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## SCIENCE & TECHNOLOGY

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### FROM THE ACS MEETING

## BRUSHING UP ON POLYMERS

Applications for polymers anchored to flat and nanoparticle surfaces are beginning to emerge

[MICHAEL FREEMANTLE, C&EN LONDON](#)

A novel class of materials with "smart surfaces" that can adapt to their environment and be tailored for a wide range of uses--including adhesives, microfluidics, lithography, and chromatography--is emerging from the application of state-of-the-art polymerization techniques.

The materials, known as polymer brushes, consist of polymer chains tethered at one end, usually by covalent bonds, to a surface or interface.

"The surface is commonly an inorganic substrate such as gold or silicate, but can also be a polymer surface," according to William J. Brittain, professor of polymer science at the [University of Akron](#), in Ohio.

A symposium on the topic was held at the ACS national meeting in New Orleans last month. It was cosponsored by the Divisions of Polymer Chemistry and Polymeric Materials: Science & Engineering. The symposium was organized by Brittain; University of Houston associate chemistry professor Rigoberto C. Advincula; Duke University senior research scientist Kenneth C. Caster; and Jürgen Rühle, professor of chemistry and physics of interfaces at the University of Freiburg, in Germany.

Polymer brushes covalently attached to the surface of a substrate are prepared by "grafting-to" or "grafting-from"



**ANALYSIS** Boyes (sitting) and Brittain examine polymer brushes prepared by living radical polymerization techniques.

UNIVERSITY OF AKRON PHOTO

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radical grows until it is deactivated to form a dormant species. Reactivation of this species allows the polymer chain to resume its growth.

At [Michigan State University](#), a polymerization group led by chemistry professor Gregory L. Baker and a surface analysis group led by associate chemistry professor Merlin L. Bruening have been working together to fabricate novel polymer films using ATRP.

"ATRP from a surface yields polymer brushes with relatively uniform molecular weights and affords control over brush thickness through variation of polymerization time," Bruening told C&EN. "We have recently used ATRP in aqueous solution to prepare giant poly(2-hydroxyethyl methacrylate) brushes with thicknesses approaching 1 mm.

"We are now trying to exploit this synthesis to develop unique polymer brush coatings for capillary electrochromatography," he said. "The length of these brushes increases the ratio of stationary phase to mobile phase in electrochromatography and should provide increased capacity for open-tubular capillary separations."

In recent work, for example, the group employed two ATRP steps to synthesize densely double-grafted brush copolymers. In the first step, ATRP is used to prepare poly(2-bromopropionyloxyethyl methacrylate) (BPPEM), which is used as a macroinitiator. Poly(ethylene glycol) methyl ether with a methacrylate end group (PEO-MA) is then grafted by ATRP from the macroinitiator. The product is P[BPPEM-graft-(PEO-MA)].

Cross-linked, double-grafted brushes behave as supersoft rubbers that mechanically resemble hydrogels, Matyjaszewski observed.

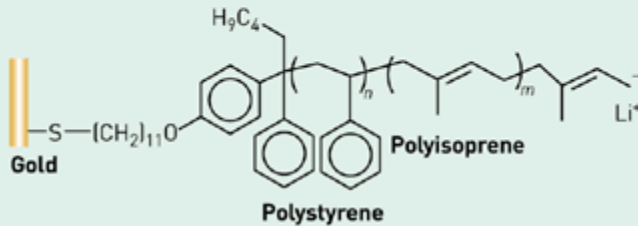
"They may be potentially used in many applications from tissue engineering and wound healing to cosmetics and specialty coatings," he said.

ATRP is also being used to graft polymer brush layers from the surfaces of inorganic nanoparticles.

"This approach provides the means to control not only the final material's surface functionality, as one can also do with small organic ligands, but also its mechanical, optical, or charge carrier properties," noted Timothy E. Patten, associate professor of chemistry at the University of California, Davis. "The development of hybrid polymer/inorganic nanoparticles should facilitate the preparation of an entire new category of materials with structures that are controllable on the nanometer scale."

## BLOCK COPOLYMER

Polystyrene-polyisoprene brush is prepared by living anionic surface initiated polymerization



**PATTEN'S GROUP** has prepared composite nanoparticles using surface-initiated ATRP of organic soluble and hydrophilic monomers from silica, germanium, and core/shell cadmium sulfide/silica nanoparticles.

"The properties of the final material can be varied by changing the inorganic core, the interior polymer layer, and the exterior or chain-end layer," he said.

In work soon to be published in *Chemistry of Materials*, Patten describes the synthesis of germanium nanoclusters terminated with organic groups containing acetals, alcohols, esters, and polymer chains grafted using ATRP. He carried out the work with Susan M. Kauzlarich, chemistry professor at UC Davis; assistant professor of chemistry Robin S. Tanke at the University of Wisconsin, Stevens Point; and coworkers.

Brittain, at the University of Akron, has been using ATRP to synthesize various types of polymer brushes on silicon substrates, including electrically charged diblock copolymer brushes containing blocks of poly(acrylic acid) and polystyrene or poly(methyl acrylate).

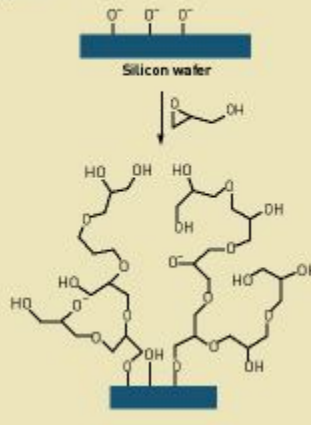
He is currently working with postdoctoral research associate Stephen G. Boyes on the preparation and properties of polyelectrolyte brushes containing silver.

"Starting from a diblock with the upper block composed of poly(acrylic acid), which is prepared by hydrolysis of a precursor poly(tert-butyl acrylate) block, the acid group can be ionized with silver acetate," Brittain explained.

"Subsequent hydrogenation reduces the silver ions to silver particles, which are observed in atomic force microscopy analysis. Our current work is aimed at creating ordered arrays of silver particles by starting with a patterned diblock copolymer brush."

## HYPERBRANCHED

Brush formed by ring-opening polymerization of glycidol



A group at the Institute of Microsystem Technology at the University of Freiburg led by Rhe is investigating the use of surface-initiated polymerization to prepare tailor-made coatings on solid substrates.

"We are currently working on the generation of functional polymer brushes-- that is, brushes that carry a number of functional groups--for the preparation of functional coatings," Rhe told C&EN. "Examples are brushes with liquid-crystalline side chains or brushes which can render surfaces ultrahydrophobic."

Last year, Rhe showed how surface-initiated radical-chain polymerization can be used to generate perfluorinated water- and oil-repellent surfaces on porous silica substrates [*Langmuir*, **18**, 6133 (2002)]. He carried out the work in collaboration with a team of South Korean scientists that included a group at the Korea Research Institute of Chemical Technology, Taejon, led by In Jun Park.

The repellent surface consists of a film of poly (perfluoroalkylethyl acrylate) brushes that are grafted from self-assembled azochlorosilane initiators attached to the "micro-rough" silica surface. Rhe and his Korean coworkers showed that the perfluorinated polymer films can be grown with controlled thicknesses without changing the roughness of the surface. They demonstrated the repellent nature of the surfaces by measuring the wetting of the surface-modified materials by water, oil, and other test liquids.

The group is also using its grafting-from approach with monolayers of azo-initiators to generate high-sensitivity DNA sensors consisting of oligonucleotide probes attached to polymer brushes.

"Brush-based DNA chips allow more probe molecules per surface area to be immobilized on the chip, and the wetting properties of the surfaces can be chemically tailored to give optimal printing performance," Rhe said. "Such tailoring is not possible with conventional chips based on self-assembled monolayers."

Cambridge University chemistry lecturer Wilhelm T. S. Huck and Ph.D. student Majad Khan have used anionic ring opening multibranching polymerization to prepare hyperbranched polyglycidol brushes on silicon wafers. Most polymer brushes described to date consist of linear chains, they note. There are only a few papers reporting the formation of surface-initiated hyperbranched polymers.

"Earlier work by our group exploited aqueous ATRP to grow brushes in a fast, yet controlled way from a variety of surfaces," Huck said. "In our latest work, we use surface Si-OH groups to directly initiate a ring-opening polymerization of glycidol to form hyperbranched brushes. The advantages of

this approach are the rapid introduction of high densities of functional groups and the elimination of any surface preparation."

Huck and Khan use a novel one-pot procedure to covalently link the polyglycidol brushes to the silicon substrate, which involves treating the wafer with sodium methoxide solution and the glycidol monomer. They show that the polymer brushes can easily be modified through esterification of the alcohol groups.

Another form of anionic polymerization, known as living anionic surface initiated polymerization (LASIP), is being used to grow homopolymer and block copolymer brushes from gold surfaces, as well as silica and clay nanoparticles. The work is being carried out by Advincula's group at the University of Houston and coworkers at the University of Tennessee, Knoxville, and the University of Athens, Greece [[\*Langmuir\*, \*\*18\*\*, 8672 \(2002\)](#)].

The team tethers 1,1-diphenylethylene, an initiator precursor, onto the surfaces using self-assembled monolayer techniques. The precursor is then activated by an n-butyl lithium anion for polymerization of monomers such as styrene, isoprene, butadiene, methyl methacrylate, and ethylene oxide.

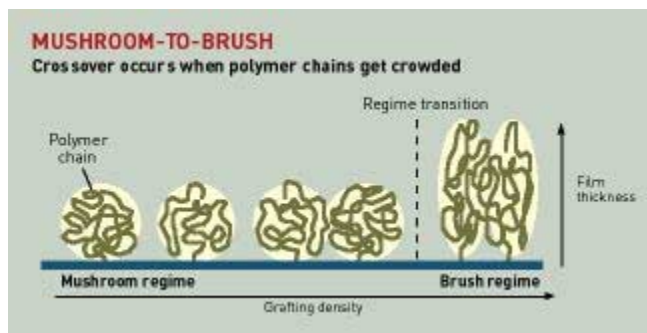
"This anionic grafting-from surface polymerization approach enables us to investigate the chemistry, mechanism, and architectures of macromolecules that have been prepared by conventional anionic polymerization in solution and apply them to surfaces," Advincula said.

Application of anionic polymerization and carbanion chemistry to silica and clay nanoparticles, he pointed out, requires special filtration and polymerization methods under high vacuum because of the living nature of the anions and the aggregation properties and sensitivity to impurities.

At the Technical University of Braunschweig, Germany, chemistry professor Henning Menzel is using a transition-metal initiated living polymerization technique to prepare polypeptide brushes.

"We use nickel-mediated grafting-from polymerization of  $\alpha$ -amino acid-N-carboxyanhydrides to prepare films of  $\alpha$ -helical polypeptides on modified surfaces of polystyrene beads," he said. "We use the beads because they have a large and easy-to-functionalize surface."

The polypeptides are rodlike, and the brushes are expected to behave differently from conventional flexible polymer brushes, Menzel explained. The polypeptide helices in the films are unidirectional and therefore have a permanent dipole that results in piezoelectric properties.



**POLYMER CHAINS** anchored at a solution/substrate interface exist as brushes only if the grafting density--that is, the number of polymer chains per unit area--is sufficiently high to force the chains to adopt elongated conformations. At lower grafting densities, the chains are less crowded and exist independently in the so-called "mushroom" regime. Such films are thinner than polymer brush films.

A group led by Jan Genzer, assistant professor of chemical engineering at North Carolina State University, has used combinatorial studies to probe the so-called mushroom-to-brush crossover of polyacrylamide grafted from silica substrates [*J. Am. Chem. Soc.*, **124**, 9394 (2002)]. The results show that the thickness of the polymer film is independent of the grafting density in the mushroom regime but gradually increases with increased grafting density in the brush regime.

"We have developed means of forming polymer brush assemblies on substrates where the grafting density changes continuously from very small to very large," he said. "We have also pioneered new means of forming surface-tethered polymer assemblies with a gradual variation of the brush molecular weight."

Such gradient techniques are particularly valuable for investigating the physicochemical characteristics of surface-anchored polymers, such as wetting of the substrate.

Despite the recent flurry of activity in the field, only limited data exist on the properties of nanometer-thick brush layers, according to Vladimir V. Tsukruk, professor of materials science and engineering at Iowa State University.

"It is frequently assumed that properties of grafted layers are similar to those in bulk," he said. "However, recent atomic force microscopy studies have shown that surface stiffness depends strongly upon the type of aggregation and overall shape of individual, grafted hyperbranched macromolecules and nanosized surface aggregates."

In work yet to be published, Tsukruk and coworkers have studied the reorganization of binary polymer brushes consisting of two incompatible polymers: polymethylacrylate and poly(styrene-co-2,3,4,5,6-pentafluorostyrene). The work was carried out in collaboration with a group at the Institute

of Polymer Research in Dresden, Germany, led by chemistry professor Sergiy Minko.

The team randomly grafted each polymer, one after another, onto a silicon wafer using a grafting-from approach to produce dense mixed-brush layers.

"We observed that these binary brushes can be switched reversibly and repeatedly from a smooth, glassy brush layer to a spongy, gel-like rubbery layer by treatment in different solvents," Tsukruk told C&EN. "This reorganization of brush microstructure results in dramatic changes in surface elasticity. The elastic modulus changes 10-fold. The thickness, surface roughness, and macroscopic properties such as wettability and optical appearance also change dramatically."

One of the primary aims of polymer surface science today, he remarks, is to create dynamic versatile polymer layers that do not merely protect surfaces.

"Polymer brush layers composed of mobile anchored polymer chains should enable a new class of materials with 'smart surfaces' to be developed for use as liquid repellents, adhesives, lubricants, and antifogging coatings," Tsukruk concluded. "It may also be possible in the future to develop polymer brush materials that mimic biologically compatible surfaces. Such materials could lead to dramatic breakthroughs in drug delivery and fighting disease."

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