FUNCTIONALIZATION OF SILICA MICRO-CAPILLARIES AND
SILICA NANOPARTICLES via POLYMER BRUSHES

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FUNCTIONALIZATION OF SILICA MICRO-CAPILLARIES AND SILICA NANOPARTICLES via POLYMER BRUSHES

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ABSTRACT

Polymer brushes were synthesized on the interior of micro-capillaries to study the influence of brushes on solvent flow through a confined space. The synthesis of several polymer brush coatings was performed in fused silica micro-capillary tubing by atom transfer radical polymerization using the “grafting from” approach. Characterization of the polymer coatings inside of the capillaries was challenging due to inaccessibility of the sample geometry. Fluorescence spectroscopy was used as a technique to verify that covalently-attached polymer brushes were present. Capillary rise measurements demonstrated that the Zisman critical surface energy changes as the polymer coatings were modified from either a hydrophilic or a hydrophobic surface. The hydrophilic and hydrophobic nature of polymers leads to flow in micro-capillaries that can be manipulated and controlled in a passive fashion without external stimulus.

Backpressure measurements were performed to show how selective solvents can be used to alter the backpressure required for flow. The measurements were used to correlate the flow of good/bad solvents with different polymer coatings; we speculate how these solvents alter brush conformation as an explanation for differentiated backpressure measurements. An analogous study involved capillaries functionalized with small molecule silanes which supported the hypothesis that the polymer brush is in an extended (solvated) state in good solvent and in a collapsed state in bad solvent.
Preferential flow experiments were designed to measure the preferred path an aqueous solvent would take when comparing two capillaries containing polymer coatings of different surface energies. Water flow preferred the hydrophilic, higher surface energy coated capillary when comparing capillaries of the same internal diameter. When the difference in internal size became too large, the surface energy effect was overwhelmed and the aqueous solvent flowed down the larger, hydrophobic capillary.

The second portion of this dissertation describes the in situ formation of functionalized silica nanoparticles. The reactive stabilizers used in the study were [3-(2-bromoisobutyryl)propyl]triethoxysilane and [3-(2-bromoisobutyryl)propyl]ethoxydimethylsilane. Both stabilizers have an ATRP initiator at the non-condensable end yielding an initiator-immobilized silica nanoparticle. With the initiator-functionalized silica nanoparticles, ATRP synthesis was performed with styrene, tert-butyl acrylate and methyl acrylate. The size of these functionalized silica nanoparticles was controlled by varying the reactive stabilizer concentration and the time of addition.

This work was extended by using preformed polymer chains as the reactive stabilizer. The polymer chain contained a monoethoxysilane-functional group which condensed to form hybrid polymer/silica nanoparticles. The relationships among the molecular weight, time of addition and concentration of the polymeric stabilizer to the nature of the resulting nanoparticle were studied. The large polymer reactive stabilizers did not afford the control in particle size observed with the small molecule reactive stabilizers.
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CHAPTER I
INTRODUCTION

Polymer chains attached to surfaces have garnered much attention in recent years because of their ability to add a vertical dimension to thin films when compared with the self-assembled monolayers, and because polymers have the added value of functional groups incorporated within the chains.\(^1\) By assembling the polymer chains, which are tethered to a surface or interface, with a high enough grafting density, the chains are then forced to stretch normal from the grafting site to avoid segmental overlap.\(^2,3\) The stretched conformations seen in polymer brushes occur under equilibrium conditions.

Polymer brushes can be fixed to a surface by using physisorption or chemisorption techniques.\(^4\) In the physisorption approach, a functionalized homopolymer or diblock copolymer were one end or one block preferentially adheres to an appropriate surface while the other end stretches from the surface.\(^5\) A major disadvantage of this technique is that the chains are thermally and solvolytically unstable due to the relatively weak van der Waals forces or hydrogen bonding that anchors the chains to the surface. The chemisorption technique involves the covalent attachment of the polymer chain to a surface, \textit{via} “grafting to” or “grafting from” methods, resulting in a more environmentally stable film. In the “grafting to” method, preformed, end-functionalized polymer chains are reacted with a functionalized surface to form a tethered
polymer film. The “grafting from” method involves the in-situ polymerization from an initiator-functionalized surface. Physisorption and “grafting to” methods use preformed polymer chains; thus, molecular weight and molecular weight distribution can be well controlled. The grafting density tends to be lower due to the inter-steric hindrance occurring during the grafting process. In the “grafting from” method, a number of different polymerization methods can be used to achieve higher grafting densities. Using this method, there is less control over the molecular weight and molecular weight distribution, and the uniformity of the tethering density is unknown.

Because brush thickness is dependent on molecular weight, controlled polymerization techniques can be used to produce brushes with tunable film thicknesses and provide means for preparation of multi-block brushes through sequential monomer addition. Herein, a controlled radical polymerization technique, atom transfer radical polymerization (ATRP), is used in the synthesis of the polymer brushes via the “grafting from” method. ATRP combines the control of a living polymerization with the less stringent conditions of a free-radical polymerization. Even though ATRP is strictly not a true “living” polymerization, it is still possible to control molecular weight, molecular weight distribution, chain architecture, chain end functionality, and copolymer composition. A living polymerization is defined as a polymerization that proceeds in the absence of chain transfer or termination.

Previously, Granville and Brittain reported the synthesis of a tethered poly(methyl acrylate)-b-poly[(3H, 3H, 3H, 2H, 2H-pentafluoro)propyl acrylate] (Si/SiO₂/PMA-b-PPFA) brush from a 2-2.5 μm porous silica substrate. The order of the blocks in the diblock brush was determined by the order of polymerization from the
surface. For example, a Si/SiO\textsubscript{2}/PMA-b-PPFA brush was synthesized by first forming a Si/SiO\textsubscript{2}/PMA brush on the surfaces, followed by the polymerization of PFA from the Si/SiO\textsubscript{2}/PMA brush. A self-assembled monolayer was first deposited onto a porous glass frit followed by the ATRP of methyl acrylate and then pentafluoropropyl acrylate to yield an AB diblock copolymer brush. Upon addition of PMA, the porous glass frit had a static water contact angle of 90\(^\circ\); after the addition of PPFA top block, the static water contact angle increased to 135\(^\circ\). The diblock copolymer brush was exposed to selective solvent treatment and was found to undergo reversible surface rearrangement to bring about hydrophilic and hydrophobic surfaces. When the glass frit was treated with ethyl acetate, a good solvent for PMA and a bad solvent for PPFA, the static water contact angle was 90\(^\circ\). The higher than typical PMA contact angle was brought about because of the rough nature of the frit; a typical static water contact angle is \~60\(^\circ\).\textsuperscript{1} The PMA layer was brought to the surface while the PPFA block was buried underneath the PMA in order to minimize its interaction with the solvent. The water droplet permeated the glass frit after several minutes. The frit was then immersed in \(\alpha,\alpha,\alpha\)-trifluorotoluene, a good solvent for both PPFA and PMA, leaving a hydrophobic, fluorine-rich surface. The water contact angle was 135\(^\circ\); however, the water droplet remained stable even after several hours and did not permeate the porous glass frit.

The permeability control is an intriguing aspect of this work, given the relative dimensions of the frit pores (200 nm) and the typical length of the diblock brush (20-30 nm). The stimuli-responsive nature of the fluorinated diblock works as a chemical gate that is responsive to selective solvents, thermal annealing, or supercritical carbon dioxide\textsuperscript{1}. Permeability control with frits that possessed different pore dimensions was
then studied; frits with specifically, 0.9-1.4 μm, 10-20 μm, and 70-100 μm average pore dimensions were investigated.\textsuperscript{10} Like the 2-2.5 μm frit, water permeated the frit when only modified with a PMA homopolymer brush. After the addition of the PPFA block, higher static water contact angles were observed. As the average pore size increased, the water repellency decreased. The static contact angles for 0.9-1.4 μm, 2-2.5 μm, 10-20 μm, and 70-100 μm glass frits were 145°, 135°, 113° and 99°, respectively.

These experiments on glass frits demonstrate that polymer brushes have the potential to act as passive flow controls in micro-channels. The research described herein uses ATRP as a controlled radical polymerization technique to prepare homopolymer and diblock copolymer brushes from the surface of flat and cylindrical silica surfaces. The goal of this research was to grow covalently-attached polymer chains from the surface of micro-capillaries and explore the use of diblock brush rearrangement as a control mechanism in micro-fluidic and lab-on-chip devices. First, the various polymer brushes had to be synthesized and characterized inside of 75 μm silica capillaries. Characterization tends to be difficult due to the inaccessibility of the interior. Creative experiments were designed to exploit the unique characteristics that the polymer brushes possess when confined in micro-channels.

The second half of this work consists of the in-situ functionalization of silica nanoparticles. The synthesis of silica is a heterogeneous condensation polymerization and the particles are stabilized by “electrostatic stabilization” from the charges formed in-situ on the surface during the reaction. An alternative to electrostatic stabilization is steric stabilization where specific non-reactive molecules, widely known as stabilizers, are added during condensation polymerization that adsorb to the surface and thus prevent
coagulation. A variant of steric stabilizers is a reactive stabilizer that will participate in the condensation reaction in addition to functioning as a stabilizing group. These stabilizing groups can be a monomer, initiator or polymer. By varying the time of addition or concentration of the reactive stabilizer, it was possible to control the particle size and ultimately produce inorganic/organic hybrid nanoparticles.
2.1 Introduction to Polymer Brushes

Polymer brushes are described as polymer chains tethered to a surface or interface which have a sufficiently high grafting density such that the chains are forced to stretch away from the tethering site. Stretching can be much further than the typical unstretched size of the chain. Typical polymer chains adopt a random-walk conformation while polymer brushes tend to stretch normal from the grafting surface when the grafting density is sufficiently high. Polymer brushes will stretch in the presence of solvent as well as in the dry state. In the presence of a good solvent, the polymer chains will stretch away from one another in order to minimize contact between their neighboring chains. In the absence of solvent, the polymer chains will stretch away from the tethering site to avoid overfilling incompressible space.

The polymer brush tethering site may vary depending on the application; the interface may be a solid substrate or the interface between two solvents, between solvent and air, or between melts or solutions of homopolymers. Figure 2.1 depicts various polymer brush systems where the polymer chains in each system exhibit the characteristic nature of polymer brushes extending away from the grafting site. Tethering of the polymer chains can be reversible or irreversible. On a solid surface, the polymer chains
can be chemically bonded to the surface or may be absorbed onto the surface, i. e. physisorption. For interfaces between fluids, the attachment may be achieved in which one part of the chain prefers one medium and the rest of the chain prefers another, as illustrated by the behavior of polymer micelles and amphiphilic diblock copolymers.

![Chemically bonded chains at solid interface][1]

![Diblock copolymer at a fluid-fluid interface][2]

![Graft copolymer at a fluid-fluid interface][3]

![Absorbed chains on a solid interface][4]

![Polymer micelle][5]

![Diblock copolymer melt][6]

**Figure 2.1. Examples of polymer brush systems.**

Polymer brushes have been widely studied over the past decades due to their novel properties.\(^{11-15}\) Polymer brushes were first used by van der Waarden\(^ {16,17}\) to prevent flocculation of carbon black particles. By grafting hydrocarbon polymer chains to colloidal carbon black particles, flocculation did not occur because the immobilized polymer chains preferred the solvent of the suspension compared to the particle, i. e. steric stabilization. Since then, polymer brushes have been used to tailor surface properties in applications for adhesive materials,\(^ {18}\) surface lubricants,\(^ {19}\) chromatographic devices,\(^ {20}\) surface compatibilizers,\(^ {6}\) inhibitors of surface corrosion,\(^ {21}\) surface modifiers,\(^ {22}\) and colloidal mixture stabilizers.\(^ {2}\)
2.2 Atom Transfer Radical Polymerization

Atom transfer radical polymerization (ATRP) is a controlled radical polymerization technique, which was used in the synthesis of our surface-bound polymer. ATRP is established as a controlled polymerization technique based on the work of Sawamoto\textsuperscript{23} and Matyjaszewski.\textsuperscript{24,25} The controlled polymerization technique allows for the synthesis of well-defined polymers with control over the molecular weight, molecular weight distribution, and molecular architecture. ATRP was used because it requires less stringent conditions when compared with anionic and cationic polymerization techniques and is more tolerant of polar functional groups.

The fundamental mechanism for ATRP comes from atom transfer radical addition (ATRA). In ATRA, also known as the Kharasch reaction, a transition metal complex catalyzes the addition of an alkyl halide across a carbon-carbon double bond as shown in Scheme 2.1.\textsuperscript{26} A radical is generated by the transfer of a halogen atom from the alkyl halide to the transition metal complex. The radical can then add to the carbon-carbon double bond to form a radical species which is less stable than the original radical, so that the halogen atom is transferred back to the product radical and thus forms a stable adduct. The halogen transfer should be kinetically dominant and faster than competing reactions such as radical termination and telomerization.\textsuperscript{26} Since the product radical in ATRA is much less stable than the initial radical, it forms a stable bond with the halogen in the metal complex. This halide capping reaction is more reversible in ATRP because the initial radical adds to the vinyl monomers that can stabilize the product radical and thus creating a product radical with a similar stability to the initial radical.\textsuperscript{27}
Otsu et al.\textsuperscript{28} suggested that the bimolecular termination process in conventional free radical polymerization would be minimized if the dormant chain end would undergo a reversible dissociation into a transient radical species and a persistent radical; these persistent radicals are more stable and do not initiate polymerization (Scheme 2.2). If the equilibrium constant for the reversible dissociation ($k_d$) is sufficiently small, a small concentration of the reactive transient radicals would exist and termination would be minimal. The propagating transient radicals are short-lived species, which quickly couple with a persistent radical. Since dissociation is sufficiently slow, the incorporation of monomer by propagation is limited to a low number of monomer units per dissociation cycle; if dissociation is fast, there would be many monomer addition cycles and the chain growth would occur in a stepwise fashion and proceeding until all of the monomer has been consumed.\textsuperscript{29} The persistent radical effect (PRE) minimizes irreversible bimolecular termination during a radical polymerization by limiting the number of propagating radicals. The concentration of stable radicals will increase relative to reactive propagating radicals because some of the propagating radicals undergo homocoupling and cross-coupling while the unreactive stable radicals can only undergo reversible cross-
coupling with reactive alkyl radicals. A build up of persistent radicals occurs because they do not react with themselves but combine with the transient radicals and the transient radicals also react with themselves irreversibly. Thus, the concentration of persistent radicals increases; this is the persistent radical effect.

\[ \text{Scheme 2.2. Reversible dissociation into a transient radical species and a persistent radical.} \]

The controlled nature of ATRP requires that the equilibrium between dormant and active species lies toward the dormant species. With a large number of persistent radicals, the number of chain termination reactions is greatly reduced, and uniform chain growth occurs as a result of fast initiation and rapid reversible deactivation. PRE helps establish the reversible activation/deactivation equilibrium with rate of deactivation much larger than the rate of activation (Scheme 2.3), this allows one to carryout controlled polymerizations using ATRP. The cross-coupling reaction between stable radicals and alkyl radicals becomes faster than the homocoupling of alkyl radicals because of the concentration increase of the stable free radicals; thus, the rate of deactivation is much faster than the rate of activation. The cross-coupling reaction is reversible unlike the homocoupling reaction between alkyl radicals which in turn, keeps the chain ends “alive” since the chain ends can be reversibly activated and deactivated.
In ATRP, the radicals are generated through a reversible redox process catalyzed by a transition metal complex, $M_t^\eta$-Y/Ligand (Scheme 2.3). The rate constants $k_{\text{act}}$ and $k_{\text{deact}}$ describe the activation and deactivation, respectively, of the reversible radical generation process. The radicals react reversibly with the oxidized metal complex (deactivator) to form the dormant species and the original metal complex (activator) by abstracting the halogen atom. The growth of the polymer chains occurs by the addition of monomer to the intermediate radicals with a rate constant $k_p$, and the rate of propagation is first order in radical concentration. The termination reactions ($k_t$) that occur during the polymerization result from radical coupling and disproportionation reactions and this occurs by a second order reaction dependence in radical concentration. This termination is minimized by shifting the equilibrium of the reaction to the dormant state and lowering the concentration of growing radicals. The concentration of reactive alkyl radicals is kept low due to the PRE. Chain transfer reactions could also occur in ATRP, as in conventional free radical polymerizations, but since the reactions are rarely carried out to high or complete conversion, the effects of any chain transfer reactions are negligible.

![Scheme 2.3. Mechanism of transition-metal catalyzed ATRP.](image)

Typical monomers polymerized in ATRP include styrenes, acrylates, methacrylates, and vinylpyridines. In order for ATRP to be controlled, the monomer must form a stabilized propagating radical that results from monomer addition. Each
monomer has its own unique atom transfer equilibrium constant, $K_{eq}$, between the active
and dormant species where $K_{eq} = k_{act}/k_{deact}$, so the amount and reactivity of the transition
metal catalyst needs to be adjusted accordingly.\textsuperscript{31} If there is a small equilibrium constant,
then the polymerization will be slow because of a low instantaneous radical
concentration. Conversely, a large equilibrium constant will lead to a larger radical
concentration and will increase the rate of termination.

The initiating molecule must contain a transferable (pseudo)halogen (X in
Scheme 2.3) and this halogen is required to rapidly and selectively transfer between the
growing chain and the transition metal complex. The amount of initiator added to the
polymerization determines the number of growing polymer chains in the system as long
as initiation is fast and chain transfer and chain termination are negligible. Alkyl halide
initiators are generally used in ATRP; they contain an activating substituent on the $\alpha-$
carbon such as aryl, carbonyl, or allyl. Figure 2.2 depicts alkyl halide initiators that are
commonly used in ATRP. Bromine and chlorine are the typical halogens used in ATRP
due to their bond strengths. The general order of bond strength for alkyl halides is: R-F >
R-Cl > R-Br > R-I. The C-F bond is too strong to undergo facile homolytic cleavage
while the reactive C-I may lead to a variety of side reactions.\textsuperscript{32}

![Figure 2.2. Initiators used in ATRP.](image-url)
The catalyst also affects the position of the atom transfer equilibrium and the dynamics of the exchange between the dormant and active species. To be an efficient transition metal catalyst, the metal center must have at least two accessible oxidation states separated by one electron. Furthermore, the metal center should have an affinity toward the halogen, the coordination sphere around the metal should be expandable upon oxidation to selectively accommodate a (pseudo)halogen, and the ligand should complex the metal relatively strongly.\textsuperscript{31} Copper is commonly used in ATRP because of its wide versatility and low cost, but iron, molybdenum, nickel, palladium, rhenium, rhodium, and ruthenium have also been used in ATRP.\textsuperscript{31}

Ligands are used to solubilize the transition metal catalyst and adjust the redox potential of the metal complex for suitable reactivity for atom transfer.\textsuperscript{31} Nitrogen based ligands, such as 2,2'-bipyridine, $N$-alkyl-2-pyridylmethanimine, and $N,N,N',N',N'$-pentamethyldiethylenetriamine (PMDETA) (Figure 2.3) are commonly used in copper-mediated ATRP. The use of multidentate amines, e. g. PMDETA, results in faster polymerization rates because they form copper complexes with lower redox potentials.
when compared with bipyridine-based ligands. The lower redox potential leads to higher activation rates for the dormant alkyl halide.  

ATRP can be carried out in bulk or solution, either in homogeneous or heterogeneous solutions. When selecting a solvent, there should be no chain transfer to solvent and interaction with the catalyst should be minimized. ATRP can be carried out in either polar or non-polar solvents. In ATRP, as the temperature is increased, the rate of polymerization increases due to the radical propagation rate constant and the atom transfer equilibrium constant increasing. Chain transfer and other side reactions may become more pronounced with the increase in temperature.

2.3 Synthesis of Polymer Brushes

The formation of polymer brushes is typically prepared by physisorption or chemical bonding. Figure 2.4 depicts the different mechanisms of formation. Physisorption on a solid surface is achieved by having either a functionalized end-group or by having a diblock copolymer with one block having a strong interaction with the surface and the other block having a weak interaction. Covalent attachment of the polymer brush can be done by either the “grafting to” or “grafting from” method. In the “grafting to” method, the polymer chain is synthesized with a functional end-group first. This end group is then reacted with an appropriate functionalized substrate to form the polymer brush. In the “grafting from” method, an immobilized initiator is attached to a substrate followed by polymerization to form the polymer brush. With the advancement of controlled/“living” polymerization techniques, it is possible to synthesize polymer chains with controlled lengths and structures.
2.3.1 Preparation of Polymer Brushes via Physisorption

Physisorption of polymer chains onto a solid substrate is a reversible process. It is achieved by the presence of selective solvents or selective surfaces, giving rise to selective solvation and selective adsorption, respectively. The polymer brush structure depends on the selectivity of the solvents and the nature of the copolymers, the architecture of copolymers, the length of each block and the interactions between the blocks and surface. An ideal solvent, using selective solvents in the adsorption of polymer chains to a surface, would precipitate one block onto the surface while acting as a good solvent for the second block. The second block forms the polymer brush in solution. In the physisorption of polymer chains to the surface using selective surfaces, one block is preferentially adsorbed on the surface and the second block forms the polymer brush.
Although formation of polymer brushes by adsorption is relatively easy, these polymer brushes exhibit thermal and solvolytic instability as well as poor control of grafting density. This instability arises from weak interactions between the polymer chain and the substrate. The interactions between the polymer chain and the substrate are either van der Waals or hydrogen bonding. Upon the addition of different solvents, desorption could occur. If the films are heated above their glass transition temperature or melting temperature, dewetting can occur along with the formation of polymer droplets. To overcome these deficiencies, the polymer chains can be covalently attached to the surface of the substrate.

2.3.2 Preparation of Polymer Brushes via “Grafting to” Approach

The “grafting to” approach refers to a preformed, end-functionalized macromolecule that is capable of reacting with a reactive substrate to generate a covalently tethered polymer brush. The preformed polymer can be synthesized by a number of techniques such as anionic, cationic, controlled free radical, and ring-opening metathesis polymerization. These polymerization techniques allow for the facile conversion of the active chain ends to the desired functionality (hydroxyl, carboxyl, amino, thiol, etc.). By using living/controlled polymerization techniques, it is possible to synthesize polymer chains possessing narrow molecular weight distribution, which allows for a uniform brush layer thickness, as well as controlled molecular weight and also formation of diblock copolymers.

Depending on the substrate, silica or gold, the surfaces possess functionalities that can undergo condensation reactions with polymer chains containing thiol, hydroxyl, or
carboxyl functionalities. These and other surfaces can be modified with self-assembled monolayers (SAMs) and other coupling agents to introduce various surface functionalities.

Tran et al.\textsuperscript{39} synthesized polyelectrolyte brushes using the “grafting to” technique. They first anionically polymerized styrene using \textit{sec}-butyllithium in benzene. The end-functionalized polymer was created by terminating the living polymer chain end with a trichlorosilane group. The polymer brush was created by spin-coating a thin layer of polystyrene onto a cleaned silicon wafer and annealed at 160 °C. The polystyrene brush was then converted to a poly(styrenesulfonate) brush by a soft sulfonation reaction using acetyl sulfate. The authors found that the brush was vulnerable to degrafting either during the sulfonation reaction or after the polyelectrolyte brush was subjected to water treatments.

Using a different method, Sumerlin et al.\textsuperscript{40} grafted a series of polymers onto gold surfaces. The polymer chains were synthesized using the reversible addition-fragmentation chain transfer (RAFT) free radical polymerization technique. The resultant dithioester end-capped chains were converted to thiol-functionalities by addition of NaBH\textsubscript{4} in water. The reaction was performed in the presence of a gold substrate so that conversion and surface attachment \textit{via} the sulfur linkage was a one-step process.

A major disadvantage in using the “grafting to” approach is the fact that the grafting density is limited. The limited grafting density is due to the diffusion of large polymer chains to the reactive sites on the surface of the substrate.\textsuperscript{4} The lower grafting density results in lower brush thicknesses. The steric hindrance for surface attachment increases as the tethered polymer film thickness increases. The low grafting density
allows for small molecules to diffuse to the tethering site and result in brush degrafting; therefore, it may be necessary to backfill the surface with oligomers of the same polymer or other small molecules. To overcome many of these problems, the “grafting from” approach is an attractive way to prepare thick polymer brushes with a higher grafting density.

2.3.3 Preparation of Polymer Brushes via “Grafting from” Approach

The “grafting from” approach has attracted attention because of its ability to form thicker brush layers while maintaining a relatively high grafting density. In this method, an initiator is immobilized onto the surface followed by in situ surface-initiated polymerization to generate the tethered polymer brush. Surface immobilized initiators can be generated by treating the substrate with plasma or glow discharge in the presence of a gas\textsuperscript{13,41-44} or with initiator containing SAMs on the substrates.\textsuperscript{45-48} As Figure 2.5 shows, as the chains are growing from the surface, the only limit to propagation is diffusion of monomer to the chain ends, thus resulting in thick tethered polymer brushes with a high grafting density.

In the following discussion, only the atom transfer radical polymerization (ATRP) technique will be used to illustrate the synthesis polymer brushes via the “grafting from”
approach. Anionic polymerizations,\textsuperscript{49-52} cationic polymerizations,\textsuperscript{53-55} ring-opening metathesis polymerizations (ROMP),\textsuperscript{56-58} conventional free radical polymerizations,\textsuperscript{45-48,59,60} controlled radical polymerization such as RAFT,\textsuperscript{61,62} and nitroxide-mediated polymerizations (NMP)\textsuperscript{63,64} have also been used to successfully grow polymer brushes from surfaces.

ATRP offers control over the brush thickness \textit{via} molecular weight control, narrow polydispersities allowing for a smooth brush, and the ability to control the architecture of the brush compared to conventional free radical polymerization. It also requires less stringent conditions compared to anionic and cationic polymerization conditions; it is more tolerant to impurities. ATRP is typically limited to methacrylates, acrylates, styrenes, acrylonitriles, and vinylpyridine monomers, but RAFT has the added advantage of being able to polymerize all monomers that are capable of undergoing conventional free radical polymerizations. Another drawback of ATRP is that the polymer synthesized has to be purified in order to remove the metal catalyst.

Ejaz et al.\textsuperscript{65} were among the first to utilize ATRP to synthesize polymer brushes. The ATRP initiator, \textsuperscript{2-(4-chlorosulfonylphenyl)}ethyltrimethoxysilane, was deposited onto the silica substrate by a Langmuir-Blodgett technique. Polymerization of methyl methacrylate (MMA) was then carried out in the presence of CuBr/4,4’-di-\textit{n}-heptyl-2,2’-bipyridine (dnNbpy) as the catalyst complex to produce a PMMA brush with a high grafting density. In addition, sacrificial initiator was added to establish the ATRP equilibrium which leads to a controlled polymerization. Matyjaszewski and coworkers\textsuperscript{66} described the ATRP synthesis of polymer brushes in the absence of sacrificial initiator (Scheme 2.4). Polymer chains were grown in the presence of the proper ratio of
activating and deactivating transition-metal species, which resulted in a controlled radical polymerization. The use of deactivator has the added advantage of not producing free polymer which likely becomes entangled with the polymer brush. However, one advantage of the free initiator technique is that it produces free polymer in solution whose molecular weight can be analyzed and used to estimate the molecular weight of the polymer brush.\(^67\)

Ayres and coworkers\(^68\) synthesized an AB diblock copolymer polyampholyte polymer brush utilizing ATRP and the “grafting from” approach, as shown in Scheme 2.5. Formation of poly(acrylic acid)-block-poly(4-vinylpyridine) resulted in a brush that exhibited stimuli-responsive behavior with respect to pH, showing both polyelectrolyte and polyampholyte effects. Free polymer was also formed in solution by using free initiator, ethyl 2-bromoisobutyrate (E2BriB), while 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) was used as the ligand. 4-Vinylpyridine segments were quaternized to form a mixed weak/strong or annealed/quenched polyelectrolyte system which exhibited a brush thickness dependence on the pH.
2.4 Surface Modification of Silica Capillaries

The inner walls of capillaries have been modified to reduce or eliminate analyte-wall interactions, to alter electroosmotic flow, or to improve reproducibility in capillary electrophoresis. Modification of silica capillaries is possible due to the presence of silanol groups located at the surface. On smooth, heat-stabilized amorphous silica surface there are 4-5 silanol groups/nm$^2$. The polymeric wall coatings are synthesized either by physisorption or covalent attachment. There are a limited number of surface characterization techniques that can be applied to the inside of capillary. In electrophoresis, the coated capillaries are characterized by the analyte separation before and after the coating process.

Physisorbed wall coatings are typically prepared by rinsing the tubing with a solution containing small molecules or polymers. The coating must constantly be regenerated by adding a small amount of the coating to the separation medium.
Polymeric surfactants,\textsuperscript{74,75} charged polymers,\textsuperscript{76-78} and neutral polymers\textsuperscript{79-82} are materials used to coat dynamic capillaries.

Permanent, covalently attached coatings eliminate electroosmotic flow and wall-analyte interaction and do not require regeneration. Covalent coatings are prepared by first cleaning the capillary walls, then the attachment of a bifunctional molecule where one end is capable of covalent attachment to the wall and the other is used to facilitate a polymerization. The coating is followed by the polymerization of the monomer. Hjertén\textsuperscript{83} was one of the first to apply this process to coat capillaries. A bifunctional silane, $\gamma$-methacryloxypropyltrimethoxysilane, was used as the anchoring molecule, where the trimethoxysilane group reacted with silanol groups on the wall surface and the methacrylate group was used in the polymerization (Scheme 2.6). A polyacrylamide coating was formed \textit{via} free radical polymerization. The coating was characterized by separation of a mixture of aromatic carboxylic acids; the separation efficiency was superior to an uncoated capillary. There was also a dramatic reduction in peak broadening between the uncoated and coated capillary, which was attributed to electroendosmosis or analyte absorption to the walls.

\begin{center}
\includegraphics[width=\textwidth]{Scheme_2.6.png}
\end{center}

\textbf{Scheme 2.6.} Preparation of surface-attached polyacrylamide.
Free radical polymerization techniques tend to leave unreacted monomer as well as polymer entangled with the attached polymer coating. Since the polymerization occurs in solution, variable coating thickness and increased solution viscosity arises, hampering the removal of the polymerization solution from the capillary. Controlled free radical polymerization techniques allow for surface confined polymerization, enabling control over the film thickness and eliminating chances of clogging the capillary.

Wirth et al.\textsuperscript{84} used ATRP to confine the growth of the polymer to the surface which enabled the film thickness to be controlled. By using controlled polymerization techniques, they were able eliminate problems associated with polymers grown in solution. The capillary was cleaned using a 1.0 M KOH aqueous solution followed by rinsing with water and drying under nitrogen. A SAM of 1-trichlorosilyl-2-(m,p-chloromethylphenyl)ethane was used to initiate the polymerization. ATRP conditions were used to polymerize acrylamide from the surface of the capillary. Capillary electrophoresis was used to confirm the presence of the polymer coating by superior separation of analytes. They demonstrated that the peaks remained sharp after repetitive analysis (100x) indicating stable polymer coatings.

2.5 Silica Nanoparticles

In this research, the functionalization of silica nanoparticles is restricted to a colloidal silica system. The colloidal silica is composed of discrete particles synthesized \textit{via} the Stöber process\textsuperscript{85} using tetraethyl orthosilicate (TEOS). For silica to be in a colloidal state, the particle size must be sufficiently small (<1 µm) so that the particles do not feel the affects of gravitational forces but large enough (>1 nm) to display noticeable
deviations from the normal solution properties. The formation of the silica particle occurs via a nucleation and growth process, which can be catalyzed by acids or bases. Once the particles are formed, aggregation must be prevented in order to keep the nanoparticles homogeneously dispersed in a matrix. Stability of nanoparticles can be achieved by electrostatic and/or steric interactions. The general method to control the nanoparticle size is by control of the relative kinetics of nucleation and growth.

2.5.1 Mechanism of Formation and Growth of Silica Nanoparticles

The formation of silica nanoparticles, using the Stöber synthesis, involves nucleation, polymerization, and particle growth. The major difference between acid- or base-catalyzed systems is that under acidic conditions, hydrolysis is relatively faster than condensation, while under basic conditions, condensation is faster relative to hydrolysis and thus more siloxane linkages are formed.\(^{86}\)

\[
\text{OH}^- + \equiv\text{Si-OR} \rightarrow \left[ \equiv\text{Si-OR} \right]^- \\
\equiv\text{Si-OH} + \text{OR}^- \quad \equiv\text{Si-OH} + \equiv\text{Si-OH} \rightarrow \equiv\text{Si-O-Si}^- + \text{H}_2\text{O} \\
\equiv\text{Si-OR} + \equiv\text{Si-OH} \rightarrow \equiv\text{Si-O-Si}^- + \text{ROH} \quad \text{where: } R = \text{H or } \text{C}_2\text{H}_5
\]


In the formation of silica particles using a tetraalkoxysilane, the synthesis proceeds via hydrolysis promoted by a catalyst in the presence of a low molecular weight alcohol. Equation 1 shows the formation of silanol groups from the hydrolysis of tetraalkoxysilane.

\[
\equiv\text{SiOR} + \text{H}_2\text{O} \rightarrow \equiv\text{SiOH} + \text{ROH} \quad (1)
\]
In base-catalyzed hydrolysis, the hydroxyl ion is a strong nucleophile which attacks the silicon atom because it carries the highest positive charge (Scheme 2.7). Alkoxy substituent groups on the silicon atom are less electron withdrawing and increase the steric hinderance of the attacking nucleophile, resulting in slower hydrolysis of the silane molecule when compared with hydroxyl substituents. As a result, after the loss of each alkoxy group, the rate of the hydrolysis reaction increases. The hydrolyzed silica then proceeds through a condensation reaction to produce a \( \text{SiO}_2 \) network by either silanol-silanol condensation or silanol-ether condensation (Scheme 2.8). The reaction occurs through a base-catalyzed nucleophilic attack on silicon resulting in an intermediate pentavalent silicon complex.\(^{87}\) The particle increases in size through aggregation of small colloids or by addition of low molecular weight particles.\(^ {88}\) Scheme 2.9 shows the overall synthesis of Stöber silica by the condensation of TEOS.

\[
\text{Hydrolysis}
\]

\[
\text{Condensation}
\]

\[
\text{Polycondensation}
\]

Scheme 2.9. Synthesis of Stöber silica particles.
Particle formation is broken down into two stages: nucleation and growth. The growth of a silica particle starts when the silicic acid undergoes a dehydrating condensation polymerization in the presence of alkali which forms nuclei. The silicic acid then polymerizes around the nuclei and the particle grows as shown in Scheme 2.10. There is a discrepancy about how the growth of the particle occurs once a stable nucleus is formed.

The first model that describes the silica particle growth is known as the monomer addition model.\textsuperscript{89,90} In this model, competition between nucleation and growth is controlled by the hydrolysis that releases the active monomer. A slow hydrolysis reaction inhibits nucleation but promotes growth of the particles by the addition of hydrolyzed monomers to the particle surface. Matsoukas et al.\textsuperscript{89} and Byers et al.\textsuperscript{91} found that a few percent of the ethoxy groups never leave the TEOS molecule supporting the fact that the growth rate is limited by the hydrolysis of TEOS.

In the controlled aggregation model, nucleation occurs throughout the reaction and the nuclei (primary particles) will aggregate together to form larger particles and produce a narrow size distribution.\textsuperscript{92,93} In this model, the silane is completely hydrolyzed at the start of the reaction and the silica particles form through a size-dependent, controlled, coagulative nucleation and growth mechanism.\textsuperscript{92} The controlled aggregation
model is supported by $^{29}$Si NMR data that confirms that only the singly hydrolyzed TEOS monomer, $[(\text{OH})\text{Si}(\text{OC}_2\text{H}_5)_3]$ is detected. Scheme 2.10 represents the controlled aggregation model where small unstable particles aggregate until a critical size is reached. Nucleation continues throughout the reaction and the newly formed small particles are taken-up by the larger, stable particles.

There are discrepancies in both models. If one assumes that all the TEOS is hydrolyzed in the first few minutes and that nucleation is continuous, then the surface of the silica particles should not be smooth. At this time, neither model can be proven because the primary particle size has not been directly measured. But Green et al. speculate that both growth mechanisms occur, where controlled aggregation is responsible for the overall particle growth particle and monomer addition smoothes the surface of the particle.

2.5.2 Stability of Silica Nanoparticles

During nanoparticle formation, the silica particles must be stabilized to prevent agglomeration and precipitation, which is typically accomplished by the addition of stabilizers. Typical stabilizers used are ionic and non-ionic surfactants or polymers. The stabilizing effect can be achieved by two mechanisms, electrostatic and/or steric interactions. Electrostatic stabilization is based on Coulombic repulsion between particles caused by the electrical double layer formed by absorbed ions. Steric stabilization prevents agglomeration by the formation of a polymer layer between particles.
2.5.3 Control of Particle Size

The particle size is usually controlled by varying the kinetics of nucleation and growth. The nucleation process is affected by changes in the concentration of the reagents, temperature, solvent viscosity, and type and concentration of the stabilizing agent. In general, larger particles are produced when there are a smaller number of nuclei present, while smaller particles are formed when there is a high supersaturation of reagents and a fast nucleation rate.

Rahman et al.\textsuperscript{102} studied the effect of concentration of TEOS, ammonia, and temperature on the particle size of the silica nanoparticle synthesized using the Stöber process. They demonstrated that increasing TEOS concentration resulted in larger silica particles. This reflects an increase in primary particle concentration during the induction period. Larger concentrations of ammonia resulted in a hydrolysis rate increase of TEOS leading to larger particle sizes.\textsuperscript{103} By increasing the temperature, the particle size decreased as a result of the increase in the nucleation rate.\textsuperscript{104}

It has been shown that particles synthesized in ethanol are larger than those synthesized in methanol under identical conditions.\textsuperscript{96,105} The nuclei generated in methanol are smaller due the higher supersaturation ratio of the hydrolyzed monomer.\textsuperscript{96}
CHAPTER III

EXPERIMENTAL

3.1 General ATRP-Functionalization of Silica Capillaries

The following explains the procedure and conditions used in the ATRP functionalization of silica capillaries.

3.1.1 Materials

2-Hydroxyethyl methacrylate (HEMA, Aldrich, 98%), methyl acrylate (MA, Aldrich, 99%), methyl methacrylate (MMA, Aldrich, 99%), pentafluorostyrene (PFS, Aldrich, 99%), styrene (S, Aldrich, 99%), tert-butyl acrylate (t-BA, Aldrich, 99%), n-butyl acrylate (n-BA, Aldrich, 99%), tert-butyl methacrylate (t-BMA, Aldrich, 99%), ethyl 2-bromoisobutyrate (E2Br-iB, Aldrich, 98%), and N,N,N',N',N"-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) were passed through a column of activated basic alumina (~150 mesh, Aldrich) before use. 2-(6-Methacryloyloxyhexyl)-thioxantheno[2,1,9-dej]isoquinoline-1,3-dione (Hostasol) was donated by Professor David Haddleton from the University of Warwick. Anhydrous anisole (Aldrich, 99%), anhydrous acetone (Aldrich, 99.8%), anhydrous methyl alcohol (Aldrich, 99.8%), anhydrous o-xylene (Aldrich, 97%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, Aldrich, 97%) and copper(II)bromide (Aldrich, 99%)
were used as received. Copper(I) bromide (CuBr, Aldrich, 98%) was purified prior to use according to a literature procedure. For the purification, sulfuric acid (EM Science), sulfurous acid (Aldrich), glacial acetic acid (EM Science), absolute ethanol (Pharmco), and anhydrous diethyl ether (Fisher) were used as received. [11-(2-Bromo-2-methyl)propionyloxy]undecyltrichlorosilane was synthesized as described in the literature. For the synthesis procedure, anhydrous tetrahydrofuran (THF, Aldrich, 99%), ω-undecylenyl alcohol (Aldrich, 98%), triethylamine (TEA, Aldrich, 99.5%), 2-bromoisobutyryl bromide (Aldrich, 98%), anhydrous magnesium sulfate (Fisher), trichlorosilane (Aldrich, 99%), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karsted’s catalyst, Aldrich, 3 wt% solution in xylene), and silica gel 60 (63-200 mesh, EMD) were used as received. Dichloromethane (EMD), isopropyl alcohol (EMD), methyl alcohol (EMD), tetrahydrofuran (EMD), toluene (EMD), brilliant cresyl blue (Aldrich, dye content: 65%), and ethylene glycol (Aldrich, ≥ 99%) were used as received. Water was purified by the Millipore Mill-Q system. Undeactivated fused silica capillary (250 µm i.d. × 363 µm o.d., 75 µm i.d. × 363 µm o.d., and 50 µm i.d. × 363 µm o.d.) was purchased from Western Analytical Products, Inc.; silicon wafers were purchased from Wafer World Inc., and silicon attenuated total reflection (ATR) crystals (25 mm × 5 mm × 1 mm) were purchased from Harrick Scientific. The silica substrates were cleaned using sulfuric acid (EMD) and hydrogen peroxide (Fisher, 30%).

A syringe pump, Model NE-1000 from New Era Pump Systems, Inc., was used in the backpressure and preferential flow experiments. A PX305-015GI pressure transducer was connected to a DP25B-E process panel meter supplied by Omega Engineering.
UV/VIS measurements were obtained using an HP 845x UV/VIS spectrophotometer; spectra were recorded over the range of 480 - 700 nm.

3.1.2 Characterization Methods

FTIR-ATR spectra were recorded using a Bruker Tensor 27 spectrometer with a modified 4XF beam condenser (Harrick Scientific). Spectra were recorded at 4 cm\(^{-1}\) resolution and 32 scans were collected.

Contact angles were determined using a Rame Hart NRL-100 goniometer equipped with an environmental chamber and tilting base mounted on a vibrationless table (Newport Corp.). Distilled water purified by a Millipore Milli-Q system was used as the test liquid using a 10 µL drop. The humidity was kept at 100%, and measurements were done at room temperature. Advancing and receding contact angles were determined using the tilting stage method at a 35° tilt angle.

Ellipsometry measurements were performed on a Gaertner model L116C ellipsometer with a He-Ne laser (\(\lambda = 633\) nm) and a fixed angle of incidence of 70°. For layer thickness calculations, refractive indices of \(n = 1.455\) for silicon oxide,\(^{107}\) \(n = 1.508\) for initiator layer,\(^{107}\) \(n = 1.512\) for PHEMA,\(^{107}\) \(n = 1.480\) for PMA,\(^{107}\) \(n = 1.489\) for PMMA,\(^{107}\) \(n = 1.473\) for PPFS,\(^{108}\) \(n = 1.589\) for PS,\(^{107}\) \(n = 1.463\) for P(t-BA),\(^{107}\) \(n = 1.527\) for PAA,\(^{107}\) \(n = 1.463\) P(t-BMA),\(^{107}\) \(n = 1.463\) PMAA,\(^{107}\) and \(n = 1.466\) for P(n-BA)\(^{107}\) were used and the average of ten measurements was recorded. Data was analyzed with Gaertner Scientific Corporation software 2GC5A + 2SubCA Automatic Ellipsometry Program for IBM PC. The thicknesses of the polymer brushes were obtained by subtracting the combined thickness of silicon oxide and initiator layers from the total
measured value. Two- and three-layer models should have been used in the analysis of film thickness to minimize the amount of error in the measurements. The 1-layer model that was used averaged the refractive indices of the silica substrate, the SiO$_2$ layer and the ATRP initiator layer when measuring the thickness of the polymer film; this method had an error between 10-20% depending on the number of layers being measured. When measuring the thickness of a diblock copolymer, the error was increased because the refractive index would be an average of the silica substrate, the SiO$_2$ layer, the ATRP initiator layer and the first polymer layer. The 2-layer model will account for the substrate, the SiO$_2$ layer and the ATRP initiator layer when measuring the first polymer film layer. The 3-layer model will account for three out of the four layers (the substrate, the SiO$_2$ layer, the ATRP initiator layer or the first polymer layer) when measuring the second polymer film layer in a diblock copolymer brush which will minimize the error.

Solution $^1$H NMR spectra were recorded on a Varian Gemini-300 MHz spectrometer. Samples were dissolved in CDCl$_3$.

Fluorescence spectroscopy measurements were made on a Jobin Yvon T6400 triple monochromator that was equipped with an argon ion laser. An excitation wavelength of 457.8 nm and a power of 0.67 mW were used. The laser was aligned so that it was shown down through the capillary. The equipment was located at the Department of Polymer Science, The University of Akron.

Capillary rise measurements were recorded using a traveling telescope cathetometer M912 from Gaertner Scientific. Ethylene glycol was used as the probe fluid which was allowed to rise overnight in order to come to its equilibrium height. An average of ten measurements was recorded.
3.1.3 Synthesis and Preparation of Reagents

The following explains the synthesis and preparation of reagents used in the ATRP functionalization of silica capillaries.

3.1.3.1 Synthesis of the Surface-Immobilized ATRP Initiator

[11-(2-Bromo-2-methyl)propionyloxy]undecyltrichlorosilane was synthesized according to a literature procedure. A round-bottom flask with a stir bar was placed into an ice bath. 2-Bromoisobutyryl bromide, 6.8 mL (55.0 mmol), was added dropwise to the flask which contained 50 mL of anhydrous THF, 10.0 mL (49.9 mmol) of \(\omega\)-undecylenyl alcohol and 8.2 mL (58.8 mmol) of triethylamine (TEA). The solution was allowed to warm to room temperature and was left to stir overnight. The resulting solid was filtered and the solution was collected. The THF was removed under reduced pressure to afford a yellow oil. The product was diluted with 200 mL of dichloromethane and the solution was washed three times with deionized (DI) water. The organic extracts were combined and dried using anhydrous magnesium sulfate. Once the solids were filtered off, the dichloromethane was removed using reduced pressure and the product, 10-undecen-1-yl 2-bromo-2-methylpropionate, was analyzed using \(^1\)H NMR. \(^1\)H NMR spectroscopy (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 5.68-5.81 (m, 1H); 4.84-4.95 (m, 2H); 4.10 (t, 2H); 1.97 (q, 2H); 1.86 (s, 6H); 1.56-1.67 (m, 2H); 1.22-1.38 (m, 12H).

In a round-bottom flask, a stir bar, 10-undecen-1-yl 2-bromo-2-methylpropionate (34.5 mmol), 0.08 mL (0.2 mmol) of Karsted’s catalyst and 7.4 mL (73.2 mmol) of trichlorosilane were added. The mixture was heated to a gentle reflux for 4 h. The reaction was monitored by \(^1\)H NMR for disappearance of the double bond indicating
completion of the silylation reaction. The excess trichlorosilane was removed via bulb-to-bulb vacuum distillation, and resultant product was diluted with 100 mL of dichloromethane and passed through a silica gel column. The remaining solvent was removed under reduced pressure to yield a yellow oily liquid. $^1$H NMR spectroscopy (300 MHz, CDCl$_3$) $\delta$ (ppm): 4.15-4.19 (t, 2H); 1.93 (s, 6H); 1.56-1.73 (m, 4H); 1.28-1.44 (m, 16H). The initiator was diluted with anhydrous toluene to give a 25% w/w solution and placed in the freezer.

3.1.3.2 Purification of CuBr

Copper(I) bromide was purified according to the literature.$^{106}$ CuBr was ground into a paste using 1 N H$_2$SO$_4$, and then it was stirred into 500 mL of 1 N H$_2$SO$_4$ for 30 minutes at room temperature. The solution was filtered, ensuring that a constant stream of nitrogen gas was constantly flowing over the CuBr. It was then washed five times with 25 mL of glacial acetic acid, three times with 30 mL of anhydrous ethanol, and six times with 15 mL of diethyl ether. The resulting CuBr was dried under reduced pressure overnight.

3.1.3.3 Substrate Preparation

ATR crystals, silicon wafers, and capillaries were cleaned by treatment with freshly prepared “piranha” solution (70/30, v/v, concentrated H$_2$SO$_4$/30% aqueous H$_2$O$_2$)$^9$ at 90 °C for 2 h. The capillary was fitted and sealed in a cylindrical water jacket while one end of the capillary was placed into the “piranha” solution and the other was sealed in a vacant Schlenk flask. The “piranha” solution was introduced to the capillary by
reduced pressure while heating with circulating, hot water through the water jacket. The samples were then removed and rinsed with copious amounts of DI water followed by drying in an air stream. ATR-FTIR and ellipsometry were used to analyze the clean, flat substrates. Initiator deposition onto the cleaned substrates was performed immediately after cleaning and analysis.

3.1.4 Substrate Immobilization of ATRP Initiator

A freshly cleaned end of the capillary, silicon wafer, and ATR crystal were placed into a dried Schlenk flask. Anhydrous toluene (15 mL) and a 25% w/w solution of the diluted initiator solution (0.5 mL) were added to the flask, and it was sealed. The opposite end of the capillary was placed through a rubber septum that was sealed onto a Schlenk flask. The flow of solution was induced through the capillary via a combination of positive nitrogen and reduced pressure at opposite ends. The reaction proceeded for 18 h at room temperature. The silicon wafer, ATR crystal, and capillary were washed with toluene, sonicated in toluene for 15 min, followed by rinsing in toluene and dried using a stream of air.

3.1.5 General ATRP Preparation to form Homopolymer, Copolymer, and Diblock Copolymer Brushes on Flat Surfaces and in Silica Capillaries

Described below is the specific procedure for the surface-initiated ATRP of a PS homopolymer brush. This procedure can be adapted for all the monomers listed in Table 3.1. The capillary was fitted and sealed in a cylindrical water jacket, leaving the two ends to be fitted into Schlenk flasks. A 50 mL Schlenk flask was used to hold one end of
the capillary, silicon wafer, and ATR crystal and was placed in an oil bath. The oil bath
and the circulating water bath were set to the desired temperature (90 °C). The opposite
end of the capillary was fitted into a small Schlenk flask and sealed. The flasks were
degassed and back-filled with nitrogen three times and left under a nitrogen atmosphere.
CuBr (0.38 mmol), solvent (anisole, 152 mmol), monomer (styrene, 118 mmol), and a
magnetic stir bar were added to a separate 100 mL Schlenk flask and sealed. The
solution was subjected to three freeze-pump-thaw cycles using nitrogen as the backfill
gas. PMDETA (0.77 mmol) was added to the solution via a syringe, and it was stirred at
the polymerization temperature until it became homogeneous (~15 min). Free initiator
(E2BriB, 0.16 mmol) was added via a syringe to the flask containing the silicon wafer,
ATR crystal, and capillary, followed by transfer of the CuBr/ligand solution via cannula.
The polymerization was allowed to proceed at 90 °C for 8 h. At the end of the reaction,
the wafers and capillary were removed and rinsed with dichloromethane, THF, and
isopropanol. To remove untethered polymer chains, the silicon wafer and ATR crystal
were placed in a Soxhlet extractor and extracted with THF for 24 h, followed by
sonicated in THF for 30 min, followed by drying with an air stream. The capillary was
treated by rinsing with THF or methanol for 24 h and then sonication for 15 min and
drying with nitrogen. Methyl alcohol was substituted for THF when washing P(HEMA).
Table 3.1 contains the monomers that were polymerized in this work and the
concentrations of the reagents used.
Table 3.1. Reagents, concentrations and conditions used in the ATRP preparation of polymer brushes.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Solvent</th>
<th>PMDETA (mmol)</th>
<th>CuBr (g)</th>
<th>E2BriB (mmol)</th>
<th>Temp. (ºC)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEMA</td>
<td>methyl alcohol</td>
<td>0.51&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.36</td>
<td>0.15&lt;sup&gt;b&lt;/sup&gt;</td>
<td>25</td>
<td>3</td>
</tr>
<tr>
<td>MA</td>
<td>anisole</td>
<td>0.90</td>
<td>0.49</td>
<td>0.46</td>
<td>90</td>
<td>6</td>
</tr>
<tr>
<td>MMA</td>
<td>anisole</td>
<td>0.94</td>
<td>0.47</td>
<td>0.47&lt;sup&gt;b&lt;/sup&gt;</td>
<td>60</td>
<td>6</td>
</tr>
<tr>
<td>PFS</td>
<td>o-xylene</td>
<td>0.53</td>
<td>0.27</td>
<td>0.27</td>
<td>90</td>
<td>18</td>
</tr>
<tr>
<td>S</td>
<td>anisole</td>
<td>0.77</td>
<td>0.38</td>
<td>0.16</td>
<td>90</td>
<td>8</td>
</tr>
<tr>
<td>t-BA</td>
<td>acetone</td>
<td>0.45</td>
<td>0.3</td>
<td>0.15</td>
<td>60</td>
<td>6</td>
</tr>
<tr>
<td>n-BA</td>
<td>anisole</td>
<td>0.75</td>
<td>0.39</td>
<td>0.31</td>
<td>90</td>
<td>5</td>
</tr>
<tr>
<td>t-BMA</td>
<td>acetone</td>
<td>0.60</td>
<td>0.30</td>
<td>0.30&lt;sup&gt;b&lt;/sup&gt;</td>
<td>60</td>
<td>4</td>
</tr>
<tr>
<td>MMA</td>
<td>anisole</td>
<td>0.94</td>
<td>0.47</td>
<td>0.47&lt;sup&gt;b&lt;/sup&gt;</td>
<td>60</td>
<td>6</td>
</tr>
<tr>
<td>Hostasol</td>
<td>anisole</td>
<td>0.047</td>
<td>0.39</td>
<td>0.31</td>
<td>90</td>
<td>5</td>
</tr>
</tbody>
</table>

<sup>a</sup> HEMA used HMTETA in place of PMDETA

<sup>b</sup> HEMA, t-BMA, MMA and MMA/Hostasol used CuBr<sub>2</sub> in place of E2Br-iB
Preparation of diblock copolymers was conducted in a similar manner to that for the homopolymer brushes. The order of the blocks in the diblock brush was determined by the order of polymerization from the surface. For example, a Si/SiO$_2$/PS-$b$-P($t$-BA) brush was synthesized by first forming Si/SiO$_2$/PS brush on the surface, followed by the polymerization of $t$-BA from the Si/SiO$_2$/PS brush. The same concentrations that were used in the homopolymer brush syntheses were used in the diblock copolymer syntheses.

3.1.6 Typical Procedure for Deprotection of the tert-Butyl Group to Acrylic Acid

A P($t$-BA)-modified silicon wafer, P($t$-BMA)-modified silicon wafer and an ATR crystal were placed on a watch-glass while the capillary was placed inside a glass column. These were then inserted into an oven preheated to 190-200 °C for 2 h under reduced pressure. The silicon wafer, ATR-crystal, and capillary were rinsed with DI water and then submerged in DI water overnight following a literature procedure.$^{109}$

3.2 Silane-Functionalization of Silica Capillaries

The following explains the procedure and conditions used in the silane-functionalization of silica capillaries.

3.2.1 Materials

$N$-(3-Triethoxysilylpropyl)gluconamide (TSPG, Gelest), 3-aminopropyl-trimethoxysilane (APTS, Gelest), hexadecyltriethoxysilane (HDTs, Gelest), (tridecafluoro-1,1,2,2-tetrahydrooctyl)triethoxysilane (13FTS, Gelest), anhydrous toluene (Aldrich), anhydrous trifluorotoluene (Aldrich), $N,N$-diisopropylethylamine (DIPEA,
Aldrich, 99%), absolute ethanol (Pharmco), toluene (EDM), dichloromethane (EDM), hexane (EDM), and ethylene glycol (Aldrich, ≥ 99%) were used as received.

3.2.2 Deposition of Functionalized Silanes

A freshly cleaned end of the capillary, silicon wafer, and ATR crystal were placed into a dried Schlenk flask. The appropriate amount of the reagents was added to the flask and the flask was sealed. The opposite end of the capillary was placed through a rubber septum that was sealed around a Schlenk flask. The flow of solution was induced through the capillary via a combination of positive nitrogen and reduced pressure at opposite ends. Table 3.2 contains the reagents, concentrations and conditions used for the silane depositions. The silicon wafer, ATR crystal, and capillary were washed with and then sonicated in toluene and ethanol for 30 min each, immersed in toluene and ethanol and then dried using a stream of air.

<table>
<thead>
<tr>
<th>Silane</th>
<th>Solvent</th>
<th>DIPEA (mmol)</th>
<th>Temperature (ºC)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>APTS&lt;sup&gt;a&lt;/sup&gt;</td>
<td>toluene</td>
<td>10.0</td>
<td>1.2</td>
<td>27</td>
</tr>
<tr>
<td>TSPG&lt;sup&gt;b&lt;/sup&gt;</td>
<td>ethanol</td>
<td>10.0</td>
<td>-</td>
<td>27</td>
</tr>
<tr>
<td>HDTS&lt;sup&gt;c&lt;/sup&gt;</td>
<td>toluene</td>
<td>10.0</td>
<td>1.7</td>
<td>60</td>
</tr>
<tr>
<td>13FTS&lt;sup&gt;d&lt;/sup&gt;</td>
<td>trifluorotoluene</td>
<td>10.0</td>
<td>1.7</td>
<td>60</td>
</tr>
</tbody>
</table>

<sup>a</sup> 3-aminopropyltrimethoxysilane (APTS)
<sup>b</sup> N-(3-Triethoxysilylpropyl)gluconamide (TSPG)
<sup>c</sup> hexadecyltriethoxysilane (HDTS)
<sup>d</sup> (tridecafluoro-1,1,2,2-tetrahydrooctyl)triethoxysilane (13FTS)
3.3 Backpressure Measurements on Functionalized Silica Capillaries

A 20 mL syringe was filled with a solvent and mounted on the syringe pump. A 21 gauge needle was used to join 0.254 mm i.d. polyethylene tubing to the syringe while the opposite end was attached to a Swagelok® tee-junction using Swagelok® fittings. A 30 cm length of functionalized capillary was attached to the opposite end of the tee-junction using a graphite ferrule. The pressure transducer was attached to the tee-junction so that it was perpendicular to the capillary. A two-neck test-tube was used to collect the sample and to keep the capillary parallel. For the 250 µ and the 75 µ capillaries, the flow rate was 1.0 and 0.5 mL/h, respectively. The experiments were allowed to run for 24 h at room temperature and the highest pressure during 24 h was used for comparison.

3.4 Preferential Flow Experiments on Functionalized Silica Capillaries

A 0.06% w/w solution was made using brilliant cresyl blue and purified distilled water. A 1 mL syringe was filled with solution and mounted on the syringe pump. 0.254 mm i.d. polyethylene tubing was connected between the syringe and a 1/16 in. Swagelok® union. A small section of 250 µ capillary was connected to the union and a fused silica “Y” connector (Supelco). The functionalized silica capillaries, one hydrophilic and one hydrophobic, were inserted into each arm of the “Y” connector to determine biased flow through the capillaries. Each end of the capillaries was inserted into the lower arm of a specially designed two-arm test-tube and sealed with a rubber septum. The upper arm had a small section of 250 µ capillary inserted and sealed with a rubber septum to serve as a pressure vent. Figure 3.1 details the setup for the preferential
flow experiments. Before the capillaries were inserted, 3 g of purified water was placed in the tube which was then immersed in an oil bath. The water was heated to 40 °C to ensure a constant humidity for all experiments. The flow rate was 5.0 µL/h for all experiments. The output of both capillaries was analyzed by UV/VIS to evaluate the concentration of dye which was used to determine differential flow. Before use, the capillaries were dried in an oven at 120 °C under reduced pressure for a minimum of 24 h.

Figure 3.1. Schematic for the setup of the preferential flow experiments.

3.5 In situ Functionalization of Silica Nanoparticles

The following explains the materials, procedures, experimental setup and conditions used for the in situ functionalization of silica nanoparticles.
3.5.1 Materials

Styrene (S, Aldrich, 99%), methyl acrylate (MA, Aldrich, 99%), tert-butyl acrylate (t-BA, Aldrich, 98%), \(N,N',N',N''\)-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), and ethyl 2-bromoisobutyrate (Et2Br-iB, Aldrich, 98%), were passed through a column of activated basic alumina (~150 mesh, Aldrich) prior to use. CuBr (Aldrich, 98%) was purified as described above and from the literature. Anhydrous anisole (Aldrich, 99.8%), anhydrous toluene (Aldrich, 99.8%), anhydrous tetrahydrofuran (THF, Aldrich, 99.8%), absolute ethane (Pharmco), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karsted’s catalyst, Aldrich, 3 wt% solution in xylene), 2-bromoisobutyryl bromide (Alfa Aesar, 96%), allyl alcohol (Aldrich, 99+%), triethoxysilane (Aldrich, 95%), dimethylethoxysilane (Alfa Aesar, 94%, A.C.S. reagent), sodium bicarbonate (EMD), hydrofluoric acid (HF, Aldrich, 48%), triethylamine (TEA, Aldrich, 99.5%), tetraethoxysilane (TEOS, Aldrich, 99%), ammonia (Aldrich, 28% aqueous solution), Aliquat 336 (Aldrich), and silica gel 60 (63-200 mesh, EMD) were used as received. The synthesis of the reactive stabilizers [3-(2-bromoisobutyryl)propyl]triethoxysilane (BPTS) and [3-(2-bromoisobutyryl)propyl]ethoxydimethylsilane (BPMS) followed literature procedures.

3.5.2 Characterization Methods

Gel permeation chromatographic (GPC) analysis was carried out using a Waters 501 pump, Waters HR1, HR4E and HR5E styrigel columns, a Waters 410 differential refractometer and a Viscotek 760A multi-angle light scattering detector. THF used as the eluant at a flow rate of 1.0 mL/min at 30 °C. The bromine content of the initiator-coated
silica particles was determined by elemental analysis (Galbraith Laboratories). FT-IR
spectra were recorded on a Digilab, Excalibur 300 series instrument and a Bruker Tensor
27 spectrometer; 32 scans were collected using KBr pellets. Thermogravimetric analysis
(TGA) was performed in a nitrogen atmosphere on a Hi-Res TGA 2950
thermogravimetric analyzer (TA instruments) over the temperature range of 23-1000 °C
at a heating rate of 10 °C/min. Transmission electron microscopy (TEM) was performed
using a FEI Techani 12; samples were prepared on a carbon-coated copper grid.

3.5.3 Synthesis of Reagents

The following explains the synthesis and preparation of reagents used in the in
situ functionalization of silica nanoparticles.

3.5.3.1 Synthesis of Difunctional Reactive Stabilizer

The synthesis of the reactive stabilizers [3-(2-bromoisobutyryl)propyl]-triethoxysilane BPTS and [3-(2-bromoisobutyryl)propyl]ethoxydimethylsilane BPMS
followed a literature procedures. A round-bottom flask with a stir bar was placed in an
ice bath. 2-Bromoisobutyryl bromide, 20.0 mL (158.2 mmol), was added dropwise to the
flask which contained 150 mL of anhydrous THF, 7.0 mL (104.2 mmol) of allyl alcohol,
and 14.6 mL (104.2 mmol) of TEA. The solution was allowed to warm to room
temperature and was left to stir overnight. The resulting solid was isolated by filtration
and the solvent was removed under reduced pressure. The product was diluted with 300
mL of dichloromethane and sequentially washed two times with 1 N aq HCl aqueous
solution (2 x 250 mL), two times with saturated aq NaHCO₃ solution (2 x 250 mL), and
two times with water (2 x 500 mL). The organic phase was collected and dried using anhydrous magnesium sulfate. The solids were removed by filtration, and the solvent was removed using reduced pressure to give a yellow oil, which was purified by distillation at 90 °C under vacuum to yield allyl 2-bromoisobutyrate (ABI) (90% yield). \(^1\)H NMR spectroscopy (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 5.80-6.00 (m, 1H); 5.15-5.33 (m, 2H); 4.63 (d, 2H); 1.94 (s, 6H).

In a round-bottom flask, a stir bar, ABI (10.6 g, 50 mmol), 0.02 mL (0.025 mmol) of Karsted’s catalyst, and triethoxysilane or dimethylethoxysilane (65 mmol) were added. The reaction was heated at a gentle reflux at 80 °C. The reaction was monitored by \(^1\)H NMR spectroscopy for the disappearance of double bond indicating completion of silylation. Unreacted silane was removed by vacuum distillation at 60 °C to yield BPTS or BMPS as a yellow oily liquid (85% yield). \(^1\)H NMR spectroscopy (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): BPTS: 4.19 (t, 2H); 3.83 (m, 6H); 1.94 (s, 6H); 1.75 (m, 2H); 1.2 (t, 9H); 0.71 (t, 2H); BPMS: 4.15 (m, 2H); 3.62 (q, 2H); 1.90 (s, 6H); 1.70 (m, 2H); 1.19 (t, 3H); 0.28 (m, 6H); 0.01 (s, 2H).

3.5.3.2 ATRP Preparation of Triethoxy and Monoethoxy- Functionalized Styrene and \(\textit{\text{tert}}\)-Butyl Acrylate

In a 1000 mL Schlenk flask, 0.63 g (0.44 mmol) of CuBr, 130 mL of toluene, 50.0 mL (436 mmol) of styrene, and a stir bar were added. Toluene (10 mL) and 5.02 mL (0.01 mmol) of BPMS were added to a 100 mL Schlenk flask while 10 mL of toluene and 5.0 mL (2.18 mmol) of PMDETA were added to a separate 100 mL Schlenk flask. Each solution was subjected to 3 freeze-pump-thaw cycles and backfilled with nitrogen. The
solution containing the PMDETA was transferred to the flask containing the CuBr via cannula, and it was stirred at the polymerization temperature until it became homogeneous (~15 min). The initiator solution was then transferred via cannula, and the polymerization was allowed to proceed for 48 h at 80 °C. The polymer was purified by passing it through a column of silica gel and the solvent was removed using reduced pressure. The reagents and amounts used for the ATRP polymerization of tert-butyl acrylate were as follows: 200 mL of acetone, 50.0 mL (341 mmol) of tert-butyl acrylate, 0.49 g (0.34 mmol) of CuBr, 1.6 mL (0.71 mmol) of PMDETA and 4.8 mL (0.013 mmol) of BPMS at 60 °C for 6 h.

3.5.4 Synthesis of Functionalized Nanoparticles

The following describes the procedure and conditions used in the Stöber synthesis of the functionalized silica nanoparticles.

3.5.4.1 Initiator-Coated Silica Particles

Initiator coated silica nanoparticles were synthesized by the hydrolytic condensation of TEOS in the presence of BPTS or BPMS as the reactive stabilizer. Ethanol (50 mL), 3.0 mL (0.013 mmol) of TEOS, and 3.3 mL (0.085 mmol) of ammonium hydroxide were added to a round-bottom flask equipped with a stir bar. The reactive stabilizer was added (10% concentration, w/w, relative to TEOS) at varying time intervals of (0 min, 10 min, 1 h, 3 h and 6 h and at 1 h) and varying the concentration of reactive stabilizer, (0%, 1%, 2%, 5%, 10%, 15% and 20%). The reaction was allowed to proceed at room temperature for 24 h. After completion of the reaction, the particles
were isolated by centrifugation (3,500 rpm for 15 min) from the reaction mixture. The particles were washed with THF, ethanol, and water (three washings of each) to remove the catalyst and unreacted initiator. The silica particles were dried overnight in a vacuum oven at 70°C.

3.5.4.2 Polymer-Coated Silica Particles

Polymer coated silica nanoparticles were synthesized by the hydrolytic condensation of TEOS in the presence of a triethoxysilane-functionalized polymer as the reactive stabilizer. In the first attempt to study the effect of the time of addition of the polymer reactive stabilizer, 50 mL of ethanol, 100 mL of THF, 3.0 mL (0.013 mmol) of TEOS, and 3.3 mL (0.085 mmol) of ammonium hydroxide were added to a round-bottom flask equipped with a stir bar. The reactive stabilizer (monoethoxy-functionalized PS dissolved in 50 mL of THF) was added (10% concentration, w/w, relative to TEOS) at varying time intervals of 0 min, 10 min, 1 h, 3 h and 6 h. When monoethoxy-functionalized P(t-BA) was used in the effect of time study, 50 mL of ethanol, 3.0 mL (0.013 mmol) of TEOS, and 3.3 mL (0.085 mmol) of ammonium hydroxide were added to a round-bottom flask equipped with a stir bar. A 10% concentration of monoethoxy-functionalized P(t-BA) dissolved in 50 mL of ethanol was added at the same intervals as before. For the effect of concentration of reactive stabilizer study, 0%, 1%, 2%, 5%, 10%, 15% and 20% concentrations were used, and were added at 1 h after the start of the reaction. Functionalized PS (dissolved in 50 mL of THF) was used in this study, but no THF was added to the reaction mixture until the polymer was added. All reactions were allowed to proceed at room temperature for 24 h. After completion of the reaction, the
particles were isolated by centrifugation from the reaction mixture. The particles were washed with THF, ethanol and water (five washings of each) to remove the catalyst and untethered polymer. The silica particles were dried overnight in a vacuum oven at 70 °C.

3.5.5 General Procedure for Surface-Initiated ATRP

The initiator coated silica particles (1 g) were added to a 100 mL Schlenk flask along with a magnetic stir bar. The flask was evacuated and back-filled with nitrogen three times and left under a nitrogen atmosphere. CuBr (0.037 g, 0.25 mmol), anisole (7.0 mL) and monomer (7.0 mL) were added to a separate 100 mL Schlenk flask along with a magnetic stirrer bar and the flask was sealed with a rubber septum. Three freeze-pump-thaw cycles were performed and back filled with nitrogen. PMDETA, 0.10 mL of (0.48 mmol), was added to the mixture via syringe and the solution was allowed to stir at the polymerization temperature until it became homogeneous, approximately 15 min. Free initiator E2Br-iB, 0.022 mL (0.15 mmol), was added via syringe to the flask containing the silica nanoparticles followed by the transfer of the polymerization solution via cannula. The solution was allowed to stir for the duration of the polymerization. The polymerization times and temperatures were as follows: styrene: 10 h, 110 °C; tert-butyl acrylate: 24 h, 75 °C; methyl acrylate: 9 h, 90 °C. To remove free polymer, the polymerized solution was sonicated and centrifuged in THF five times. The silica particles were dried overnight in a vacuum oven at 70 °C.
3.5.6 Degrafting of Polymer Brush from Silica Nanoparticles

In a polyethylene beaker, 100.0 mg of the silica polymer hybrid nanoparticles were dispersed in 1 mL of toluene. Aliquat 336 (10.0 mg), phase transfer catalyst, and 1 mL of 49% aqueous HF solution were added to the dispersion of particles. The reaction was allowed to stir at room temperature overnight. The polymer was recovered by precipitation into hexanes.
4.1 Functionalization of Silica Capillaries

For the functionalization of silica capillaries, an ATRP surface-immobilized initiator was first deposited onto the inner surface followed by the ATRP polymerization of the monomers. The capillaries were then characterized by capillary rise prior to undergoing manipulation of flow experiments.

4.1.1 Synthesis and Characterization of Surface-Immobilized ATRP Initiator

In this work, ATRP was used to form polymer brushes via the “grafting from” method through surface-initiated polymerizations. An α-bromoester-type initiator was used because of its versatility in the formation of a range of polymer brushes.\textsuperscript{111-115} The ATRP initiator used was [11-(2-bromo-2-methyl)propionyloxy]-undecyltrichlorosilane, which was reported by Matyjaszewski and coworkers.\textsuperscript{66} The synthesis is shown in Scheme 4.1.
Deposition of the trichlorosilane self-assembled monolayer proceeded as shown in Scheme 4.2. The theoretical thickness of the initiating layer is 2.0 nm based on normal bond angles and lengths, and takes into account a 10° tilt of the initiator chain, which has been shown for self-assembled monolayers of trichlorosilanes. The deposited initiator layer thickness was observed to be 2.0 ± 0.2 nm using ellipsometry. The measurements were in good agreement with the theoretical thickness and indicate that the initiator deposited predominantly via the horizontal polymerization or covalent attachment mechanisms rather than through vertical polymerization, Figure 4.1. This initiator layer was also characterized by water contact angles; the advancing and receding water contact angles were 85° and 70°, respectively. The static water contact angle for a perfect clean silicon wafer was 3°. The value for the advancing contact angle of the α-bromoester-initiator correlates reasonably well with the literature value.
Figure 4.1. Possible side reactions of trichlorosilanes with silicon substrates.

ATR-FTIR was also used to characterize the initiator layer,\textsuperscript{66} Figure 4.2. The absorbencies at 2928 cm\textsuperscript{-1} and 2854 cm\textsuperscript{-1} are assigned to the asymmetric and symmetric C-H stretching vibrations of the CH\textsubscript{2} groups in the alkyl chain. An absorbance assigned to the C-H stretching vibrations of the CH\textsubscript{3} groups is barely visible as a shoulder near 3000 cm\textsuperscript{-1}, and the absorbance at 1737 cm\textsuperscript{-1} is assigned to the carbonyl stretching vibration of the ester group. The two absorbencies at 1465 cm\textsuperscript{-1} and 1271 cm\textsuperscript{-1} are related to the bending absorption of methylene and methyl groups, respectively.
Figure 4.2. ATR-FTIR spectrum of surface-immobilized, ATRP initiator.

4.1.2 Synthesis and Characterization of Tethered Homopolymer and Diblock Copolymer Brushes

Scheme 4.3 illustrates the general ATRP “grafting from” approach used to synthesize the tethered homopolymer and diblock copolymer brushes. Here the synthesis of Si/SiO$_2$/PMA homopolymer brush is shown. Similar synthesis procedures were used to form other polymer brushes.

Due to the challenges in characterizing the polymer brushes grown on the inside of the capillaries, silicon wafers and ATR crystals were used to model the reactions.
Ethyl 2-bromoisobutyrate (E2Br-iB) was added as the “free initiator” and served two purposes: one, molecular weight can be obtained from the polymer formed in solution which has been shown to correlate well with the surface-bound polymer;\textsuperscript{61,118} two, it also provides a high enough concentration of the deactivating Cu(II) species to control the polymerization in solution and at the surface.\textsuperscript{65,119,120} The simultaneous solution polymerization can cause an increase in the viscosity of the solution and obstruct the capillary. To eliminate this problem, Cu\textsuperscript{II}Br can be used because there is no free polymer formed in solution.\textsuperscript{66} The polymer brushes on flat surfaces were extracted using a good solvent for that polymer in order to remove any free polymer formed in solution.

![ATR-FTIR spectrum of Si/SiO\textsubscript{2}/PMA.](image)

The conditions in Scheme 4.3 afforded a methyl acrylate (MA) polymer with a $M_n$ of 23,000 g/mol and PDI of 1.2. The corresponding Si/SiO\textsubscript{2}/PMA brush exhibited a thickness of 13 ± 2 nm from ellipsometry and had advancing and receding water contact.
angles of $67^\circ$ and $50^\circ$, respectively. The ATR-FTIR spectrum of Si/SiO$_2$/PMA is shown in Figure 4.3. The absorbance at 3000 cm$^{-1}$ is assigned to O-CH$_3$ stretching while the absorbance at 2954 cm$^{-1}$ is assigned to the C-H stretching vibration of the methyl group. The absorbencies at 2928 cm$^{-1}$ and 2846 cm$^{-1}$ are assigned to the asymmetric and symmetric C-H stretching vibrations of the CH$_2$ groups in the alkyl chain, respectively. The absorbance at 1732 cm$^{-1}$ is assigned to the carbonyl stretching vibration of the ester group, while the absorbance at 1434 cm$^{-1}$ is related to the bending absorption of methylene groups. THF was used for the extraction of untethered polymer chains.

![ATR-FTIR spectrum of Si/SiO$_2$/P($n$-BA)](image)

Figure 4.4. ATR-FTIR spectrum of Si/SiO$_2$/P($n$-BA).

The conditions used for the polymerization of $n$-butyl acrylate ($n$-BA), 90 °C for 5 h, afforded a polymer with a $M_n$ of 25,000 g/mol and PDI of 1.2. The corresponding Si/SiO$_2$/P($n$-BA) brush exhibited a thickness of 13 ± 2 nm from ellipsometry and had advancing and receding water contact angles of $92^\circ$ and $74^\circ$, respectively. The ATR-
FTIR spectrum of Si/SiO$_2$/P(n-BA) is shown in Figure 4.4. The absorbance at 2962 cm$^{-1}$ is assigned to the C-H stretching vibration of the methyl group. The absorbencies at 2933 cm$^{-1}$ and 2870 cm$^{-1}$ are assigned to the asymmetric and symmetric C-H stretching vibrations of the CH$_2$ groups, respectively, in the alkyl backbone and side chain. The absorbance at 1735 cm$^{-1}$ is assigned to the carbonyl stretching vibration of the ester group, while the two absorbencies at 1458 cm$^{-1}$ and 1400 cm$^{-1}$ are related to the bending absorption of methylene and methyl groups, respectively.$^1$ THF was used for the extraction of untethered polymer chains.

The conditions used for the polymerization of styrene (S), 90 °C for 8 h, afforded a polymer with a $M_n$ of 21,000 g/mol and PDI of 1.2. The corresponding Si/SiO$_2$/PS brush exhibited a thickness of 17 ± 3 nm from ellipsometry and had advancing and receding water contact angles of 92° and 80°, respectively. The ATR-FTIR spectrum of
Si/SiO$_2$/PS is shown in Figure 4.5. The absorbencies above 3000 cm$^{-1}$ are attributed to the C-H stretching vibrations of the aromatic ring. The absorbencies at 2928 cm$^{-1}$ and 2846 cm$^{-1}$ are assigned to the asymmetric and symmetric C-H stretching vibrations of the CH$_2$ groups in the alkyl chain. The absorbencies at 1600 cm$^{-1}$, 1490 cm$^{-1}$, and 1445 cm$^{-1}$ are assigned to the stretching vibration of the C-C bonds in the aromatic ring.$^{11}$ THF was used for the extraction of untethered polymer chains.

![ATR-FTIR spectrum of Si/SiO$_2$/PPFS.](image)

Figure 4.6. ATR-FTIR spectrum of Si/SiO$_2$/PPFS.

The conditions used for the polymerization of pentafluorostyrene (PFS) were 90 °C for 8 h. Cu$^{II}$Br was used in the reaction, so there was no free polymer in solution to analyze the molecular weight. The corresponding Si/SiO$_2$/PPFS brush exhibited a thickness of 4 ± 1 nm from ellipsometry and had advancing and receding water contact angles of 94° and 83°, respectively. The ATR-FTIR spectrum of Si/SiO$_2$/PPFS is shown in Figure 4.6. The absorbencies at 2928 cm$^{-1}$ and 2852 cm$^{-1}$ are assigned to the
asymmetric and symmetric C-H stretching vibrations of the CH₂ groups in the alkyl chain, respectively. The absorbencies at 1654 cm⁻¹ assigned to the stretching vibration of the C-C bonds in the fluorinated benzyl ring. The absorbencies at 1499 cm⁻¹ and 1456 cm⁻¹ are assigned to the =C-F stretching vibration. The absorbance at 1302 cm⁻¹ is related to the stretching of the C-F bond. Dichloromethane was used for the extraction of untethered polymer chains.

The conditions used for the polymerization of hydroxyethyl methacrylate (HEMA) were room temperature for 2 h. Cu^{II}Br was used in the reaction, so there was no free polymer in solution to analyze the molecular weight. The corresponding Si/SiO₂/P(HEMA) brush exhibited a thickness of 26 ± 4 nm from ellipsometry and had advancing and receding water contact angles of 51° and 36°, respectively. The ATR-FTIR spectrum of Si/SiO₂/P(HEMA) is shown in Figure 4.7. The broad absorbance at

Figure 4.7. ATR-FTIR spectrum of Si/SiO₂/P(HEMA).
3430 cm\(^{-1}\) corresponds to the O-H stretching vibration. The absorbencies between 2926 cm\(^{-1}\) and 2851 cm\(^{-1}\) are assigned to the asymmetric and symmetric C-H stretching vibrations of the CH\(_2\) groups in the alkyl chain. The absorbance at 1726 cm\(^{-1}\) is assigned to the carbonyl stretching vibration of the ester group, while the two absorbencies at 1453 cm\(^{-1}\) and 1391 cm\(^{-1}\) are related to the bending absorption of methylene and methyl groups, respectively.\(^\text{112}\) Methanol was used for the extraction of untethered polymer chains.

![Figure 4.8. ATR-FTIR spectrum of Si/SiO\(_2\)//P(t-BA).](image)

The conditions used for the polymerization of tert-butyl acrylate (t-BA), 60 °C for 6 h, afforded a polymer with a \(M_n\) of 95,0100 g/mol and PDI of 1.2. The corresponding Si/SiO\(_2\)//P(t-BA) brush exhibited a thickness of 26 ± 4 nm from ellipsometry and had advancing and receding water contact angles of 90° and 75°, respectively. The ATR-FTIR spectrum of Si/SiO\(_2\)//P(t-BA) is shown in Figure 4.8. The absorbance at 2978 cm\(^{-1}\) is assigned to the C-H stretching vibrations of the CH\(_3\) groups. The absorbencies at 2931
cm\(^{-1}\) and 2864 cm\(^{-1}\) are assigned to the asymmetric and symmetric C-H stretching vibrations of the \(\text{CH}_2\) groups in the alkyl chain. The absorbance at 1729 cm\(^{-1}\) is assigned to the carbonyl stretching vibration of the ester group, while the two absorbencies at 1451 cm\(^{-1}\) and 1365 cm\(^{-1}\) are related to the bending absorption of methylene and methyl groups, respectively.\(^{109}\) THF was used for the extraction of untethered polymer chains.

![Figure 4.9. ATR-FTIR spectrum of Si/SiO\(_2\)//PAA.](image)

The Si/SiO\(_2\)//PAA homopolymer brush was formed by the pyrolysis of a Si/SiO\(_2\)//P(t-BA) homopolymer brush at \(\sim 200 \, ^\circ\text{C}\) for 2 h.\(^{109}\) The corresponding brush thickness decreased by approximately 40% to 11 ± 2 nm based on ellipsometry and the advancing and receding water contact angles decreased to 55° and 44°, respectively. The thickness change correlates to the mass loss of the –C(\(\text{CH}_3\))\(_3\) groups and agrees with literature values reported by Wu and coworkers.\(^1\) The ATR-FTIR spectrum of Si/SiO\(_2\)//PAA is seen in Figure 4.9. The broad absorbance at 3248 cm\(^{-1}\) results from the
O-H stretch from the carboxylic acid group. The absorbencies at 2924 cm\(^{-1}\) and 2854 cm\(^{-1}\) are assigned to the asymmetric and symmetric C-H stretching vibrations of the CH\(_2\) groups in the alkyl chain. The loss of the CH\(_3\) stretch and the methyl deformation doublet indicates the loss of the tert-butyl group. The absorbance at 1759 cm\(^{-1}\) decreased in intensity and broadened when compared to the FTIR of Si/SiO\(_2\)//P(t-BA) and is assigned to the carbonyl stretching vibration of the ester group.\(^{109}\)

![ATR-FTIR spectrum of Si/SiO\(_2\)//P(t-BMA).](image)

The conditions used for the polymerization of tert-butyl methacrylate (t-BMA) were 60 °C for 4 h. Cu\(^{II}\)Br was used in the reaction, so there was no free polymer in solution to analyze the molecular weight. The corresponding Si/SiO\(_2\)//P(t-BMA) brush exhibited a thickness of 37 ± 5 nm from ellipsometry and had advancing and receding water contact angles of 91° and 74°, respectively. The ATR-FTIR spectrum of Si/SiO\(_2\)//P(t-BMA) is shown in Figure 4.10. The absorbance at 2975 cm\(^{-1}\) is assigned to
the C-H stretching vibrations of the CH$_3$ groups. The absorbencies at 2933 cm$^{-1}$ and 2852 cm$^{-1}$ are assigned to the asymmetric and symmetric C-H stretching vibrations of the CH$_2$ groups in the alkyl chain. The absorbance at 1724 cm$^{-1}$ is assigned to the carbonyl stretching vibration of the ester group, while the two absorbencies at 1455 cm$^{-1}$ and 1367 cm$^{-1}$ are related to the bending absorption of methylene and methyl groups, respectively.$^{109}$ THF was used for the extraction of untethered polymer chains.

![Graph showing ATR-FTIR spectrum of Si/SiO$_2$/PMAA.](image)

**Figure 4.11.** ATR-FTIR spectrum of Si/SiO$_2$/PMAA.

The Si/SiO$_2$/PMAA homopolymer brush was formed by the pyrolysis of a Si/SiO$_2$/P(t-BMA) homopolymer brush at ~200 °C for 2 h.$^{109}$ The corresponding brush thickness decreased by approximately 40% to 26 ± 4 nm based on ellipsometry and the advancing and receding water contact angles decreased to 43° and 21°, respectively. The thickness change correlates to the loss of the mass of the –C(CH$_3$)$_3$ groups within the brush and agrees with literature values reported by Wu and coworkers.$^1$ The ATR-FTIR
spectrum of Si/SiO$_2$/PMAA is seen in Figure 4.11. The absorbance at 2980 cm$^{-1}$ is assigned to the C-H stretching vibrations of the CH$_3$ groups. The absorbencies at 2931 cm$^{-1}$ and 2858 cm$^{-1}$ are assigned to the asymmetric and symmetric C-H stretching vibrations of the CH$_2$ groups in the alkyl chain. The loss of the CH$_3$ stretch and the methyl deformation doublet indicates the loss of the tert-butyl group. The two absorbencies at 1458 cm$^{-1}$ and 1393 cm$^{-1}$ are related to the bending absorption of methylene and methyl groups, respectively. The doublet at 1761 cm$^{-1}$ appeared and was broader when compared to the FTIR of Si/SiO$_2$/P(t-BMA) and is assigned to the carbonyl stretching vibration of the carboxylic acid group.$^{109}$

![ATR-FTIR spectrum of Si/SiO$_2$/PMMA](image)

**Figure 4.12.** ATR-FTIR spectrum of Si/SiO$_2$/PMMA.

The conditions used for the polymerization of methyl methacrylate (MMA) were 60 °C for 6 h. Cu$^{II}$Br was used in the reaction, so there was no free polymer in solution to analyze the molecular weight. The corresponding Si/SiO$_2$/PMMA brush exhibited a
thickness of 25 ± 4 nm from ellipsometry and had advancing and receding water contact angles of 89° and 79°, respectively. The ATR-FTIR spectrum of Si/SiO$_2$/PMMA is shown in Figure 4.12. The absorbance at 2994 cm$^{-1}$ is assigned to the C-H stretching vibrations of the CH$_3$ groups. The absorbencies at 2951 cm$^{-1}$ and 2837 cm$^{-1}$ are assigned to the asymmetric and symmetric C-H stretching vibrations of the CH$_2$ groups in the alkyl chain. The absorbance at 1728 cm$^{-1}$ is assigned to the carbonyl stretching vibration of the ester group, while the two absorbencies at 1444 cm$^{-1}$ and 1387 cm$^{-1}$ are related to the bending absorption of methylene and methyl groups, respectively. THF was used for the extraction of untethered polymer chains.

![Figure 4.13. ATR-FTIR spectrum of Si/SiO$_2$/PMMA-co-Hostasol.](image)

The conditions used for the copolymerization of methyl methacrylate and the Hostasol monomer (MMA-co-Hostasol; Scheme 4.5) were 60 °C for 6 h. Cu$^{II}$Br was used in the reaction, so there was no free polymer in solution to analyze the molecular
weight. The corresponding Si/SiO$_2$/P(MMA-co-Hostasol) brush exhibited a thickness of 23 ± 24 nm from ellipsometry and had advancing and receding water contact angles of 75° and 59°, respectively. The ATR-FTIR spectrum of Si/SiO$_2$/P(MMA-co-Hostasol) is shown in Figure 4.13. The absorbance at 2946 cm$^{-1}$ is assigned to the C-H stretching vibrations of the CH$_3$ groups in the alkyl chain and the pendent group. The absorbencies at 2816 cm$^{-1}$ and 2763 cm$^{-1}$ correspond to the C-H stretching vibration of the CH$_2$ group next to the nitrogen in the pendant group. The absorbance at 1741 cm$^{-1}$ is assigned to the carbonyl stretching vibration of the ester group, while the absorbance at 1446 cm$^{-1}$ is related to the bending absorption of methylene groups. THF was used for the extraction of untethered polymer chains.

The data in Table 4.1 summarizes the physical data for the polymer systems. The polymer that was analyzed for molecular weight analysis was the free polymer that was obtained by polymerization in solution. Thickness and contact angle measurements were made from the flat silica wafer. It was assumed that the polymer brushes on the interior surfaces of the capillaries were comparable to those of the flat surfaces.
Table 4.1. Characterization of polymer brushes on flat surface.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molecular Weight&lt;sup&gt;a&lt;/sup&gt; (g/mol)</th>
<th>PDI</th>
<th>Thickness&lt;sup&gt;b&lt;/sup&gt; (nm)</th>
<th>Water Contact Angle&lt;sup&gt;c&lt;/sup&gt; (&lt;º)</th>
<th>Static</th>
<th>Advancing</th>
<th>Receding</th>
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<tr>
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<td>1.2</td>
<td>13</td>
<td>61</td>
<td>67</td>
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<td></td>
</tr>
<tr>
<td>P(n-BA)</td>
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<td>1.2</td>
<td>13</td>
<td>83</td>
<td>92</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>P(HEMA)</td>
<td>—</td>
<td>—</td>
<td>26</td>
<td>44</td>
<td>51</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>PS</td>
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<td>1.2</td>
<td>17</td>
<td>86</td>
<td>92</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>PPFS</td>
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<td>—</td>
<td>4</td>
<td>91</td>
<td>94</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>P(t-BA)</td>
<td>95,000</td>
<td>1.2</td>
<td>26</td>
<td>83</td>
<td>90</td>
<td>75</td>
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</tr>
<tr>
<td>PAA</td>
<td>—</td>
<td>—</td>
<td>11</td>
<td>53</td>
<td>55</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>P(t-BMA)</td>
<td>—</td>
<td>—</td>
<td>37</td>
<td>82</td>
<td>91</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>PMAA</td>
<td>—</td>
<td>—</td>
<td>26</td>
<td>33</td>
<td>43</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>PMMA</td>
<td>—</td>
<td>—</td>
<td>25</td>
<td>82</td>
<td>89</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>PMMA-co-Hostasol</td>
<td>—</td>
<td>—</td>
<td>23</td>
<td>68</td>
<td>75</td>
<td>59</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Molecular weights were determined from the free polymer in solution

<sup>b</sup> Error on thickness measurements was ± 14%

<sup>c</sup> The standard deviation of contact angles was ± 2º
Preparation of the diblock copolymer brushes was carried out in a similar manner to that of the homopolymer brushes. Scheme 4.4 illustrates the synthesis of Si/SiO$_2$/PS-\textit{b}-PAA diblock copolymer brush, while Figure 4.14 shows the FTIR-ATR spectra of the surface-immobilized ATRP initiator to the surface followed by the synthesis of each block of the copolymer brush, Si/SiO$_2$/PS-\textit{b}-PAA. A solution deposition of the bromoisobutyrate initiator to a silica substrate was performed by self-assembly. Figure 4.14a displays the ATR-FTIR spectrum of the immobilized initiator with absorbencies at 2927 and 2854 cm$^{-1}$ (C–H stretching and CH$_2$ stretching vibrations) and 1732 cm$^{-1}$ (carbonyl stretching vibration of the ester group). Upon synthesis of the PS homopolymer brush, Figure 4.14b shows the presence of absorbencies at 3030, 3061 and
3084 cm\(^{-1}\), all attributed to aromatic C–H stretching vibrations. The absorbencies at 1600 cm\(^{-1}\), 1490 cm\(^{-1}\) and 1437 cm\(^{-1}\) are assigned to the stretching vibration of the C-C bonds in the aromatic ring.

![ATR-FTIR spectra](image)

Figure 4.14. ATR-FTIR spectra of (a) Si/SiO\(_2\)//bromoisobutyrate initiator, (b) Si/SiO\(_2\)//PS, (c) Si/SiO\(_2\)//PS-\(b\)-P(\(t\)-BA) and (d) Si/SiO\(_2\)//PS-\(b\)-PAA.

Table 4.2 shows the representative advancing and receding contact angles for the PS homopolymer brush of 92\(^\circ\) and 74\(^\circ\), respectively, which has a brush thickness of 22 ± 3 nm. With the addition of the second block, P(\(t\)-BA), Figure 4.14c shows the carbonyl stretching absorbance at 1726 cm\(^{-1}\) corresponding to the addition of \(t\)-BA and a doublet at 1367 cm\(^{-1}\) and 1392 cm\(^{-1}\) due to the symmetric methyl deformation mode. There was little change in the contact angles, but Table 4.2 shows a 10 ± 5 nm increase in brush thickness. The absence of any contact angle change was due to both PS and P(\(t\)-BA) being hydrophobic. The Si/SiO\(_2\)//PS-\(b\)-P(\(t\)-BA) chains were converted to Si/SiO\(_2\)//PS-\(b\)-
PAA chains via pyrolysis.\textsuperscript{109} After pyrolysis (Figure 4.15d), there is a broadening of the absorbance at 1726 cm\textsuperscript{-1} and a loss of the absorbencies associated with the pendant methyl groups. The advancing and receding contact angles decreased from 91° and 72° for P(\(t\)-BA) to 61° and 47°, respectively, for PAA as shown in Table 4.2. The polymer brush thickness has decreased from 10 nm to 6 ± 5 nm after pyrolysis. This was approximately a 40% decrease in the outer most polymer brush layer which correlates well with literature.\textsuperscript{1}

\begin{table}[h]
\centering
\caption{Contact angle and ellipsometry data for the PS-based diblock copolymer brush on a flat surface.}
\begin{tabular}{lcccc}
\hline
Brush structure & Water & Ethylene glycol & Block thickness (nm) \\
 & \text{contact angle\textsuperscript{a} (°)} & \text{contact angle\textsuperscript{a} (°)} & \\
 & \(\theta_s\) & \(\theta_d\) & \(\theta_r\) & \(\theta_a\) \\
\hline
Si/SiO\textsubscript{2}///OH & 3\textsuperscript{b} & 9 & - \\
Si/SiO\textsubscript{2}///ATRP initiator & 78 & 89 & 72 & 55 & 5 ± 1 \\
Si/SiO\textsubscript{2}///PS & 85 & 92 & 74 & 57 & 22 ± 3 \\
Si/SiO\textsubscript{2}///PS-\textit{b}-P(\(t\)-BA) & 83 & 91 & 72 & 68 & 10 ± 5 \\
Si/SiO\textsubscript{2}///PS-\textit{b}-PAA & 56 & 61 & 47 & 44 & 6 ± 5 \\
\hline
\textsuperscript{a} The standard deviation of contact angles was ± 2° \\
\textsuperscript{b} Static contact angle was recorded for this value
\end{tabular}
\end{table}

4.1.3 Characterization of Capillary Coatings

Due to the inability to chemically characterize the inner diameter of capillaries, analysis has been challenging. Common characterization techniques typically employed to study polymer brushes on flat surfaces and nanoparticles could not be used. Silicon wafers and ATR crystals were used to follow the surface-initiated polymerizations. The internal diameter of the micro-capillaries used was 75 \(\mu\)m unless otherwise stated.
Fluorescence spectroscopy was used to prove that polymer brushes were attached to the inside of the capillary, while capillary rise experiments were used to demonstrate changes in the surface energy of the capillaries after each synthetic step. With this technique, it was possible to evaluate if the synthesis of homopolymers and diblock copolymers occurred.

\[
\text{Si} - \text{SiO}_2 \rightarrow \text{PMMA-co-Hostasol.}
\]

Scheme 4.5. ATRP synthesis of Si/SiO\(_2\)/PMMA-co-Hostasol.

In the synthesis of Si/SiO\(_2\)/PMMA-co-Hostasol (Scheme 4.5), the monomer feed ratio was 100:1, MMA:Hostasol, and CuBr\(_2\) was used instead of the free initiator E2Br2 to eliminate the chance for free polymer becoming adsorbed onto the capillary walls. The capillaries were subjected to an exhaustive washing by sonication and rinsing with dichloromethane, THF, and isopropanol. Figure 4.15a, Si/SiO\(_2\)//OH, shows the fluorescence spectrum of a freshly cleaned inner capillary, and the capillary in Figure 4.15b (Si/SiO\(_2\)//PMMA) has a PMMA homopolymer brush coated inner surface. Both
spectra show no fluorescence, but Si/SiO$_2$/PMMA-\textit{co}-Hostasol (Figure 4.15c) shows a large absorbance emission between 510 and 540 nm. The experiments was conducted such that the laser was directed down through the capillary. The absorption from the backscattered light was measured. This large emission absorbance provides evidence that the copolymer was present within the inside walls of the capillary. Since no emission was seen in the clean or PMMA-coated capillaries, the fluorescence observed was attributed to the Hostasol-functionalized methacrylates. The polyimide coating on the outside of the capillary, which provides strength and flexibility to the capillary, was removed by dissolution in hot sulfuric acid to ensure that it would not contribute to the any absorbance emission. Also, to confirm that no residual polymerization solution or polymer chains resided inside the capillary, hot toluene was passed through the capillary and the solution and the capillary were separately analyzed. No fluorescence emission was detected from the solvent and the same emission spectrum was seen as before for the Si/SiO$_2$/PMMA-\textit{co}-Hostasol-coated capillary.
Equation (2) relates capillary rise to surface tension. From this equation, the treatment of capillary rise and surface tension ($\gamma$) has been deduced,

$$\gamma = \frac{\Delta \rho gh r }{2 \cos \theta}$$

where $\Delta \rho$ is the difference in densities of the liquid and gas phases, $g$ is the acceleration due to gravity, $h$ is the height that the liquid rises in the capillary, $r$ is the radius of the capillary, and $\theta$ is the contact angle between the capillary wall and the meniscus.

Ethylene glycol was used as the probe fluid due to its medium surface tension value of 49.89 mN/m when compared to surface tension of water at 73.56 mN/m; most common organic solvents have a surface tension ranging from 17.98 to 34.96 mN/m.

These latter organic solvents have a tendency to completely wet a polymer surface due to the reduction of surface free energy. In capillary rise, the equilibrium height was reached...
when the forces due to surface tension are equal to the weight of the probe fluid.

Ethylene glycol was used as the probe fluid and was allowed to rise for 24 h; measurements were made using a traveling telescope cathetometer. Fluid was allowed to rise up the capillary overnight before the measurements were recorded because the process for the probe fluid to rise up a polymer coated capillary tends to be slow.123

A number of polymer brush systems were studied via capillary rise as a way to characterize the various polymer coatings (Table 4.3). As the inner capillary surface was modified from a hydrophilic surface to a hydrophobic surface and back to a hydrophilic surface, these changes in surface energy could be followed as shown in Figure 4.16. A freshly cleaned surface, using a ‘piranha solution,’ left the silica covered with hydroxyl groups which allowed the ethylene glycol to completely wet the surface of the capillary. This complete wetting leads to a large capillary rise (24.17 cm) corresponding to a small contact angle between the capillary wall and the probe fluid, as derived from equation 2. As the silica surface was modified to become more hydrophobic (Si/SiO$_2$/PS and Si/SiO$_2$/PS-$b$-$P(t$-BA)), the capillary rise (6.64 and 4.04 cm, respectively) was lower due to the unfavorable energy interactions between the polymer and the probe fluid. Upon pyrolysis of Si/SiO$_2$/PS-$b$-PAA, the outermost polymer layer was converted to PAA which produced a large capillary rise (23.86 cm) for the Si/SiO$_2$/PS-$b$-PAA-modified capillary.
By comparing the data in Table 4.2 with the capillary rise data (Figure 4.16), the changes in surface energies were able to be followed. As the capillary coating became more hydrophobic, the capillary rise decreased, but when the outermost polymer layer became hydrophilic, the capillary rise increased. This same trend can also be seen from the water and ethylene glycol contact angle data (Table 4.2), indicating that capillary rise measurements can be used to follow changes in surface energies in a series of surface reactions in micro-capillaries which is equivalent to using contact angle measurements on flat surfaces.

As seen in Table 4.3, the data follows the expected pattern apart from the Si/SiO$_2$/PPFS system. The lowest water contact angles (and thus, the more hydrophilic
compositions) have the highest Zisman critical surface energy which corresponds to the capillary system with the greatest capillary rises (Si/SiO$_2$/OH, Si/SiO$_2$/P(HEMA) and Si/SiO$_2$/PAA). The polymer systems that are more hydrophobic, Si/SiO$_2$/PS, Si/SiO$_2$/PPFS, and Si/SiO$_2$/P(t-BA), have a higher water contact angle, a lower Zisman critical surface energy and a lower capillary rise. Si/SiO$_2$/PPFS does not follow the expected trend and this could be a result of the polymer brush thickness being low and/or the polymer brush grafting density being sufficiently lower when compared to the other capillary systems. These differences can also be seen on flat surfaces where an increase in surface roughness can cause a change in the contact angle that was measured. de Gennes et al.\textsuperscript{124} described how gravity forces (tend to thin the layer) and long range van der Waals forces (tends to thicken the layer) affect the thickness of the brush which, in turn, affect the height of the capillary rise. These effects, when comparing the same polymer coated capillaries polymerized at different periods in time, show small differences in the measured results in capillary rise experiments. The important finding from these experiments was that it was possible to follow changes in surface energies following multi-step surface modification using capillary rise measurements.

The Zisman critical surface energy ($\gamma_c$) was used to estimate the surface energy of the polymer films on flat surfaces by measuring the advancing water contact angle. This data was used to correlate the changes seen between the contact angles measured on flat surfaces and the contact angles calculated from the capillary rise measurements. By measuring the capillary rise of the probe fluid at each step in the reaction, it was possible to follow the change in Zisman critical surface energy of each layer of the polymer brush. The same trends that were seen when measuring the water contact angle on flat surfaces
were seen by the capillary rise measurements as the film’s surface energy changes (Table 4.3).

The contact angle between the probe fluid, ethylene glycol, and the wall of the capillary was calculated using Equation 2. These values were then compared with ethylene glycol static contact angles (Table 4.4). It can be seen that as the capillary coating goes from a clean surface (Si/SiO$_2$/OH) to a progressively hydrophobic surface (Si/SiO$_2$/ATRP Initiator, Si/SiO$_2$/PS and Si/SiO$_2$/PS-$b$-P(t-BA)) the capillary rise decreases which causes the calculated contact angle and the static ethylene glycol contact angle to increase. The results indicate that the interior coating of the capillary is becoming more hydrophobic as suggested by $\gamma_c$ from Table 4.3. Again, as the second block of the Si/SiO$_2$/PS-$b$-P(t-BA) diblock was converted to Si/SiO$_2$/PS-$b$-PAA, the calculated contact angle decreased to 12°, signifying a hydrophilic coating. The decrease was also seen on flat surfaces.
Table 4.3. Comparison of physical properties for polymer-coated, capillary surfaces.

<table>
<thead>
<tr>
<th>Brush structure</th>
<th>Static water contact angle $^a$, $\theta_s$ (°)</th>
<th>Advancing water contact angle $^a$, $\theta_a$ (°)</th>
<th>Zisman critical surface energy $^b$, $\gamma_c$ (mN/m)</th>
<th>Capillary rise (cm)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/SiO$_2$/OH</td>
<td>3</td>
<td>4</td>
<td>95.2</td>
<td>24.17</td>
</tr>
<tr>
<td>Si/SiO$_2$/ATRP Initiator</td>
<td>78</td>
<td>89</td>
<td>31.8</td>
<td>7.92</td>
</tr>
<tr>
<td>Si/SiO$_2$/PS</td>
<td>85</td>
<td>90</td>
<td>31.1</td>
<td>6.64</td>
</tr>
<tr>
<td>Si/SiO$_2$/PS-b-P(\text{-}BA)</td>
<td>83</td>
<td>92</td>
<td>29.6</td>
<td>4.04</td>
</tr>
<tr>
<td>Si/SiO$_2$/PS-b-PAA</td>
<td>56</td>
<td>61</td>
<td>52.7</td>
<td>23.6</td>
</tr>
<tr>
<td>Si/SiO$_2$/PPFS</td>
<td>90</td>
<td>94</td>
<td>28.1</td>
<td>12.61</td>
</tr>
<tr>
<td>Si/SiO$_2$/P(HEMA)</td>
<td>48</td>
<td>49</td>
<td>61.6</td>
<td>23.01</td>
</tr>
<tr>
<td>Si/SiO$_2$/P(\text{-}BA)</td>
<td>84</td>
<td>92</td>
<td>29.6</td>
<td>5.63</td>
</tr>
<tr>
<td>Si/SiO$_2$/PAA</td>
<td>49</td>
<td>32</td>
<td>74.3</td>
<td>23.55</td>
</tr>
<tr>
<td>Si/SiO$_2$/PMA</td>
<td>60</td>
<td>72</td>
<td>44.5</td>
<td>10.93</td>
</tr>
</tbody>
</table>

$^a$ The standard deviation of contact angles measured on flat surfaces was $\pm 2^\circ$

$^b$ $\gamma_c$ was calculated by plotting $\theta_a$ vs. $\gamma_c$ from the data reported by Vogler$^{125}$; error was $\pm 0.1$ mN/m

$^c$ Ethylene glycol was used as the probe fluid and was allowed to rise for 24 h. Measurements were made using a traveling telescope cathetometer. The error on capillary rise measurements was $\pm 0.05$ mm
Table 4.4  Physical properties for polymer-coated capillaries and flat surfaces.

<table>
<thead>
<tr>
<th>Brush structure</th>
<th>Static water contact angle&lt;sup&gt;a&lt;/sup&gt;, $\theta_s$ (°)</th>
<th>Static ethylene glycol contact angle&lt;sup&gt;a&lt;/sup&gt;, $\theta_s$ (°)</th>
<th>Calculated contact angle&lt;sup&gt;b&lt;/sup&gt;, (°)</th>
<th>Capillary rise (cm)&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/SiO$_2$/OH</td>
<td>3</td>
<td>2</td>
<td>8</td>
<td>24.17</td>
</tr>
<tr>
<td>Si/SiO$_2$/ATRP Initiator</td>
<td>78</td>
<td>56</td>
<td>71</td>
<td>7.92</td>
</tr>
<tr>
<td>Si/SiO$_2$/PS</td>
<td>85</td>
<td>57</td>
<td>74</td>
<td>6.64</td>
</tr>
<tr>
<td>Si/SiO$_2$/PS-b-P(t-BA)</td>
<td>83</td>
<td>68</td>
<td>80</td>
<td>4.04</td>
</tr>
<tr>
<td>Si/SiO$_2$/PS-b-PAA</td>
<td>56</td>
<td>44</td>
<td>12</td>
<td>23.86</td>
</tr>
<tr>
<td>Si/SiO$_2$/PPFS</td>
<td>90</td>
<td>67</td>
<td>59</td>
<td>12.61</td>
</tr>
<tr>
<td>Si/SiO$_2$/P(HEMA)</td>
<td>48</td>
<td>7</td>
<td>19</td>
<td>23.01</td>
</tr>
<tr>
<td>Si/SiO$_2$/P(t-BA)</td>
<td>84</td>
<td>63</td>
<td>77</td>
<td>5.63</td>
</tr>
<tr>
<td>Si/SiO$_2$/PAA</td>
<td>49</td>
<td>9</td>
<td>15</td>
<td>23.54</td>
</tr>
<tr>
<td>Si/SiO$_2$/PMA</td>
<td>60</td>
<td>47</td>
<td>63</td>
<td>10.93</td>
</tr>
</tbody>
</table>

<sup>a</sup> The standard deviation of contact angles measured on flat surfaces was ± 2°

<sup>b</sup> Capillary contact angles calculated using Equation 2

<sup>c</sup> Ethylene glycol was used as the probe fluid and was allowed to rise for 24 h. Measurements were made using a traveling telescope cathetometer. The error on capillary rise measurements was ± 0.05 mm
4.1.4 Synthesis and Characterization of Silane-Functionalized Silica Capillaries

The silica capillaries were coated using either a hydrophilic or hydrophobic functionalized triethoxysilanes in order to study the effect that the monomolecular, thin coatings would have on the ability to manipulate flow. The silanes used (Figure 4.17) were selected based on their extreme surface energy differences in order to help better understand the mechanism behind the manipulation seen in flow. APTS and TSPG are both hydrophilic in nature and have a surface energy\(^\text{121}\) around 40 dynes/cm while HDTs and 13FTS are both considered hydrophobic coatings and have a surface energy\(^\text{121}\) around 20 dynes/cm.

![Chemical structures of triethoxysilanes used for the functionalization of capillaries.](image)

Self-assembly techniques were used to deposit the silanes on the silica surfaces. Toluene was chosen as the solvent because of its ability to consistently prepare monolayers with high grafting densities.\(^\text{117,126}\) The base, ethyldiisopropylamine (EDIPA), facilitates covalent attachment between silanes and surface silanols which leads to higher
Table 4.5 summarizes the physical properties from the silane depositions on flat surfaces and in the micro-capillaries. The deposition of APTS resulted in a film thickness of 9 nm from ellipsometry and produced advancing and receding contact angles of 67° and 46°, respectively. A height of 22.9 cm was measured from the capillary rise measurements. Figure 4.18 shows the ATR-FTIR spectrum of the APTS monolayer. The absorbencies at 2932 cm\(^{-1}\) and 2889 cm\(^{-1}\) are assigned to the asymmetric and symmetric C-H stretching vibrations of the CH\(_2\) groups in the alkyl chain. The absorbencies at 1638 cm\(^{-1}\) and 1560 cm\(^{-1}\) result from N-H bending from the primary amine, while the absorbance at 1488 cm\(^{-1}\) is related to the bending absorption of methylene groups. The two absorbencies at 1119 cm\(^{-1}\) and 1034 cm\(^{-1}\) occur from the C-N stretching vibration.\(^{130}\)

![Figure 4.18. ATR-FTIR spectrum of surface-deposited APTS.](image)
The deposition of TSPG resulted in a film thickness of 10 nm from ellipsometry and produced advancing and receding contact angles of 38° and 17°, respectively. A height of 22.2 cm was measured from the capillary rise measurements. Figure 4.19 shows the ATR-FTIR spectrum of the APTS film. The broad absorbance at 3484 cm\(^{-1}\) corresponds to the O-H stretching vibration. The absorbencies at 2930 cm\(^{-1}\) are assigned to the asymmetric and symmetric C-H stretching vibrations of the CH\(_2\) groups in the alkyl chain. The absorbencies at 1645 cm\(^{-1}\) and 1547 cm\(^{-1}\) result from carbonyl stretching vibration of the amide group and N-H bending from the secondary amide, respectively. The absorbance at 1079 cm\(^{-1}\) is related to the C-O stretching vibration.\(^{131}\)

![ATR-FTIR spectrum of surface-deposited TSPG.](image)

The deposition of HDTS resulted in a film thickness of 3 nm from ellipsometry and produced advancing and receding contact angles of 101° and 90°, respectively. A height of 3.7 cm was measured from the capillary rise measurements. Figure 4.20 shows
the ATR-FTIR spectrum of the HDT monolayer. The absorbencies at 2926 cm\(^{-1}\) and 2849 cm\(^{-1}\) are assigned to the asymmetric and symmetric C-H stretching vibrations of the CH\(_2\) groups in the alkyl chain. The smaller absorbencies at 1460 cm\(^{-1}\) and 1374 cm\(^{-1}\) are a result of bending absorption from the methylene and methyl groups, respectively.\(^{132}\)

![ATR-FTIR spectrum](image)

Figure 4.20. ATR-FTIR spectrum of surface-deposited HDTs.

The deposition of 13FTS resulted in a film thickness of 4 nm from ellipsometry and produced advancing and receding contact angles of 93° and 75°, respectively. A height of 3.2 cm was measured from the capillary rise measurements. Figure 4.21 shows the ATR-FTIR spectrum of the 13FTS monolayer; the absorbencies at 1243 cm\(^{-1}\) and 1075 cm\(^{-1}\) are assigned to the C-F stretching vibration.\(^{133}\)
4.2 Manipulation of Flow through Capillaries

In order to study how polymer brushes can affect the flow of a fluid through the capillaries, backpressure experiments and preferential flow experiments were designed. The experiments show how differences in surface energies of the coatings can alter the
flow of the fluid. By changing the polymer coating, the pressure required for flow through the column can be manipulated as a result of the change in surface energy. Depending on the hydrophobicity of the polymer coating, differential flow between two capillaries can be altered.

4.2.1 Backpressure Experiments

The backpressure experiments shows that the pressure required for the flow of a solvent can be adjusted by changing the polymer coating. By adjusting the surface energy of the interior walls of the capillary, the backpressure for flow can be increased or decreased. Figure 4.22 shows a schematic of the backpressure experiment while Figure 4.23 shows the actual experimental setup used in the laboratory. A syringe pump was used to control the flow rate while a pressure transducer, located directly behind the capillary, was connected to a digital meter and recorded the backpressure. The experiments ran for 24 h and the highest pressure observed was recorded as the backpressure.

Figure 4.22. Schematic for the setup of the backpressure experiments.
In the first set of experiments (Figure 4.24), a 250 µm capillary was used and each 30 cm section was coated with either Si/SiO₂//OH (clean), Si/SiO₂//ATRP Initiator (SAM), Si/SiO₂//P(t-BMA) (P(t-BMA)) or Si/SiO₂//PMAA (PMAA). Three solvents were used (pure water, ethanol and hexane) and the flow rate was 1.00 mL/h. Figure 4.24 shows the results from the backpressure measurements using a 250 µm capillary. The flow of water through the functionalized capillaries resulted in an increase in backpressure when going from a clean capillary to a PMAA-functionalized capillary. When ethanol was used as the solvent, the backpressure was higher than for water because of its higher viscosity (Table 4.6), but as the capillary coatings went from hydrophobic to hydrophilic, the backpressure decreases. The backpressure did not vary significantly between the different capillary coatings when hexane was used as the solvent.
Figure 4.24. Backpressure measurements for 250 µm functionalized capillary, flow rate = 1.00 mL/h: coatings consisted of Si/SiO$_2$/OH (clean), Si/SiO$_2$/ATRP Initiator (SAM), Si/SiO$_2$/P(t-BMA) (P(t-BMA)) and Si/SiO$_2$/PMAA (PMAA).

Water and ethanol are both known as good solvents for PMAA, but they show contrasting results as the capillary coating goes from P(t-BMA) to PMAA. Since ethanol has the highest viscosity of the three solvents (Table 4.6) it requires greater pressure for flow and has the highest backpressure for a clean capillary.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Viscosity (centipoise)</th>
<th>Surface Tension @ 25 °C (dynes/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.911</td>
<td>73.56</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.057</td>
<td>23.39</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.296</td>
<td>17.98</td>
</tr>
</tbody>
</table>

Table 4.6. Viscosity and surface tension data for selected solvents for backpressure experiments.
Water has a much larger surface tension when compared to ethanol which can account for the contrasting effects seen in the backpressure measurements. Hydrogen bonding also plays a role in interpreting the data. The increase in pressure, from SAM to P(t-BMA), could be due to hydrogen bonding interactions occurring between the water molecules and the carbonyl group of the P(t-BMA). The pressure increases further when the coating was converted to PMAA. Greater hydrogen bonding interactions would be occurring between the water molecules and the carbonyl groups plus the hydroxyl groups within PMAA chains, when compared with P(t-BMA), because of the tert-butyl groups being converted to hydroxyl groups via pyrolysis. The decrease in backpressure seen with ethanol was a result of it becoming a better solvent for the polymer layer. In ethanol, the polymer chains are being solvated and act as a lubricant, reducing drag between the fluid and the wall of the capillary. Hexane has the lowest viscosity and surface tension (Table 4.6) of all the solvents leading to the lowest values in backpressure. The low surface tension allows hexane to completely wet all of the capillary coatings resulting in little change between the polymer films.
Figure 4.25. Backpressure measurements for a 75 µm functionalized capillary, flow rate = 0.5 mL/h: a) water, b) ethanol, c) acetone, d) decane, e) methylene chloride; coatings consisted of Si/SiO$_2$/OH (clean), Si/SiO$_2$/ATRP Initiator (SAM), Si/SiO$_2$/P(t-BA) and Si/SiO$_2$/PAA.
In the second set of experiments, 30 cm sections of a 75 µm capillary were used with the intention to see an enhanced effect in the changes in backpressure from one coating to the next due to the smaller internal diameter. The capillary coatings consisted of Si/SiO$_2$/OH (clean), Si/SiO$_2$/ATRP Initiator (SAM), Si/SiO$_2$/P(t-BA) (P(t-BA)), Si/SiO$_2$/PAA (PAA); water, ethanol, acetone, decane, and methylene chloride were used as the solvents (see Table 4.7 for properties of solvents). In order to describe the flow down the capillary, the Reynolds number$^{134}$ calculated (Equation 3) for this system was 2.36. At such a low value, instabilities are suppressed by viscous effects and the flow of the solvent is laminar.$^{134}$ Where $Re$ is the Reynolds number, $\rho$ is the fluid density, $V$ is the fluid velocity, $D$ is the density and $\mu$ is the viscosity.

\[
Re = \frac{\rho V D}{\mu}
\]  

(3)

The results of the experiments can be seen in Figure 4.25. With water and ethanol as the solvent (Figure 4.25a and Figure 4.25b, respectively), the backpressure increased as the capillary coating changed from SAM to PAA. However, when acetone was the solvent, Figure 4.25c, the backpressure decreased as the capillary coating changed from clean to PAA. There was little change in backpressure when decane or methylene chloride was used as the solvent, as shown in Figure 4.25d and Figure 4.25e, respectively.
Table 4.7. Viscosity and surface tension data for selected solvents.\textsuperscript{122}

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Viscosity (centipoise)</th>
<th>Surface Tension @ 25 °C (dynes/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.911</td>
<td>73.56</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.057</td>
<td>23.39</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.308</td>
<td>23.04</td>
</tr>
<tr>
<td>Decane</td>
<td>0.920</td>
<td>23.41</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>0.417</td>
<td>28.77</td>
</tr>
</tbody>
</table>

The increase in backpressure seen with water as the solvent can be explained by the increase in hydrogen bonding between the solvent and the polymer coating. The strongest hydrogen bonding is between water and PAA, which creates the largest amount of drag during flow causing the larger backpressure. Water is also known to be a good solvent for PAA\textsuperscript{107} which would cause the polymer brush to be solvated and increase solvent/polymer interactions. Ethanol also shows an increase in backpressure as the coating changes from clean to PAA and has a larger backpressure altogether because of its higher viscosity value (Table 4.7). Ethanol is also a good solvent for PAA\textsuperscript{107} which solvates the polymer brush leaving it fully extended. This full extension and solvent/polymer interactions leads to a rise in the backpressure.

Acetone shows a decrease in the backpressure from one coating to the next. Acetone in a good solvent for P(t-BA) but a bad solvent for PAA\textsuperscript{107}; this would leave the P(t-BA) polymer brush extended and having a larger backpressure value compared to PAA in which the polymer chains would be in a more collapsed state and have a lower backpressure. Acetone has the lowest overall backpressure readings due to it having the lowest viscosity (Table 4.7). Decane was chosen as a solvent because of its higher viscosity and lack of hydrogen bonding interactions between it and the polymer coatings.
Even though it has a slightly higher viscosity than water, decane’s backpressure measurements are lower than water’s. The lower values can be attributed to the lack of hydrogen bonding between the solvent and the capillary coating. However, there was little change in the measurements when comparing between the different coatings which was due to decane being a poor solvent for all of the coatings. Methylene chloride also shows little change between the backpressure values when comparing between the capillary coatings because of its lack of hydrogen bonding and it being a poor solvent for the capillary systems.

![Backpressure measurements for 75 µm silane-functionalized capillaries](image)

Figure 4.26. Backpressure measurements for 75 µm silane-functionalized capillaries, flow rate = 0.5 mL/h; coatings consisted of Si/SiO$_2$/OH (clean), Si/SiO$_2$/TSPG, Si/SiO$_2$/APTS and Si/SiO$_2$/13FTS, Si/SiO$_2$/HDT.

Hydrophilic and hydrophobic functionalized triethoxysilanes (Figure 4.17) were used to study the difference between thin film coatings versus thicker polymer coatings. When a 75 µm capillary was modified with both the hydrophilic and hydrophobic
functionalized silanes, the backpressure dropped compared with a clean capillary when water was used as a probe fluid, as shown in Figure 4.26. This drop in pressure was a result of the loss of hydrogen bonding interactions between the water and the surface of the silica capillary. There was little change between the silane-functionalized capillaries suggesting that the effect that the solvent has on the polymer brushes causes the increase in backpressure. The backpressures for the silane coatings were noticeably lower than those for the polymer coatings with water or water as the solvent. Again, ethanol has a higher backpressure values because of its higher viscosity (Table 4.7). There was a large drop in backpressure when going from a clean capillary to the triethoxysilane-functionalized capillaries for both probe fluids. This decrease is a result of SAMs reducing the interaction between the fluid and the capillary wall. As with water, ethanol has little effect on the backpressure readings when the different silane-functionalized capillaries were compared. Since there is no expansion or collapse occurring with the functionalized-silane coatings, the decrease in backpressure is a result of the reduction in the drag that the probe fluid sees against the capillary walls when compared with a clean capillary. The thin films that formed from the functionalized-silanes do not become solvated and expand as polymer brushes do in good solvent.

In summary, the pressure required for flow through a confined space can be manipulated by modifying the interior surface. When using a good solvent for the polymer film, the backpressure increases due to solvation effects between the solvent and the polymer brush; however, if a poor solvent is used, the backpressure decreases due to a collapse in the polymer brush. Dimitrov et al.\textsuperscript{135,136} used molecular dynamics simulations to show how polymer brushes confined in cylindrical tubes are affected by solvents.
Their work shows that the polymer brush reorganizes itself depending on whether or not the probe fluid wets the brush. When functionalized silane films were deposited on the walls, the backpressure dropped significantly when compared to a clean silica capillary. There was virtually no difference in backpressure between the hydrophilic and hydrophobic silanes supporting the explanation that conformation of the polymer brush is responsible for the changes in backpressure.

4.2.2 Preferential Flow Experiments

The preferential flow experiments were designed to study how differences in surface energies of a coating could be used to control the direction of flow, as illustrated in Figure 4.27. In our apparatus, a syringe pump was used to pump a water solution, at a very low flow rate (0.5 µL/h), through a silica “Y” junction to the capillaries allowing the solution to flow down the capillaries. A water soluble dye, brilliant blue, was used in order to analyze the preferred flow by UV/VIS. A two arm test tube was constructed where the exit of the capillary was inserted through a rubber septum and a small section of 250 µm capillary was used as a vent. The vent was used to keep pressure from building up within the test tube. Pure water (3.0 g) was weighed out in each test tube, and it was inserted into an oil bath and heated to 40 °C. The reservoir of water, in this test tube, provided constant humidity and was used in UV/VIS analysis.
Figure 4.27. Schematic of the setup for the preferential flow experiments.

Figure 4.28. Actual laboratory setup for the preferential flow experiments.
Figure 4.29 shows the comparison between Si/SiO$_2$/PAA and Si/SiO$_2$/P(\(r\)-BA) coated capillaries. It was formed that flow only occurred down the hydrophilic capillary, Si/SiO$_2$/PAA. The experiment was repeated five times and each run was for 24 h; each trial showed similar results. Flow between Si/SiO$_2$/P(HEMA) and Si/SiO$_2$/P(\(n\)-BA) coated capillaries also showed a preference for the hydrophilic capillary, as shown in Figure 4.30. This experiment was also conducted five times. Even after 24 h, no aqueous solution traveled down the hydrophobic capillary. These results suggest that water flowing at a very slow rate favors the polymer capillary with the highest surface energy. The experiments shown in Figure 4.29 and Figure 4.30 demonstrate that the results are reproducible. When new functionalized capillaries were made and the systems were interchanged, as shown in Figure 4.31, flow of the aqueous solution still preferred the hydrophilic capillaries of Si/SiO$_2$/PAA and Si/SiO$_2$/P(HEMA).
Figure 4.29. Preferential flow results between Si/SiO$_2$/PAA and Si/SiO$_2$/P($t$-BA) functionalized capillary, i.d. = 75 µm, flow rate = 5.0 µL/h, time = 24 h.
Figure 4.30. Preferential flow results between Si/SiO$_2$/P(HEMA) and Si/SiO$_2$/P(n-BA) functionalized capillary, i.d. = 75 µm, flow rate = 5.0 µL/h, time = 24 h.
The functionalized triethoxysilanes in Figure 4.17 were used to coat the internal walls of the capillaries in order to study the effect of film thickness. The functionalized silanes, in principle, should be monolayers and thus possess lower film thicknesses than the polymer brushes. According to the functionalized film thickness in Table 4.5, it was assumed that HDTS and 13FTS formed monolayers due to the reasonable low thickness measurements of 3 and 4 nm, respectively; calculated thicknesses were 2.5 and 1.6 nm, respectively. It appears however that APTS (9 nm) and TSPG (10 nm) self-polymerized
due to the higher observed thicknesses compared to those calculated,\textsuperscript{116} 1.0 and 2.4 nm, respectively. First, silane-functionalized capillaries were compared with one another, as shown in Figure 4.32. The same results were seen when comparing the silane-functionalized capillaries with the polymer-functionalized capillaries; flow only occurred down the hydrophilic capillary. Figure 4.33 compares silane-functionalized capillaries versus polymer-functionalized capillaries. In Figure 4.33a and Figure 4.33b, Si/SiO\textsubscript{2}/TSPG was compared with Si/SiO\textsubscript{2}/P(t-BA) and Si/SiO\textsubscript{2}/P(n-BA), respectively. In these two experiments, the hydrophilic silane film thicknesses should be 10 to 15 nm lower than the polymer films, based on analogous depositions on flat substrates. Flow was seen to only occur down the hydrophilic silane-functionalized capillary. In Figure 4.33c and Figure 4.33d, Si/SiO\textsubscript{2}/PAA and Si/SiO\textsubscript{2}/P(HEMA) are compared with Si/SiO\textsubscript{2}/HDTAPS. The polymer brushes represent thicker inner films with a hydrophilic nature while the silane-functionalized capillaries contain thinner inner layers with a hydrophobic character. Flow of the aqueous solution only occurred down the thicker, hydrophilic polymer coated capillaries demonstrating that the difference in surface energy was the major factor for the preference of flow and not the film thickness.
Figure 4.32. Preferential flow results between a) Si/SiO$_2$//APTS and Si/SiO$_2$//HDTs, b) Si/SiO$_2$//APTS and Si/SiO$_2$//13FTS, c) Si/SiO$_2$//TSPG and Si/SiO$_2$//HDTs, d) Si/SiO$_2$//TSPG and Si/SiO$_2$//13FTS functionalized capillary, i.d. = 75 µm, flow rate = 5.0 µL/h, time = 4 h.
Figure 4.33. Preferential flow results between a) Si/SiO$_2$/TSPG and Si/SiO$_2$/P(t-BA), b) Si/SiO$_2$/TSPG and Si/SiO$_2$/P(n-BA), c) Si/SiO$_2$/PAA and Si/SiO$_2$/HDTS, d) Si/SiO$_2$/P(HEMA) and Si/SiO$_2$/HDTS functionalized capillary, i.d. = 75 µm, flow rate = 5.0 µL/h, time = 4 h.

The same polymer coatings as before were polymerized inside of 50 µm i.d. silica capillaries in order to look at the effect of capillary size. First, 50 µm hydrophilic and hydrophobic coated capillaries were compared. Figure 4.34 shows that the aqueous solution preferred to flow down the hydrophilic-coated capillary as before. The 50 µm hydrophilic polymer-coated capillary was then compared with 75 µm hydrophobic polymer coated capillary to determine if the surface energy effect could still direct flow even with a large difference in the internal diameter of the capillary. Figure 4.35 shows
that flow occurred down the 75 µm, hydrophobic polymer-coated capillary in both experiments. Because flow occurred down the larger, hydrophobic capillary, it appears that changes in the internal diameter of the silica overwhelm the effect seen by differences in surface energy of the coating.

Figure 4.34. Preferential flow results between a) Si/SiO₂/PAA and Si/SiO₂/P(t-BA), b) Si/SiO₂/PAA and Si/SiO₂/P(n-BA), c) Si/SiO₂/P(HEMA) and Si/SiO₂/P(t-BA), d) Si/SiO₂/P(HEMA) and Si/SiO₂/P(n-BA) functionalized capillary, i.d. = 50 µm, flow rate = 5.0 µL/h, time = 4 h.
Figure 4.35. Preferential flow results between a) 50 µm - Si/SiO₂/PAA and 75 µm - Si/SiO₂/P(t-BA), b) 50 µm - Si/SiO₂/PAA and 75 µm - Si/SiO₂/P(n-BA), c) 50 µm - Si/SiO₂/P(HEMA) and 75 µm - Si/SiO₂/P(t-BA), d) 50 µm - Si/SiO₂/P(HEMA) and 75 µm - Si/SiO₂/P(n-BA) functionalized capillary, flow rate = 5.0 µL/h, time = 4 h.

An experiment was designed so that a pressure transducer was placed directly behind the “Y” junction to ensure that there was positive pressure applied to the aqueous solution in the capillaries. There was 2.21 kPa of backpressure on the hydrophilic and hydrophobic capillaries and flow was observed predominately in the more hydrophilic capillary. This positive pressure demonstrates that there is more than wetting or wicking action involved in the preference of flow down the hydrophilic capillary. It was also
observed that a liquid drop would form at the exit end of the capillary and, upon
discharge, another drop would immediately form.

Figure 4.36. Preferential flow results comparing flow between similar 75 µm capillaries:
a) Si/SiO$_2$/PAA, b) Si/SiO$_2$/P(HEMA), c) Si/SiO$_2$/P(t-BA) and d) Si/SiO$_2$/P(n-BA).

A set of controlled experiments was run that compared two similar 75 µm
capillaries which contained the same polymer coating. Figure 4.36 displays the results
when comparing two PAA-coated capillaries (Figure 4.36a), two P(HEMA)-coated
capillaries (Figure 4.36b), two P(t-BA)-coated capillaries (Figure 4.36c) and two P(n-
BA)-coated capillaries (Figure 4.36d). Each test showed analogous results, in which the
flows between the comparable coatings were “the same”. These results affirm that the preference in flow seen is a consequence of the difference in capillary coatings.

In summary, the flow of the aqueous media occurred only down the capillary with the hydrophilic polymer coating when comparing capillaries with the same internal diameter. The capillaries were also coated with hydrophilic and hydrophobic functionalized silanes and flow only occurred down the hydrophilic capillaries. The thickness of the film did affect the preference of flow down the capillary that had the higher surface energy. It appears that the large difference between the surface energies of the coatings is responsible for the direction of flow. However, when capillaries of different internal diameter were compared, flow occurred down the larger hydrophobic capillary. When similar polymer coated capillaries were compared, approximately identical flow results were seen; suggesting that the extreme difference in the capillary coatings results in preferential flow. The results suggest that there is a limit in which the differences in surface energies can be overcome and the difference in size prevails.

4.3 In situ Functionalization of Silica Particles

The in situ formation of functionalized silica nanoparticles was investigated. The primary focus was control of particle size. Difunctional reactive stabilizers were used to simultaneously functionalize the silica nanoparticles and prohibit the continued growth of the particles. The reactive stabilizers used in the study were [3-(2-bromoisobutyryl)-propyl]triethoxysilane (BPTS) and [3-(2-bromoisobutyryl)propyl]ethoxydimethylsilane (BPMS), which each have a triethoxysilane-functionality and an ATRP initiating group at the non-condensable end. Condensation with tetraethoxysilane yielded silica
nanoparticles with a surface-immobilized initiator. The sizes of these functionalized silica nanoparticles were controlled by varying the time of initiator addition and initiator concentration. With the initiator-functionalized silica nanoparticles, ATRP synthesis of homopolymer and diblock copolymers was performed to produce organic-inorganic nanomaterials. This work was extended to the condensation of triethoxysilane- and monoethoxysilane-functionalized polymers to prepare polymer coated particles with size control.

4.3.1 Synthesis and Characterization of Difunctional Reactive Stabilizers

The synthesis and characterization of the precursor to the silica nanoparticles with surface-immobilized initiator has been reported by Patten and coworkers.\textsuperscript{110} The synthesis is a two step process (Scheme 4.6) that first involves the reaction of allyl alcohol with an acyl bromide. The second step is a hydrosilylation to form either a monoethoxy- or triethoxysilane. The product is a reactive stabilizer that is used in a silicate condensation process with tetraethoxysilane.

![Scheme 4.6. Synthesis of BPTS and BPMS.](image)

4.3.2 Synthesis and Characterization of Initiator-Functionalized Nanoparticles

Silica nanoparticles were synthesized by a sol-gel technique and by a condensation technique using alkoxy silanes, as shown in Scheme 4.7. In the sol-gel
process, silicic acid is polymerized to form primary particles, which subsequently aggregate to form larger particles. In the condensation technique, silica particles are formed by the simultaneous hydrolysis and condensation of sodium silicates or alkoxy silanes. Complete hydrolysis is achieved in the presence of an acid or base catalyst. As condensation proceeds, small three-dimensional siloxane networks are gradually formed. Stöber et al.\textsuperscript{85} reported the controlled synthesis of spherical silica particles by hydrolytic condensations of tetraethoxysilane using ammonia as a catalyst. The condensation reaction was influenced by the type of the alkoxy silane, presence of an electrolyte and pH. Ying et al.\textsuperscript{86} studied the effect of pH and found that under acidic conditions, the rate of hydrolysis was faster; however, it slows down with increasing siloxane linkages. This leads to weakly branched polymeric networks. Under basic conditions the condensation process is accelerated relative to hydrolysis, resulting in increased condensation with an increasing number of siloxane linkages. This produces a highly branched network structure, which is accompanied by cyclic structures. A basic catalyst was used in our research and produced higher yields and opaque particles when compared with the experiments in which an acidic catalyst was used. Opacity of the particle was brought about by the high degree of crosslinking, which was due to the differing mechanisms of hydrolysis and condensation that occur in acidic versus basic catalyzed systems.\textsuperscript{86}

\begin{equation}
\text{EtO-Si-OEt} + \text{EtO-Si-OEt} \xrightarrow{\text{NH}_3, \text{EtOH}} \text{O-Si-OEt} \xrightarrow{\text{RT, 24h}} \text{O-Si-OEt}
\end{equation}

\text{R = -OEt = BPTS}
\text{R = -Me = BMPS}

Scheme 4.7. ‘In situ’ synthesis of initiator-immobilized silica particles.
Silica nanoparticles were synthesized in the presence and absence of reactive stabilizer to evaluate the relationship between reactive stabilizer and particle size. It was predicted that particle growth would be prevented by decreased condensation due to lower TEOS concentrations. As predicted, the addition of BPTS or BPMS resulted in a marked difference in the sizes of particles, Figure 4.37 and Figure 4.40. The size of the particles in the absence of BPTS was ~350 nm. However the size reduced to 10-20 nm with the addition of BPTS at the beginning of the reaction.

4.3.2.1 Effect of Concentration of Initiator Reactive Stabilizer

![TEM images of silica nanoparticles](image)

Figure 4.37. TEM analysis of silica nanoparticles synthesized using [3-(2-bromoisobutyryl)propyl]ethoxydimethylsilane, effect of concentration.

The stabilizer effect on silica particle synthesis can be seen by varying the stabilizer concentration, with respect to TEOS, under similar reaction conditions. As the relative BPTS concentration increased, a decrease in particle size was observed (Figure 4.37). The decrease in size was a result of particle steric stabilization and decreased
particle growth due to the decrease of the number of propagating groups on the surface. Since BPTS contains three condensable groups, it was speculated that not all of the condensable groups are reacting with a single particle. This resulted in the “raspberry-like” structure shown in the Figure 4.38. This structure disappeared and core shell structure resulted upon using BPMS, which has only one condensable group.

![Figure 4.38. TEM analysis of silica nanoparticles synthesized using [3-(2-bromoisobutyryl)propyl]triethoxysilane: a) 15% relative to tetraethoxysilane (TEOS) as stabilizer, b) 20% relative to TEOS as stabilizer.](image)

Table 4.8 contains the tabulated results from a comparison study between BPTS and BPMS on the effect of concentration of the reactive stabilizer on the size of particle under similar reaction conditions. BPTS reactive stabilizer resulted in smaller particles (Figure 4.39) because of its ability to react with the surface of the growing particle faster at low concentration. Since it has three condensable ethoxy groups, BPTS can react with a particle and limit continued propagation when compared with BPMS. Elemental analysis of bromine was performed on BPMS particles (Table 4.8). As the concentration of BPMS increased, the bromine concentration increased while the particle size decreased. The decrease in size was due to the BPMS reactive stabilizer attaching to the
particle and inhibiting its growth. As the concentration in BPMS was increased, the reduction in growth was magnified, confirmed by the increase in bromine content.

<table>
<thead>
<tr>
<th>Concentration, %</th>
<th>BPTS&lt;sup&gt;b&lt;/sup&gt; Average particle size (nm)</th>
<th>BPMS&lt;sup&gt;c&lt;/sup&gt; Average particle size (nm)</th>
<th>Elemental analysis of bromine (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>350</td>
<td>350</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>200</td>
<td>300</td>
<td>0.69</td>
</tr>
<tr>
<td>2</td>
<td>180</td>
<td>280</td>
<td>1.15</td>
</tr>
<tr>
<td>10</td>
<td>160</td>
<td>200</td>
<td>5.03</td>
</tr>
<tr>
<td>15</td>
<td>150</td>
<td>160</td>
<td>6.58</td>
</tr>
<tr>
<td>20</td>
<td>150</td>
<td>150</td>
<td>7.55</td>
</tr>
</tbody>
</table>

<sup>a</sup> Concentration relative to tetraethoxysilane (TEOS)
<sup>b</sup> [3-(2-bromoisobutyryl)propyl]triethoxysilane (BPTS)
<sup>c</sup> [3-(2-bromoisobutyryl)propyl]ethoxydimethylsilane (BPMS)
4.3.2.2 Effect of Addition Time of Initiator Reactive Stabilizer

Figure 4.40. TEM analysis of silica nanoparticles synthesized using [3-(2-bromoisobutyryl)propyl]triethoxysilane, effect of time of addition.
Another parameter that was crucial in controlling particle size was the time of reactive stabilizer addition. It was observed that particle size could be controlled by the time of stabilizer addition as seen in Figure 4.40. Smaller particles were formed with early stabilizer addition due to the presence of the noncondensing end of the BPTS after reaction with the preformed particles which then hindered particle growth. In the absence of either reactive stabilizer, the particles grew to ~350 nm. However, the size of the particles was reduced to 10-20 nm for both BPTS and BPMS. As the time of addition increased, the particles have additional time to grow before the reactive stabilizers prohibit growth. Both stabilizers showed a similar trend of increasing size as the time of addition increased, as shown in Figure 4.41.

Figure 4.41. Effect of stabilizer addition time on the size of the particles: [3-(2-bromoisobutyryl)propyl]triethoxysilane (BPTS) and [3-(2-bromoisobutyryl)propyl]ethoxydimethylsilane (BPMS).
4.3.2.3 Polymerization and Characterization of Initiator-coated Particles

The initiator immobilized silica particles were used for ATRP of MA, S and \( t \)-BA.

The results are tabulated in Table 4.9. Six different block copolymer-modified silica particles were synthesized by alternating the choice of monomers and choice of the initial block composition. The initiator-coated silica particles, using TGA and heating to 1000 \(^\circ\)C at 10 \(^\circ\)C/min, showed a weight loss of 7\% (Figure 4.42a) while the FTIR spectrum displayed the characteristic carbonyl stretching at 1730 cm\(^{-1}\) (Figure 4.43a). Weight loss measured after diblock copolymer synthesis was in the range of 24-34\%. Figure 4.42 displays the trace for the TGA results from Si/SiO\(_2\)/PMA-\( b \)-PS functionalized silica nanoparticles which shows a weight loss of 23.9\% for the PMA homopolymer and 34.3\%.

**Table 4.9. Characterization of polymer-coated, silica nanoparticles.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>GPC Analysis</th>
<th>TGA(^a) (Final weight loss, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( M_n ), g/mol</td>
<td>PDI</td>
</tr>
<tr>
<td>Si/SiO(_2)/PS-( b )-PMA</td>
<td>PS 7,000</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>PMA 6,000</td>
<td>1.3</td>
</tr>
<tr>
<td>Si/SiO(_2)/PS-( b )-P(( t )-BA)</td>
<td>PS 10,000</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>P(( t )-BA) 16,000</td>
<td>1.3</td>
</tr>
<tr>
<td>Si/SiO(_2)/PMA-( b )-PS</td>
<td>PMA 10,000</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>PS 27,000</td>
<td>1.2</td>
</tr>
<tr>
<td>Si/SiO(_2)/P(( t )-BA)-( b )-PMA</td>
<td>PMA 11,000</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>P(( t )-BA) 18,000</td>
<td>1.1</td>
</tr>
<tr>
<td>Si/SiO(_2)/P(( t )-BA)-( b )-PS</td>
<td>P(( t )-BA) 13,000</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>PMA 12,000</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>PS 10,000</td>
<td>1.2</td>
</tr>
</tbody>
</table>

\(^a\) TGA measurements were performed in a nitrogen atmosphere over the temperature range of 23-1000 \(^\circ\)C at a heating rate of 10 \(^\circ\)C/min.
for the PMA-\textit{b}-PS diblock copolymer. The free polymer that was polymerized in solution was used to determine the molecular weight and polydispersity index which was 1.3 or less. The ability to prepare diblock copolymers confirms that the polymerizations were controlled. FTIR data confirms the presence of the Si/SiO\textsubscript{2}/PMA-\textit{b}-PS diblock copolymer; absorptions at 1730 cm\textsuperscript{-1} (carbonyl group) and 1454 cm\textsuperscript{-1} (bending absorption of the methylene groups) appeared after the polymerization of MA. Upon polymerization of the styrene monomer, Figure 4.43c, absorbencies appeared at 3030 cm\textsuperscript{-1} and above due to aromatic hydrogen stretching.

Figure 4.42. TGA data of a) ATRP-functionalized silica, b) PMA-functionalized silica and c) PMA-\textit{b}-PS functionalized silica.
4.3.3 Synthesis and Characterization of Polymer-functionalized Nanoparticles

Using the BPTS and BPMS initiators, the polymerization of styrene and tert-butyl acrylate, using ATRP, was carried out to make a difunctional polymer that was capable of reacting with the growing silica particles. The in situ polymer-functionalization of the particle would eliminate the need for further post-reactions. The same techniques used to synthesize the initiator-coated particles were used to form core-shell hybrid particles with an ability to control their size.

BPTS was first used to synthesize PS using ATRP. However, there was a high molecular weight absorbance in the GPC chromatogram with $M_n = 2,000,000$ g/mol (Figure 4.44a). The main absorbance at a retention volume of 19.5 mL had a $M_n = 63,000$ g/mol. It was speculated that the high molecular weight polymer was from the
condensation of triethoxy end-groups during the ATRP polymerization. To confirm this hypothesis, a sample of the PS was dissolved in toluene and treated with HF. The HF reacts with the silica bonds but does not degrade the polymer. Figure 4.44b shows that after treatment with HF, the high molecular weight absorbance was absent. This experiment supports the hypothesis that condensation of the triethoxy groups did occur during polymerization.

![Figure 4.44. GPC chromatogram of a) triethoxy-functionalized PS and b) PS after treatment with HF.](image)

As a result of the formation of the high molecular weight absorbance from the condensation of triethoxysilane groups, BPMS ATRP initiator was used. Figure 4.45a displays the GPC chromatogram for the resulting monoethoxysilane-functionalized PS. There was no high molecular weight absorbance observed; however, there was a high molecular weight shoulder ($M_n = 50,000$ g/mol) instead. This shoulder was
approximately double the molecular weight of the main absorbance \( (M_n = 25,000 \text{ g/mol}) \), indicating that monoethoxy groups were condensing to form a dimer. A sample was treated with HF to investigate this hypothesis. Figure 4.45b clearly shows the loss of the high molecular weight shoulder, indicating that dimer had formed during the polymerization process. The number average molecular weight of this absorbance is approximately the same as before HF treatment. By using the monoethoxysilane initiator, only homopolymer chains would be condensed onto the particle during particle formation. It also eliminates the chance of forming the “raspberry” like structures when using the triethoxysilane-functionalized PS at higher concentrations.

Figure 4.45. GPC chromatogram of a) monoethoxy-functionalized PS and b) PS after treatment with HF.
4.3.3.1 Effect of Molecular Weight of Polymer Reactive Stabilizer

The effect of the molecular weight of the monoethoxy-functionalized PS was studied by synthesizing silica particles under similar conditions. The functionalized PS was added 1 h after the start of the reaction using a 0.01% molar concentration. The number average molecular weight ranged from 4,000 to 54,000 g/mol. No evidence of surface-attached polymer was observed by FTIR (Figure 4.46); we speculate that this was a result of using such a low concentration of the PS precursor. The TGA data in Figure 4.47 indicates that all of the polymer coated silica particles had approximately the same weight percent of PS attached to them. There was also no difference in the size of the particles formed which ranged from 170 – 250 nm (Figure 4.48).

Figure 4.46. FTIR spectra of PS-functionalized silica particles: a) Si/SiO$_2$/PS ($M_n = 54,000$ g/mol), b) Si/SiO$_2$/PS ($M_n = 26,000$ g/mol), c) Si/SiO$_2$/PS ($M_n = 17,000$ g/mol) and d) Si/SiO$_2$/PS ($M_n = 4,000$ g/mol).
Figure 4.47. TGA data of PS-functionalized silica particles: a) Si/SiO$_2$/OH, b) Si/SiO$_2$/PS ($M_n = 54,000$ g/mol), c) Si/SiO$_2$/PS ($M_n = 26,000$ g/mol), d) Si/SiO$_2$/PS ($M_n = 17,000$ g/mol) and e) Si/SiO$_2$/PS ($M_n = 4,000$ g/mol).
4.3.3.2 Effect of Time of Addition Polymer Reactive Stabilizer

In the first attempt to control the particle size by varying the time of addition of the monoethoxy-functionalized PS reactive stabilizer; however, all the particles were approximately the same size. The number average molecular weight of functionalized PS was 3,600 g/mol, and its PDI was 1.4. Figure 4.49 displays the particles and their sizes that were synthesized. The time of addition of the dissolved PS, 10% concentration relative to the TEOS concentration, ranged from 0 min to 6 h from the start of the reaction. THF was added at the beginning of the reaction mixture to ensure that the dissolved PS did not precipitate.
Figure 4.49. TEM images of PS-functionalized silica nanoparticles, for experiments with THF added at the onset of the reaction; effect of time of addition of PS reactive stabilizer.

In the absence of monoethoxy-functionalized PS, the particles were only 10-20 nm in diameter. Upon the addition of functionalized PS, the particle size increased by approximately 20-30 nm. It was expected that larger particles would have grown in the absence of the functionalized polymer. The presence of larger particles was seen but they were not present in large quantities for the experiments with functionalized PS. We speculate that the addition of THF, at the onset of the reaction, interfered with particle formation. In all cases, particle yield was extremely low, 50 mg or less. The low yields and the absence in particle growth suggest that the presence of THF limits nucleation and growth. The TGA data (Figure 4.50) resulted in approximately the same weight loss between the PS-functionalized silica nanoparticles ranging between 87-89%. In the absence of PS, the silica particles also showed a weight loss of 88.9%. FTIR did not reveal the presence of PS on the samples.
Figure 4.50. TGA data for PS-functionalized silica nanoparticles prepared in the presence of THF: a) no PS added, b) PS added at 0 min, c) PS added at 10 min, d) PS added at 1 h, e) PS added at 3 h and f) PS added at 6 h.
In order to alleviate the need for THF within the system, P(t-BA) was synthesized because it is soluble in ethanol, the solvent commonly used in this condensation process. A sample was prepared in an analogous fashion to PS; the monoethoxy-functionalized P(t-BA) was characterized by a number average molecular weight of 2,400 g/mol and a PDI of 1.4. By increasing the time of addition of the monoethoxy-functionalized P(t-BA), the particle size was expected to increase. However, under similar conditions, there was no change in the size of the particles when the functionalized P(t-BA) was added at varying intervals between 0 min and 6 h, (Figure 4.51). In the absence of the reactive stabilizer, the particle size was 160 nm, but when the reactive stabilizer was added, all the samples were characterized by a particle size of approximately 75 nm. The TGA data in Figure 4.52 indicates that the P(t-BA)-functionalized silica had a weight loss of 17.7% when the polymer was added at 0 min and 15.7% when the polymer was added at 6 h. When no polymer was added during the silica synthesis, the particles displayed a weight
loss of 2.3%. There was no evidence of P(t-BA) on the silica particles when analyzed with FTIR. When the P(t-BA) coated silica was treated with HF (Figure 4.53), the number average molecular weight of the isolated polymer was 1,100 g/mol and displays a similar retention volume as that of a low molecular weight shoulder on the chromatogram of the precursor P(t-BA) homopolymer prior to functionalization. It appears as if the majority of the functionalized P(t-BA) used in the experiments may have been in the dimer form, which would explain why no evidence of the polymer was seen using FTIR. If the polymer was in the dimer form, then it would not be able to react with the silica particles effectively. The yield of the reaction did increase to about 800 mg for each sample which was considerably higher when compared to the silica particles synthesized in the presence of THF.
Figure 4.52. TGA data for P(t-BA)-functionalized silica nanoparticles:
a) no P(t-BA) added, b) P(t-BA) added at 0 min, c) P(t-BA) added at 10 min,
d) P(t-BA) added at 1 h, e) P(t-BA) added at 3 h and f) P(t-BA) added at 6 h.
Figure 4.53. GPC chromatograms of a) P(t-BA) homopolymer from solution polymerization and b) P(t-BA) chains cleaved from silica particles using HF.
4.3.3.3 Effect of Concentration of Polymer Reactive Stabilizer

By changing the concentration of the polymer reactive stabilizer with respect to the TEOS concentration, it was hypothesized that if the particle size would decrease as the polymer concentration increased. Monoethoxy-functionalized PS with a number average molecular weight of 4,000 g/mol and a PDI of 1.4 was used. As seen from Figure 4.54, the particle size did not decrease as expected. In the absence of the polymer reactive stabilizer, the particle size was 130 nm, but in the presence of the of the polymer stabilizer, the particle size ranged from 40 nm to 80 nm. The TGA data in Figure 4.55 shows an increase in weight loss as the concentration increases indicating that there is an increase in the amount of polymer reacting with the particles. However, there was no evidence of PS on the silica particles when analyzed with FTIR. When the PS-coated silica was treated with HF (Figure 4.56c), the recovered polymer was analyzed by GPC. The number average molecular weight was 2,600 g/mol and displays a similar retention
volume as that of a low molecular weight shoulder on the chromatogram of the precursor PS homopolymer (Figure 4.56a) prior to silica functionalization. A sample of the monoethoxy-functionalized PS homopolymer was also treated with HF (Figure 4.56b); the number average molecular weight was 2,400 g/mol. From the GPC analysis and HF treatment, only the monoethoxy-functionalized homopolymer reacted with the particles not any polymer that was in dimer form. Particle yield was approximately 200 mg for each experiment.
Figure 4.55. TGA data for PS-functionalized silica nanoparticles prepared with polymer added at 1 h: a) no PS added, b) 1% PS added, c) 2% PS added, d) 5% PS added, e) 10% PS added, f) 15% PS added and g) 20% PS added.
In summary, silica nanoparticles with an immobilized ATRP initiator or PS and P(t-BA) chains were prepared by an ‘in situ’ condensation method. The reactive stabilizer was a bromoisobutyrate-functionalized alkoxysilane or a polymer-functionalized alkoxysilane. Reaction with tetraethoxysilane produces functionalized silica nanoparticles in one step. When a bromoisobutyrate-functionalized alkoxysilane reactive stabilizer was used, particle size ranges from 10 - 350 nm. Particle size was controlled by varying the amount of reactive stabilizer used and the time period of addition during the condensation process. Potentially, other types of polymerization initiators could be used in this process. Marini and coworkers\textsuperscript{137} observed similar effects in the condensation of TEOS with vinyltriethoxysilane. The silica nanoparticles with surface-immobilized initiator were used to prepare homo and diblock copolymers via ATRP. The free polymer from solution revealed number average molecular weights
between 6,000 and 27,000 g/mol. Bromine analysis also confirmed the presence of the ATRP initiator on the silica particle.

The work was then extended to study the effect that polymer-functionalized alkoxy silanes would have on particle size. By varying the molecular weight of the functionalized PS, 4,300 – 53,900 g/mol, the size of the particles did not change. The particles ranged from 180 nm to 250 nm for all molecular weights. The effect of time of addition of the functionalized PS produced 50 nm silica particles. It appeared, that by adding THF at the beginning of the reaction, nucleation and growth of the particles were limited. Functionalized P(t-BA) was then studied because it was soluble in ethanol and did not require an additional solvent to be added to the reaction. Again, the silica particle size was not controlled by varying the time of addition of the ethoxy-functionalized polymer. The particle size was 75 nm for all experiments. By changing the concentration of the functionalized PS, the particle sizes were approximately 60 nm in all cases.

The same time frame and concentrations were used in all experiments to compare the effect of small molecule reactive stabilizer with large functionalized polymers. The use of small molecule reactive stabilizers gave control over particle size. Larger polymer molecules resulted in particles with less than 100 nm each time. The larger polymer chains did not allow the particles to grow; however, no evidence of polymer on the surface of the particles was seen using FTIR. From analysis of the GPC chromatograms, there may only be a small percent of the functionalized homopolymer present which could react with the growing silica particle since the majority of the polymer used appeared to be in the dimer state. The low percentage of polymer available for
condensation could explain the lack of evidence in FTIR analysis and the loss of size control.
CHAPTER V
SUMMARY AND CONCLUSION

The objective of this research was to functionalize and characterize the surface of micro-capillaries with polymer brushes and study how the flow of a solvent can be manipulated. Atom transfer radical polymerization (ATRP) was used to synthesize polymer chains from initiators immobilized on the interior surface of the capillary. ATRP afforded control over the thickness of the brush by controlling the molecular weight, and it allowed for the formation of diblock copolymer brushes. Inspired by literature work that demonstrated that polymer brushes could control the permeability of a water droplet through a glass frit, polymer brushes were used to vary the backpressure of flow through a capillary and direct flow of a solvent down a desired path.

The characterization of the polymer brushes in a confined space proved to be more challenging when compared to flat or spherical surfaces due to the inaccessibility of the interior of the capillary. Fluorescence spectroscopy measurements confirmed the presence of the polymer brushes within the capillary. Capillary rise measurements were used to follow the changes in surface energy of the thin films. The capillary rise measurements correlated well with the water contact angles measurements made on flat surfaces. By comparing the capillary rise data from the silica capillaries with the water
contact angle from flat surfaces, it was possible to follow the changes in surface energy as various polymerization steps were carried out to modify the capillaries.

Experiments were designed to study if polymer brushes could be used to manipulate the flow of a solvent through confined spaces. We observed that backpressure increased with the capillary flow of a good solvent for the polymer brush due to the solvating effect of the good solvent. When a bad solvent for the polymer film was used, the backpressure decreased. In this situation, the polymer brush would be in a collapsed configuration and there would be less interaction occurring between the solvent and the polymer brush. The solvating/collapsed configuration of the polymer brush during flow hypothesis was strengthened when small molecule functionalized silanes were used to produce thinner films as compared with the polymer brushes. There was virtually no change in the backpressure measurements when the various solvents were ran through the hydrophilic and hydrophobic coatings suggesting that solvent-polymer interactions are largely responsible for the changes in backpressure. With a good solvent for the polymer brush system, the brush becomes solvated and its thickness increases resulting in an increase in backpressure. When a bad solvent for the brush system is used, the polymer brush adopts a collapsed state in order to minimize its interaction with the solvent, lowering the backpressure.

 Preferential flow experiments were designed to study the effect that the surface energy of the films would have on the flow of an aqueous solution. When a silica capillary, that contained a hydrophilic polymer coating, was compared with a capillary that contained a hydrophobic polymer coating (internal diameters were the same), flow of the aqueous solution preferred only the hydrophilic polymer-coated capillary. The same
result occurred repeatedly as long as there was an extreme difference between the surface energies of the polymer coatings or thinner films. Larger i.d. (75 µm) capillaries containing a hydrophobic coating were also compared with smaller i.d. (50 µm) capillaries containing a hydrophilic coating to investigate if this surface energy effect could overcome the large difference in size. It was observed that flow traveled preferentially down the larger hydrophobic capillary each time, demonstrating that there is a limit in the ability for low surface energy materials to restrict flow as seen in the study of the glass frits. From this study, it was found that by having large differences in the surface energies of coatings flow can be directed in micro-channels. If there is a large difference in the size of the micro-channels, the surface energy effects will be overwhelmed by the difference in size.

In the second portion of this work, the in situ functionalization of silica nanoparticles was studied. The goal of this research was to simultaneously produce functionalized silica particles and have the ability to control their size using a reactive stabilizer. The reactive stabilizer consisted of small and large difunctional alkoxy silanes molecules. The small molecule consisted of an ATRP initiator at the non-condensable end and either a monoethoxysilane or triethoxysilane end group which could condense onto the surface of the silica particles. The large molecule consisted of a monoethoxysilane-functionalized polymer. Using functionalized polymers during the in situ synthesis of the silica particles would eliminate the need for further post-polymerization reactions.

The average sizes of the silica nanoparticles were controlled by varying the time of addition of the small reactive stabilizer. The average particle sizes ranged from 10 –
350 nm. By increasing the time of addition, the sizes of the silica particles increased due to the longer time allowed for nucleation and growth. The sizes of the particles were also controlled by varying the concentration of the small molecule reactive stabilizer. Here, the size of the particle decreased as the concentration of the reactive stabilizer increased. In both cases, we speculate that the condensable end (ethoxysilane group) would condense onto the particle while the non-condensable end (ATRP initiating group) prohibited continued growth of the particles. Evidence of the bromine containing ATRP initiator on the silica nanoparticles was supported by FTIR and TGA measurements, as well as the ability to synthesize homopolymer and diblock copolymer brushes using the “grafting from” approach. Bromine analysis of the silica particles demonstrated that the bromine content increased as the concentration of the reactive stabilizer increased, thus supporting our hypothesis that the ATRP initiator is present on the particles.

Larger, ethoxysilane-functionalized polymer molecules were also used as the reactive stabilizer during the in situ functionalization of the silica nanoparticles. When using polystyrene or poly(tert-butyl acrylate), the particle size was not controlled by changing the time of addition or changing the concentration of the reactive stabilizer. The average particle size was approximately 70 nm when the polymer reactive stabilizers were used. There was no evidence for the polymer on the surface via FTIR, but TGA analysis showed a weight loss of roughly 15% in both studies.

The use of small, difunctional reactive stabilizers in this in situ method is an effective method to produce functionalized silica particles with the ability to control the sizes of those particles by changing the time of addition or the concentration of the reactive stabilizer. The ability to synthesize polymer brushes from the surface of those
particles demonstrates the successful functionalization of the silica nanoparticles. However, when the same experiments were attempting using a larger, difunctional polymer reactive stabilizer, the particle size was uncontrolled and determination of the location of the polymer was ineffective. Upon treatment of the polymer coated silica particles with HF and subsequent analysis with GPC, the number average molecular weight was found to be about half compared to the GPC molecular weight of the polymer prior to condensation. The majority of the polymer polymerized appeared to be in the dimer form, which would limit the amount of the polymer that would be able to condense onto the silica nanoparticles leading to a reduction in particle size control.
REFERENCES


(60) Biesalski, M.; Rühe, J. Macromolecules 2003, 36, 1222-1227.


(80) Chiari, M.; Cretich, M.; Damin, F.; Ceriotti, L.; Consonni, R. Electrophoresis 2000, 21, 909-916.


(85) Stöber, W.; Fink, A.; Bohn, E. J. Colloid Interface Sci. 1968, 26, 62-69.


(101) Sondi, I.; Goia, D. V.; Matijević, E. J. Colloid Interface Sci. 2003, 260, 75-81.


(114) Edmondson, S.; Huck, W. T. S.  

(115) Boyes, S. G.; Brittain, W. J.; Weng, X.; Cheng, S. Z. D.  


(117) Fadeev, A. Y.; McCarthy, T. J.  


(120) Zhao, B.; Brittain, W. J.  


(123) Legait, B.; de Gennes, P. G.  

(124) Brochard-Wyart, F.; de Gennes, P. G.  

(125) Vogler, E. A.  

(126) Fadeev, A. Y.; McCarthy, T. J.  

(127) Kinkel, J. N.; Unger, K. K.  

(128) Buszewski, B.; Jurasek, A.; Garaj, J.; Nondek, L.; Novak, I.; Berek, D. J.  

(129) Tripp, C. P.; Hair, M. L.  

(130) Mohapatra, S.; Pramanik, N.; Mukherjee, S.; Ghosh, S. K.; Pramanik, P.  

(131) Chen, Y.; Zhang, Z.; Sui, X.; Brennan, J. D.; Brook, M. A.  


Figure A1. GPC chromatogram of the free polymer from the ATRP polymerization of polymer coated capillaries a) Si/SiO$_2$/PS, b) Si/SiO$_2$/PMA, c) Si/SiO$_2$/P(t-BA) and d) Si/SiO$_2$/ P(n-BA).
Figure A2. GPC chromatogram of the free polymer from the ATRP diblock copolymerization of Si/SiO$_2$/PS-$b$-PMA and Si/SiO$_2$/PS-$b$-P(t-BA) from silica nanoparticles: a) PS, b) PMA and c) P(t-BA).

Figure A3. GPC chromatogram of the free polymer from the ATRP diblock copolymerization of Si/SiO$_2$/PMA-$b$-PS and Si/SiO$_2$/PMA-$b$-P(t-BA) from silica nanoparticles: a) PMA, b) PS and c) P(t-BA).

Figure A4. GPC chromatogram of the free polymer from the ATRP diblock copolymerization of Si/SiO$_2$/P(t-BA)-$b$-PS and Si/SiO$_2$/P(t-BA)-$b$-PMA from silica nanoparticles: a) P(t-BA), b) PS and c) PMA.
Figure A5. TGA analysis on PS based diblock copolymers polymerized from silica nanoparticles: a) Si/SiO$_2$//ATRP Initiator and b) Si/SiO$_2$//PS-$b$-PMA.

Figure A6. TGA analysis on PMA based diblock copolymers polymerized from silica nanoparticles: a) Si/SiO$_2$//PMA-$b$-PS and b) Si/SiO$_2$//PMA-$b$-P(t-BA).

Figure A7. TGA analysis on P(t-BA) based diblock copolymers polymerized from silica nanoparticles: a) Si/SiO$_2$//P(t-BA)-$b$-PS and b) Si/SiO$_2$//P(t-BA)-$b$-PMA.
Figure A8. GPC chromatogram of PS used in the effect of molecular weight study.

Figure A9. GPC chromatogram of PS used in the effect of time study when THF was added at the beginning of the reaction.
Figure A10. GPC chromatogram of a) effect of time study using P(t-BA) reactive stabilizer and b) effect of concentration study using PS.

Figure A11. FTIR data of a) effect of time study using P(t-BA) reactive stabilizer and b) effect of concentration study using PS.
Figure A12. $^1$H NMR spectrum (CDCl$_3$) of 10-undec-1-yl 2-bromo-2-methylpropionate.

Figure A13. $^1$H NMR spectrum (CDCl$_3$) of [11-(2-bromo-2-methyl)propionyloxy]-undecyltrichlorosilane.
Figure A14. $^1$H NMR spectrum (CDCl$_3$) of allyl 2-bromoisobutyrate.

Figure A15. $^1$H NMR spectrum (CDCl$_3$) of [3-(2-bromoisobutyryl)propyl]triethoxysilane (BPTS).
Figure A16. $^1$H NMR spectrum (CDCl$_3$) of [3-(2-bromoisobutyryl)propyl]ethoxydimethylsilane (BPMS).