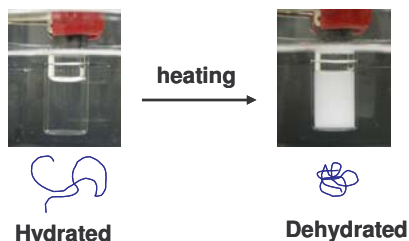


Polymer Chemistry, Surface Chemistry, Materials Chemistry

Our research involves the synthesis and study of responsive polymers and polymer brushes that can undergo spontaneous changes in structures and properties upon application of external stimuli. Three classes of environmentally responsive polymeric systems, thermosensitive water-soluble polymers, well-defined mixed homopolymer brushes, and thermoresponsive polymer brush-grafted particles, are being developed and investigated in our laboratory. In general, we use "living"/controlled polymerization techniques (atom transfer radical polymerization, nitroxide-mediated radical polymerization, reversible addition-fragmentation chain transfer polymerization, ring-opening polymerization, etc.) to synthesize polymers and polymer brushes with controlled molecular weights, narrow polydispersities, and defined architectures. These soft materials have potential applications in controlled encapsulation and triggered release of substances, surface-responsive materials, smart catalysis, biotechnology, and nanotechnology.

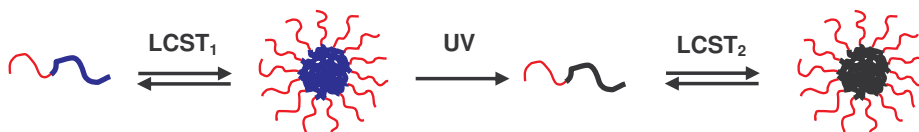
Thermosensitive Water-Soluble Polymers

Thermosensitive water-soluble polymers undergo a phase transition in water from a soluble (hydrated) to an insoluble (dehydrated) state when the temperature is above a critical point (lower critical solution temperature, LCST, Scheme 1) or below a certain value (upper critical solution temperature, UCST). These types of polymers, especially those exhibiting the LCST behavior, have attracted growing interest in recent years and a variety of applications have been reported ranging from the creation of smart surfaces, to drug delivery, and catalysis. By using living radical polymerization techniques, our laboratory has developed a new class of thermosensitive water-soluble polystyrenics and polyacrylates with a short oligo(ethylene glycol) group as a pendant from each repeating unit. The LCST can be readily tuned by varying the length and end group of oligo(ethylene glycol) pendant or the type of polymer backbone.



Scheme 1. An aqueous solution of a thermosensitive polymer turns cloudy when $T > LCST$.

We are especially interested in multi-responsive water-soluble block and star copolymers. A series of well-defined block copolymers that can respond to two external stimuli (temperature (T)/T, T/light, T/pH, or T/specific molecule) have been synthesized; they can undergo multiple micellization and dissociation transitions in water. For example, thermo- and light-sensitive block copolymer poly(ethylene oxide)-*b*-poly(ethoxytri(ethylene oxide)-*co*-*o*-nitrobenzyl acrylate) dissolves molecularly in cold water, and undergo micellization when the temperature is increased above the LCST of the thermosensitive block (Scheme 2). Upon UV irradiation, the micelles are dissociated into the molecular dissolved unimers (Scheme 2). Further increasing temperature induces micellization again. We are also pursuing the applications of these

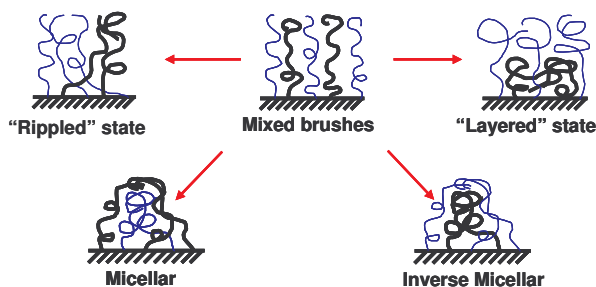


Scheme 2. Thermo- and light-sensitive block copolymer PEO-*b*-P(TEGEA-*co*-*o*-NBA) undergoes multiple micellization and dissociation transitions in water in response to temperature changes and UV irradiation.

these thermosensitive water-soluble polymers in controlled release of substances, "smart" catalysis, etc.

Environmentally Responsive Mixed Homopolymer Brushes

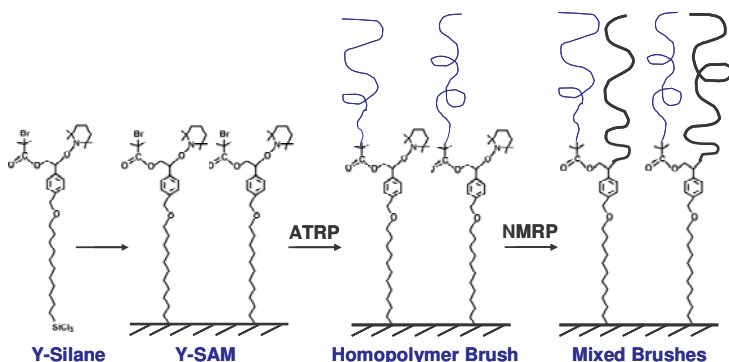
Mixed homopolymer brushes, composed of two chemically distinct homopolymers randomly or alternately immobilized via covalent bonds on a solid surface with high grafting densities, represent a new class of environmentally responsive materials. In addition to the stretched conformations assumed by surface-tethered polymer chains, microphase separation between two immiscible polymers and/or between polymers and solvents occurs, enriching their phase



Scheme 3. Various Nanostructures from Self-Assembly of Mixed Homopolymer Brushes.

behavior. Theoretical studies have discussed whether symmetric mixed homopolymer brushes on a flat substrate phase separate laterally forming a "rippled" state or vertically producing a "layered" state under equilibrium melt conditions (Scheme 3), and have predicted that the "rippled" structure 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 overall and relative 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 4). Two different living radical polymerization techniques, ATRP and NMRP, were

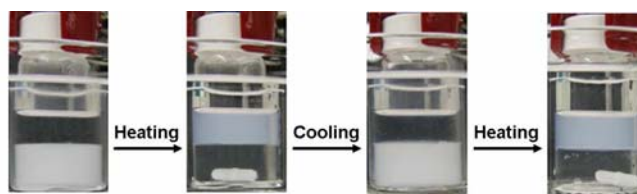


Scheme 4. Synthesis of Well-defined Mixed homopolymer brushes from a Y-initiator-functionalized silica surface.

used to grow two different polymers from asymmetric difunctional initiator-terminated self-assembled monolayers (Y-SAMs) on flat substrates and nanoparticles. The Y-initiators were designed to ensure that the two initiators were alternately immobilized on the substrate. These brushes have been shown to respond to environmental changes, exhibiting different surface morphologies and surface properties. We have found from transmission electron microscopy studies that mixed poly(*t*-butyl acrylate)/polystyrene brushes undergo lateral microphase separation in melt, producing a nearly bicontinuous, random wormlike pattern. The ongoing work includes the study of self-assembly of mixed brushes by combinatorial methods, the formation of well-ordered nanoscale patterns via directed self-assembly, phase morphologies of mixed brush-grafted silica particles in homopolymer, polymer blend, and diblock copolymer matrices, etc.

Thermo-Responsive Polymer Brush-Grafted Particles (Thermosensitive Hairy Particles)

Hairy particles, composed of a layer of polymer chains that are densely grafted by one end via a covalent bond (i.e., polymer brushes) on the core, are an intriguing class of nanostructured materials. The structures and properties of both core and brush layer can be tailored for a variety of applications, e.g., sensors and supported catalysts. Using surface-initiated ATRP, we have synthesized thermosensitive poly(methoxyoligo(ethylene glycol) methacrylate) brushes on silica particles, and have found that the phase transition of polymer brushes from a hydrated state to a dehydrated state begins at a lower temperature and continues over a broader temperature range compared with that of the corresponding free polymer in water. These thermoresponsive hairy particles can be reversibly and quantitatively transported between water and ethyl acetate phases upon temperature changes (Scheme 5) and the transport rates can be greatly enhanced by the use of pre-mutually saturated solvents. As a demonstration of the application of thermosensitive hairy particles in catalysis, we have synthesized Pd nanoparticles inside the core of hairy polymeric particles. The supported Pd efficiently catalyzes mono- and bi-phasic hydrogenation reactions and the catalytic activity can be modulated by the phase transition of hairy layer, resulting in a non-Arrhenius-type dependence of rate constant on temperature. Currently, we are developing multi-responsive hairy particles and thermosensitive polymer brush-supported organic catalysts on particles.



Images of H₂O and ethyl acetate layers after consecutive heating at 60 °C and cooling in an ice/water bath. The conc. of particles: 1.0 mg/mL.

Scheme 5. Temperature-induced reversible transport of thermosensitive hairy particles.

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