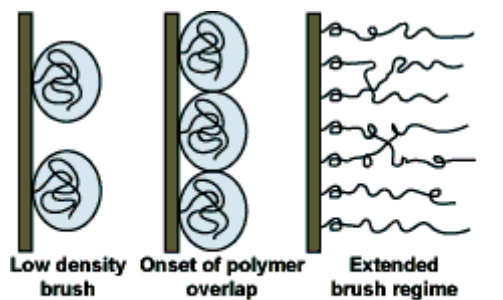


# Polymer Brushes

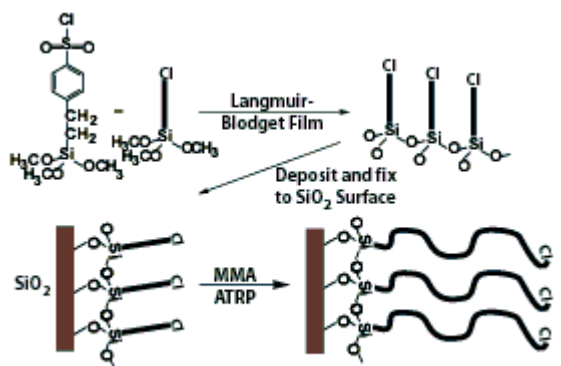
## Functional Polymer Monolayers

Polymer brushes are polymer monolayers attached to a solid support. Surfaces formed from polymer brushes have potential applications as low friction biological surfaces,<sup>1</sup> nanoparticles organizers,<sup>2</sup> nanoparticle stabilizers for NMR contrast agents,<sup>3</sup> biological mimetic and antifouling surfaces,<sup>4</sup> and high dielectric polymers coatings.<sup>5</sup> At high grafting density, adsorbed polymers change their conformation from a globule to an extended chain. This unusual conformation change is induced by polymer-polymer repulsions when they are confined to a small area. This was first described by Alexander<sup>6</sup> in 1977 and de Gennes<sup>7</sup> in 1980, but it was not until 1986 that Tirrell<sup>8</sup> showed experimental evidence for the extended chain conformation.



**Figure 1** Polymer brushes at three different surface graft densities.

Tirrell synthesized a polystyrene block polyvinyl pyridine copolymer. In a nonpolar solvent like toluene, the “sticky” polyvinyl pyridine block adsorbed onto a mica substrate while the polystyrene could extend into the solvent system. Tirrell’s synthesis is typical of the “grafting to” approach, where polymer chains are first synthesized followed by surface adsorption. In the “grafting to” approach, attached chains cover the surface at high density and prevent further chain adsorption. Another approach is the “grafting from” method.<sup>9</sup> Here, polymer initiators are attached to a surface, and polymerization proceeds from the surface with the addition of monomer. The reactive sites move with the growing chain allowing complete access of monomer to the initiator sites (fig 2).<sup>10</sup>

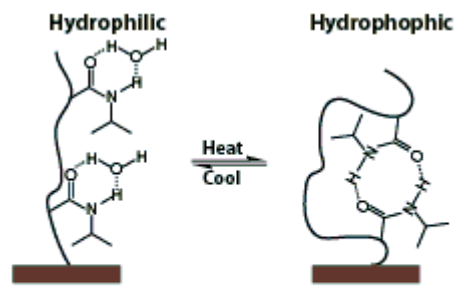


**Figure 2** The grafting from approach using ATRP.

### Surface Responsive Brushes

Polymer brushes can interact with the surrounding solvent and expand and contract depending on solvent quality. This allows brushes to act as nanoactuators, opening and closing valves in response to various conditions. Ito has used polymer brushes to synthesize porous membranes that can open and close in response to pH,<sup>11</sup> light,<sup>12</sup> and temperature.<sup>13</sup> In each case an external stimuli increases the polarity of the surface bound polymers. The brush polymers then expands in the aqueous solvent and acts as a pore gating system.

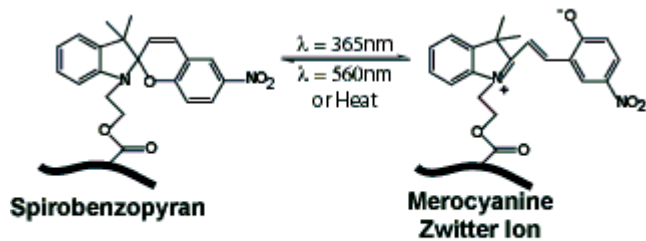
Poly(N-isopropyl acrylamide)[pNIPAAm] is a polymer commonly used for temperature-mediated responses.<sup>14</sup> It has a lower common solution temperature (LCST) induced by rearrangement of hydrogen bonding in the amide backbone causing it to become hydrophobic at higher temperatures (fig 3). Jiang has shown that super hydrophobic switching can be achieved when pNIPAAm polymer is attached to a patterned silica surface.<sup>15</sup> Such surfaces display water contact angles that vary greatly with temperature. At 25°C a water droplet spreads completely



**Figure 3.** Hydrogen bonding change in thermoresponsive polymer.

changes the LCST of the overall polymer. Such polymers can display isothermal switching if the ionization changes the LCST from above to below the ambient temperature or vice versa. For instance Yamaguchi showed that copolymer brushes of N-isopropyl acrylamide and benzyl-18-crown-6 (fig 4 left) could respond to the presence of  $Ba^{2+}$  to induce pore closure similar to Ito's gating systems.<sup>16</sup> Such a polymer brush has been exploited for an ion specific osmotic pressure gating system. Such an osmotic pressure control valve could be used as an osmotic pump for a drug delivery.

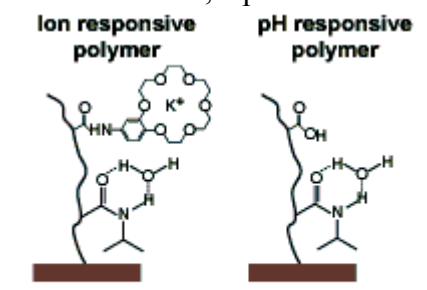
Random copolymers of methyl methacrylate and spirobenzopyran (pMMA-co-SP) are well known.<sup>17</sup> Spirobenzopyran can undergo a photoinduced isomerization from a neutral species to a zwitterion upon exposure to UV light (fig 5). The polarity of the zwitterion is greater than the neutral spirobenzopyran allowing brushes of pMMA-co-SP to rearrange in response in non-polar solvents. This has been exploited by Bell and Braun to create light patternable surfaces.<sup>18</sup> Such surfaces show differential absorption of brush coated silica particles and could be used for ordered 2-D patterned surfaces over large areas.



**Figure 5** Polarity change through zwitterion formation of spirobenzopyran upon UV treatment.

onto the hydrophilic surface, if the temperature is raised to 40°C a contact angle of 149.3° can be measured indicative of an extremely hydrophobic surface. The surfaces are stable over multiple cycles with little to no loss in contact angle measurements over 20 cycles. These surfaces could be used for purposes as mundane as self cleaning surfaces or as complex as controlling cellular motility.

Random copolymers of pNIPAAm can also be used for multiple responsive polymers (fig 4).<sup>14</sup> The copolymer contains a monomer which, upon ionization,



**Figure 4.** Copolymer systems which respond to multiple stimuli.

Recently polymer brush surfaces have been developed which are capable of responding to ions released from cell tissue<sup>19</sup>. Such a response could only be generated through specific chemical interactions and the combination of rapid recognition and rearrangement. As our knowledge of responsive surfaces increases, it could usher in a new type of tissue engineering based on cell signal responses at the growing surface.

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