NOVEL P-(SBMA) GRAFTED GLASS FIBER FILTERS AND GLASS SLIDES FOR OIL-WATER SEPARATION AND UNDERWATER SELF-CLEANING APPLICATIONS

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OIL-WATER SEPARATION AND UNDERWATER SELF-CLEANING
APPLICATIONS

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Thesis

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ABSTRACT

Oil-water separation is a major problem in industries such as oil-production and waste-water treatment where millions of gallons of oil-contaminated water are produced. Therefore a nontoxic, quick, effortless, cost-efficient, and ready-to-go technique is required. Superhydrophilic and underwater superoleophobic sulfobetaine methacrylate (SBMA) surfaces were successfully prepared using surface-initiated atom transfer radical polymerization (SI-ATRP) and were characterized by contact angle measurements and ellipsometry. The contact angles obtained for the p-(SBMA) grafted glass slides in-air (8-13°) and underwater (162-169°) allow them to be classified as superhydrophilic and superoleophobic respectively. The p-(SBMA) grafted glass fiber filters showed exceptional results at separating water from oil without even allowing miniscule amounts of visible oil to permeate through. The p-(SBMA) grafted glass fiber filters can be used for oil-water separation purposes, while the p-(SBMA) grafted glass slides can be used for self-cleaning, while both can be used for antifouling applications.
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CHAPTER I

RESEARCH OBJECTIVES

There is always a superior technique desirable to overcome various problems and disadvantages associated with oil-water separation. There is an increasing amount of environmental awareness, and more stricter and tighter regulations are created by the Environmental Protection Agency. There is also a tremendous increase in the production of oily waste waters from industries and accidental oil spills. Compared to other traditional large-scale oil-water separation techniques, membrane filtration has its own disadvantages such as membrane fouling, low efficiency, and high costs. Therefore an enhanced technique is needed to help solve these problems. Since most of the filters created and used for membrane filtration are hydrophobic and oleophilic in nature, the oils can easily foul the surfaces and therefore leading to increasing amount of oil and material waste. The main objective of this research was to successfully graft the hydrophilic SulfoBetaine Methacrylate (SBMA) monomer onto the glass fiber filter and glass slide surfaces to help overcome the above mentioned disadvantages.

Other goals are to characterize the surfaces to determine the optimum film thickness and therefore the best reaction conditions to achieve the best separation, and finally, to be able to show the separation of oil-water mixtures.
Oil-water separation has been a worldwide challenge for a long time, due to increasing environmental awareness and tighter regulations, as well as increased production of industrial wastewater and accidental oil spills [1]. In recent years, for effective oil-water separation, more attention has been paid to creating hydrophobic-oleophilic “oil-removing” surfaces over hydrophilic-oleophobic “water-removing” surfaces. However, due to their intrinsic oleophilic characteristic resulting from high surface energy, oil-removing surfaces are easily fouled and blocked up by oils. This creates a significant disadvantage because the adhered oils greatly affect the separation efficiency and are harder to remove, therefore increasing oil and material waste [2-4]. Therefore it is essential to create novel materials for oil-water separation that are easily produced, recycled, have high resistance to organic contaminants such as oils, have high separation efficiency, and low operating costs.

Various substrates have been studied for oil-water separation including; filter paper [5], manganese oxide nanowire [6], metal meshes, [1, 7-11], polyurethane/PS composite [12], textiles [13-15], silicon [16], and plastics [17]. However, some disadvantages exist over using these substrates such as low flexibility of metal meshes, and poor mechanical stability of filter paper and polymer films. Several methods have
been used to improve surface hydrophilicity and thereby achieving antifouling properties such as; surface coating [18], surface graft polymerization [19], and spray casting [10]. Superoleophobic surfaces are generally shown to require the use of both hydrophilic material; “surface chemistry,” and hierarchical surface structures; “surface roughness,” [15] however, we report using only surface chemistry to achieve underwater superoleophobicity. Table 1 lists the different materials, methods, and oil-water separation criteria used by several groups. To the best of our knowledge, modified glass fiber filters have not been utilized as oil-water (water-removing) separation media, however they have been used as oil-removing coalescing media.[20]

Commercially used techniques for separating oily waste water include; gravity separation and skimming, air-floatation, coagulation, de-emulsification, centrifugation and flocculation. However these have several disadvantages compared to membrane filtration such as; low separation efficiency, high operating costs, corrosion, re-contamination problems, and fouling. [21]

There are several potential applications that require a hydrophilic/oleophobic surface such as oil-water separation, underwater marine antifouling, and antifogging. Several groups have successfully achieved hydrophilic-oleophobic surfaces [14, 22-25], however, they have only been used to study self-cleaning and antifouling properties of the surface. Since the substrates studied were all solids, no oil-water separation studies could be performed. The fact that amphiphilic surfaces in air turn to superhydrophilic-superoleophobic underwater shows that oil contaminants can be washed away when immersed in water, therefore useful as self-cleaning and can be used against marine ship fouling.[26]
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Table 1: Literature Review Summary of Various Materials, Methods and Criteria Already Used
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<th>Surface Property</th>
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Table 1: Literature Review Summary of Various Materials, Methods and Criteria used (cont.)
Over the past decade, there has been a great interest in biomimetics; that is to learn from nature and to fabricate micro- and nanohierarchical structures with chemical modification to achieve specific results such as in-air hydrophilicity and underwater hydrophobicity. Fish scales are composed of calcium phosphate and a thin layer of mucus that provide the fish with a superoleophobic surface underwater. However, when the fish are in air, they are oleophilic, therefore showing that the water surrounding the fish scales leads to a change in wettability. A further investigation of the surface showed surface roughness, therefore presenting its oleophobicity.[24]

Herein we report a simple novel technique to fabricate, for the first time, a superhydrophilic glass fiber filter for the separation of oil and water from oil-water mixtures, by utilizing surface-initiated atom-transfer radical polymerization (SI-ATRP). In addition to the polymer being covalently attached to the surface, ATRP is a superior technique to utilize because it has several distinct advantages over the other mentioned techniques such as; controllable uniform film thickness, narrow molecular weight distribution, and high surface coverage due to minimal steric hindrance of incoming monomers [27]. A general characteristic of a zwitterionic structure is the fact that they carry a positive charge as well as a negative charge on the same segment side chain, but maintain overall neutrality. As shown in Figure 1, zwitterionic poly-(sulfobetaine methacrylate) (p-(SBMA)) is a superhydrophilic and an ultralow fouling material. [28] These characteristics are ascribed by its hydration ability due to the electrostatic attractions between charges on the side groups of the polymer and the water molecules. These cross-linked networks lead to the insolubility of p-(SBMA) in water [29]. Azzaroni
et al. [30] studied the phase transition mechanism of p-(SBMA) brushes grafted from gold substrates and found that the self-associated regime develops hydrophobic surface characteristics after passing through the hydrophilic, non-associated regime, and the ionically cross-linked regime. They found that increasing the temperature reverses the self-association state. Polzer et al. [31] found that p-(SBMA) shell on cross-linked polystyrene surfaces exhibited reversible swelling upon heating which was further enhanced upon addition of salt. The p-(SBMA) shell thickness increased upon heating and showed good reproducibility upon further cooling-reheating. Several groups have successfully achieved hydrophilic-oleophobic surfaces [22-25], however, they have only been used to study self-cleaning and antifouling properties. Since the substrates studied were all solids, no oil-water separation studies could be performed.

The fact that amphiphilic surfaces in air turn to superhydrophilic-superoleophobic underwater, shows that oil contaminants can be washed away when immersed in water, therefore useful as self-cleaning and can be used against marine ship fouling. [32] The innovation can also be used for applications such as; oil retention barriers for oil-spill clean-ups, waste-water treatment, remote operation of oil-water separation units, underwater marine antifouling, anti-fogging films, self-cleaning coatings, microfluidic devices, and cell and protein adhesion control on surfaces. Superoleophobic surfaces can also significantly reduce loses of residual fuel in fuel tanks and pipes.
Figure 1: Molecular structure of superhydrophilic p-(SBMA) monomer. The electrostatic interactions between the charges on the side groups of the polymer and the water molecules result in high hydration ability.

2.1 Introduction to Atom Transfer Radical Polymerization (ATRP)

Compared to traditional radical polymerizations, controlled/living free radical polymerization techniques have advantages with the most important being that a living process provides reliable control over the polymer molecular weight and also provides narrow polydispersities. The most important characteristic is the lack of irreversible terminating side reactions. [33, 34] This enables the degree of polymerization to increase linearly with the extent of the reaction. [35] Conversely, conventional surface-initiated free radical polymerizations result in a wide molecular weight distribution of the grafted polymer; mainly due to termination reactions.[36]
There is increasing research, in regard to, the use of controlled/living polymerization such as cationic [37, 38], anionic [39, 40], ring-opening [41], nitroxide-mediated [42-44], reversible addition fragmentation chain transfer (RAFT) [45], and atom transfer radical polymerization (ATRP) [46]. From these methods, ATRP is preferred because it does not require harsh conditions and is tolerant of functional groups and impurities that are disadvantageous to other “living” polymerizations. ATRP was discovered by Matyjaszewski [47, 48] and Sawamoto [49] in 1995 and since then has widely been used to create polymers with low polydispersities and controlled molecular weight.

There are two common methods for the attachment of polymerization initiators as shown in Figure 2. The first, a one-step process, relies on the reactions between an end-functionalized initiator and native functional groups originally present on the substrate surface. [50, 51] The other, a two-step process, involves the formation of a monolayer consisting of functional groups that are active toward the terminally functionalized initiator. [46] The anchoring layer is attached to the surface via covalent bonds while the reactive groups in the loops and tails of the attached macromolecules are not attached to the surface. [52] These free groups serve as reactive sites for subsequent attachment of the initiators and thereby further chemical modification reactions can be made.

There are two common methods used to execute surface polymerization to obtain surface functionalized polymer chains. One is the “grafting to” technique, and the other is the ‘grafting from’ technique. The “grafting from” technique refers to polymerization of the grafts from a macroinitiator equipped with pendant functionality which provides well-defined polymer brushes with a high surface coverage because of minimal steric
hindrance of incoming monomers, imposed by the grafted chains, to the active sites on the surface. [27, 53-55] Conversely, the “grafting to” technique refers to when a growing chain is attached onto a polymer backbone, therefore resulting in low surface coverage due to steric crowding of reactive sites. [27, 56]

Figure 2: One-step method is used to synthesize and graft the ATRP initiator directly onto the glass surface while the two-step method is used to react the initiator with the hydroxyl-terminated SAM.
The ATRP reaction scheme, as shown in Figure 3, consists of the ATRP catalyst, a transition metal species (\(M_t^n\)), a ligand (L), and a counterion or another ligand (Y) which is able to form ionic or covalent bonds with the metal center. The transition metal complex (\(M_t^n/L\)) is responsible for the homolytic cleavage of an alkyl halogen bond \(R-X\); from which the corresponding higher oxidation state metal halide complex (\(M_t^{n+1}X/L\)) and an organic radical are generated. The radical can either terminate by coupling or disproportionation (kt, not shown), propagate with vinyl monomer (kp), or be reversibly deactivated (kdeact) in this equilibrium by \(M_t^{n+1}X/L\) to form a halide-capped dormant polymer chain. [57, 58] Termination of the radical is reduced as a consequence of the persistent radical effect (PRE) which provides a self-regulating effect in certain controlled/living radical polymerization (CRP) systems. In such systems, a steady state of growing radicals is established through the activation-deactivation process rather than initiation-termination process as found in typical radical polymerization systems.[59] This results in the equilibrium (\(K_{ATRP}=k_{act}/k_{deact}\)) to strongly shift towards the dormant species (rate constant of activation \(<<\) rate constant of deactivation).

\[
\begin{align*}
R-X + M_t^n\text{-Y/Ligand} & \xrightleftharpoons[k_{deact}]{k_{act}} R^* + X-M_t^{n+1}\text{-Y/Ligand} \\
\end{align*}
\]

Figure 3: Reaction Scheme for a typical ATRP reaction.
The molecular weight in ATRP is controlled as a result of the fast activation/deactivation cycles that guarantee a low stationary concentration of free radicals which minimize termination reactions. [60] The initiator/growing chain with the halide end group is activated by the Cu(I) (activator) species giving rise to the growing chain radical, which is rapidly deactivated by Cu(II)X (deactivator). Several metal/ligand systems have previously been utilized to catalyze this process to polymerize monomers such as styrene, (meth)acrylates, and acrylonitrile. [61-63]

The rate of ATRP is internally first order in monomer, externally first order with respect to initiator and activator, Mt^n, and negative first order with respect to deactivator, X-Mt^{n+1}. The actual kinetics however, depends on factors such as solubility of activator and deactivator, their possible interactions, and variation of their structures and reactivity’s with concentration and composition of the reaction medium.

2.2 Sulfo betaine Methacrylate (SBMA)

Zwitterionic poly-(sulfo betaine methacrylate) p-(SBMA), Figure 4, is a superhydrophilic and an ultralow fouling material. These characteristics are ascribed by its hydration ability due to the electrostatic attractions between charges on the side groups of the polymer and the water molecules. These cross-linked networks lead to the insolubility of p-(SBMA) in water therefore making it a very distinctive material. The exceptionally high dipole moments of zwitterionic groups ascribes a range of distinctive properties because of the strong inter- and intramolecular dipolar interactions that give rise to the self-association of the polymer chains.[64] Figure 4 shows the high hydrophilic property of SBMA, where eight different water molecules are interacting with a single
SBMA monomer, as found experimentally by Wu et al.[65]. It has been shown to be used as a supersorbent and for antimicrobial wound dressing applications. [28] It has also been shown to be used against underwater fouling by marine life.[32]

Dong Zhixin et al. [64] performed phase behavior experiments on p-(SBMA) grafted silica nanoparticles. They found p-(SBMA) to have a phase transition (UCST) during the heating process as measured using UV-visible spectrophotometer and DLS. The p-(SBMA) grafted silica nanoparticles suggested an aggregated state at temperatures below 26 °C, and a phase transition occurring within 26-54°C, followed by a good dispersion of the nanoparticles in the solution without polymer chain associations above 54 °C. More on this subject is discussed in the results and discussion section.
2.3 Film Thickness Measurement

Thin films on substrates are mostly characterized by the use of Ellipsometry and Atomic Force Microscopy (AFM). Ellipsometry is easier to use than AFM, but in some cases, like transparent substrates, ellipsometry is not useful because it provides inaccurate results. Therefore AFM, Appendix 1, can be used to measure the film thickness, even though it is mostly used to characterize surface topography.

Ellipsometry is widely used in the semiconductor and microelectronics industries as a quick and precise measurement technique for process characterization and control. It is also used in research industries to characterize optical properties of thin films and substrate materials. Ellipsometry measures the change of polarization upon reflection which is determined by the sample’s properties such as; thickness, refractive index, and dielectric function. Its high resolution allows it to be used for thicknesses ranging from one nanometer to several micrometers. The samples, however, must be composed of a small number of distinct, well-defined layers that are optically isotropic and uniform. A typical setup is shown in Figure 5. The light source emits electromagnetic radiation which is polarized as it passes through a polarizer. After reflecting off the sample, it passes through another polarizer which is called an analyzer, after which the reflection enters the detector.
Contact angle measurements were performed using a goniometer which can also measure advancing and receding contact angles, and surface tensions. The angle a droplet, at equilibrium, makes with the solid interface is known as the contact angle. General contact angle measurements are performed at the liquid/solid/vapor interface and the liquid1/solid/liquid 2 interface. The contact angle of a drop on a solid surface depends on the mechanical equilibrium of the drop under the action of the interfacial tensions (Figure 6); liquid/vapor, $\gamma_{LV}$, solid/liquid, $\gamma_{SL}$ and solid/vapor, $\gamma_{SV}$.
Figure 6: Schematic showing a drop on a surface with the three interfacial tensions and the contact angle as described by Young’s equation.

This relation is described by Young’s equation:

$$\cos \theta_C = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$  \hspace{1cm} (1)

where $\theta_C$ is the equilibrium contact angle. The contact angle at equilibrium is in between the advancing and receding angles which refer to the maximum and minimum contact angles, respectively. However, the advancing and receding angles are not identical because of surface roughness or inhomogeneity on the surface. This is referred to as contact angle hysteresis which is generally exhibited by all surfaces. Erroneous results would be obtained if Young’s equation is used to interpret such angles because it neglects the roughness. Contact angle hysteresis reflects the irreversibility of the
wetting/dewetting cycle. “It is a measure of energy dissipation during the flow of a droplet along a solid surface.” [66] Some factors that affect contact angle hysteresis include adhesion hysteresis, inhomogeneity and surface roughness. Some conclusions about the relationship between contact angle hysteresis and roughness can be made; it is known that the energy gained for surfaces during contact is greater than the work of adhesion for separating the surfaces, due to so called adhesion hysteresis.

The droplets may slide or roll on the surface if the hysteresis value is low, therefore facilitating the removal of contaminant particles. These surfaces tend to have low tilt angles which refers to the minimum angle the surface must be tilted in order for the liquid droplet to roll off. [66-68]. Low sliding angles are important in liquid flow applications such as in micro/nanochannels and surfaces with self-cleaning ability. Surfaces with contact angle hysteresis or a low tilting angle of less than < 10º are generally referred to as self-cleaning surfaces. The surfaces are typically categorized by their contact angles as shown in Table 2. Surfaces formed by polar molecules have a high energy and therefore tend to be hydrophilic. Conversely, surfaces formed by non-polar molecules have a low energy and tend to be hydrophobic.
In order to have low drag force, and for applications requiring the self-cleaning feature, in addition to the high contact angle, superhydrophobic surfaces should also have very low water contact angle hysteresis. The lotus leaf is known to be self-cleaning with a CA > 150, which is also known as the Lotus effect. However, the leaf surface is oleophilic; therefore oil easily wets the surface. [69]

Generally, the hydrophobic/oleophobic contact angles on a smooth surface are about 100°-120°, but due to roughness and/or hierarchical micro/nano-structures, they can be as high as 160° as found on the lotus leaf surface. [70, 71] The contact angles on rough and inhomogeneous surfaces are described by the Wenzel and Cassie-Baxter models. In the Wenzel model, the surface area of the solid increases as a result of surface roughness, and this in turn increases the contact angle of the surface. The Wenzel equation (Eqn. 2) provides the contact angle, \( \theta \), for a droplet that is in contact with a rough surface without any air pockets:

\[
\cos \theta = R_f \cos \theta_f
\]  

where \( \theta_f \) is the contact angle of the liquid droplet on a solid surface and \( R_f \) is the roughness factor which is defined as

<table>
<thead>
<tr>
<th>Type of Surface</th>
<th>Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very hydrophilic</td>
<td>&lt; 20</td>
</tr>
<tr>
<td>Hydrophilic</td>
<td>&lt; 90</td>
</tr>
<tr>
<td>Hydrophobic</td>
<td>&gt; 90</td>
</tr>
<tr>
<td>Superhydrophobic</td>
<td>&gt; 150</td>
</tr>
</tbody>
</table>

Table 2: Surface Properties Based on Contact Angle Measurements.
where $A_F$ is the flat solid-liquid contact area or a projection of the solid-liquid area, $A_{SL}$, on the horizontal plane.

Conversely, the Cassie-Baxter model suggests that trapped air under the water droplet results in the surface being hydrophobic. The Cassie-Baxter equation provides the contact angle for a complex interface, which includes air pockets and the solid-liquid contact area $f_{SL}$:

$$\cos \theta = R_f f_{SL} \cos \theta_f - 1 + f_{SL}$$

### 2.4.1 Industrial Applications of Contact Angles

Contact angle measurements provide a better understanding of the interactions between solids and liquids, or between immiscible liquids. Correlations of surface tension of solids with contact angle data can be vastly found in literature. The solid-liquid interactions play an important role in understanding the chemical and physical processes in many industries. The adhesion between different composite structures such as; glass-metal, leather-fabric, and wood-paper, and the wetting of adhesive on a substrate can be accessed by contact angle measurements. Therefore the determination of the contact angle is important to industries such as the paint and coatings.

Composite materials made of reinforcing fibers and polymeric (resin) matrix systems have replaced many of the traditional metals and other heavier and weaker materials, and have begun to be used in a wide range of products in aerospace, automotive and sporting goods industries. Using contact angle measurements, it is
possible to optimize the adhesion force between the fiber and resin matrix system, and to find the right formulation of the resin matrix with proper wetting properties against the fiber.

Textile industries also utilize contact angle measurements for surface treatments provided to products such as carpets and surgical gowns such as anti-static or anti-stain coatings. The wettability of single fibers and fabrics as well as their hydrophobicity and washability can be checked by contact angle measurements. Medical and pharmaceutical industries utilize contact angle measurements to check the wettability of surface-modified biomaterials such as eye lenses, catheters, dental prosthetics and body implants. These biomaterials should be biocompatible otherwise they are rejected by the human body.

2.5 Creating –Phobic Surfaces

Hydrophobic and oleophobic surfaces have been created using micro- and nanostructure fabrication using methods such as etching, lithography, deposition and self-assembly. Self-assembly is superior to the other methods because they are costly, can be easily contaminated with chemicals and are less controllable. Generally stated, two main requirements are needed to achieve -phobic surfaces; surface roughness and surface chemistry (low surface energy). Keeping these requirements in mind, two methods can be used to create phobic surfaces; first, it is possible to maintain a rough surface from an initially phobic material, and second, to modify a rough -phillic surface by modifying the surface chemistry or coating a phobic material upon it. Surface energy is given more consideration because both slightly –phobic, and highly –phobic materials tend to exhibit the same wetting behavior when roughened.
2.6 Natural -ophobic Surfaces

Many plants have been known to possess water-repellent properties and therefore called hydrophobic. The Lotus (\textit{Nelumbo nucifera}) leaf is the most studied plant. Like other plants, the epidermis is covered by a thin extracellular membrane called the cuticle. The cuticle is further comprised of a composite material mainly made from a cuticle network and hydrophobic waxes. SEM images reveal that the lotus leaf is covered by papillae, which, in turn, are covered by an additional layer of epicuticular waxes. The hydrophobicity achieved ascribes the leaf with self-cleaning ability. [72]

Fish scales consist of hierarchical structures consisting of sector-like scales with diameters of 4-5mm which are further covered with papillae 100-300 µm in width. [24] Natural model examples for drag reduction are the sharks. Shark skin is covered by very small individual tooth-like structures, called dermal denticles, which are ribbed with longitudinal grooves (aligned parallel to the local flow direction of water). These grooved scales reduce the formation of vortices on a smooth surface, therefore resulting in water moving efficiently over their surface. [66] The water surrounding these structures can help prevent marine fouling from marine organisms, and also play a role in the defense against adhesion and growth from organisms such as bacteria and algae.[73] The fish and shark skin are easily wet by oil when exposed to it
in-air. However, when underwater, the oil comes off, and therefore the surfaces are self-cleaning and anti-fouling.
CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

Unwoven glass fibers with an unknown porosity, average fiber diameter of 6.5µm and 1.4mm thickness were provided by Hollingsworth & Vose while glass slides were obtained from Corning (2947-3x1). The monomer, N-(3-sulfopropyl)-N-(methacryloxyethyl)-N,N-dimethlyammonium betaine (SBMA, H2C=C(CH3)-COOCH2CH2N(CH3)2(CH2)3SO3), 2,2’-Bipyridyl (99%), Copper (I) bromide (99.99%), Tetrahydrofuran (99%), Methanol (99.8%), and Oil Red O die were purchased from Sigma-Aldrich and used as received. Hexadecane (99%) was purchased from Alfa Aezar. Sodium Hydroxide was purchased from Fisher Scientific. Ethanol (absolute 200 proof) was purchased from Pharmco-AAPER. DI-Water was purified to a minimum resistivity of 18.0 MΩ-cm by a Millipore filter system.

The initiator, (11-(2-Bromo-2-methyl)-propionyloxy) Undecyltrichlorosilane (Br-PUCS) was synthesized through the reaction of 1,3-propanesultone and 2-(dimethylamino)ethyl methacrylate using a method published previously.[74] $^1$H-NMR (300 MHz, CDCl3) $\delta$: 1.23-1.45 (br m, 16H); 1.54-1.75 (m, 4H); 1.93 (s 6H); 4.16 (t, 2H) ppm.
3.2 SAM Preparation and Initiator Immobilization

Glass slides were cut into $\frac{1}{2} \times 1$ inch pieces while glass fibers were cut into 1 inch (diameter) pieces from an 8.5 inch $\times$ 11 inch sheet. Prior to use, the back side of the glass substrates was roughened using sandpaper and both substrates were washed with DI-Water and EtOH two times. Both substrates (5-7 per glass dish) were immersed in a 20 wt% NaOH solution for approximately 24 hours, and were subsequently washed with DI-Water and ethanol multiple times, and then air dried. As shown in Figure 2, for ATRP initiator immobilization, the substrates were immersed in 15 ml ethanol solution containing 10 $\mu$l BrTMOS initiator and left for approximately 24 hours. The substrates were then sequentially washed with THF and ethanol two times and then air dried prior to p(SBMA) grafting.

3.3 Surface Polymerization of SBMA

One of each type of substrate, with immobilized initiator, along with SBMA monomer (0.2960g) and bpy ligand (0.0620g) were placed into a test tube. Cu(I)Br (0.0310g) was added just before starting the reaction, and the test tube was sealed with a natural rubber septum. The reaction vessel was quickly filled with nitrogen and degassed two times. Using a syringe under nitrogen protection, a degassed solution (7ml) of methanol was added followed by a degassed solution of DI-Water (7ml). After reacting the samples for the predetermined time, the substrates were removed and washed with DI-Water and ethanol multiple times, and then air dried prior to storage in a dessicator. The polymerization scheme is shown in Figure 7.
3.4 Scanning Electron Microscopy (SEM)

The surface morphology of the p-(SBMA) grafted fibers was characterized using an FEI Quanta 200 scanning electron microscope. Dried fiber samples were cut into 1cm² squares and affixed onto aluminum stubs using double-sided adhesive conductive carbon
tape. The fiber morphology was then resolved and captured under low vacuum conditions at 30 kV.

3.5 Film Thickness

Ellipsometry is widely used to measure the thickness of a thin film on a substrate and it measures the change of polarization upon reflection or transmission from the sample. Film thicknesses were measured using a variable angle spectroscopic ellipsometer (J.A. Woollam Co. Ellipsometer, running WVASE 32 Version 3.610). The phase factor (Δ) and amplitude factor (Ψ) were measured in air at room temperature in the wavelength range from 300 nm to 1000 nm at 10nm intervals. This wavelength range was repeated for incident angles ranging from 65° to 75° in 5° intervals. Measurements were made on the smooth side of the sample while the back side was roughened using sandpaper prior to preparing the SAM. This was done to prevent backside reflections caused by scattering of the light, and thereby simplifying data analysis.

3.6 Contact Angle Measurements

Contact angle measurements were made using a Rame-Hart Goniometer. A spectroscopic cell was used for the underwater measurements which contained a prism stand. The glass sample was placed on the stand upside down, and subsequently filled with DI-Water. As shown in Figure 8, a curved needle containing hexadecane was placed under the sample and the solution was pushed out of the syringe until an oil droplet formed. The oil droplet either floated up by itself or was made to detach the needle tip by gentle agitation of the needle. In doing this, the oil droplet is ‘captured’ underneath the sample, and a contact
angle can be measured. The in-air contact angle measurements had an approximate drop size of 3-5\( \mu l \) and the underwater contact angle measurements had an approximate oil drop size of 10-15\( \mu l \). At least two areas were measured on each sample; with five consecutive measurements for each droplet. The underwater contact angles were measured with the Drop Image software, while the in-air contact angles were measured using ImageJ software.

Figure 8: Schematic of underwater contact angle measurement with a sample placed upside down on top of a prism stand and a liquid droplet (oil) is released underneath via a syringe.

3.7 Oil/Water Separation Tests

Dead-end filtration tests were performed in the apparatus as shown in Figure 9 to separate oil/water mixtures. The sample, which rests on the stainless steel mesh, is placed inside
the cell, which in turn rests on the lip. The opening at the bottom of the cell is about 1½ cm because ½ cm is used to create the lip on which the sample rests. Because of the flexibility of the filter samples when wet, a stainless steel mesh was used for structural support. Another piece of glass tubing (outer diameter of ~1 inch and 3 inches tall) is inserted into the cell to hold the sample in place. An O-ring embedded inside the cell is used to prevent the solution from leaking out between the glass tube and the cell. 10ml of DI-Water was poured into the tube using a glass funnel to hydrate the filter. Thereafter, a DI-Water and hexadecane solution (2:1 volume ratio, 20:10 ml) was rigorously mixed by hand in a glass bottle, and then poured down the tube with the aid of a glass funnel. The permeate was collected in a graduated cylinder from which the levels were recorded at various times for the water, oil, and the total permeate solution. The Oil Red O dye was added to the oil for visual purposes only. Hexadecane was used as a foulant as it has very low surface energy and is therefore prone to aggressively wet surfaces. [75]
Figure 9: Image of the separation setup of the cell, which contains the sample and the stainless steel mesh. Another piece of glass tubing is placed on top to hold the sample in place.

3.8 Water Absorption

Water absorption of the p-(SBMA) grafted samples was characterized by comparing the dry and hydrated samples. Dry p-(SBMA) grafted and control samples were weighed first and then soaked in water. After certain time periods, the hydrated samples were withdrawn from water, and the excess surface water was removed with Kimwipe. The samples were weighed again and the water absorption was calculated using the following equation:

\[
Water\ Absorption\ (\%) = \left(\frac{W_S - W_D}{W_D}\right) \times 100\% \tag{5}
\]

where \(W_S\) represents the weight of the filter after water uptake and \(W_D\) represents the weight of the dry filter.
CHAPTER IV

RESULTS AND DISCUSSION

4.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy measurements were carried out to characterize the surface morphologies of the glass fiber filter; both before and after p-(SBMA) grafting. The images were obtained using a field-emission scanning electron microscope (quanta 200 by FEI Corp.). Figure 10 shows the SEM micrographs of the control and the p-(SBMA) grafted glass fiber filters. Figure 10a is a typical image of the porous unwoven glass fiber substrate with a fiber diameter of 6.5µm and a pore range of 50-350 µm. Figure 10b and 10c are the 5min and 1 hour p-(SBMA) grafted samples respectively. The diameters of the p-(SBMA) grafted glass fibers are ~ 6.5 µm, thus showing no significant change after the ATRP grafting step. There is also no grafting within the pores, therefore ensuring free passage of solution within the pores. It was difficult to distinguish the control, and p-(SBMA) grafted samples under the 5 µm scale, possibly due to sample/brightness so checking for nanoscale roughness was inconclusive. The fiber surfaces also don’t exhibit roughness at the 5 µm scale (Figure 10c inset), thereby implying that oleophobicity is mostly achieved via surface chemistry and not surface roughness. Atomic force
microscopy (AFM) cannot be used to characterize the glass fiber filters because they are soft and the results would be insignificant.

Figure 10: SEM micrographs of the glass fiber samples for the control, a), and the p-(SBMA) grafted samples b) and c) with reaction times of 5 min and 1 hour respectively. The inset in 10c) shows the 1 hour p-(SBMA) grafted sample at the 5µm scale.

4.2 Surface Polymerization of SBMA

Figure 11a) shows the ATRP reaction taking place inside the test tubes. The solution turns to dark brown when the solvent is added to the test tube. The brown color articulates that the reactions are underway and that there is no oxygen present in the reaction vessel. If oxygen were present, which is unwanted, the color would be light green due to the oxidation of copper. Figure 11b) shows the image of the glass fiber filters and glass slides after the ATRP step. Both types of samples are clean and additionally the glass slides remain transparent, as shown on the edges of the slides;
while the center region is roughened with sand paper. In order for the surface to be transparent, the roughness details should be smaller than the wavelength of visible light (about 400-700 nm) as found by Nakajima et al. [76]. The amount of SBMA monomer used (converted) was estimated using a grafting density of 0.39 chains/nm$^2$ [85], and the results (not shown) showed very minute conversions in the order of 1/1750 for the 5 minute sample and 1/906 for the 24 hour p-(SBMA) grafted samples. An accurate % monomer conversion can be obtained by Gas Chromatography.

Figure 11: Images showing ATRP reactions going on in the test tubes a), and the cleaned glass fiber filters and glass slides after the ATRP step b).

4.3 Film Thickness

For a thick glass substrate (~1mm), the fact that the incident beam could possibly penetrate the substrate and get reflected from its back surface cannot be ignored. Back side reflections may interfere with the primary reflection from the front of the substrate.
and adds incoherently at the detector, which may disturb the polarization state and result in incorrect analysis. Therefore, one side; the “back side,” was roughened with sandpaper prior to SAM preparation and thereby allowing measurements to be made on the smooth side. This was done to prevent backside reflections caused by scattering of the light, and thereby simplifying data analysis. A two layer model was used to determine the polymer thicknesses; the bottom glass layer (Corning 7059), and the top polymer layer (Cauchy).

Ellipsometric measurements were conducted in air at room temperature using a variable angle spectroscopic ellipsometer (J.A. Woollam Co. Ellipsometer, running WVASE 32 Version 3.610) from 300nm-1000nm at 10nm intervals. This wavelength range was repeated for incident angles of 65°, 70° and 75°. From the ellipsometry results (Figure 12), it can be seen that the p-(SBMA) polymer thickness increases with the ATRP time therefore confirming that ATRP of p-(SBMA) onto the substrates is successful. The film thickness increases rapidly from 14nm to 25nm at 5 minutes, and 2 hours respectively, thereafter a fairly constant thickness of 26-27nm is achieved up to 24 hours. The slowly increasing film thickness rate can be a consequence due to either the deactivation of materials and/or termination of long polymer chains via self-association. Even though the p-(SBMA) film thickness increases over time, as shown in the ellipsometry results, the in-air water contact angles do not become more superhydrophilic with time. This is due to the p-(SBMA) chains entangling together via intermolecular interactions, and as a consequence, reduce the interactions between the surface and water, and therefore an increase in hydrophobicity is seen with contact angles greater than 10° and also a slowdown in film thickness is seen for higher reaction times. Other groups have found p-(SBMA) thicknesses ranging from 10-15nm [32, 77, 78] and 15-90nm [79].
where the differences could be due to the different amounts of materials used such as catalyst and ligand, or it could be due to the use of different initiators and substrates.

Figure 12: p-(SBMA) film thickness measured as a function of time using Ellipsometry. The measurements, conducted at room temperature and ambient conditions, were measured at incidence angles of 65°, 70°, and 75° from 300-1000.

4.4 Contact Angle Measurements

The wettability of the p-(SBMA) grafted slides was fully characterized via contact angle measurements. Compared to the untreated “control” sample, represented as the 0
reaction time, the in-air water contact angle measurements, shown in Figure 13 on the p-(SBMA) grafted glass slide samples resulted in an increase towards superhydrophilicity with contact angles ~8-13°. The p-(SBMA) grafted samples also resulted in superoleophilicity (not shown). Similarly, underwater oil contact angles on the p-(SBMA) grafted glass slides resulted in an increase towards superoleophobicity with contact angles ~162-169°. This increase in superoleophobicity is acquired due to water being trapped at the solid-oil-water interface, thus effectively preventing strong adhesion of oils. Underwater tilt angles and contact angle hysteresis were not measured because of the difficulty of measuring underwater; however it is well known that -phobic surfaces have low contact angles and low hysteresis. Additionally, if the sample stand for the goniometer was not perfectly leveled, the oil droplet would start moving, thus suggesting very low tilt angles for the p-(SBMA) grafted samples. On the contrary, the characterization of the p-(SBMA) grafted glass fiber filters was not possible due to its flexibility, however, the fiber mats also showed amphiphilicity in air.
Figure 13: In-air water contact angle measurements a), and underwater hexadecane contact angle measurements b), for control and p-(SBMA) grafted samples at different reaction times. The error bars represent the standard deviation.
Analysis of variance (ANOVA) was performed to check for statistical differences among the contact angle values obtained for the p-(SBMA) grafted glass slides, Table 3. ANOVA is a statistical technique that can be used to test whether there are significant differences between the average values, or the means, across several population groups. The model tests whether or not groups of data have the same or differing means by comparing the amounts of distribution experienced by each of the groups to the total amount of distribution in the data. By using the sum of squares and the mean of squares, the model provides an f-ratio which is used to obtain the probability value (p-value).

Table 3 ANOVA results showing the relationship between p-(SBMA) grafting reaction times and in-air contact angles for the p-(SBMA) grafted samples only.

<table>
<thead>
<tr>
<th>Source</th>
<th>Degrees of Freedom</th>
<th>Sum of Squares</th>
<th>Mean of Squares</th>
<th>F-Ratio</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatments</td>
<td>5</td>
<td>21.555</td>
<td>4.311</td>
<td>1.262</td>
<td>&gt; 0.05</td>
</tr>
<tr>
<td>Error</td>
<td>6</td>
<td>20.500</td>
<td>3.417</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>11</td>
<td>42.055</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The null hypothesis (H₀) to test, states that all reaction times lead to the same contact angle value. ANOVA was performed with a Type 1 error (α = 0.05) to obtain a value of 4.39, making p-value > 0.05, therefore showing that the results are not statistically significant and thus the null hypothesis cannot be rejected. This means there
are no significant differences in the in-air contact angle values obtained for the different p-(SBMA) reaction times.

The control sample was also statistically compared to the p-(SBMA) grafted samples. The ANOVA results are presented in Table 4 for a Type 1 error ($\alpha = 0.05$), which give a value of 3.87, making $p$-value $< 0.05$. Therefore, there are statistically significant differences among the reaction times, meaning there is a significant difference in the contact angle obtained for the p-(SBMA) grafted samples and the control sample. A further analysis using Tukey’s ‘HSD’ Method was used to compare the control sample pair-wisely with each of the p-(SBMA) grafted samples. All results conclude that the control sample leads to a higher in-air contact angle compared to p-(SBMA) grafted samples.

Table 4 ANOVA results showing the relationship between p-(SBMA) grafting reaction times and in-air contact angles for the p-(SBMA) grafted, and control samples.

<table>
<thead>
<tr>
<th>Source</th>
<th>Degrees of Freedom</th>
<th>Sum of Squares</th>
<th>Mean of Squares</th>
<th>F-Ratio</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatments</td>
<td>6</td>
<td>614.816</td>
<td>102.47</td>
<td>18.63</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Error</td>
<td>7</td>
<td>38.500</td>
<td>5.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>13</td>
<td>653.316</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.5 Properties of the Grafted Zwitterionic Films

As noticed from the contact angle measurements, the in-air contact angles increase after a certain time as the reaction time increases, and also as seen from the ellipsometry results, the film thickness increases quickly initially and then gradually reaches a plateau. These are attributes of the grafted zwitterionic films. Azzaroni et al. observed that thin brush films displayed a very hydrophilic surface, while increasing thickness thereafter resulted in a linear increase in hydrophobicity. They referred to these two regimes as the “non-associated” and “self-associated” regimes respectively.

The grafted polymer chains bear high dipole moment side groups and will therefore exist in the self-associated conformation. The electrostatic interactions on the other hand lead to interchain and/or intrachain ionic crosslinks and loops respectively as caused by the closely associated opposite charges. However when in water, salvation counteracts the electrostatic effects which in turn forces the opposite charges to repel each other.
Azzaroni et al. concluded that the differences between thin, hydrophilic swollen brushes and thick, hydrophobic, collapsed brushes are a result of several factors such as; stabilization of the high dipole moments with choice of solvent, steric factors related to the polymer backbone and favorable interactions of sulfonate groups with water rather than with quaternary ammonium groups. These factors change when the brushes are significantly thicker. The amount of zwitterionic groups increases as the film thickness increases, therefore the probability of ion-pairing or self-association between the positive and negative charges is also increased. This leads to an increase in the polymer volume fraction and then after reaching some critical height where the first ion-pairing events begin, the self-association becomes more favorable and leads to a collapse of the chains. This has been referred to as the supercollapsed state by Khokhlov et al. In this state the
chains are very dense in which they form intrachain and interchain ion pairs as shown in Figure 14 b) and c) respectively.

4.6 Oil/Water Separation Tests

All samples used were fresh, therefore, after they were cleaned and dried after performing ATRP reactions. As shown in the experimental setup for dead-end filtration (oil-water separation), the p-(SBMA) grafted glass fiber samples were placed inside the cell on a SS mesh that was used for structural support purposes only. After hydrating the samples with DI-Water, the DI-Water/hexadecane mixture was poured, thereafter the water selectively permeated through the filter while the oil was retained above the sample. The results are shown in Figures 15 and 16, where it can be seen that even samples grafted with p-(SBMA) for 5 minutes can be effectively used to completely prevent the oil from permeating through the filter, while allowing the water to quickly permeate within seconds. The SEM images showed no grafting between fibers, thus ensuring free passage of the solution.
Figure 15: Oil-water separation data of p-(SBMA) grafted samples at various reaction times. The total permeate was measured, a), along with the amount of oil in the total permeate solution, b). 10ml of DI-Water was used to hydrate the samples, followed by an addition of DI-Water: hexadecane solution (20ml: 10ml).

Although the separation happened within seconds, the results in Figure 15b show that most of the oil in the control sample permeates through within 20 minutes, while the oil is retained for p-(SBMA) grafted samples for over 24 hours. The intrusion pressure indicates the maximum height that the sample can support, however it was not studied in this experiment. This means that below the intrusion pressure, the oils will not be able to permeate through the samples [1] of which we can see an example in Figure 16b.
Figure 16: The before and after images of the control sample 16a, b and the 5 minute sample 16c, d. The filter was fitted inside the cell between the SS mesh and top glass tube. A mixture of DI-water and hexadecane was poured into the top glass tube. The water selectively permeates through the filter while the oil is retained on the top.

Due to the in-air superoleophilic property of the p-(SBMA) grafted samples, the samples were first hydrated with 10ml of DI-Water. This prevents the samples from absorbing the oil on contact and further inhibits the permeation of oil through the filter by capillary effects. Hexadecane was used as a foulant as it is a very aggressive foulant with a low surface energy.[75] During the oil-water separation, the underwater superoleophobic property of the p-(SBMA) grafted samples prevents oil droplets from adhering therefore making recycling of oil and materials very easy. This can be
represented by the Cassie-Baxter state where water and/or air are trapped at the solid/liquid 1/liquid 2 interface. [15] This can be further explained by the high repellency between the non-polar (hexadecane) and polar (water, p-(SBMA)) molecules.

Good separation results (not shown) are still obtained if the samples are not initially hydrated, however some amount of oil permeates through the sample at the initial step of pouring the oil-water mixture. The oil stops permeating thereafter, theoretically, when the entire sample is hydrated with water due to its superhydrophilic property. The samples, due to their underwater oleophobicity property, prevent oil from further permeating for over 24 hours. On the contrary, the control sample allowed most of the oil and water to permeate through within a few minutes. In addition to the samples being easily cleaned with DI-Water and Ethanol, the separation requires no additional force other than gravitational force. This demonstrates that the filters are a good candidate for industrial oil-water separation. Besides intrusion pressure, another factor that contributes to the effective separation is water absorption. Due to its superhydrophilic property, the filters tend to swell during the separation, so water absorption tests were performed.

4.7 Water Absorption

The contact angle measurements on the p-(SBMA) grafted glass slides show that the surface is superhydrophilic. To get a different perspective on the hydrophilicity of the p-(SBMA) grafted fibers, water absorption experiments were performed. The water absorption level based on the weight difference of the dry and hydrated filters was
determined. The 5 min p-(SBMA) grafted samples exhibited the highest average water absorption of 1237 %, more than 1.22 times compared with the control glass fibers that only absorbed 1011% water (Figure 17). Similarly, the 10 min sample exhibited average water absorption of more than 1.20 times compared to control. Thereafter, the average % water absorption values were only 1.05 and 1.06 times more than the control sample for the 1 hour and 24 hour samples respectively. Some factors affecting the amount of water absorption include; high surface area-to-volume ratio of the fiber filters, water molecules being held between polymer chains via electrostatic interactions, and also being trapped within the porous structure of the fiber filter. These factors facilitate the increase of water absorption of the p-(SBMA) grafted fiber mats compared to the control samples.

![Figure 17: Water absorption of p-(SBMA) grafted glass fiber filters at different reaction times compared to control glass fiber filters.](image-url)
The decrease in water absorption after the 10 min sample is a consequence of the p-(SBMA) grafted zwitterionic films. As discussed above, after a certain film thickness, the zwitterionic films tend to self-associate with themselves due to an increase in the amount of zwitterionic groups. When this happens, the chains tend to interact more with each other than with water molecules, therefore an increase towards hydrophobicity is seen. Therefore, the decrease in water absorption can be ascribed to the properties of the grafted p-(SBMA) zwitterionic chains.

Analysis of variance (ANOVA) was performed to check for statistical differences among the water absorption % values obtained for the p-(SBMA) grafted glass fiber filters. The results are presented in Table 5.

Table 5: ANOVA results showing the relationship between p-(SBMA) grafting reaction times and percentage of water absorption as compared to the control sample.

<table>
<thead>
<tr>
<th>Source</th>
<th>Degrees of Freedom</th>
<th>Sum of Squares</th>
<th>Mean of Squares</th>
<th>F-Ratio</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatments</td>
<td>4</td>
<td>328,144.831</td>
<td>82,036.208</td>
<td>6.706</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Error</td>
<td>35</td>
<td>428,186.831</td>
<td>12,233.907</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>39</td>
<td>756,331.662</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ANOVA was performed with a Type 1 error (\(\alpha = 0.05\)) to obtain a value of 3.06, making \(p\)-value <0.05, therefore showing that the results are statistically significant and thus the null hypothesis is rejected. This means there are significant differences in the water absorption (%) between the control and p-(SBMA) grafted glass fiber samples. A further analysis using Tukey’s ‘HSD’ Method was used to compare the control samples
pair wisely with each of the p-(SBMA) grafted samples. The 5 min and 10 min reaction times showed statistically significant differences when compared pair wisely to the control sample. Since they both exhibit significance in the water absorption level, the 5 min and 10 min samples are able to absorb more water than the control sample. The 1 hour and 24 hour reaction times led to insignificant differences when compared pair wisely to the control. Therefore, the 1 hour and 24 hour samples absorb almost the same amount of water as the control sample.

4.8 Self-Cleaning Tests

The p-(SBMA) grafted glass slides complement the underwater antifouling characteristics. The samples were placed in hexadecane oil, and subsequently placed in water to test the underwater self-cleaning ability. Figure 18 shows images of the control glass slide, and the 5 min glass slide. As can be seen for the control sample (18a), the oil droplets quickly gather together and the surface is easily fouled underwater, and even after shaking the sample rigorously, the sample still remained fouled. On the contrary, the 5 min p-(SBMA) grafted sample (18b) showed excellent results at self-cleaning. The sample was barely fouled, initially, and mild shaking of the sample resulted in complete self-cleaning ability of the surface. These observations suggest that the surfaces are self-cleaning and antifouling underwater. Liu et al. [24] saw a similar observation with fish scales, where the fish exhibit oleophilicity in air and oleophobicity underwater, and therefore are self-cleaning. The fish scales were found to be consisting of nanoscale roughness, which created the underwater superoleophobicity, however, we report superoleophobicity achieved only via surface chemistry.
Jung et al. [23] and Liu et al. [24] performed experiments in a solid-water-oil interface. They found that hydrophilic and oleophilic surfaces can switch into an oleophobic surface in water. As a result, oil contaminants are washed away when immersed in water. This effect can be employed for underwater oleophobicity and self-cleaning that can be used against marine ship fouling.

Underwater superoleophobicity is a great application for marine antifouling as well as antifouling coatings as suggested by Genzer et al. [73]. The reversibility of the surface properties in different environments is a very good feature to have; such as a hydrophilic/oleophilic material in air switching into an oleophobic material under water. As a result, oil contaminants are washed away when immersed in water. This effect leads to underwater oleophobicity and self-cleaning that can be used against marine ship fouling. [26]
Figure 18: Self-cleaning tests performed on the control a) and 5 min b) glass slides, before 1) and after 2) shaking. The samples were first dipped in hexadecane oil; dyed with Oil Red O dye, and subsequently placed underwater in DI-Water.

The same story cannot be articulated for the glass fiber samples because due to their intrinsic oleophilicity in air and sorbent properties, the samples are easily fouled with oil. Placing them underwater does not result in a self-cleaning surface. However,
very vigorous shaking by hand results in oil being released from the surface, but it is still retained inside the filter. On the other hand, if the glass fiber filters are initially hydrated, then passing them through an oil layer does not result in fouling, therefore, they are self-cleaning only if hydrated. Surprisingly, the control sample behaves the same way. This can be attributed to the absorbing nature of the filter; when the filter is fully swelled, it cannot absorb more liquid, and it is harder for oil molecules inside the fiber to come out when surrounded by water molecules.

Even though fish and sharks are easily wetted by water, they are known to be well protected from oil contamination during oil spills. The fish scales are shown to be consisting of microscale hierarchical roughness [24] and the shark skin, a natural model for a low-drag surface, is covered by small individual tooth-like scales termed dermal denticles. In turbulent flow conditions, vortices are created on the surface, which increase fluid drag. These structures lift and constrain the naturally occurring vortices, and therefore reduce the transfer of momentum and shear stress. [23] The water surrounding these structures can lead to protection from marine fouling and play a role in the defense against adhesion and growth of marine organisms. Algae.[80]

4.9 Applications

Several applications require the separation of oil-contaminated waters produced from various industries such as petrochemical, food, metallurgical and pharmaceutical industries. The self-cleaning ability of p-(SBMA) grafted samples opens up potential applications related to self-cleaning windows, windshields, exterior paints for buildings, navigation ships, utensils, roof tiles, solar panels, and applications requiring antifouling
from biological and organic contaminants and a reduction of drag in fluid flow, e.g. in micro/nanochannels and ships. [23] To reduce pressure drop and volume loss in micro/nanochannels, it is desirable to reduce the drag force in the solid-liquid interface.

An additional application the p-(SBMA) grafted samples can be used for is to create anti-fogging films/surfaces. Increasing hydrophilicity and advancing contact angles of $< 40^\circ$ are experimentally shown to prevent fogging on surfaces.[81, 82] Moisture will tend to form a transparent continuous thin film on surfaces with advancing contact angles $< 40^\circ$. On the contrary, the moisture forms discrete droplets on surfaces with advancing contact angles $> 40^\circ$. These droplets scatter light and create a translucent fog. A big concern when dealing with anti-fogging surfaces is fouling from oils. These oils are left onto the surfaces via residues from fingerprints or oil contaminates from the air, and thus creating another surface which induces fogging. Since the p-(SBMA) grafted glass slides exhibit very hydrophilic surfaces and are self-cleaning, they can potentially be used as anti-fogging coatings involving cold windshields, eyeglasses, SCUBA goggles, infrared microscopes and applications that rely on maximizing solar flux.[81]

The innovation can also be used for applications such as; oil retention barriers for oil-spill clean-ups, hydraulic fracturing, waste-water treatment, remote operation of oil-water separation units, underwater marine antifouling [82] self-cleaning coatings, microfluidic devices, [11] cell and protein adhesion control on surfaces [28]. Superoleophobic surfaces can also reduce significant loses of residual fuel in fuel tanks and pipes.
CHAPTER V

FUTURE/RELATED WORK

5.1 Particle Size Distribution

Since the oil and water mixtures in this study are readily immiscible, we would like to perform emulsion experiments to test the oil-water separation aptitude of the micro emulsions, and hope to be able to determine the particle size limits for the separation to be successfully achieved. Depending on the results, a further step would be to look into coalescence filtration so that the efficiency of p-(SBMA) grafted filters for oil-water separation can be enhanced. Since the substrate is made of glass, further modification of the fibers would allow for directional collection of the micro droplets. Finally, intrusion pressure that determines the pressure needed for the oil to flow through the pores between the p-(SBMA) grafted fibers will be calculated.

5.2 SBMA-PS Block Copolymer

Since ATRP is a living polymerization of a controlled nature, it has been possible to create diblock copolymers. [60] The subsequent initiation of a different monomer by the first block results in a diblock copolymer, which could be made into multiblock copolymers with subsequent addition of different monomer. We would like to add an
oleophobic block copolymer and therefore achieve both, in-air hydrophilic-oleophobic, and underwater hydrophilic-oleophobic filter. For this case, initial hydration of the samples would not be necessary, thus reducing costs, and also due to the lightness of the glass fiber filters, they could be used as sorbents to remove water from oil.

5.3 Grafting P-(SBMA) onto Different Substrates

Since p-(SBMA) is a great material due to its superhydrophilicity and anti-fouling properties, it would be excellent if it could be grafted onto different substrates such as hydrophobic polymers and metals. The grafting of p-(SBMA) is possible on these surfaces following the same procedure; however, depending on the substrate chemistry, a different initiator is needed in order to covalently attach the p-(SBMA) chains to the surface. A future work is to perform some experiments with regard to p-(SBMA) grafted polyvinylidene fluoride (PVDF). Chang Y. (2011) et al., and Chiang Y.-C. et al. have successfully grafted SBMA onto PVDF using ATRP and plasma-induced methods respectively. Because the substrates are not glass, a different technique is required to generate hydroxyl groups onto the substrate surface, onto which the initiator is covalently attached thereafter. An initiator is required for the grafting of SBMA onto the substrates for both of these methods, but Chen Y. et al. realized and utilized the secondary fluoride of PVDF to directly graft the SBMA. This method is superior because no initiator is required.
CHAPTER VI

CONCLUSIONS

In conclusion, a novel superhydrophilic and underwater superoleophobic p-(SBMA) grafted glass fiber filters have successfully been engineered for the use of oil-water separation. For the p-(SBMA) grafted glass slide samples, the in-air water contact angles were around 8-13º while underwater oil contact angles were around 162-169º. The 5 min glass fiber filter showed slightly better water absorption properties when compared with control sample, with absorbing more than 1.12% water than the control sample. P-(SBMA) grafted glass slides also exhibit underwater superoleophobicity and therefore self-cleaning properties, which can be used against fouling from organic material, marine life, and cell and bacteria adhesion. On top of being non-toxic, the fabrication of the samples is very easy and inexpensive compared to other techniques, while the separation is rapid and can be manufactured to be readily deployable.

Being able to have successfully demonstrated the grafting of SBMA monomer onto the glass surfaces, the objectives of the research were therefore successfully met. The results show that all three disadvantages; membrane fouling, low efficiency, and high costs are successfully addressed and can be reduced for large-scale operation of oily waste waters. The results have decreased the amount of the disadvantages if not totally eliminated them.


APPENDIX

ATOMIC FORCE MICROSCOPY (AFM)

Atomic Force Microscopy (AFM) is also used to measure the film thicknesses on some instances, for example when using plain glass samples. It is a very high-resolution type of scanning probe microscopy which is widely used to measure the surface roughness of a material. AFM provides a 3D profile of the surface on a nanoscale by measuring the forces between the cantilever (<10nm) and the surface at very short distances (0.2-10nm probe-sample separation). The forces can be described using Hooke’s Law:

\[ F = -k x \]  

where F is the force, k is the spring constant and x is the cantilever deflection.

The amount of force between the sample and the probe is dependent on the stiffness of the cantilever and the distance between the probe and the sample surface.

To measure the film thickness, a scratch is made on the sample surface, and by using AFM, the thickness is measured by taking the difference between the bottom of the scratch zone and the average of both sides away from the scratch; because some residue will arise near the top of the scratch as shown in Figure A-1.
Figure. A-1. Example of an AFM scan profile across the scratch made by a razor blade.