles (Janus particles), development of sensors by use of polymer brushes on the basis of molecular recognition, etc. These projects provide an opportunity to those who are interested in polymer synthesis, surface chemistry, polymer physical chemistry, materials science, and analytical chemistry.

**Figure 1:** $^1$H NMR spectra of mixed poly(acrylic acid) (PAA)/polystyrene (PS) brush-grafted silica nanoparticles dispersed in (a) CDCl$_3$, a selective solvent for PS, (b) $N,N$-dimethylformamide-$d_7$ (DMF-$d_7$), a good solvent for both PAA and PS, (c) CD$_3$OD, a selective solvent for PAA. A drop of DMF-$d_7$ was added into the particles prior to CDCl$_3$ and CD$_3$OD to increase the concentration of the dispersed particles.

**Thermosensitive Water-Soluble Polymers**

Thermosensitive water-soluble polymers undergo phase transition in aqueous solutions from a soluble to an insoluble state when the temperature is above a critical point (lower critical solution temperature, LCST) or below a certain value (upper solution critical temperature, UCST). These types of polymers, especially those exhibiting the LCST behavior, have attracted considerable attention and a variety of applications have been reported ranging from creation of smart surfaces, to drug delivery, and catalysis. We have developed a series of new thermosensitive water-soluble polystyrenics and polyacrylates with short pendant oligo(ethylene glycol) groups by nitroxide-mediated radical polymerization using a $\alpha$-hydrido alkoxyamine as initiator (Scheme 3). The high level of alkoxyamine chain end retention allowed the synthesis of diblock copolymers, which were found to exhibit intriguing thermo-induced self-association in water. Our current effort in this field is directed to the synthesis of doubly thermosensitive polymers with various architectures (ABC triblock, ABC mikto-arm star, multi-arm star copolymers, and hyperbranched polymers) and the study of their thermo-induced micellization in

![Scheme 3](image-url)
water by UV-Vis spectrometry, variable temperature $^1$H NMR spectroscopy, dynamic light scattering, differential scanning calorimetry, and transmission electron microscopy. We are also exploring the polymers that can respond to two different stimuli (temperature/light, temperature/specific metal ion, etc.). Applications of these environmentally sensitive polymers in thermoregulated catalysis and controlled release will be pursued.

**Multi-Responsive Soft Nanocages**

Hollow polymeric nanoparticles with the size in the range of tens to hundreds of nanometers are of great scientific and technological importance due to their potential applications in controlled release of substances (drugs, fragrances, pesticides, etc.), confined nano-reactors for spatially restricted organic/inorganic synthesis, photonic crystals, and catalysis. We are currently developing a general method to fabricate multi-responsive hollow polymeric nanoparticles by use of surface-initiated living radical polymerization. The hollow nanoparticles will be engineered to respond to multiple external stimuli including pH, temperature, specific metal ions, glucose, etc., making them ideal for applications in triggered release of substances. An example is shown in Scheme 4.

![Scheme 4](image)

**Representative publications:**


