NOVEL PERFLUOROPOLYETHERS AS FOULING-RELEASE COATINGS

by

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ABSTRACT

ZHAOKANG HU: Novel Perfluoropolyethers as Fouling-release Coatings
(Under the direction of Professor Joseph M. DeSimone)

Perfluoropolyethers (PFPE’s) and copolymers exhibit low surface tensions, low moduli and excellent thermal and chemical stabilities, which make them promising candidates as fouling-release coating materials. The objectives of this research primarily involve functionalizing PFPE precursors to form reactive macromonomers which can be photochemically crosslinked to form elastomer materials. To explore structure/property relationships, different functional endgroups such as methacrylate and styrene were used to modify PFPE telechelic diols of variable molecular weights to yield crosslinkable difunctional PFPE macromonomers. The method allows for control of the crosslink density of crosslinked PFPE elastomer materials via UV curing, which can provide materials with different mechanical and surface properties.

These difunctional PFPE’s were incorporated into hydrophilic dimethacrylate-functionalized poly(ethylene glycol) (PEG-DMA) to form amphiphilic networks via UV curing. These network materials varied from optically transparent to opaque as a function of molecular weight and composition ratio. The different solubility of these two components resulted in the amphiphilic materials with microphase to macrophase separation. Strong inhibition of non-specific protein adsorption could be achieved with these network materials compared with an oligo(ethylene glycol)-based self-assembled monolayer coated surface.
Multifunctional PFPE macromonomer was obtained via the modification of PFPE tetrol precursor with methacrylate endgroups. In order to achieve durable PFPE elastomer materials, fluorinated difunctional crosslinker was incorporated and copolymerized with the PFPE macromonomer to further increase crosslink density. The partial incompatibility of the two components resulted in samples with microphase separation. This fundamental research helps both to understand the compatibility and miscibility behavior of fluorinated components and to optimize the design of perfluorinated systems for obtaining enhanced mechanically durable materials as long-term fouling-release coatings.
ACKNOWLEDGEMENTS

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Chapter 1

Introduction to Applications of Polymeric Materials on Biofouling Prevention
1.1 Introduction

Biofouling, or biological fouling, is the detrimental buildup and accumulation of micro- or macro-organisms that attach onto submerged structures, especially on ship hulls and pier pillars. Biofouling is divided into two categories: microfouling from biofilm formation and bacterial adhesion and macrofouling resulting from the attachment of larger organisms. The main culprits of biofouling are algae, diatoms, barnacles, mussels, polychaete worms, bryozoans, and seaweed. Together, these organisms form a marine biofouling community.

Marine biofouling can form enormous masses that severely diminish the maneuverability and carrying capacity of ocean vessels and thus incur huge functional and monetary costs in maintenance. On a poorly treated ship hull surface, marine biofouling can amount up to 330 pounds per square meter in only a six-month period of time at sea. A 40,000 square meter tanker can increase its weight by 6,000 tons during this time due to the accumulation of these organisms. The extra weight caused by biofouling leads to a significant increase in hydrodynamic drag as the vessel moves through water, which increases fuel consumption by as much as 30% to 40%. Additionally, marine biofouling can speed up the corrosion process in structures and materials causing accelerated operational failures and the premature loss of structures or equipment. By adding other costs such as hull cleaning, paint removal, and repainting, the total cost for the US Navy alone is estimated to be more than $1 billion per annum. Most importantly, the effective control of the biofouling is of considerable significance in military to minimize the acoustic signature and therefore the detectability of submarines.
Biofouling is also found in membrane systems, such as osmosis membranes and membrane biosensors used for microfiltration or ultrafiltration of municipal and industrial wastewater. The buildup of a layer of fouling on these membranes will strongly influence the performance of a membrane in crossflow filtration. Biofouling causes the narrowing of the inner diameter and in some cases completely plugs the porous structure on the membrane surface. This results in decreased separation efficiency or can even shut down the entire filtration process. Biofouling can also occur in oil pipelines carrying oils with entrained water such as used oils, cutting oils, and hydraulic oils. Given the significant economic impact of biofouling in marine and the related industries, it is necessary to develop an approach to effectively prevent biofouling problems.

1.2 Conventional Approaches to Prevention Biofouling

1.2.1 Organotin-based Anti-fouling Paints

One of the earliest methods of solving the biofouling problem was to scrape the ship hull. This solution, although simple and relatively effective, poses a problem by spreading invasive species. It is illustrated with the population explosion of zebra mussels (Dreissena polymorpha) in the Great Lakes region. To counter the spread of invasive species, many areas have established hull-cleaning laws, stating that any material removed from ship hulls must be collected and disposed of properly.

When cleaning (or scraping) becomes time consuming or ineffective, marine industries turn to the widely accepted method of controlling and preventing biofouling by using anti-fouling paints containing heavy metal compounds. One class of the most popular
anti-fouling paints is organotin containing paints, specifically tributyltin paints (TBT). They kill marine organisms (e.g. algae, barnacles, and other marine organisms) by releasing tin biocides to interfere with major biological processes such as growth, reproduction and immunity, on a cellular level. A number of organotin compounds have been extensively used as ingredients in TBT anti-fouling paints, which includes bis(tributyltin) oxide or tributyltin oxide, tributyltin sulfide, bis(tributyltin) adipate, tributyltin methacrylate, tributyltin fluoride, and tributyltin acetate (Scheme 1-1).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis(tributyltin) oxide (Tributyltin oxide)</td>
<td><img src="image1" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Tributyltin sulfide</td>
<td><img src="image2" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Tributyltin methacrylate</td>
<td><img src="image3" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Tributyltin fluoride</td>
<td><img src="image4" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Bis (tributyltin) adipate</td>
<td><img src="image5" alt="Chemical Structure" /></td>
</tr>
</tbody>
</table>

Table 1-1. Chemical structures of main TBT containing compounds.
The release mechanism of tributyltin can be described by the following equation for the reaction of the tin biocides (Bu₃SnX) with water:

\[ \text{Bu}_3\text{SnX} + \text{H}_2\text{O} \rightarrow \text{Bu}_3\text{Sn(H}_2\text{O})^+ + \text{X}^- \]

In most practical applications, TBT compounds are chemically bound with monomers which can copolymerize with other comonomers to form a polymer matrix that forms an anti-fouling paint. This approach allows manufacturers to formulate products with a controllable biocide release rate in seawater. One example is the copolymer of tributyltin methacrylate (TBTM) with methyl methacrylate (MMA). The TBT biocides are slowly released, initiated by a hydrolysis reaction, which cleaves the TBT biocides from the copolymer backbone into the marine environment, as shown in Scheme 1-1.⁹

![Scheme 1-1.](image)

**Scheme 1-1.** The hydrolysis reaction that takes place between the tributyltin methacrylate/methyl methacrylate copolymer and seawater releases the TBT⁺ cation biocides into the seawater to prevent biofouling.

Because most anti-fouling paints are hydrophobic, seawater interacts at the coating surfaces only. When a ship hull is in motion, the water gradually wears away the top layer of the compound, which allows the TBT containing anti-fouling paints to function for a long period of operational time. However, as it is widely known, the TBT biocides are toxic not only to biofouling organisms, but also to non-target organisms. Since TBT biocides cannot
decompose rapidly in seawater, they accumulate in sediment, particularly in areas with a high volume of ship traffic such as harbors and ports. Many incidences of deformities in some shellfish have been linked to their presence, even when present at extremely low concentrations.\textsuperscript{10}

1.2.2 Other Non-tin Anti-fouling Paints

Due to the strong ecotoxicity of tin biocides and the negative ecological influences observed worldwide, a global prohibition was imposed on the application of organotin containing anti-fouling paints on ships by the International Maritime Organization (IMO) in 2003.\textsuperscript{11} An essential requirement of any tin-free anti-fouling product is that the replacement must be environmentally compatible, from which no tin biocide will leach out to be harmful to untargeted marine organisms. Many of these new anti-fouling paints require supplements of copper or zinc compounds as biocides to function effectively. One example of these compounds is zinc pyrithione (ZPT) (Figure 1-1), which known as an effective bactericide, fungicide and algicide. Such properties have led it to be used as a booster biocide in modern anti-fouling paints to protect against mildew and algae.\textsuperscript{12}

By replacing zinc with copper, one obtains another commonly used non-tin biocide, copper pyrithione (Figure 1-1). It is less soluble in seawater compared to zinc pyrithione and has been shown to be less effective than zinc pyrithione in cooler ($< 15^\circ$C) waters. But in many applications, copper pyrithione offers advantages over zinc pyrithione. For example, copper pyrithione is more stable than zinc pyrithione when incorporated in paint products, and therefore is less likely to cause gelation during storage.\textsuperscript{13} Due to the lack of statistical data, the potential ecotoxicological risks to the marine environment from the use of these
copper or zinc containing alternative anti-fouling paints cannot be estimated presently. This has raised concerns that they may affect the marine ecosystem similarly to the tin-containing paints by leaching ecologically harmful metal ions.\textsuperscript{14} A more environmental friendly approach is to use synthetic polymeric materials as nontoxic coatings that can either inhibit the attachment of marine organisms or minimize the adhesion strength of those organisms that do attach and grow on the ship hull surfaces.

![Chemical structures of zinc pyrithione (1) and copper pyrithione (2).](image)

**Figure 1-1.** Chemical structures of zinc pyrithione (1) and copper pyrithione (2).

### 1.3 Polymeric Coatings to Prevent Biofouling

In recent years, with advances in macromolecular synthesis and self assembly techniques, several polymeric surfaces have been designed and explored either as anti-fouling coatings which can resist the attachment of biofouling, or fouling-release coatings, on which the adhesion force of the attached organisms is very weak so that the biofouling can be easily removed. The settlement and adhesion of marine organisms on these polymer surfaces was found to be affected by chemical,\textsuperscript{15,16} topographic,\textsuperscript{17,18} and biological cues,\textsuperscript{19} and can vary from one species to another. Synthetic approaches allow for a platform to study these effects systematically.
1.3.1 Polymeric Anti-fouling Coatings

1.3.1.1 Oligo(ethylene glycol) Self-assembled Monolayers

Oligo(ethylene glycol) (OEG) is well known within the biomaterials community to have good protein resistance. A number of such materials with different OEG-functionalized surfaces have been extensively studied. Most of fundamental studies have been rooted on a well studied model: self-assembled monolayer (SAM) containing OEG-terminated alkanethiols covalently bonded onto gold substrates through reaction between sulfur and gold, as seen in Figure 1-2. An effective OEG-terminated SAM construction consists of three to six ethylene glycol repeat units with one end attached to an alkyl chain (C11) and the other end capped with a functional head group that can be varied to be either hydrophobic or hydrophilic in character.

It is believed that the hydration of the OEG chains induced by a low interfacial energy between the OEG groups and water molecules plays an important role in conferring anti-fouling characteristics to a surface. The interfacial energy between water and the polar OEG segments is below 5 mJ/m². According to the mechanism of protein resistance proposed by Andrade and de Gennes, the water molecules associated with the hydrated OEG chains are compressed out of the OEG layer as the protein approaches the surface. Thermodynamically, the removal of water from the OEG chains is unfavorable, which will eventually prevent protein adsorption on OEG surface. Brash and co-workers have reported that chain density is one of the key contributors to resist protein adsorption. As long as the surface is completely covered by ethylene glycol units, the chain length and the entropic effects associated with the molecular architecture do not have a strong influence on anti-
fouling activity. Although the mechanism of OEG-terminated SAM to resist protein adsorption is still under debate, research on these materials provides fundamental understanding of the relationship of material structure with its anti-fouling properties and furthers the design of materials for applications as anti-fouling coatings.

![Diagram of OEG-terminated SAM](image)

**Figure 1-2.** Scheme of a typical OEG-terminated SAM construction.

### 1.3.1.2 Poly(ethylene glycol)-based Polymers

As a derivative of the OEG-SAM system, the anti-fouling properties of poly(ethylene glycol) (PEG)-based polymers are well documented. A recent advance in hydrophilic PEGylated coatings is the use of bio-inspired polymers prepared from methoxy-terminated PEG and the adhesive amino acid L-3,4-dihydroxy-phenylalaine (DOPA), as seen in Figure 1-3, which was used to mimic muscle adhesive protein to enhance the adhesion of PEG to a titanium substrate. Biofouling assays for the settlement and release of the diatom *Navicula*
perminuta and settlement, growth, and release of zoospores and sporelings (young plants) of the green alga *Ulva* were carried out. The methoxy-terminated PEG-DOPA modified titanium surfaces exhibited decreased attachment of both *Navicula perminuta* and zoospores.

![Figure 1-3](image)

**Figure 1-3.** Methoxy-terminated PEG, conjugated to DOPA tripeptide to promote adhesion to metal, glass and other substrates.

As previously discussed, self-assembled monolayers with only a few EG units per molecule have shown resistance to non-specific protein adsorption.23 This gives credence to the hypothesis that the formation of a hydration layer near the surface is a more general basis for protein resistance of PEGylated polymers than the steric repulsion mechanism that is usually invoked in the case of longer PEG chains. Jiang et al. argued this hypothesis by producing hyperbranched PEG-like structures on a silicon rubber and compared the anti-fouling properties with linear PEG grafts (Scheme 1-2).35 Both of the surfaces are expected to be highly hydrated due to the densely packed hydroxyl and ethylene glycol groups. It was found that linear PEG molecules were much more effective in preventing bacterial attachment than branched architectures. The strong steric repulsion generated by linear molecular arrangements was attributed to the better anti-fouling ability.
Scheme 1-2. PEG-like hyperbranched polymer with anti-fouling properties.

Meanwhile, Benhabbour et al. have investigated the protein adsorption on a PEGylated gold surface (HS-PEG$_{650}$-OH) modified by aliphatic polyesters with multiple peripheral OH groups.$^{36}$ Adsorption of both $^{125}$I-radiolabeled fibrinogen and lysozyme onto the dendronized surfaces showed that protein adsorption increases upon introduction of dendrons to the PEG functionalized surfaces. Furthermore, protein adsorption continued to increase with increasing dendron generation as shown in Figure 1-4. They have proposed that the PEG chain flexibility is the key factor in the mechanism of protein resistance. On the dendronized surface, the PEG chain flexibility was impeded by the intra- and intermolecular hydrogen bonding of the grafted dendrons.
**Figure 1-4.** Modified PEGylated gold surface with aliphatic polyester dendrons.

PEGylated polymers and OEG-terminated SAM are currently among the best protein resistant surfaces. Their long term stability in a biological environment is crucial for the practical application as anti-fouling coatings. However, those molecules containing ethylene glycol repeat units have hydrolytically unstable linkages in their backbones which can undergo oxidative decomposition and chain cleavage in the presence of oxygen and transition metal ions found in most biochemically relevant solutions. This significantly limits these materials for any practical application as marine anti-fouling coatings.
1.3.1.3 Zwitterionic Polymers

Inspired by the anti-fouling properties of blood cell membranes, polymers incorporating zwitterionic molecules, which are electrically neutral but carry formal positive and negative charges on different atoms such as phosphatidylcholines, have also been studied as anti-fouling surfaces.\(^{40,41}\) Polymethacrylates and polymethacrylamide with different pendant zwitterionic groups were synthesized by Kitano \textit{et al.} via controlled radical polymerization (Figure 1-5).

\[\text{Figure 1-5.} \text{ Anti-fouling polymers with zwitterionic side chains and disulfide groups for attachment to gold substrates.}\]

The resulting oligomers formed self-assembled monolayers, and when brushed on gold substrates they were found to resist non-specific adsorption of proteins.\(^{42}\) Using Raman spectroscopy and Attenuated Total Reflection Infrared spectroscopy (ATR-IR), it was determined that the surfaces of the zwitterionic polymers did not perturb the native hydrogen bonded network of water in the vicinity of surfaces.\(^{43,44}\) In contrast, the ionic groups and
counterions of polyelectrolytes, such as poly(sodium acrylate) and poly (sodium ethylenesulfonate), strongly perturbed the structure of water in their hydration shells.\textsuperscript{45,46} This led to the proposal that the existence of the native hydrogen bonded network of water near the surface is a necessary feature for anti-fouling properties of these surfaces.\textsuperscript{47}

Via atom transfer radical polymerization (ATRP), Jiang et al. prepared zwitterionic polymer brushes of sulfobetaine methacrylate (SBMA) and carboxybetaine methacrylate (CBMA) monomers from glass slides (Scheme 1-3).\textsuperscript{48} They found that the zwitterionic polymer brushes reduced fibrinogen adsorption to a comparable level of that on PEGylated surfaces. These surfaces also resisted adhesion of bovine aortic endothelial cells and prevented biofilm formation of Gram positive and Gram negative bacteria.\textsuperscript{49} The hydration of the charged groups on the zwitterionic materials was attributed to their anti-fouling characteristics.\textsuperscript{50}

\begin{center}
\textbf{Scheme 1-3} The process of surface grafting polyCBMA via ATRP from the silanized glass surface covered with initiators.
\end{center}
1.3.1.4 Polymer with Oligosaccharide Grafts

Surfaces coated with oligosaccharide grafted polymers mimic the anti-fouling properties of the cell surface glycocalyx, which provides a physical basis for maximizing entropic repulsion that minimizes nonspecific interactions of proteins and cells in the serum with the cell surface. Marchant et al. have designed and synthesized maltose dendrons, and further attached these materials to a poly(vinlyamine) backbone to create a non-adhesive glycocalyx-like saccharide coating over a biomaterial surface (Figure 1-6). Where R =

![Diagram](attachment:image.png)

*Figure 1-6. Dendritic saccharide polymers as anti-fouling materials.*
The resulting dendritic polymers were adsorbed onto octadecyltrichlorosilane-pretreated glass coverslips. The interfacial energy can be minimized with a significant reduction in contact angle from 105° on the neat silane-treated surface to 48° on the oligosaccharide grafted surface. The dendritic architecture enabled dense surface coverage by glycosylated molecules thus eliminating potential defect areas. This structure was observed to successfully suppress platelet adhesion. The steric barrier provided by the highly hydrated dendrons was thought to be responsible for the suppressed non-specific adsorption of plasma proteins.

1.3.1.5 Polyoxazoline Polymers

Polyoxazolines have received renewed interest as biomaterials. These hydrophilic and relatively non-toxic polymers are promising as anti-fouling coatings for biomedical applications. Konradi et al. have investigated the anti-fouling properties of comblike polymers with poly(2-methyl-2-oxazoline) side chains and a polycationic poly(L-lysine) backbone (Figure 1-7). These polymers were designed to be analogous to the PEG-based comb polymers previously investigated by Textor and coworkers. With an optimal side chain grafting density, the resulting adsorbed monolayers of the copolymer on metal oxide surfaces could eliminate protein adsorption from full human serum to below 2 ng/cm². Polyoxazolines also equaled the protein repellant properties of the best PEGylated coatings. However, these polymer coatings are formed on metal oxide surfaces via electro-static interactions and are thus prone to desorption at high salt concentration. Covalent attachment is preferred to overcome this limitation.
1.3.1.6 Block Copolymers with Amphiphilic Side Chains

Block copolymers possessing perfluoroalkyl tagged oligo(ethylene glycol) moieties as side chains (Figure 1-8) were synthesized and studied as anti-fouling coatings. Upon spray coating and annealing in air, X-ray adsorption studies indicated that the perfluoroalkyl terminated PEG block migrated to the non-polar air interface of the coating when exposed in air because of the low surface energy perfluoroalkyl groups. Further surface enrichment of the perfluoroalkyl terminated PEG block occurred when the coating was exposed to a polar environment like water resulting in a polymer-water interfacial energy of about 4 mJ/m². Such a molecular architecture readily allowed a dynamic switch in surface wettability. These surfaces, that combined the non-adhesive properties of hydrophobic fluoroalkyl groups with the anti-fouling characteristics of hydrophilic PEGylated groups, resulted in weak adhesion of Ulva and Navicula, low settlement density of barnacle larvae, and strong resistance to protein adsorption. A multistep reaction was involved in the synthesis of this block
copolymer. The relatively low yield makes it difficult to apply this material as a coating on a large scale. A bilayer coating strategy was applied to enhance the adhesion of this coating to a glass slide by using a polystyrene-poly(ethylene-butylene)-polystyrene block copolymer as the adhesive layer of coating. However, it should be noted that the immiscibility of the fluorinated blocks and the styrene blocks may weaken the adhesion force between the fluorinated coating and the block copolymer bottom coatings.

![Comblike block copolymer with amphiphilic side chains.](image)

**Figure 1-8.** Comblike block copolymer with amphiphilic side chains.

### 1.3.1.7 Hyperbranched Amphiphilic Fluoropolymers

Based on the hypothesis that nanoscale heterogeneities in topography will create a surface that is unfavorable for protein adsorption, Gudipati et al. have investigated surfaces of hyperbranched fluorinated polymers containing PEGylated groups.\(^6^1\) Coatings based on these hyperbranched amphiphilic polymers were covalently attached to glass slide substrates.
via thermal curing. At an optimal composition ratio of fluorophilic and hydrophilic monomers in the polymer, low protein adsorption and high fouling-release were achieved. The thermodynamically driven phase separation of the amphiphilic networks along with the so-called three-fold complexity (topography, morphology, and composition) is hypothesized to be responsible for the significant anti-fouling activity of these materials.

It is assumed that the small size of the heterogeneities is also an important factor to enhance the resistance of protein adsorption and marine organism adhesion. Based on this assumption, Powell et al. have recently optimized the synthesis of hyperbranched fluoropolymers via atom transfer radical polymerization of an inimer, a molecule possessing both a monomer group and an initiator functionality, as shown in Scheme 1-4. They proposed that a coating prepared using the resulting polymer would possess surface heterogeneities small enough in size to enhance resistance to protein adsorption and cell adhesion. While a heterogeneous surface is expected to provide a greater surface area for interaction with proteins, the design principle of hyperbranched amphiphilic polymer coatings is that the non-uniformity of surface characteristics would adversely affect the ability of a protein molecule to adsorb and unfold on the surface. However, definitive evidence for the fact that a nanoscale variation in surface topography and chemistry can impart superior resistance to protein adsorption is still lacking.
1.3.2 Fouling-release Coatings

Unlike anti-fouling coatings, fouling-release coatings do not need to inhibit the attachment and growth of fouling organisms on a surface. Instead, the accumulated fouling organisms can be released from fouling-release coating surfaces by hydrodynamic forces such as those generated on a ship hull by the ship moving through the water. In the 1970s, Baier et al. investigated the relationship of protein adhesion onto surfaces with varying surface energies. Their finding demonstrated that the relative protein adhesion decreased as the surface energy decreased, with the lowest data point of ~ 25 mN/m being the surface energy of a poly(dimethylsiloxane) (PDMS) elastomer. As the surface energy was further decreased to less than 25 mN/m, an increase in protein adhesion was observed for fluoropolymers such as poly(tetrafluoroethylene) (PTFE). However, this study took only
surface energy into account and ignored other factors such as modulus, surface roughness, coating thickness, chemical composition, and chain rearrangement. A similar study was performed by Brady et al. who investigated the combinatorial effect of a polymer’s critical surface tension ($\gamma_c$) and modulus (E) on relative adhesion. The experiment revealed the relative adhesion of pseudobarnacles (a proxy for barnacles) on these surfaces is related to $(\gamma_c E)^{1/2}$ (Figure 1-9). These findings thus suggest that a low modulus and low critical surface tension correspond to a lower adhesion. Recent research of polymeric surfaces as fouling-release coatings have been focused on synthetic flexible elastomeric materials such as silicon or fluorinated polymers because these materials possess low critical surface tension as well as low modulus.

Figure 1-9. Relative adhesion plotted as a function of $(\gamma_c E)^{1/2}$, where $\gamma_c$ and E are the critical surface energy and the elastic modulus, respectively, poly(tetrafluoroethylene (PTFE), poly(dimethylsiloxane) (PDMS), Poly(vinylidene fluoride) (PVDF), polyethylene (PE), polystyrene (PS), poly(methyl methacrylate) (PMMA), and Nylon-66.
1.3.2.1 Polysiloxane-based Polymers

One of the most popular non-toxic fouling-release coating materials is polysiloxanes. Polysiloxanes are very hydrophobic and possess low polarity, low glass transition temperature, low surface energy, and low modulus that all contribute to the effectiveness of these materials as fouling-release coatings. Because the initial attachment of marine organisms to a substrate is enhanced by hydrogen bonds formed by polar surface groups to these organisms, hydrophobic polysiloxane surfaces are ideal for fouling-release coatings. The adhesion of marine organisms onto polysiloxane surfaces is sufficiently weak, such that the attachment point can be broken by the weight of the fouling organisms, movement of a vessel through water, or via a water jet.

Silastic® T2 is a commercially available polysiloxane-based product by Dow Corning Corporation. It is a two-component material consisting of Silastic® T2 poly(dimethyl siloxane) resin and Silastic® T2 poly(methyl silane) curing agent. The Silastic® T2 coating can be easily obtained through a hydrosilation reaction by thermally curing the mixture of 10 parts by weight of resin and 1 part of curing agent under 50 °C for 5 h (Scheme 1-5). The silicone elastomer made from Silastic® T2 has low critical surface tension (~ 23 mN/m) and low Young’s modulus (2.47 MPa). With good fouling-release properties and low cost, coatings based on silicone have been widely used as a standard control material in biofouling evaluation processes. However, silicone elastomeric materials are not solvent resistant and consequently are easily swollen in many organic solvents resulting in coatings with poor mechanical strength and reduced operational time. There is a great need to improve the mechanical strength of silicones to obviate current problems with cutting, tearing, and
puncturing. Improvements are also needed in the chemistry of bonding silicones to ship hulls.\textsuperscript{77}

\begin{center}
\begin{minipage}{0.5\textwidth}
\begin{center}
\textbf{Scheme 1-5.} The curing of Silastic\textsuperscript{®} T2 by Dow Corning Corporation.
\end{center}
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\begin{center}
\begin{align}
A & \quad 50^\circ\text{C for 5 h, Pt} \\
& \quad A:B = 10:1 \text{ by weight}
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\subsection*{1.3.2.2 Fluorinated Polysiloxane Polymers}

Fluoropolymers are of great interest as fouling-release coatings because of their low critical surface tension and high flexibility.\textsuperscript{61,78} Intersleek\textsuperscript{®} 900 (International Paint Ltd.) is a commercially available fouling-release coating based on fluoropolymers. Despite the promise of Intersleek 900, very few samples of fluorinated polymers have been successfully commercialized as fouling-release coatings. However, the use of fluorinated additives is attractive to build up the mechanical strength of siloxane films. Incorporating fluorinated segments can serve to further decrease surface tension of the polysiloxane surface resulting in a surface with potentially better fouling-release properties. Furthermore, low energy fluorinated groups easily migrate to the surface of the silicone film due to their non-polar
character thus serving to further reduce surface tension.\textsuperscript{79} It is also possible to attain significant control of surface segregation or rearrangement according to different external environment, which is thought to be related to the fouling-release performance of materials.\textsuperscript{58,80} However, traditional fluorinated polymers are not well miscible with polysiloxanes and thus the amount of fluorinated additives in these systems must be kept very low in order to avoid phase separation and achieve homogeneous materials.\textsuperscript{81}

Weber \textit{et al.} produced three surfaces through crosslinking $\alpha,\omega$-bisepoxy-alkyl substituted fluorinated polysiloxanes.\textsuperscript{82} To understand the relationship between the chemical nature of polysiloxane coatings (e.g., surface tension, glass transition temperature ($T_g$), crosslinking chemistry) and fouling-release properties, the pendant groups of the siloxane backbone were varied in the degree of fluorination: $1H,1H,2H,2H$-perfluorooctyl (1), $3,3,3$-trifluoropropyl (2), and methyl (3) (Scheme 1-6). The polysiloxanes were then end capped with epoxy groups to increase the adhesion of the coating materials to the substrates. Both anti-fouling and fouling-release properties were evaluated on these films. \textbf{Film 1} demonstrated the lowest surface energy and superior anti-fouling resistance to barnacle \textit{Balanus Amphitrite} (hard foulers) compared to \textbf{Films 2 and 3}. However, the adhesion of barnacles to all three of the films was too high for removal without breakage from their baseplates. In addition, the three coatings did not inhibit settlement of \textit{Enteromorpha} spores or the growth of sporelings (soft foulers). The removal of spores was greatest from \textbf{Film 2} containing the $3',3',3'$-trifluoropropyl pendant groups though. The highest percentage of sporelings was released from the non-fluorinated surface of \textbf{Film 3} with methyl pendant groups, which possessed the highest $T_g$ and surface energy of the three coatings. Although \textbf{Films 1 and 2} have low surface energies, their $T_g$’s are high compared to that of PDMS (\textsuperscript{~}}
Therefore a reduction in the $T_g$ of the coatings produced superior fouling-release behaviors.

Scheme 1-6. Crosslinked films from $\alpha,\omega$-bisepoxy-alkyl substituted fluorinated oligosiloxanes.

1.3.2.3 Siloxane-Polyurethane Copolymers

To address issues related to poor mechanical properties and weak substrate adhesion of PDMS coatings, a series of linear and H-type siloxane-polyurethane block copolymers have been synthesized with a variable PDMS molecular weight and length of end-capped poly(ε-caprolactone) (PCL). The chemical structures of the synthetic PDMS-PCL block copolymers are shown in Figure 1-10. The polyurethane coatings were formulated using a trifunctional alcohol (polycaprolactone triol) and an isocyanurate. In marine biofouling assays, coatings prepared using hydroxyalkyl carbamate-terminated PDMS showed lower
adhesion of barnacles than those prepared using the dihydroxyalkyl carbamate-terminated PDMS. Low molecular weight PDMS showed a higher removal of soft fouling than high molecular weight PDMS but the opposite trend was seen in barnacle adhesion assays with the higher molecular weight PDMS resulting in greater removal.

![Formulation ingredients in a siloxane-polyurethane coating system.](image)

**Figure 1-10.** Formulation ingredients in a siloxane-polyurethane coating system.

### 1.3.2.4 Anti-fouling and Fouling-release Dual-functional Polymers

Polysiloxane-based elastomeric surfaces have been widely used in commercial fouling-release coating products. However, some marine organisms like diatoms (unicellular algae) show strong adhesion to PDMS, and it is well known that marine biofilms dominated by diatoms are not easily released from PDMS-based fouling-release coatings. As such, it is of interest to generate non-toxic polymeric coatings with an advanced ability to resist attachment of some ocean organisms while simultaneously showing weak adhesion force to the other attached organisms such that they can be easily removed.
Chio and coworkers developed a novel approach to obtain anti-fouling and fouling-release coatings based on dual-functional siloxane polymers. To incorporate anti-fouling characteristics into polysiloxane-based coatings while maintaining low or no environmental toxicity, methacrylate/acrylate modified trichosan, an organic biocide, was chemically bound to the polysiloxane matrix through a hydrosilation reaction (Figure 1-11). Static immersion tests were carried out and compared with the commercial product Intersleek® 425 (fouling-release coating) and Interspeed® BRA 642 (copper ablative anti-fouling coating). After 29 days of water immersion, the results showed that the test coatings based on acrylic trichosan reduced macrofouling and thus the performance was close to that of the copper ablative coatings. The average barnacle adhesion strength on these acrylic trichosan containing dual-functional polysiloxane coatings was comparable or slightly higher than the Intersleek® 425 control. It is not clear why the methacrylate trichosan containing coatings did not provide any benefit compared to either anti-fouling or fouling-release performance.

Figure 1-11. General structure of biocide-based dual functional silicone resin.
1.3.2.5 Xerogel Coatings

Sol-gel processed xerogel materials are readily prepared by the hydrolysis of metal or semimetal alkoxides with tunable surface characteristics, such as surface composition, surface area, and surface wettability. Sol-gel-derived xerogel films can be applied to surfaces by a variety of means including spraying, brushing, dip coating, and spin coating. Tang et al. investigated cell attachment and adhesion properties of xerogels with tailored wettability. These xerogels were prepared using alkoxyalkane precursors containing the non-polar n-propyl, n-octyl and 3,3,3-trifluoropropyl groups, as well as the polar ethylenediamine and methoxy groups (Figure 1-12).

![Figure 1-12. Precursors for sol-gel synthesis of fouling-release coatings.](image)

Coatings with the semifluorinated n-propyl group showed a higher settlement of both algal zoospores and barnacle cyprid larvae. Coatings incorporating the n-octyl group showed the highest removal of eight-day old Ulva sporelings. The fluorinated coatings showed only a moderate release of Ulva spores and sporelings (adult spores), lower than or similar to xerogels containing the n-propyl and n-octyl groups. In comparison to the previously introduced block copolymers with long semifluorinated side chains that showed good release
of green algae, the data from the fluorinated xerogel coatings suggests that relatively longer semifluorinated alkyl side chains may give better fouling-release performance.

1.3.2.6 Perfluoropolyether-based Coatings

Just like some of other coatings, fluoropolymers based coatings are relatively easily scratched or otherwise damaged by physical impact. As such, there is still a significant amount of space to improve the performance of fluoropolymers in this field. Recently, DeSimone et al. discovered a series of fouling-release coatings by using perfluoropolyether (PFPE)-based elastomers. This unique class of materials demonstrated flexibilities similar to that of PDMS because of low barriers to rotation of the flexible C-O bond, while offering the high chemical resistance and low surface energy of fluoropolymers via the C-C and C-F bonds. The combination of low surface energy and flexibility makes PFPE ideal candidates for fouling-release coatings. A large number of random terpolymers were synthesized with various monomers in order to isolate the various structure/property relationships for optimization in the application of fouling-release coatings (Figure 1-13). The terpolymer contained three monomers: an alkyl (meth)acrylate, glycidyl methacrylate, and methacryldiamide perfluoropolyether (PFPE) macromonomer. The variable alkyl moiety enables the $T_g$ of the materials to be tuned from -60 °C to 125 °C. This provides a means of isolating the effect of modulus and $T_g$ on the anti-fouling performance of the polymer. By varying the incorporated amount of the curable functional groups and curing conditions the relative effect of the crosslink density can be evaluated. Crosslinking also provides mechanical stability to the polymer matrix. The low surface tension induced by incorporating a PFPE macromonomer into polymer surfaces plays a critical role in the
material’s function as a fouling-release coating. The number of spores settled on test surfaces was less than on standards, being approximately 10% and 25% of glass and the PDMS elastomer Silastic® T2, respectively. Percentage removal from PFPE surfaces was greater than from the PDMS control after exposure to a wall shear stress of 53 Pa in a water channel.

Figure 1-13. Perfluoropolyether-based random terpolymers.
1.4 Alternative Approaches

1.4.1 Micro-engineered PDMS elastomeric Surfaces

In addition to various chemical approaches, surface topography has also been shown to play a role in mechanical defense against macrofouling on a larger scale.\textsuperscript{94} Settlement studies and field observations have led many researchers to conclude that the settlement of a wide range of cells \textsuperscript{95-97} and organisms including bacteria,\textsuperscript{98} algal spores,\textsuperscript{99-101} and invertebrate larvae\textsuperscript{102} is sensitive both to the size and periodicity of the surface topography. It has been demonstrated that \textit{Ulva} spores are very selective in settlement behavior on engineered PDMS microtopographies such as the Sharklet AF\textsuperscript{TM}, which is a patterned PDMS surface inspired by the skin of sharks, as seen in Figure 1-14a.\textsuperscript{103} The studies show that spores prefer to settle on surfaces that provide a topography with dimensions on the same order of the maximum width of the free swimming spore body, 5 \textmu m or greater.\textsuperscript{18} The topography effect was further studied by analyzing the effect of feature size, geometry, and roughness on spore settlement by testing a variety of engineered PDMS surfaces.\textsuperscript{66} The results showed uniform surfaces of either 2 \textmu m diameter circular pillars (Figure 1-14c) or 2 \textmu m wide ridges (Figure 1-14d) reduced settlement by 36\% and 31\%, respectively, compared to a standard flat PDMS surface. The largest reduction (77\%) in spore settlement was obtained with the Sharklet AF\textsuperscript{TM} topography (Figure 1-14a). While these surfaces studied demonstrated the anti-fouling potential of microtopographical surfaces, the underlying mechanism responsible for reduced fouling still remains unknown.
Figure 1-14. SEM images of engineered topographies on a PDMS elastomer surface. (a) 2 µm ribs of lengths 4, 8, 12, and 16 µm combined to create the Sharklet AF™; (b) 10 µm equilateral triangles combined with 2 µm diameter circular pillars; (c) hexagonally packed 2 µm diameter circular pillars; (d) 2 µm wide ridges separated by 2 µm wide channels.66

1.4.2 Ambiguous Alternative Monolayers

Previous studies indicate that marine organisms possess different settlement and adhesion behavior based upon the variable hydrophilicity of polymeric surfaces.34,104,105 For example, Ulva zoospores prefer to settle on hydrophobic surface compared to hydrophilic surfaces.104 However, the adhesion strength of settled spores is stronger on hydrophilic compared to hydrophobic surfaces15 (with the exception for OEG containing SAMs 65). The difference in settlement and adhesion has suggested the development of “ambiguous” surfaces which present both hydrophilic and hydrophobic domains to settle cells or organisms. In recent years, a number of novel coatings have been studied as anti-fouling/fouling-release coatings in which the surfaces undergo phase separation to create amphiphilic domains.58, 61, 106 However, it is difficult to control the size of a specific domain from the biofouling prevention point of view. The optimum design of ambiguously
segregated surfaces requires information regarding the scale at which settling cells and marine organisms detect hydrophilic or hydrophobic domains. By using photolithographic techniques, Ober et al. created micropatterns of alternating PEGylated and fluorinated monolayer (fluorooctatrichlorosilane) stripes of different widths on silicon surfaces (Figure 1-15). The response of zoospores to the combination of hydrophilic and hydrophobic domains was explored. For a strip width of 2 or 5 µm, the level of settlement on the patterned squares was low and similar to the pure PEGylated background. On the other hand, squares with strips above 5 µm had high levels of spore settlement, especially on fluorinated strips. The results imply that fluorinated strips of ≤ 5 µm were of insufficient size to attract spores. This technique allows for precise control of the size, geometry, and surface chemistry of the materials. The result of this investigation provides the first definitive evidence that marine organisms can discriminate between surface domains of different wettability and of a specific size.

Fluorooctatrichlorosilane (FOTS): F(CF$_2$)$_6$CH$_2$CH$_2$SiCl$_3$

Figure 1-15. Cartoon of micropatterns of alternating PEGylated and fluorinated monolayers stripes of variable widths on a silicon surface. $^{60}$
1.4.3 Nanoparticle/Polymer Composites

In order to improve the mechanical performance of polymeric coatings without impairing the anti-fouling and/or fouling-release performance, nanoparticles have been incorporated into polymer matrices to form nanoparticle/polymer composites.\textsuperscript{107} Wooley’s previous work has shown that the Young’s modulus was increased four-fold after incorporating 5 wt % of silica into a hyperbranched polymer matrix. In a related study by Nechers,\textsuperscript{108} instead of silica nanoparticles, acrylic-functionalized copper nanoparticles were chemically incorporated into a poly(phenoxylethyl acrylate) matrix to enhance the anti-fungal and anti-bacterial properties of the materials. The experimental results indicated the antimicrobial activity of acrylic-modified copper nanoparticles matches well with conventionally used biocides. If researchers can optimize the control on the release rate of copper nanoparticle biocides this strategy may show potential for the development of antibacterial paints and coatings to reduce biofouling on ship hulls. However, as stated previously, the possible toxicity associated with copper must be taken into account.

\begin{center}
\includegraphics[width=\textwidth]{Scheme1-7.png}
\end{center}

\textit{Scheme 1-7.} Preparation of acrylic functionalized copper nanoparticles.
1.5 Research Objectives

As a unique class of fluoropolymers, PFPE materials have been established as high performance materials, which combine low surface tensions (9 - 16 mN/m), tunable modulus, as well as excellent thermal and chemical stabilities with the practical ease of solventless processibility. The objective of this research involves the synthesis and physical characterization of PFPE-based materials and evaluation of these materials as fouling-release coatings to prevent biofouling on ship hulls. Chapter 2 explores structure-property relationships of a series of photochemically cured PFPE elastomeric materials, specifically the effect of variable molecular weight, crosslink density, and functional endgroup on controlling the materials’ physical properties such as phase separation, mechanical strength, surface tension, and the fouling-release potential. Chapter 3 builds on this work and utilizes low molecular weight PFPE’s to achieve amphiphilic networks through blending with hydrophilic PEG’s. A variety of composition ratios were used to form blends that range from optically transparent to opaque. Chapter 4 focuses on developing a new strategy to obtain mechanically durable PFPE network materials by synthesizing multifunctional PFPE macromonomer as well as incorporating a fluorinated crosslinker as filler to increase the modulus of photochemically crosslinked systems.
1.6 References


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Chapter 2

Synthesis and Characterization of Photochemically Crosslinked Perfluoropolyether-based Elastomers
2.1 Introduction

Tailored polymeric materials have been studied as leading candidates for marine anti-fouling/fouling-release coatings since the ban of traditional anti-fouling coatings containing tributyltin (TBT) in 2003.\textsuperscript{1} Most of the efforts to design environmentally benign fouling-release coatings have focused on improving polydimethylsiloxane (PDMS).\textsuperscript{2-6} Baier and Brady \textit{et al.} indicated that the relative adhesion on different polymeric surfaces decreased linearly with decreasing surface energy down to approximately 25 mN/m.\textsuperscript{7,8} Combining low modulus (2.4 MPa for fully cured Sylgard 184\textsuperscript{®}) with low critical surface tension (approximately 25 mN/m), flexible PDMS elastomers have proven to be promising fouling-release coating materials.\textsuperscript{7,9} Accumulated fouling organisms are readily ‘released’ from these coatings by hydrodynamic forces, such as those generated by a ship moving through the water. However, it is well known that PDMS is not compatible with many organic solvents and lipid-rich materials. As a result, PDMS coatings are prone to swelling that, lead to premature mechanical failure, severely limiting the use of these materials in many applications.\textsuperscript{10} Furthermore, PDMS-based fouling release coatings accumulate slime dominated by algal cells, which are not ‘released’ by the hydrodynamic conditions generated by the majority of vessels. Such slimes impose significant hydrodynamic drag on vessels moving through the water.

In an effort to address this concern, a number of researchers have made progress towards next-generation fouling-release coatings by investigating fluorinated polymeric materials. The incorporation of fluorinated groups into a polymeric matrix is very attractive due to their unique properties, such as chemical and thermal stability in various environments, as well as good weathering resistance, low surface tension, hydrophobicity and
Recent work by Wooley et al. has shown that a hyperbranched fluoropolymer matrix with crosslinked poly(ethylene glycol) (PEG) performed well as a fouling-release coating. A class of comb-like amphiphilic graft copolymers discovered by Ober et al. that are composed of PEGylated perfluoroalkyl side chains demonstrated low adhesion strength to both the green macroalga, Ulva and the slime-forming diatom, Navicula. Furthermore, a fluorinated silicone has been synthesized by Chaudhury et al. as a fouling-release coating with tunable release properties by reacting an allyl amide terminated perfluoropolyether oligomer with silicones via a platinum catalyzed hydrosilation reaction. This material has not been evaluated for its resistance to biofouling has not been tested yet, but fluorinated-silicone copolymer blends have recently been shown in laboratory assays to have improved fouling-release properties for both algae and barnacles compared to silicone alone. Early work by Yarborough et al. demonstrated the synthesis of a series of thermally crosslinkable perfluoropolyether (PFPE) graft terpolymers containing various alkyl (meth)acrylate monomers with glycidyl methacrylate as a cure-site monomer, showing promise as both fouling-resistant and fouling-release materials. While these fluorinated polymers showed improved biofouling performance as marine coatings compared to a standard PDMS elastomeric coating, most of them involved either multistep reactions or complicated surface modifications. More recently, the synthesis of functionalized PFPE’s was optimized via a photochemical crosslinking (UV curing) process with the practical ease of solventless processibility. The advantages offered by the UV curing technique are of great interest in coating operations because they do not require the use of solvents, can be complete in a few seconds, are energy efficient, and use simple equipment. This chapter describes the synthesis and characterization of a series of photochemically cured PFPE-based coatings.
elastomeric networks. In order to investigate the structure/property relationships, different functional endgroups such as methacrylate and styrene were used to modify the PFPE diol precursor of variable molecular weight to form crosslinkable difunctional PFPE macromonomers. A styrenyl PFPE/styrene sulfonic ester copolymer network (sPFPE-SS) was also prepared by photochemically crosslinking a blend of distyrenyl-modified PFPE (sPFPE) with a fluorinated derivative of a styrene sulfonic ester monomer (SS) to study its effect on the mechanical and surface properties. The properties of these materials including the thermal stability, glass transition temperature (T_g), modulus, contact angle, surface tension, and antifouling/fouling-release performance were systematically studied.

2.2 Experimental Section

2.2.1 Materials

The solvent 1,1,1,3,3-pentafluorobutane (Solkane 365 MFC) was purchased from Micro-Care and used as received. The 1 and 4 kg/mol PFPE diols (Fluorolink D10 and Fomblin ZDOL 4000, respectively) were purchased from Solvay Solexis. The 4-vinylbenzenesulfonyl chloride monomer was purchased from TCI America. All the other chemicals were purchased from Aldrich and used as received.

2.2.2 Synthesis of α,ω-dimethacrylate-modified Perfluoropolyether Macromonomer (PFPE-DMA)

The synthesis of the PFPE-DMA macromonomer has been reported previously. Briefly, telechelic PFPE diol (Fluorolink D10 or Fomblin ZDOL 4000) was first dissolved in 1,1,1,3,3-pentafluorobutane and allowed to react with a 1:2.05 molar ratio of 2-
isocyanatoethyl methacrylate (IEM) at 45 °C for 24 h, using 0.1 wt % tetrabutyltin diacetate (DBTDA) as a catalyst. The solution was then passed through a chromatographic column filled with alumina (2 x 10 cm). The photo initiator, α-hydroxycyclohexyl phenylketone (HCPK, 0.2 wt %), was added and the solvent was subsequently removed by rotovaporation. The product was filtered through a 0.2 micron filter to yield a clear, colorless, viscous oil. To obtain the chain extended 2 x 4 and 3 x 4 kg/mol PFPE-DMA macromonomers, the 4 kg/mol PFPE diol was first reacted with isophorone diisocyanate (IPDI) in a proper stoichiometry to yield the chain extended PFPE diols.\textsuperscript{20} The compound with diol endgroups were then modified with IEM to form the dimethacrylate reactive macromonomers as described above.

2.2.3 Synthesis of α, ω-distyrenyl-modified Perfluoropolyether Macromonomers (sPFPE)

The sPFPE was synthesized by the following procedure.\textsuperscript{21} In a typical synthesis, 30 grams of the 4 kg/mol PFPE diol (7.89 mmol) and 1.5 grams of tetrabutylammonium hydrogen sulfate (4.42 mmol) were first dissolved in 60 mL of 1,1,1,3,3-pentafluorobutane. Potassium hydroxide (15 g, 0.27 mol) dissolved in 30 mL of deionized water was then added under stirring, which was followed by the addition of 3 mL of 4-vinyl benzyl chloride (19.2 mmol). The yellow mixture was reacted under vigorous stirring at 45 °C for 48 h. After filtering out the brown solids, the product was washed with deionized water three times and then decolorized by stirring activated carbon overnight. After filtering out the activated carbon with a 0.2 micron filter, evaporation of the solvent yielded a clear, colorless, viscous oil.
2.2.4 **Synthesis of Fluorinated Styrene Sulfonic Ester Monomer (SS)**

In order to make styrene sulfonic ester compatible with sPFPE, a fluorinated tail was added to 4-vinylbenzenesulfonyl chloride. To a 150 mL round-bottom flask, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol (13.66 g, 37.5 mmol), triethylamine (10 mL), pyridine (20 mL), and 4-vinylbenzenesulfonyl chloride (7.6 g, 37.5 mmol) were added. The resulting slurry was stirred at room temperature for 20 h under argon flow. The reaction mixture was then poured into a dilute hydrochloric acid ice bath to quench triethylamine and pyridine. The aqueous solution was extracted with diethyl ether three times and the combined ether layer was washed sequentially with water, 10% NaOH solution, and 10% NaCl solution. The ether solution was then dried over MgSO$_4$ for 1 h. After removing MgSO$_4$ and solvent, the dry product was recovered as a waxy light yellow solid.

2.2.5 **Photocure of PFPE Precursors**

In a typical cure, 0.2 wt % of HCPK was first added to the PFPE macromonomers. The elastomeric films were formed by casting the PFPE macromonomers over a silicon wafer followed by UV irradiation (Electronlite UV curing chamber model No. 81432-ELC-500, $\lambda = 365$ nm) under nitrogen purge for 5 min ($\sim 38,000$ mJ/cm$^2$). To fabricate the sPFPE-SS copolymer network, the 4 kg/mol sPFPE macromonomer with 0.2 wt % of HCPK and the fluorinated styrene sulfonic precursor were mixed in the desired weight ratio (10% fluorinated styrene sulfonic ester in this study). The mixture was first heated above 40 °C to form a homogeneous solution, which was then photochemically cured as described previously.
2.2.6 Characterization

2.2.6.1 Thermal Analysis

The thermal stability of the cured PFPE elastomers was investigated with a Perkin-
Elmer Pyris I thermogravimetric analyzer (TGA). Fully cured films were first pre-
dehydrated in a vacuum oven at 110 °C overnight to remove any residual moisture and then
heated from 25 °C to 600 °C in a nitrogen atmosphere with a heating rate of 10 °C/min. The
temperature at 5% weight loss was defined as the decomposition temperature. Differential
scanning calorimetry (DSC) curves were recorded on a Seiko DSC 220 in the temperature
range from -150 °C to 100 °C, at a scanning rate of 10 °C/min. Dynamic mechanical thermal
analysis (DMTA) was performed using a PerkinElmer Pyris Diamond DMA 6100 at a fixed
frequency of 1 Hz in tension mode. The program temperature was varied from -150 °C to
150 °C with a heating rate of 2 °C/min.

2.2.6.2 Small Angle X-ray Scattering

The small angle X-ray scattering (SAXS) instrument (Anton Paar) at the University
of Minnesota was utilized to probe the microstructure in the fully cured PFPE elastomeric
films. The film was placed in a copper sample holder and the scattering was measured at
room temperature for 5 min operating at 40 kV and 50 mA. The scattering signals were not
corrected for instrumental broadening caused by the line-collimated incident beam, but were
integrated into a 1D plot of intensity versus the scattering vector, q. Finally, the scattering
intensity was normalized with respect to the incident beam intensity.
2.2.6.3 Mechanical Analysis

Stress-strain measurements were performed using rectangular samples (1 x 10 x 20 mm) at room temperature on an Instron model 5566 system using a 10 kN load cell at a crosshead speed of 5 mm/min. An extensiometer of 15 mm gauge length was used to measure the strain accurately. From the stress-strain curves, the Young’s modulus was calculated. Four replicates were performed for each sample.

2.2.6.4 Control of Relative Humidity at the Time of Cure

To control the humidity in the UV cure oven, a humidified nitrogen stream was used to purge the chamber environment while curing. The nitrogen stream was humidified by first passing the gas through a bubbler containing LiCl aqueous solutions at varying concentrations.\(^{22}\) Humidity of 19%, 42%, 58%, and 76% were generated by this method. A 100% humidity environment was induced by passing nitrogen stream through a bubbler containing deionized water. The 0% relative humidity environment was obtained by passing the nitrogen stream through a Drierite\(^{\circledR}\) desiccant tube that was pre-baked in a heating oven at 110 °C for 24 h and all connecting tubes were pre-dried in a vacuum oven for 24 h. A digital humidity meter was placed at the nitrogen outlet of the UV oven to monitor the real time humidity during the entire curing process. Once the desired humidity inside the UV chamber was reached, typically in 15 - 20 min of purging, the samples were then cured by UV irradiation for 10 min under continuous nitrogen stream.

2.2.6.5 Surface Analysis

Dynamic tensiometry measurements were performed on a NIMA Technologies DST 9005 dynamic surface tensiometer. PFPE thin films on glass coverslips measuring 22 x 22 x 0.1 mm were formed by dip-coating the coverslips in the pure PFPE liquid precursors
followed by UV irradiation as previously described. The dynamic contact angle was measured by the Wilhelmy plate method. Typically, a PFPE dip-coated glass coverslip was attached to an electrobalance via a clip and a stage with a dish of pure solvent (water) was automatically raised and lowered to allow the solvent to impinge upon the slide at a speed of 5 mm/min. The advancing and receding contact angles were recorded when the samples were immersed into and departing from the solvent, respectively. All the results were expressed as the average value of at least four independent measurements. Through analysis of the resulting force vs. depth curves, the advancing and receding contact angles as well as the dynamic contact angle hysteresis were obtained when samples were immersed into and departing from the solvent respectively. The static contact angles of n-alcohols and n-alkanes on the surfaces were measured using a KSV Instruments LCD CAM 200 optical contact angle meter at room temperature (23 °C) to calculate the critical surface tension from the Zisman method. In the Owens-Wendt-Kaelble (OWK) method, the water and hexadecane were used as polar and non-polar probe liquids, respectively.

2.2.6.6 Sample Preparation for Biofouling Evaluation

Free standing samples with a thickness of ~ 1 mm were achieved by casting the PFPE precursors containing 0.2 wt % of HCPK over a silicon wafer followed by UV irradiation under nitrogen for 5 min. To remove any unpolymerized monomers, which if present may have been toxic to the organism used in the bioassays, the samples were continuously extracted by utilizing supercritical CO₂ under 5000 psi and 50 °C for 4 h. The marine anti-fouling and fouling-release properties of these samples were then evaluated by settlement and release assays involving zoospores and sporelings (young plants), respectively, of green
fouling alga *Ulva*, through collaboration with Professor Maureen Callow at the University of Birmingham (UK).

2.3 Results and Discussion

It is attractive to study the structure/property relationship of fluorinated polymers to create the next generation of environmentally friendly anti-fouling/fouling-release coatings in a variety of applications ranging from ship hull coatings to long in-dwelling medical devices. To determine the effect of chemical structure on the fouling-release performance, telechelic PFPE diols were modified with polymerizable methacrylate endgroups via a reaction between the hydroxyl endgroups and isocyanatoethyl methacrylate to form urethane linkages (Scheme 2-1). To study the effect of crosslink density on the surface and bulk properties of the formed elastomers, PFPE diols with longer chain were formed via a chain extension reaction of the 4 kg/mol PFPE diol with isophorone diisocyanate (IPDI) in a proper stoichiometry. The resulting chain extended PFPE diols were then further modified with methacrylate endgroups to form photochemically curable precursors. As seen in Scheme 2-2, the 2 x and 3 x 4 kg/mol PFPE-DMA macromonomers were obtained by initially setting the molar ratio of PFPE diol to IPDI to 2:1 and 3:2, respectively. The effect of the functional endgroup structure was studied by forming the 4 kg/mol distyrenyl-modified PFPE precursors (4 kg/mol sPFPE) as seen in Scheme 2-3. To further explore the effect of styrene on the properties of materials, a fluorinated styrene sulfonic ester (SS) was mixed with the sPFPE precursor to form a homogenous sPFPE-SS solution with heating up to 45 °C. All of the obtained PFPE macromonomers could be photochemically cured to form elastomeric films under UV irradiation in one step.
Scheme 2-1. Synthesis of dimethacrylate-modified PFPE networks (1 or 4 kg/mol PFPE-DMA).
Scheme 2-2. Synthesis of 2 x chain extended dimethacrylate-modified PFPE network (2 x 4 kg/mol PFPE-DMA).
Scheme 2-3. Synthesis of distyrenyl-modified PFPE network (4 kg/mol sPFPE) and its copolymer network with fluorinated styrene sulfonic ester (sPFPE-SS).

2.3.1 Thermal Stability

It is well known that PFPE exhibit exceptionally high chemical and thermal stabilities imparted by the strong C-F and C-C bonds and shielding of the polymer backbone by the sheath of nonbonding electrons from the fluorine atoms. The thermal stability of all of the fully cured PFPE films was investigated by TGA with a heating rate of 10 °C/min under a
nitrogen atmosphere. As shown in Figure 2-1, all of the samples maintained consistent weights up to 250 °C.

**Figure 2-1.** TGA curves of fully cured PFPE films.

The 4 kg/mol PFPE-based elastomeric materials (4 kg/mol PFPE-DMA, 4 kg/mol sPFPE, and 10% sPFPE-SS) were observed to have higher decomposition temperatures (defined as the 5% weight loss) than the 1 kg/mol PFPE-DMA and the chain extended PFPE-DMA samples. For example, a decomposition temperature of 333 °C for the 4 kg/mol PFPE-DMA and 350 °C for the 4 kg/mol sPFPE-SS sample were recorded while the 1 kg/mol PFPE-DMA has a lower decomposition temperature of 274 °C as shown in Table 2-1. For the chain extended PFPE-DMAs, the temperature was observed to decreased from 333 °C for the non-chain extended 4 kg/mol PFPE-DMA, to 306 °C for the 2 x 4 kg/mol PFPE-DMA chain extended sample, to 283 °C for the 3 x 4 kg/mol PFPE-DMA sample. This loss in
thermal stability is likely due to the breaking of the urethane linkage units between the 4 kg/mol PFPE segments.

<table>
<thead>
<tr>
<th>Decomposition Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 kg/mol PFPE-DMA</td>
</tr>
<tr>
<td>4 kg/mol PFPE-DMA</td>
</tr>
<tr>
<td>2 x 4 kg/mol PFPE-DMA</td>
</tr>
<tr>
<td>3 x 4 kg/mol PFPE-DMA</td>
</tr>
<tr>
<td>4 kg/mol sPFPE</td>
</tr>
<tr>
<td>10% sPFPE-SS</td>
</tr>
</tbody>
</table>

Table 2-1. Decomposition temperature of cured PFPE samples.

2.3.2 Glass Transition Temperatures

The DSC curves of the fully cured PFPE samples are plotted in Figure 2-2. Two glass transition temperatures ($T_g$’s) were generally found. A similar result was previously observed by Malucelli et al. for a related system. The first glass transition ($T_{g1}$) at approximately 0 °C is believed to be related to the hydrocarbon domains from the polymerized methacrylate endgroups of the PFPE networks and the second glass transition ($T_{g2}$) at approximately -116 °C, corresponds to the fluorocarbon moieties. Without the urethane linkage groups in the polymer matrix, the $T_{g1}$ of the cured 4 kg/mol sPFPE sample is slightly lower than that of the PFPE-DMA samples presumably due to a decreased physical crosslinking formed by hydrogen bonds, which results in a higher chain mobility for the sPFPE chains. Compared to that of the 4 kg/mol sPFPE sample, a low content (10%) of the fluorinated styrene sulfonic ester monomer in the sPFPE-SS copolymer sample shows no
significant effect on the $T_g$ from the DSC profile. The detailed $T_g$ information of the studied PFPE samples has been summarized in Table 2-2.

![DSC spectra of fully cured PFPE films.](image)

**Figure 2-2.** DSC spectra of fully cured PFPE films.

Due to the high crosslink density, it is difficult to obtain the $T_g$ information for the 1 kg/mol PFPE-DMA by using DSC. However, detailed information can be collected by using the more sensitive DMTA as shown in Figure 2-3. Two $T_g$'s were clearly observed for the 1 kg/mol PFPE-DMA sample. A pronounced $T_{g1}$, at 54.5 °C, was assigned to the methacrylate crosslinking endgroups of the PFPE domains and a secondary relaxation ($T_{g2}$) at -80.4 °C was assigned to the PFPE domains of the main chains located away from the crosslinks. It is surprising to find that the DMTA trace of the higher molecular weight 4 kg/mol PFPE-DMA sample is very different from that of the 1 kg/mol PFPE-DMA sample. The $T_{g1}$ for the
crosslinked methacrylate endgroups of the 4 kg/mol PFPE-DMA sample was shifted down by almost 25 °C compared to the 1 kg/mol PFPE-DMA samples from 54.5 °C to 30 °C. Additionally, the predominant peak for $T_{g2}$ at -130.1 °C, assigned to the PFPE segments between the crosslinked methacrylate endgroups is almost 50 °C lower than that of the 1 kg/mol PFPE-DMA sample. Interestingly, the activity for the hydrocarbon domains is much weaker compared with the PFPE moieties due to the decreased concentration of methacrylate endgroups.

![Figure 2-3. DMTA spectra of fully cured PFPE films.](image)

For the chain extended PFPE-DMA samples, the predominant $T_{g2}$ peak for the PFPE segments remained unchanged at approximately -131 °C while the $T_{g1}$ for the hydrocarbon domains gradually shifted to -35.8 °C as the molecular weight was increased. This indicates that the short urethane ether methacrylate segments possess a relatively higher mobility in the
less crosslinked PFPE matrix. A single T_g at -132 °C was clearly observed as the relaxation of the PFPE moieties for the 4 kg/mol sPFPE-based samples. Instead of a peak corresponding to the hydrocarbon domains in the higher temperature region, a broad signal for the 4 kg/mol sPFPE and 10% sPFPE-SS samples was observed making it difficult to define the peak maxima.

<table>
<thead>
<tr>
<th></th>
<th>DSC (°C)</th>
<th>DMTA (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T_g2</td>
<td>T_g1</td>
</tr>
<tr>
<td>1 kg/mol PFPE-DMA</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>4 kg/mol PFPE-DMA</td>
<td>-115.3</td>
<td>0</td>
</tr>
<tr>
<td>2 x 4 kg/mol PFPE-DMA</td>
<td>-116.0</td>
<td>6.6</td>
</tr>
<tr>
<td>3 x 4 kg/mol PFPE-DMA</td>
<td>-116.3</td>
<td>n/a</td>
</tr>
<tr>
<td>4 kg/mol sPFPE</td>
<td>-116.7</td>
<td>-7.6</td>
</tr>
<tr>
<td>10% sPFPE-SS</td>
<td>-116.5</td>
<td>-6.8</td>
</tr>
</tbody>
</table>

Table 2-2. Glass transition temperatures determined by DSC and DMTA.

2.3.3 Morphology by Small Angle X-ray Scattering

The two T_g's in the thermal analysis are consistent with nanophase separation of the optically transparent PFPE networks. SAXS experiments were performed to determine the average domain size in these crosslinked samples (Figure 2-4). As reported previously, a single broad peak was observed for the 1 kg/mol PFPE-DMA sample and was attributed to nanophase separated domains of PFPE and the polymerized methacrylate endgroups. From the position of the peak in scattering intensity, a principal domain size (D) associated with aliphatic methacrylate endgroups and the PFPE domains of about 3.3 nm was calculated.
using $D = 2\pi/q$, where $q$ is the principal scattering vector. The peak in scattering intensity shifted to a lower value of $q$ for the 4 kg/mol PFPE-DMA sample, indicating a slightly larger domain size of 5.2 nm. The increased average size between the polymerized methacrylate endgroups and the PFPE domains is consistent with the increased chain length in the 4 kg/mol PFPE-DMA sample.

![Figure 2-4](image.png)

**Figure 2-4.** 1D SAXS data for fully cured PFPE samples. All of the data was acquired on the same instrument over a 2 hour time period and have not been shifted on the y-axis.

Interestingly, $q$ for the chain extended PFPE-DMA samples was essentially the same as the 4 kg/mol PFPE-DMA sample. This may be the result of either self-aggregation of the fluorophobic isophorone diisocyanate moieties or aggregation of these mid-chain moieties with the polymerized methacrylate endgroups. In both of these cases, it is expected that the observed domain size would be comparable to that of the 4 kg/mol PFPE-DMA sample.
Aggregation of the isophorone diisocyanate units and the polymerized methacrylate endgroups is consistent with the observed $T_g$’s for the chain extended PFPE-DMA samples, in which $T_{g2}$ was unchanged while $T_{g1}$, corresponding to aliphatic endgroups, varied dramatically. Additionally, a domain size of 4.8 nm was found in the 4 kg/mol sPFPE sample with styrene endgroups. Similarly, the domain size of the 10% sPFPE-SS sample was approximately 5.7 nm, likely due to the domain swelling upon addition of the styrene sulfonic ester.

### 2.3.4 Young’s Modulus

As stated previously, it is often desirable to tune the modulus to fit the materials to various applications. In this study, control over the modulus of the cured materials was induced by varying molecular weights and functional endgroups. The higher molecular weight PFPE macromonomers will result in crosslinked networks with lower crosslink densities upon UV curing. Additionally, strong hydrogen bond associations between the urethane groups of individual PFPE chains were thought to increase the intermolecular interactions and further enhance the mechanical strength of the crosslinked networks. The modulus was determined by the slope of the initial linear region (~ 2% elongation) of the stress-strain curve in Figure 2-5.

The modulus for the 1 kg/mol PFPE-DMA sample is 90 MPa. As the molecular weight of the PFPE-DMA samples was increased, the modulus of the resulting film was gradually decreased due to the decreased chemical and physical crosslink density. Specifically, for the highest molecular weight sample, 3 x 4 kg/mol PFPE-DMA, the modulus was only 1.5 MPa. The modulus of this system is tunable between 1.5 - 90 MPa through the curing of blends of
the different macromonomers at variable composition ratios. For example, the cured 50:50 by weight blend of the 1 kg/mol and 4 kg/mol PFPE-DMAs had a modulus of 34 MPa. It is interesting that the modulus of this system can be varied while the thermal, optical, and surface properties remain similar because all of the components of the blends have similar chemical structures. Without the urethane linkage groups in the cured PFPE matrix to form strong hydrogen bonds, the modulus of the 4 kg/mol sPFPE sample is much lower compared to that of the 4 kg/mol PFPE-DMA sample. By incorporating 10 wt % of the rigid styrene sulfonic ester monomer (SS) into the 4 kg/mol sPFPE matrix, the modulus of resulting copolymer network was slightly increased from 2.2 to 2.6 MPa, however, it is still much lower than the 4 kg/mol PFPE-DMA sample.

![Figure 2-5. Stress-strains curves of fully cured PFPE networks by Instron.](image)
2.3.5 Contact Angle Hysteresis

The performance of coating materials is often dictated by surface and interfacial properties such as wettability and adhesion. The contact angle and the surface tension are determined by the competition of these two factors. In this study, the advancing and receding contact angles at the air interfaces of the samples were measured by the Wilhelmy plate method. The dynamic contact angle hysteresis curves for all of the PFPE-DMAs were recorded by a tensiometer, as seen in Figure 2-6 with the contact angle as a function of immersion depth. The results indicate that all of the PFPE-based surfaces are highly hydrophobic with a water advancing contact angle greater than 110° and a receding contact angle from 76° to 38°. This large difference in the advancing and receding contact angles subsequently led to a large contact angle hysteresis.

![Dynamic contact angle hysteresis curves of PFPE-DMA surfaces given by Dynamic Surface Tensiometry (DST).](image)

**Figure 2-6.** Dynamic contact angle hysteresis curves of PFPE-DMA surfaces given by Dynamic Surface Tensiometry (DST).
The dynamic contact angle values are summarized in Table 2-3. For the series of PFPE-DMA samples, as the molecular weight increased, i.e., the crosslink density decreased, the advancing contact angles slightly increased, from 117° for the 1 kg/mol PFPE-DMA sample to 126° for the 3 x 4 kg/mol PFPE-DMA sample. Simultaneously, the receding contact angles dramatically decreased from 76° to 39°. As a result, it caused a huge disparity on the contact angle hysteresis. Specifically, the contact angle hysteresis is only 39° for the 1 kg/mol PFPE-DMA surface while it increased to 56° for the 4 kg/mol PFPE-DMA sample which possesses a decreased crosslink density. The contact angle hysteresis increased to 74° for the 2 x 4 kg/mol PFPE-DMA sample with an even lower crosslink density and further increased to 81° for the 3 x 4 kg/mol PFPE-DMA sample. According to the literature, the main factors contributing to contact angle hysteresis can be the surface roughness, swelling of the studied surface, and surface reorganization. It is known that PFPE is very chemically stable with a negligible water uptake of less than 1% after 2 weeks soaking in water. Our previous studies also indicated that all of the PFPE surfaces cured in this manner were ultra-flat with a surface roughness less than 1 nm. The most plausible contribution to the hysteresis in this system is therefore from the surface group rearrangement.

The dynamic contact angle hysteresis can be explained through a series of reversible, short-range interactions of the polar segments in the polymer backbone with water on the surface. The high advancing contact angles are observed as water comes in contact with the fluorocarbon dominant polymer-air interface. Once the surface is wetted, the polymer will reorganize the interface by rotating or relaxing the polar hydrophilic functionalities such as the urethane groups in the endgroups of the PFPE chains to interact with water, which can be accomplished by both forming hydrogen bonds and enhancing the dispersion interaction with
water. Additionally, the hydrogen atoms of the –CF_{2}CH_{2}O- units adjacent to the PFPE segments are acidic which allows for them to participate in similar polar interactions. Thus, the interaction of these functionalities with water would be favored, allowing the liquid molecules to penetrate and further facilitating the migration of the polar groups towards the interface. A low receding contact angle is an indication of significant surface reorganization, which results in high contact angle hysteresis.\textsuperscript{16} Compared with the chain extended PFPE-DMA samples, the lower molecular weight 1 or 4 kg/mol PFPE-DMA samples have a relatively higher crosslink density. The polymer chains were highly constrained thus making the chain rotation or reorganization on the surface of any polar moieties such as the oxygen and the urethane groups very difficult. The mobility of the polymerized polar urethane ether methacrylate endgroups of the PFPE samples was indicated by the corresponding glass transition temperature (T\textsubscript{g1}). As seen in Table 2-2, the 1 kg/mol PFPE-DMA sample possesses a higher T\textsubscript{g1} (54.5 °C) compared to all of the other PFPE-DMA samples. It suggests the polymerized polar endgroups are constrained and possess a low mobility and making it difficult for the segments to initiate the short-range relaxation and rotation needed to reorganize the surface. As a result, the material has a smaller contact angle hysteresis.

<table>
<thead>
<tr>
<th></th>
<th>Advancing (θ\textsubscript{adv})</th>
<th>Receding (θ\textsubscript{rec})</th>
<th>Hysteresis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 kg/mol PFPE-DMA</td>
<td>117.4 ± 0.8</td>
<td>76.0 ± 1.0</td>
<td>38.9</td>
</tr>
<tr>
<td>4 kg/mol PFPE-DMA</td>
<td>120.4 ± 0.5</td>
<td>64.6 ± 1.1</td>
<td>55.8</td>
</tr>
<tr>
<td>2 x 4 kg/mol PFPE-DMA</td>
<td>121.6 ± 0.5</td>
<td>47.5 ± 4.4</td>
<td>74.1</td>
</tr>
<tr>
<td>3 x 4 kg/mol PFPE-DMA</td>
<td>126.6 ± 1.5</td>
<td>38.6 ± 2.9</td>
<td>80.6</td>
</tr>
</tbody>
</table>

\textbf{Table 2-3.} Dynamic contact angle and contact angle hysteresis.
2.3.6 Effect of Humidity on Contact Angle Hysteresis

Besides the crosslink density, the impact of the relative humidity during the curing on the contact angle hysteresis was also investigated. Previous studies have shown the adsorption of the water on the PFPE surface improves the mobility of the PFPE molecules.\textsuperscript{31} But it not clear whether the relative humidity during the curing step has an effect on the enrichment of polar groups to the PFPE/air interface resulting in a large contact angle hysteresis. To this end, a humid environment inside the UV chamber was induced by passing a nitrogen purge stream through a bubbler containing LiCl solution at desired concentrations.\textsuperscript{22} The contact angle hysteresis was compared on the fully cured systems of the 1 kg/mol PFPE-DMA and the 2 x 4 kg/mol PFPE-DMA films.

As shown in Figure 2-7, the data was plotted as the relationship of the contact angle hysteresis with the relative humidity. The hysteresis was seen to increase as the relative humidity was increased. This result supports the previous hypothesis that as the humidity in the chamber is increased, more polar groups migrate to the PFPE surface and are locked into place during UV curing. This process would facilitate the penetration of water into the PFPE surface, resulting in a further increase in the contact angle hysteresis. Specifically, in this study the hysteresis was increased from 33° to 46° for the 1 kg/mol PFPE-DMA sample and from 78° to 86° for the 2 x 4 kg/mol PFPE-DMA sample. A large disparity in hysteresis as a function of humidity has not been observed on these photochemically cured PFPE surfaces, compared with those previously reported for thermally cured PFPE terpolymer surfaces, which consisted of more polar acrylate and epoxide moieties containing monomers. An increase of up to 40° in the hysteresis was observed by varying the relative humidity from 0% to approximately 100%.\textsuperscript{16} The increase observed here for both PFPE-DMAs is
approximately 10°. This smaller change in hysteresis is thought to be a result of the limited number of polar groups present in these perfluorinated polymers and the high crosslink density, which effectively constrains the chain rotation and reorganization by immobilizing the chains during the curing step.

![Graph showing contact angle hysteresis observations on PFPE surfaces cured under variable humidity environments.](image)

**Figure 2-7.** Contact angle hysteresis observations on PFPE surfaces cured under variable humidity environments.

### 2.3.7 Surface Tension

The critical surface tensions of the studied PFPE surfaces were quantified via Zisman method by measuring static contact angles of a series of n-alcohols on the fully cured PFPE surfaces. Based on the linear relationship between \( \cos \theta \) (\( \theta \), the static contact angle) and the corresponding surface tension of the probe solvent, the critical surface tension was calculated for each PFPE surface by extrapolation of the linear line to \( \cos \theta = 1 \), which ranges from 8.6 to 16 mN/m as shown in Table 2-4. The results are in good agreement with
previously reported PFPE-urethane crosslinked networks (13 - 16 mN/m),\textsuperscript{34} however, as
dynamic surfaces, it is difficult to obtain the accurate critical surface tension values for the
PFPE materials because the surfaces easily undergo environment-dependent surface
reorganization.\textsuperscript{35} As a result of the surface reorganization, the surface hydrophilicity and
hence the critical surface tension may change when probe liquids of variable polarity are
used. To study the effect of the polarity of the probe solvent on the critical surface tension,
the critical surface tension was recalculated based on the Zisman plot using less polar alkanes
as probe liquids. The surface tension values are summarized in Table 2-4 and compared to
the values obtained from the polar alcohols. Generally, the critical surface tensions show a
similar trend on these surfaces when two different series of probe liquids was used. However,
the critical surface tension obtained from the hydrophobic alkane probe liquids is lower than
that obtained from the more polar alcohol probe liquids on the same surface, except for the 4
kg/mol PFPE-DMA surfaces. This is likely attributed to the fact that the polar alcohols are
more effective at driving the PFPE surface reorganization by forming hydrogen bonds or
dipolar interactions with the polar segments in the PFPE such as the oxygen and urethane
groups at the uppermost surface.

To distinguish the contribution of the different interaction components to the surface
tension such as the van der Waals dispersive forces, dipole interactions, hydrogen bonds, etc.,
Owens, Wendt, and Kaelble (OWK) defined the solid surface tension ($\gamma_s$) as the sum of the
dispersion component ($\gamma^d_s$) and the polar component ($\gamma^p_s$) and combined it with the Young’s
equation to yield\textsuperscript{36,37}

$$\gamma_L = \frac{2\left(\gamma^d_s \gamma^d_l\right)^{1/2} + \left(\gamma^p_s \gamma^p_l\right)^{1/2}}{1 + \cos \theta}$$

(1)
Where $\theta$ is the static contact angle; $\gamma_L$ is the surface tension of a probe liquid; $\gamma_L^d$ and $\gamma_L^p$ are the dispersion component and the polar component of the liquid surface tension, respectively.

By measuring the contact angles of two different probe liquids (one polar and one non-polar) on each surface, the overall solid surface tension can be calculated based on the equation. In this study, the water and n-hexadecane were used as the polar and non-polar probe liquids, which are $\gamma_L^d = 27.6$ mN/m, $\gamma_L^p = 0$ mN/m for n-hexadecane and $\gamma_L^d = 21.8$ mN/m, $\gamma_L^p = 51.0$ mN/m for water, respectively. The surface tensions calculated from the OWK method are listed in Table 2-4. The overall surface tensions are seen to be 13 - 14 mN/m for all tested PFPE surfaces expect that the 1 kg/mol PFPE-DMA has a relatively higher surface tension of 16.3 mN/m. These results are in reasonable agreement with those given by the Zisman method.

<table>
<thead>
<tr>
<th>Critical Surface Tension $^a$ (mN/m)</th>
<th>Surface Tension $^b$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohols</td>
<td>Alkanes</td>
</tr>
<tr>
<td>1 kg/mol PFPE-DMA</td>
<td>14.5 ± 1.6</td>
</tr>
<tr>
<td>4 kg/mol PFPE-DMA</td>
<td>8.6 ± 1.5</td>
</tr>
<tr>
<td>2 x 4 kg/mol PFPE-DMA</td>
<td>15.4 ± 0.7</td>
</tr>
<tr>
<td>3 x 4 kg/mol PFPE-DMA</td>
<td>16.1 ± 0.5</td>
</tr>
<tr>
<td>4 kg/mol sPFPE</td>
<td>15.9 ± 0.6</td>
</tr>
<tr>
<td>10% sPFPE-SS</td>
<td>14.4 ± 0.9</td>
</tr>
</tbody>
</table>

$^a$ Calculated with the Zisman analysis method.

$^b$ Calculated with the Owens-Wendt-Kaelble method: $\gamma_s^d$ dispersion component, $\gamma_s^p$ polar component, $\gamma_s$ overall surface tension.

**Table 2-4.** Summary of surface tensions.
As expected, the dispersion component (11.5 – 13.6 mN/m) is the main contributor to the surface tension while the polar surface tension component was 5 – 17% of the total surface tension. Particularly for the 1 and 4 kg/mol PFPE-DMA samples, the polar component contributes in a relatively high percentage of 17% to the total surface tension. It is interesting to observe that for the PFPE-DMA series of samples, the percent contribution of the polar component to the surface tension decreased as the molecular weight of the PFPE-DMA precursors increased. This is understandable since the lower molecular weight 1 and 4 kg/mol PFPE-DMA samples contain more polar urethane ether methacrylate endgroups in the crosslinked PFPE surfaces. The surface tension calculated from the OWK method generally agrees with the observation from the advancing contact angle measurements. A lower advancing contact angle was expected on the 1 kg/mol PFPE-DMA surface because the surface possesses a relatively larger contribution from the polar component.

2.3.8 Sol Fraction Analysis by Supercritical CO$_2$ Extraction

The sol fraction in photochemically crosslinked PFPE networks may be toxic to the marine organisms used in the biofouling evaluation assays. Thus, it is critical to remove any unpolymerized monomers before any anti-fouling/fouling-release test. Due to its good solubility to fluoropolymers, supercritical CO$_2$ was used to extract any sol fraction from the crosslinked PFPE networks. Typically, the free standing 10 x 75 x 1 mm samples of the 4 kg/mol sPFPE and 10% sPFPE-SS were put into a high pressure chamber and continuously extracted with supercritical CO$_2$ at 5000 psi and 50 °C for 4 h. The sol fraction was found to be on average 5.5 wt % for the 4 kg/mol sPFPE and 5.2 wt % for the 10% sPFPE-SS sample. These values were determined by analyzing the weight loss of the samples before and after
the extraction process. The leachate appeared to be a cloudy liquid mixture consisting of water insoluble compounds. The composition of the sol fraction was identified by both $^1$H- and $^{19}$F-NMR spectra as seen in Figure 2-8. According to the literature, signals observed with the multiple peaks at -51 to -58 ppm were assigned to the fluorine in the -CF$_2$O- repeat units and peaks at -87 to -93 ppm corresponding to the fluorine in the -CF$_2$CF$_2$O- repeat units. The small peaks around -80 ppm were attributed to the fluorine in the -CF$_2$CH$_2$O- endgroups. All this information confirmed the major component in the leachate to be unpolymerized PFPE macromolecules. They could be either non-functionalized fluorinated macromolecules coming from the starting PFPE diols or the PFPE diols that had not been effectively functionalized via the reaction with the vinyl benzyl chloride. The minor compositions of the leachate were further identified by $^1$H NMR spectroscopy as seen in Figure 2-9. The peaks at 5.26 ppm (H$_a$), 5.85 ppm (H$_b$), and 6.77 ppm (H$_c$) are assigned to the vinyl protons associated with the benzyl groups. The peaks at 4.72 ppm and 3.99 ppm were assigned to the protons in the -CF$_2$CH$_2$O- linkage groups associated with the vinyl benzyl ring (H$_d$) and the PFPE chain (H$_e$), respectively. Additionally, the peaks at 4.56 ppm and 4.05 ppm were assigned to the twin peaks of H$_d$ and H$_e$ that are indicative of the presence of the unreacted vinyl benzyl chloride molecules.

The peaks at 2.43, 1.29 and 0.86 ppm were assigned to the protons in the butyl group, from the tetrabutylammonium used as a catalyst in the reaction of the PFPE diol with vinyl benzyl chloride. A small fraction of the photo initiator, $\alpha$-hydroxycyclohexyl phenylketone, was also extracted out by supercritical CO$_2$, as identified by the aliphatic peaks at 1.55 – 1.87 ppm and the aromatic protons at 8.12 and 7.40 ppm. All of the unreacted molecules in the samples can be effectively extracted using supercritical CO$_2$. 

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Figure 2-8. $^{19}$F-NMR spectrum of leachates extracted by supercritical CO$_2$.

Figure 2-9. $^1$H-NMR Spectrum of leachates extracted by supercritical CO$_2$. 
The influence of the extraction on surface properties was investigated by monitoring the change in the critical surface tension on the samples before and after the extraction process. The critical surface tension at the air interface was remeasured by Zisman method. The critical surface tensions of both surfaces were slightly decreased upon extraction by supercritical CO₂, as seen in Table 2-6. The lower critical surface tension was attributed to the removal of the polar hydrocarbon molecules near the surface and some unpolymerized PFPE molecules. As discussed in the previous section, these chains are highly susceptible to rearrangement, which exposes the polar segments to the surface and further results in a relatively higher critical surface tension. With the decreased critical surface tension imparted by supercritical CO₂ extraction, the process does not appear to damage the surface and could potentially benefit the fouling-release performance.

<table>
<thead>
<tr>
<th></th>
<th>Critical Surface Tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before Extraction</td>
</tr>
<tr>
<td>4 kg/mol sPFPE</td>
<td>15.9</td>
</tr>
<tr>
<td>10% sPFPE-SS</td>
<td>14.4</td>
</tr>
</tbody>
</table>

Table 2-5. Effect of supercritical CO₂ extraction on critical surface tension of PFPE surfaces.

2.3.9 Biofouling Results

Monolithic samples of the 4 kg/mol PFPE-DMA, 4 kg/mol sPFPE, and 10% sPFPE-SS were tested for *Ulva* spore settlement and sporeling removal. Previously conducted preliminary tests showed that only the 4 kg/mol sPFPE and 10% sPFPE-SS increased performance compared to PDMS standards, as seen in Figure 2-10. This is most because the 4 kg/mol PFPE-DMA elastomer has a relatively high modulus and a large contact angle
hysteresis even though the material possesses a similar surface tension to the 4 kg/mol sPFPE and 10% sPFPE-SS samples based on the OWK method.

![Graph](image)

**Figure 2-10.** Detachment of 8 day old *Ulva* sporelings plotted as a function of pressure. Coatings were exposed to a range of surface pressures from the water jet.

Spore settlement densities were substantially lower on the two PFPE monoliths than on the PDMS standards (Figure 2-11), but there was no significant difference between the 4 kg/mol sPFPE and the 10% sPFPE-SS surfaces. Microscopic observations indicated that the attached spores were normal and healthy on both PFPE samples. Previous studies have indicated that higher numbers of spores settle on hydrophobic surfaces compared to hydrophilic, so the present results that show a low settlement density on the hydrophobic PFPE surfaces is not typical, but nevertheless a highly desirable characteristic for a potential antifouling coating.
Figure 2-11. Density of attached spores of *Ulva* on PDMS (Silastic® T2) and PFPE monoliths after a 1 hour settlement period. Each bar is the mean of 90 counts, 30 on each of 3 replicate slides. Error bars show 95% confidence limits.

The spores were cultured on the test surfaces for 7 days during which time they germinated and grew into sporelings. Although biomass production was lower on both the PFPE surfaces than on the PDMS standard, reflecting the lower spore settlement density, all surfaces were covered by a green lawn of sporelings after 7 days. The strength of attachment of sporelings was similar on both of the PFPE monoliths and on the PDMS standards (Figure 2-12). One-way analysis of variance showed that there was no significant difference in removal from the three surfaces (F 2, 15 = 2.67 P > 0.05). Commercial fouling-release coatings based on PDMS show weak attachment strength of a wide range of fouling organisms. The fouling-release characteristics of these materials are attributed to their smooth surfaces, low modulus, hydrophobicity, and properties of surface reconstruction which are all qualities shared with the PFPE elastomers. The similar release profiles of sporelings of *Ulva* for the PFPE and PDMS materials are therefore likely to originate from their shared physical properties. In long term ocean trials, the greater mechanical durability
of the PFPE coatings would be an advantage since one of the limiting factors in silicone fouling-release performance is its softness which makes it prone to physical damage.

![Figure 2-12](image)

**Figure 2-12.** Percentage removal of sporeling biomass from PDMS (Silastic® T2) and PFPE monoliths following exposure to an impact pressure of 32 kPa produced by a water jet. Each bar is the mean percentage removal from 6 replicate slides. Error bars show the standard error of the mean derived from arcsine transformed data.

### 2.4 Conclusions

A series of novel perfluoropolyethers have been synthesized via a solventless process using liquid precursors that are capable of being photochemically crosslinked into elastomeric networks. The structure/property relationships were systematically investigated as a function of endgroup, molecular weight, and content of a comonomer. Generally two glass transitions were revealed for these PFPE-based materials with the first transition assigned to the hydrocarbon domains and the second transition at lower temperature assigned to the fluorinated domains. Through a SAXS study, the domain spacing was estimated to be 3.3 nm for the 1 kg/mol PFPE-DMA sample and approximately 5.2 nm for the 4 kg/mol PFPE-base samples. It was demonstrated that the moduli of the fully cured PFPE samples can be tuned by using precursors with various chain length to vary the crosslink density. The
contact angle hysteresis and the critical surface tension of these films have been studied. Both the crosslink density and the curing environment humidity show effect on the chain reorganization and the contact angle hysteresis. A lower crosslink density or more humid cure environment is likely to drive more polar groups towards the surface and facilitate chain reorganization that results in a larger contact angle hysteresis. The PFPE materials with low surface tension, Young’s modulus, and contact angle hysteresis show decreased zoospore settlement and comparable sporeling removal performance to PDMS elastomer standard material. The ease of fabrication, the ability to tune the properties, and the promising fouling-release performance coupled with potentially greater service lifetime could provide opportunity for these PFPE elastomers to be utilized as fouling-release coatings in marine environments.
2.5 References


(7) Brady, R. F.; Singer, I. L. *Biofouling* 2000, 15, 73.


Chapter 3

Amphiphilic Networks Based on
Blends of Perfluoropolyethers and Poly(ethylene glycol)s
3.1 Introduction

Amphiphilic networks have gained much attention and are the topic of several recent reviews.\(^1\,^2\) In these systems, hydrophilic and hydrophobic phases are combined and then chemically crosslinked thus generating an amphiphilic network. Such materials have been the target for developing novel applications such as contact lenses,\(^3\,^4\) medical devices,\(^5\,^6\) membranes,\(^7\,^8\) enzyme catalysts,\(^9\,^10\) and drug delivery.\(^11\,-\,^13\) Most amphiphilic networks extensively studied consist of a hydrophilic and a hydrophobic phase. As a unique class of materials, fluoropolymers possess a combination of properties including high thermal and chemical stability, low surface energy, and low flammability. In addition, fluoropolymers exist in forms ranging from thermoplastics to elastomers. They have found many applications in building, automotive, and petrochemical industries, microelectronics, aerospace, and optics.\(^14\) However, due to the immiscibility between fluorophilic and hydrophilic or hydrophobic segments, limited amphiphilic networks comprising fluorophilic chain segments have been reported.

Tiller et al. has reported a class of nanophasic hydrophilic/fluorophilic networks that were achieved by photochemically curing blends of a dimethacrylate-functionalized perfluoropolyether (PFPE) with perfluorosilyl-protected poly(hydroxyethyl acrylate) (PHEA), as seen in Scheme 3-1.\(^15\) This is not a straightforward method to form amphiphilic networks as it requires the perfluorosilyl protecting groups on the PHEA chain segments to be cleaved in a subsequent procedure involving soaking the cured films in hydrochloric acid and tetrahydrofuran (THF) for 24 h. The acid-deprotection step is thought to deleteriously affect the fluorinated nature of the surfaces of the network materials. Wooley et al. recently reported the formation of amphiphilic networks derived from the crosslinking of diamino-
terminated poly(ethylene glycol) with hyperbranched perfluorobenzyl ether.\textsuperscript{16,17} The unusual topology, morphology, surface, and mechanical properties have been systematically studied.\textsuperscript{12,18} Although these materials show interesting anti-fouling properties,\textsuperscript{19} they appear to be heterogeneous due to a wide degree of incompatibility along the architectural and compositional axes.\textsuperscript{20}

Scheme 3-1. Synthesis of PHEA-l-PFPE co-networks via a precursor approach (R_f = C_6H_{13} or C_8H_{17}).

Thus far in the literature the existence of a fluorophilic/hydrophilic amphiphilic network possessing good miscibility between the two components in a wide composition ratio has not been reported. Herein for the first time it was observed that the low molecular weight dimethacrylate-terminated PFPE (1 kg/mol) and dimethacrylate-terminated PEG (550 g/mol) form optically transparent liquid blends in all composition ratios. When the higher molecular weight PFPE (4 kg/mol) was mixed with PEGs (550 and 750 g/mol), a series of
milky-white emulsions formed. All liquid blends with reactive forms of these oligomers could then be photochemically cured to form optically transparent to opaque materials in one step.

3.2 Experimental Section

3.2.1 Materials

The solvent 1,1,1,3,3-pentafluorobutane (Solkane 365 MFC) was purchased from Micro-Care. The 1 and 4 kg/mol PFPE diols (Fluorolink D10 and Fomblin ZDOL 4000, respectively) were purchased from Solvay Solexis. Tetrabutyltin diacetate (DBTDA), α-hydroxycyclohexyl phenylketone (HCPK), 2-isocyanatoethyl methacrylate (IEM), poly(ethylene glycol) dimethacrylates (PEG-DMA, 550 and 750 g/mol), hexa(ethylene glycol)mono-11-mercaptoundecyl ether, canine plasma fibrinogen, bovine serum albumin (BSA), and all solvents used were purchased from Sigma-Aldrich. HyClone Phosphate Buffered Saline (PBS, 1X, 0.0067M PO₄, without calcium, without magnesium, 0.1 μm sterile filtered) was purchased from Fisher. Cell culture plates (48 well, flat bottom) used for protein adsorption research were purchased from Corning Inc.

3.2.2 Synthesis of Dimethacrylate-modified Perfluoropolyether (PFPE-DMA)

PFPE-DMA were synthesized as previously reported. Briefly, PFPE diol (1 or 4 kg/mol) was first dissolved in 1,1,1,3,3-pentafluorobutane and reacted with a 1:2.05 molar ratio of 2-isocyanatoethyl methacrylate (IEM) at 45 °C for 24 h, using 0.1 wt % tetrabutyltin diacetate (DBTDA) as a catalyst. The solution was then passed through a chromatographic
column filled with alumina (2 x 10 cm). After evaporating the solvent, the product was filtered through a 0.2 μm polyethersulfone filter to yield a clear, colorless, viscous oil.

3.2.3 Photocuring of PFPE/PEG Amphiphilic Networks

Commercial poly(ethylene glycol) dimethacrylate (PEG-DMA) with a molecular weight of 550 or 750 g/mol was first passed through a chromatographic column (alumina, 2 x 10 cm) to remove any inhibitor. Purified 550 g/mol PEG-DMA was then added into the desired amount of the 1 kg/mol PFPE-DMA macromonomer (composition weight ratios of 30/70, 50/50, and 70/30 were studied) to form a mixture, followed by the addition of 0.2 wt % of α-hydroxycyclohexyl phenylketone (HCPK) as a photoinitiator. A colorless, clear, homogeneous liquid blend of 1 kg/mol PFPE-DMA and 550 g/mol PEG-DMA was obtained after vortexing (Vortex Genie 2, Scientific Industries, Inc) the mixture for approximately 5 minutes at room temperature to dissolve the photo initiator. To achieve a fully cured PFPE/PEG network, the homogeneous PFPE/PEG liquid blend was simply cast onto a clean silicon wafer followed by subsequent UV irradiation (Electrolite UV curing chamber model No. 81432-ELC-500, λ = 365 nm) for 5 minutes under N₂ purge. This resulted in a completely clear, elastomeric material. Opaque 4k PFPE/PEG blends could be achieved following a similar protocol by blending the higher molecular weight 4 kg/mol PFPE-DMA with either the 550 or 750 g/mol PEG-DMA.
3.2.4 Characterization

3.2.4.1 Ultraviolet-visible Spectroscopy

UV-Vis transparency was measured with a Shimadzu UV-3600 UV-Vis NIR spectrophotometer over the wavelength range of 200 – 800 nm. Thin films of ca. 1 mm were measured for optical transparency with the percent transmittance at 550 nm (the solar maximum) reported.

3.2.4.2 Thermal Analysis

Dynamic mechanical thermal analysis (DMTA) measurements were performed in a PerkinElmer Pyris Diamond DMA 6100, operated at a fixed frequency (1 Hz) in tension mode. The temperature was varied from -150 °C to 150 °C with a heating rate of 2 °C/min. DSC curves were recorded with a Seiko DSC 220C in the temperature range from -150 °C to 100 °C, at a scanning rate of 10 °C/min.

3.2.4.3 Morphology Study by Microscopy

Cross sections of the clear blend samples were imaged using a Multimode Atomic Force Microscope (AFM) in tapping-mode from Veeco Metrology group equipped with Nanoscope III control station and silicon cantilevers from Mikromasch USA with resonance frequencies of about 160 kHz, spring constants of 5.0 N/m, and radii of less than 10 nm. Ultrathin cross sections of the opaque samples cut by microtome were studied at 40x magnification under unpolarized light using an optical microscope (Olympus BH2) equipped with a SpotRT camera and photographic system.
3.2.4.4 Small Angle X-ray Scattering

The small angle X-ray scattering (SAXS) instrument (Anton Paar) at the University of Minnesota was utilized to probe the microstructure in the fully cured clear 1k PFPE/550 PEG blends. The film was placed in a copper sample holder, and the scattering was measured at room temperature for 5 min, operating at 40 kV and 50 mA. The scattering signal was not corrected for instrumental broadening caused by the line-collimated incident beam but was integrated into a 1D plot of intensity versus the scattering vector, q. Finally, the scattering intensity was normalized with respect to the incident beam intensity.

3.2.4.5 Mechanical Properties

Stress-strain measurements were performed for rectangular samples (1 x 10 x 20 mm) at ambient temperature on an Instron Model 5566 System using a 10 kN load cell at a crosshead speed of 5 mm/min. An extensiometer of 15 mm gauge length was used to measure the strain accurately. The Young’s modulus was determined from the stress-strain curves. Four replicates were performed for each sample.

3.2.4.6 Swelling Measurements

Swelling measurements were performed by soaking the fully cured PFPE/PEG films in deionized water for 72 h. The weight percent swelling ratio was determined using the following equation: wt % swelling = 100% * (W_wet − W_dry) / W_dry. To accurately evaluate the weight of the dried film, the original film was dried to a constant weight in a vacuum oven at 100 °C for 24 h. The weight of the water swollen film was recorded after quickly blotting the film between two sheets of filter paper. No difference was visually observed for all the PFPE/PEG films during the soaking treatment.
3.2.4.7 Static Contact Angle Measurement

Static contact angles were measured using a KSV Instruments LCD CAM 200 Optical Contact Angle Meter at room temperature (23 °C). All measurements were carried out with drops that had a total volume of 10 μL on the surface of each fully cured film using a 1000 μL screw-top syringe.

3.2.4.8 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopic

The interfaces were examined with a Tensor 27 FTIR instrument (Bruker) using a Hyperion microscope fitted with an ATR objective with a germanium crystal as the internal reflectance element (IRE) and a MCT detector. OPUS software was employed for data processing.

3.2.4.9 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) analysis was performed using a Kratos Axis Ultra equipped with a monochromated aluminum Kα X-ray source. Photoelectrons at pass energies ranging from 20 to 80 eV were collected with a concentric hemispherical analyzer and detected with a delay line detector. All data were collected at 90° from the surface normal takeoff angle and processed with Kratos Vision software (version 2.2.6). The binding energy component in the C₁s region (CF₂CF₂O) was referenced to 293.5 eV and all other element scans were shifted accordingly.

3.2.4.10 Surface Preparation for Protein Adsorption

A Fisher brand standard glass slide (25 x 75 mm) was cut into 5 x 5 mm pieces and boiled in piranha solution (H₂SO₄ : H₂O₂ ≈ 3:1) at 90 °C for 30 minutes, followed by thorough washing in deionized water, ethanol, and subsequent drying with a stream of nitrogen. Oligo(ethylene glycol) (OEG) self-assembled monolayers (SAMs) on gold
surfaces containing hexa(ethylene glycol)mono-11-mercaptopoundecyl ether (HS-C\textsubscript{11}-EG\textsubscript{6}) were prepared from a 1 mM solution of HS-C\textsubscript{11}-EG\textsubscript{6} thiol dissolved in degassed, absolute ethanol by placing gold substrates in the solution for 24 h at room temperature.\textsuperscript{22} Untreated pieces of 5 x 5 mm gold foil (0.1 mm, Sigma-Aldrich) were used as a negative control. All studied surfaces were rinsed with deionized water and ethanol and then dried under nitrogen before applying the protein solution.

3.2.4.11 Protein Adsorption

An enzyme-linked immunosorbent assay (ELISA) was used to measure fibrinogen adsorption on the surfaces of cured PFPE/PEG films.\textsuperscript{23} The 5 x 5 mm thin films were put onto a 48-well plate and incubated in 500 \(\mu\text{L} \) of 1 mg/mL fibrinogen in PBS at 37 \(^\circ\text{C}\) for 90 minutes. The films were then removed from the protein solution, rinsed five times with PBS solution (pH 7.4) and incubated in a new 48-well plate with 500 \(\mu\text{L} \) of 1 mg/mL BSA in PBS at 37 \(^\circ\text{C}\) for 90 minutes to block the areas unoccupied by fibrinogen. The films were taken out again, washed five times with PBS and moved to another 48-well plate, followed by the addition of 500 \(\mu\text{L} \) of horseradish peroxidase (HRP) conjugated anti-fibrinogen (Antogen Bioclear, working dilution of 1:10,000) into each well and subsequently incubated at 37 \(^\circ\text{C}\) for 30 minutes. After washing five times with PBS, the samples were transferred to another clean 48-well plate and incubated in 500 \(\mu\text{L} \) of TMB substrate (containing HRP, Pierce) at 37 \(^\circ\text{C}\) for 20 minutes. The enzyme-induced color reaction was stopped by adding 500 \(\mu\text{L} \) of 1M H\textsubscript{2}SO\textsubscript{4} solution. The solution then changed color from light blue to light yellow. Finally, the absorbance of the light intensity was determined at 450 nm by a microplate reader (SpectraMax \textsuperscript{\textregistered} M5, Molecular Devices).
3.3 Results and Discussion

3.3.1 Synthesis of Amphiphilic PFPE-PEG Networks

It is surprising that the low molecular weight 1 kg/mol PFPE-DMA prepolymer was completely miscible with the low molecular weight 550 g/mol PEG-DMA at ambient temperature. Clear liquid blends of these two prepolymer s were obtained in all composition weight ratios after vortexing the mixtures for 5 minutes. Completely clear liquid blends could be formed in the composition weight ratio of 70/30 1k PFPE/750 PEG or higher when mixing the 1 kg/mol PFPE-DMA with the 750 g/mol PEG-DMA precursor. The liquid blend was slightly hazy when the composition weight ratio was decreased to 50/50 1k PFPE/750 PEG and became even hazier when further decreased to 30/70 1k PFPE/750 PEG in this case. However, kinetically stable, milky-white emulsions formed when adding the higher molecular weight 4 kg/mol PFPE-DMA into PEG-DMAs (both 550 and 750 g/mol) in the composition weight ratio of 70/30 PFPE/PEG or higher. Less stable opaque liquid blends were yielded in lower composition ratios that separated in hours. In addition, a clear liquid blend could be achieved by mixing the 1 kg/mol PFPE diol with either the 550 g/mol PEG-DMA or the 600 g/mol PEG diol at 50:50 by weight. A similar endgroup was attributed to the good miscibility between PFPE and PEG macromolecules. Additionally, the hydroxyl endgroups associated with PFPE diol enhanced the interaction with the 600 g/mol PEG diol or 550 g/mol PEG-DMA by forming hydrogen bonds. However, it is not clear why poor miscibility was observed between the 1 kg/mol PFPE-DMA and 600g/mol PEG diol at the same composition ratio.
These liquid blends were easily cured free radically to yield free-standing films in one step (Scheme 3-2). Typically, the liquid blends were first vortexed at room temperature for 5 min to dissolve the photoinitiator (0.2 wt % of HCPK). They were then cast onto a clean flat silicon wafer followed by subsequent UV irradiation for 5 min under nitrogen purge. The resulting series of amphiphilic PFPE/PEG films varied from optically transparent to opaque dependent upon molecular weight and composition ratio as shown in Figure 3-1. In each series (i.e. 1 or 4 kg/mol PFPE-DMA with 550 or 750 g/mol PEG-DMA), blends in three composition weight ratios (30/70, 50/50, and 70/30) were fabricated for systematic analytical studies.

![Synthetic scheme of PFPE/PEG networks via a precursor approach.](image)

**Scheme 3-2.** Synthetic scheme of PFPE/PEG networks via a precursor approach.
3.3.2 Transmittance of Cured Films

The optical transparency of the resulting films was quantitatively elucidated by measuring the transmittance at 550 nm. As seen in Figure 3-2a, all transparent films showed a high transmittance of ca. 98% in the range of 400 – 800 nm. For the 1k PFPE/750 PEG blends, as the composition ratio was decreased from 70/30 to 30/70, the film gradually turned hazy with the transmittance decreasing from ca. 98.1% to 83.7%. With macrophase separation for the 4 kg/mol PFPE/PEG blends (Figure 3-2b), most of visible light cannot go through the samples, resulting in a transmittance of less than 40%. The transmittance further decreased to 11.6% for the 70/30 4k PFPE/550 PEG blend and 8.0% for the 70/30 4k PFPE/750 PEG blend due to more visible light being scattered inside the samples.
Figure 3-2. Transmittance of cured films by UV-Vis: (a) 1k PFPE/PEG blends and (b) 4k PFPE/PEG blends.
3.3.3 Glass Transition Temperatures

The morphologies of the fully cured PFPE/PEG films were studied by DMTA and are shown in Figure 3-3. Two transitions were found for the cured neat 1 kg/mol PFPE-DMA sample, the glass transition ($T_g$) at 54.5 °C was assigned to the polymerized methacrylate endgroups of the PFPE domains and a secondary transition at -80.4 °C was assigned to the PFPE domains of the perfluoropolyether main chains located away from the crosslinks. For the blends of the 1 kg/mol PFPE-DMA with the 550 g/mol PEG-DMA, the methacrylate crosslinking endgroups of the PFPE segments were miscible with the PEG domains and formed a mixed phase after crosslinking, corresponding to the broad $T_g$ at 10 °C to 50 °C as shown in Figure 3-3a, which shifted to a higher temperature upon increasing the PFPE content. The secondary relaxation for PFPE domains located away from the crosslinks was severely restricted by the crosslinking from the mixed PFPE/PEG phase. In this case, the secondary transition could not be detected by either DMTA or DSC (Figures 3-3a and 3-4a). However, the broad $T_g$ for the blends indicates a level of microheterogeneity which is reflected in nanoscale phase separation.

When a higher molecular weight 750 g/mol PEG-DMA was blended with the 1 kg/mol PFPE-DMA, the methacrylate crosslinking endgroups of the PFPE segments appeared to be compatible with PEG domains while the secondary relaxation of the PFPE domains located away from the crosslinks was not perturbed to any significant extent by the miscible methacrylate crosslinked PEG rich domains. The short-range molecular motions within the PFPE domains thus became enhanced and the secondary transition became visible by DSC (although it remained invisible in DMTA) at approximately -110 °C; the transition
cannot be clearly detected for the 1k PFPE/550 PEG blend samples under similar conditions (Figure 3-4a).

**Figure 3-3.** DMTA spectra of fully cured PFPE/PEG films of varying component ratios and molar masses. (a) 1k PFPE/550 PEG, (b) 1k PFPE/750 PEG, (c) 4k PFPE/550 PEG, (d) 4k PFPE/750 PEG.

As the crosslink density was decreased by incorporating more 750 g/mol PEG-DMA into the blend networks, the effect of the restrictions from the methacrylate crosslinked phase on the secondary relaxation of the PFPE domains away from the crosslinks was decreased to the point that in the composition ratio of 50/50 1k PFPE/750 PEG the mixture became immiscible and the blend appeared to be hazy. As a result, the broad $T_g$ for the mixed phase shifted from 50 °C to -35 °C. Unlike the 1 kg/mol PFPE-DMA, a lower $T_g$ around -130 °C for the dominant PFPE phase located away from the crosslinks was observed for the 4
kg/mol PFPE-DMA, with a broad $T_g$ of the minor phase located in the vicinity of the crosslinks around 30 °C. The highly fluorophilic 4 kg/mol PFPE-DMA was immiscible with the hydrophilic PEG-DMAs, which resulted in a series of optically opaque blends with PEG-DMAs of various molecular weights in all composition ratios. Two $T_g$’s were clearly detected by both DMTA and DSC for the 4 kg/mol PFPE/PEG blends, as shown in Figures 3-3c, 3-3d, and 4-3b. As the content of the 4 kg/mol PFPE-DMA sample was increased in these blends, the secondary relaxation within PFPE domains became more pronounced with a more enhanced peak observed at -130 °C.

![DSC spectra of fully cured PFPE/PEG film. (a) PFPE 1k/PEG series and (b) PFPE 4k/PEG series.](image)

**Figure 3-4.** DSC spectra of fully cured PFPE/PEG film. (a) PFPE 1k/PEG series and (b) PFPE 4k/PEG series.
3.3.4 Bulk Morphology

The bulk morphologies of the 1 kg/mol PFPE/PEG blends were investigated by AFM on the cross sections of cryo-fractures. The AFM phase images are consistent with the observations by DMTA. Nanophase separation was observed even for the blends with a single T_g. This is not unexpected based on the DMTA data which indicates some nanophase separation in the cured clear 1 kg/mol PFPE-DMA homo-polymer.

![AFM phase contrast images](image)

**Figure 3-5.** AFM phase contrast images in tapping mode on cross sections of (a) 30/70 1k PFPE/550 PEG, (b) 50/50 1k PFPE /550 PEG, (c) 70/30 1k PFPE/550 PEG, (d) 30/70 1k PFPE/750 PEG, (e) 50/50 1k PFPE/750 PEG, and (f) 70/30 1k PFPE/750 PEG samples. In the hard tapping mode, PFPE shows dark and PEG show light.

As shown in Figure 3-5a, uniform nanophase separation occurred with a domain size of 19.7 ± 3.2 nm for the cured 30/70 1k PFPE/550 PEG sample. These domains were
completely separated by continuous walls as thin as 5 nm, which are believed to be rich in the stiffer PFPE phase. As the composition ratio was increased to 50/50 1k PFPE/550 PEG (Figure 3-5b), most of the domains remained well separated with an average domain size of 21.4 ± 5.0 nm while some of them aggregated in certain locations and smaller 10 nm domains were found between the larger domains. As the composition ratio was further increased to 70/30 1k PFPE/550 PEG (Figure 3-5c), the cross section of the sample became more homogeneous, making the domain size immeasurable.

The 1k PFPE/550 PEG blends and associated crosslinked homo-polymers were also analyzed by small-angle X-ray scattering (SAXS) in Figure 3-6. The cured 1 kg/mol PFPE-DMA sample exhibited a peak in the scattering intensity at about 2 nm⁻¹ corresponding to a domain spacing of approximately 3 nm. This is likely due to clustering of the polymerized methacrylate endgroups in the highly-fluorinated matrix thus leading to compositional heterogeneity at length scales comparable to the PFPE chain dimensions. A similar peak was not observed for the crosslinked 550 g/mol PEG-DMA sample. In the PEG-DMA case, it may be that the scattering contrast or level of incompatibility between the hydrophilic PEG chains and the hydrophobic methacrylate endgroups is not high enough to observe a well-resolved peak. The scattering data from the three 1k PFPE/550 PEG blends exhibited two similar features: (i) enhanced scattering at low q and (ii) a peak or a broad shoulder at about 1 nm⁻¹ < q < 2 nm⁻¹ (ca. 3 – 6 nm length scale). It is posited that the peak (shoulder) is again associated with scattering from the domains of the polymerized (now co-polymerized) methacrylate groups in a matrix consisting of a mixture of PEG and PFPE. However, the increased scattering intensity at 0.1 < q < 1 (ca. 6 – 60 nm length scales) suggests compositional heterogeneities over a range of larger length scales, which is consistent with
the AFM images shown in Figure 3-5. Both the scattering intensity at low q and the length scale associated with the peak (shoulder) increases with increasing PEG content. This suggests that the domain sizes on average are increasing with increasing PEG content in these blends.

![Figure 3-6](image)

**Figure 3-6.** 1D SAXS data for optically transparent films of crosslinked 1k PFPE/550 PEG blends at various composition ratios. Also shown are the corresponding crosslinked homopolymers. All the data was acquired on the same instrument over a 2 hour time period and has not been shifted on the y-axis.

For the 1k PFPE/750 PEG blends, the samples at first appeared milky when a small amount of the 1 kg/mol PFPE-DMA was incorporated but as the content of the PFPE-DMA was increased the blends became optically transparent. This phenomenon can be explained by the AFM phase images shown in Figure 3-5. In Figure 3-5d, a co-continuous morphology was observed with light PEG-enriched domains as large as 400 nm being separated by sponge-like PFPE-enriched domains of 71.7 ± 21.1 nm. As more of the 1 kg/mol PFPE-DMA was incorporated into the PEG matrix, the co-continuous biphasic system changed to a matrix fully composed of isolated polydisperse domains of 50 - 250 nm (Figure 3-5e) with some aggregated together to form larger ones. With domain sizes above several hundred
nanometers, both of the 30/70 1k PFPE/750 PEG and 50/50 1k PFPE/750 PEG blends appeared to be hazy as shown in Figure 1. As the content of the 1 kg/mol PFPE-DMA was increased to 70 wt % the cross section appeared to be less heterogeneous with uniform domains of 61.3 ± 13.5 nm resulting in a clear film (Figure 3-5f).

Due to the domain size of the macrophase-separated 4k PFPE/PEG blends being beyond the working range of AFM, optical microscopy was used to study the bulk morphologies of these opaque blends. As shown in Figure 3-7a, an ultrathin film of the 30/70 4k PFPE/550 PEG blend was found to have spherical PFPE-enriched domains randomly distributed in a continuous PEG matrix with domain sizes of 1 - 90 µm. The polydisperse PFPE-enriched domains in this blend were seen to be isolated from each other. It was particularly interesting to find some smaller spheres of 1 - 5 µm capsulated inside the larger spherical domains. The phase separation behavior looks similar for the 50/50 4k PFPE/550 PEG blend as shown in Figure 3-7b, however, no sphere as large as 90 µm was seen. Most of the domains were 40 - 50 µm in diameter. As the content of the 4 kg/mol PFPE-DMA was increased to 70 wt %, the size of the PFPE-enriched domains was decreased dramatically to less than 10 µm with most of the spheres connected to each other in Figure 3-7c.

When the higher molecular weight 750 g/mol PEG-DMA was used, the series of 4k PFPE/750 PEG blends appeared to be more heterogeneous and phase separated under optical microscopy. As seen in Figure 3-7d, for the 30/70 4k PFPE/750 PEG blend most of the spherical PFPE-enriched domains were less than 50 µm. The morphology dramatically changed though for the 50/50 4k PFPE/750 PEG blend as the cross section was mostly filled with large PFPE-enriched spheres of 40 - 100 µm while small spherical PFPE-enriched
domains were rarely seen outside of these larger ones (Figure 3-7e), instead almost all of the small PFPE-enriched domains were located inside the larger spheres. However, as the composition ratio was increased further to 70/30 4k PFPE/750 PEG, the morphology significantly changed again as the large PFPE-enriched domains disappeared and the small PFPE-enriched domains of 1 - 15 µm were dispersed in a PEG-enriched matrix as seen in Figure 3-7f. A less compatible system was generally found for the 4k PFPE/750 PEG blends with both the size and number of spherical PFPE-enriched domains greater than the counterparts in the 4k PFPE/550 PEG blends.

Figure 3-7. Morphologies of cured 4k PFPE/PEG blend cross sections by optical microscopy. (a) 30/70 4k PFPE/550 PEG, (b) 50/50 4k PFPE/550 PEG, (c) 70/30 4k PFPE/550 PEG, (d) 30/70 4k PFPE/750 PEG, (e) 50/50 4k PFPE/750 PEG, and (f) 70/30 4k PFPE/750 PEG. The thickness of the cross sections is 5 µm for the 4k PFPE/550 PEG blends and 10 µm for the 4k PFPE/750 PEG blends. The magnification is 40 x with a scale bar of 20 µm.
3.3.5 Young’s Modulus

The mechanical properties of these PFPE/PEG films were analyzed by studying the Young’s modulus, which was calculated from the slope of the initial linear section (up to 2% of elongation) of the stress-strain curve. The cured 1 kg/mol PFPE-DMA sample is a much stiffer material than the cured 550 or 750 g/mol PEG-DMA sample, which is reflected by their Young’s modulus. As seen in Table 3-1, the Young’s modulus is 89.9 ± 10.4 MPa for the cured 1 kg/mol PFPE-DMA sample, while it is 40.3 ± 2.4 MPa for the 550 g/mol PEG-DMA and 16.5 ± 0.7 MPa for the 750 g/mol PEG-DMA. As a result, the Young’s modulus of the 1 kg/mol PFPE/PEG blends should be no higher than that of the neat 1 kg/mol PFPE-DMA sample. And as the stiffer 1 kg/mol PFPE-DMA was incorporated into the blends, the materials should become stiffer with an increased Young’s modulus. The hypothesis is well explained by the results in Table 3-1.

For example, the Young’s modulus is 48.6 ± 2.2 MPa for the 30/70 1k PFPE/550 PEG, which is much higher than that of the 30/70 1k PFPE/750 PEG blend sample, 19.8 ± 0.4, and this result is mainly attributed to the lower crosslink density. As the content of the 1 kg/mol PFPE-DMA was increased to 70%, the modulus of the 70/30 1k PFPE/550 PEG was increased to 66.9 ± 4.2 MPa, almost the double that of the 550 g/mol PEG-DMA. On the other hand, the moduli of the opaque 4 kg/mol PFPE/PEG blends are much lower than those for the 1 kg/mol PFPE/PEG blends mainly due to the lower crosslink density. The increased content of the 4 kg/mol PFPE-DMA in the 4k PFPE/750 PEG blends corresponds to a decreased Young’s modulus because the cured PFPE-DMA sample is a very flexible elastomeric material with a Young’s modulus of only 7 MPa, which is even lower than that of the cured 750 g/mol PEG-DMA sample. The characteristic of tunable mechanical strength
and the unique fluorophilic/hydrophilic nature of these amphiphilic blends provide flexibility to design these materials for a variety of applications based on the specific requirements of the application.

<table>
<thead>
<tr>
<th></th>
<th>Young's Modulus (MPa)</th>
</tr>
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<tbody>
<tr>
<td>1 kg/ml PFPE-DMA</td>
<td>89.9 ± 10.4</td>
</tr>
<tr>
<td>70/30 1k PFPE/550 PEG</td>
<td>66.9 ± 4.2</td>
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<tr>
<td>50/50 1k PFPE/550 PEG</td>
<td>53.3 ± 2.7</td>
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<tr>
<td>30/70 1k PFPE/550 PEG</td>
<td>48.6 ± 2.2</td>
</tr>
<tr>
<td>550 g/mol PEG-DMA</td>
<td>40.3 ± 2.4</td>
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<tr>
<td>70/30 1k PFPE/750 PEG</td>
<td>28.1 ± 0.9</td>
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<td>50/50 1k PFPE/750 PEG</td>
<td>22.5 ± 1.4</td>
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<tr>
<td>30/70 1k PFPE/750 PEG</td>
<td>19.8 ± 0.4</td>
</tr>
<tr>
<td>750 g/mol PEG-DMA</td>
<td>16.5 ± 0.7</td>
</tr>
<tr>
<td>70/30 4k PFPE/550 PEG</td>
<td>16.9 ± 0.5</td>
</tr>
<tr>
<td>50/50 4k PFPE/550 PEG</td>
<td>23.4 ± 1.1</td>
</tr>
<tr>
<td>30/70 4k PFPE/550 PEG</td>
<td>30.2 ± 1.5</td>
</tr>
<tr>
<td>70/30 4k PFPE/750 PEG</td>
<td>10.5 ± 0.9</td>
</tr>
<tr>
<td>50/50 4k PFPE/750 PEG</td>
<td>13.1 ± 0.7</td>
</tr>
<tr>
<td>30/70 4k PFPE/750 PEG</td>
<td>14.8 ± 1.6</td>
</tr>
<tr>
<td>4 kg/mol PFPE-DMA</td>
<td>7.0 ± 0.3</td>
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</tbody>
</table>

Table 3-1. Young’s modulus of fully cured blend films by Instron.

3.3.6 Water Swelling Ratio

PEG-based materials are well known to non-specifically resist protein adsorption. However, most of the previously reported crosslinked PEG-based networks swell easily with high water uptake to form hydrogels. These swollen hydrogel networks are too brittle and
weak to be used as anti-fouling coatings.\textsuperscript{30} The PFPEs are highly water resistant due to their fluorinated structure. The hydrophobicity of PFPE coupled with its bulk properties is expected to generate amphiphilic networks that would be mechanically robust with reduced swelling when PFPE is incorporated into a PEG matrix. Herein, the water swelling ratio was carefully studied for all cured PFPE/PEG blends by evaluating the weight difference prior to and after soaking in deionized water. No obvious difference in transparency was observed for all samples after being soaked in water for 72 h.

As shown in Figure 3-8a and 3-8b, the swelling ratios for the 1 and 4 kg/mol PFPE-DMAAs were very low, even less than 1 wt % after being soaked in water for 72 h, which is negligible compared with those for the PEG homopolymers (27 wt % for the 550 g/mol PEG-DMA and 51 wt % for the 750 g/mol PEG-DMA). With the highly hydrophobic nature, the swelling ratios for all PFPE/PEG blends were decreased upon increasing the composition ratio of the PFPEs. For example, the optically transparent 30/70 1k PFPE/550 PEG blend swelled approximately 14 wt % in 72 h. But as the content of the 1 kg/mol PFPE-DMA was increased to 50 wt %, the sample swelled 7.5 wt % and the swelling was further decreased to 2.5 wt % when the content of the 1 kg/mol PFPE-DMA was increased to 70 wt % (Figure 3-8a). It is believed that the water uptake can be reduced further by increasing the crosslink density of the PFPEs. Additional studies have shown that the swelling ratios of these blends remain unchanged in water for months. The high stability and durability of these robust materials would allow them to remain operational for an extended period in an underwater environment.
3.3.7 Static Contact Angles

The surface properties of these amphiphilic blends were investigated as to what kind of interface would be achieved when hydrophilic PEG and hydrophobic PFPE are mixed to form uniform networks. High asymmetry was observed for these amphiphilic PFPE/PEG films in measuring the static contact angles at both the air and substrate interfaces. Generally, the air interface was found to be hydrophobic with a static contact angle of approximately 110° while the substrate interface was hydrophilic with a static contact angle ranging from

**Figure 3-8.** Weight swelling ratio in water for 72 h of the cured 550 g/mol PEG-DMA based blend samples (a) and 750 g/mol PEG-DMA based blend samples.
57° to 75°, varying as a function of the composition ratio and molecular weight as seen in Figure 3-9. Relatively high contact angles (>125°) at the air interfaces of the opaque 70/30 4k PFPE/550 PEG, 50/50 4k PFPE/750 PEG, and 70/30 4k PFPE/750 PEG films are believed to be caused by the high surface roughness due to macrophase separation at these interfaces.

Figure 3-9. Static water contact angles at the air and substrate interfaces of PFPE/550 PEG blend samples (a) and PFPE/750 PEG blend samples (b).
Slightly asymmetric surfaces have been previously reported on fluorinated surfaces but there have been no report in the literature describing an amphiphilic blend with such highly asymmetric interfaces without any special chemical or physical treatments.\textsuperscript{24,31,32} It is believed that the high asymmetry was induced when the interfaces were formed under various polar environments. The large disparity in the hydrophilicity of two components are the main driving force to enable the highly hydrophobic PFPE moieties to migrate to the non-polar air interface and the hydrophilic PEG to migrate in the opposite direction towards the polar silicon substrate.

### 3.3.8 Chemical Composition at Asymmetric Interfaces

The asymmetric interfaces of a fully cured 50/50 1k PFPE/550 PEG film was qualitatively studied by ATR-FTIR (Figure 3-10). Initially, the absence of signal at 1638 cm\(^{-1}\) due to the C=C double bonds of methacrylate endgroups indicates complete monomer conversion for all PFPE/PEG blends. The spectra obtained at both the air and substrate interfaces for the blends were compared with the spectra of the neat 1 kg/mol PFPE-DMA and 550 g/mol PEG-DMA films to judge whether the PFPE or PEG segments are predominate at the interfaces. Unfortunately, the CF\(_2\) stretching frequency is assigned to be around 1200 cm\(^{-1}\), which is obscured by the C-O-C stretching frequency (1200 - 1000 cm\(^{-1}\)) of both the PFPE and PEG chains,\textsuperscript{33} making it difficult to distinguish the interfaces components by analyzing the signal in this region. However, the signal intensity in 2800 - 3100 cm\(^{-1}\), corresponding to the CH\(_2\) and CH\(_3\) asymmetric stretch frequencies, is unobscured and useful for determining the interface composition to differentiate for all studied interfaces.
Figure 3-10. ATR-FTIR survey spectra for the fully cured 1 kg/mol PFPE-DMA air interface, 550 g/mol PEG-DMA air interface, and 50/50 1k PFPE/550 PEG air and substrate interfaces. The box shows a magnification of 2800 - 3050 cm⁻¹.

For the air interface of the 50/50 1k PFPE/550 PEG sample, the intensity of the peaks at 2863 and 2965 cm⁻¹ are very similar. A slightly larger peak at 2965 cm⁻¹ is a result of more methacrylate endgroups being present, indicative of more PFPE chains being present at the non-polar air interface. However, the ATR-FTIR spectrum obtained at the substrate interface of the same sample was very different from that of the air interface. The substrate interface spectra was very similar to the one obtained at the air interface of the neat 550 g/mol PEG-DMA film with a predominant peak at 2863 cm⁻¹ for the -CH₂- groups and a negligible shoulder at 2965 cm⁻¹ corresponding to the CH₃ groups, which indicated that the PEG chains are enriched at the substrate interface of the 50/50 1 kg PFPE/550 PEG blend. This observation explains the results from the static contact angle measurements that showed a disparity in hydrophilicity between the interfaces. As for the crosslinked PFPE/PEG
networks, the non-polar PFPE chains gravitate to the less polar air interface to create a highly hydrophobic surface while the PEG chains are attracted to the polar substrate interface, responsible for the hydrophilic characteristic.

The chemical compositions of the asymmetric interfaces of the cured 50/50 1k PFPE/550 PEG film were further quantitatively identified by full XPS survey scans as shown in Figure 3-11. The overall chemical composition at the air interface of the blend film was very similar to that at the air interface of the cured 1 kg/mol PFPE-DMA homo-polymer (Table 3-2). The fluorine concentration was much higher at the air interface of the blend film compared to the substrate interface of the same film.

![XPS survey spectra of the air and substrate interfaces of the 50/50 1k PFPE/550 as well as the air interface of the 1 kg/mol PFPE-DMA.](image)

**Figure 3-11.** XPS survey spectra of the air and substrate interfaces of the 50/50 1k PFPE/550 as well as the air interface of the 1 kg/mol PFPE-DMA.
High-resolution XPS spectra were taken to further reveal the local chemical disparity at both interfaces of the 50/50 1k PFPE/550 PEG film. As seen in Figure 3-12a, while two main peaks with similar intensity were found in the C$_{1s}$ spectrum at the air interface of the 50/50 1k PFPE/550 PEG film, corresponding to the overlap of fluorocarbon peaks at CF$_2$O ($\sim 294.9$ eV), CF$_2$CF$_2$O ($\sim 293.5$ eV) and the overlap of hydrocarbon peaks at C=O ($\sim 288.9$ eV), C-O-C ($\sim 286.4$ eV), and C-C ($\sim 284.9$ eV), the C$_{1s}$ spectrum of the substrate interface exhibits much higher intensity for hydrocarbon peaks, indicative of an enriching of the polar PEG component. The result given by the O$_{1s}$ spectra in Figure 3-12b is consistent to that of the C$_{1s}$ spectra in Figure 3-12a where the PFPE moiety is dominant at the air interface. The dominant peak in the O$_{1s}$ spectra was attributed to CF$_2$O ($\sim 535.9$ eV) at the air interface and to C=O ($\sim 532.5$ eV) at the substrate interface. Both the higher fluorine and nitrogen compositions were further discerned in the F$_{1s}$ (689.2 eV) and N$_{1s}$ (400.2 eV) spectra at the air interface of the blend film as shown in Figures 3-12c and 3-12d. These XPS results corroborate the results of the static contact angle measurements where it was seen that for the crosslinked PFPE/PEG networks, the non-polar PFPE chains gravitate to the less polar air interface to create a highly hydrophobic surface while the hydrophilic polar PEG chains are attracted to the polar substrate interface leading to its hydrophilic characteristic.

<table>
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<tr>
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<th>C$_{1s}$</th>
<th>O$_{1s}$</th>
<th>F$_{1s}$</th>
<th>N$_{1s}$</th>
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<tr>
<td>Air interface:</td>
<td>28.5</td>
<td>20.2</td>
<td>50.2</td>
<td>1.1</td>
</tr>
<tr>
<td>blend</td>
<td></td>
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<td>Substrate interface: blend</td>
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<td>26.2</td>
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<td>25.7</td>
<td>18.4</td>
<td>54.4</td>
<td>1.6</td>
</tr>
<tr>
<td>1kg/mol PFPE-DMA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 3-2.** Surface chemical mass compositions of the cured 50/50 1k PFPE/550 PEG film by XPS spectra.
**Figure 3-12.** Representative XPS high-resolution spectra at both the air and glass interfaces of the cured 50/50 1k PFPE/550 PEG blend. (a) C\textsubscript{1s}, (b) O\textsubscript{1s}, (c) F\textsubscript{1s}, and (d) N\textsubscript{1s}.

### 3.3.9 Protein Adsorption

Oligo(ethylene glycol) self-assembled monolayers (OEG SAMs) are a well established model for studying protein resistance behaviors.\textsuperscript{25,26} There are numerous reports on their non-specific protein resistant properties in the past two decades.\textsuperscript{27-29} However, the disadvantage of this model is that the OEG SAMs are unstable and rapidly auto-oxidize, especially in the presence of oxygen and biochemically relevant transition metal ions.\textsuperscript{28,34,35} It was also reported that grafted PEG brushes gradually lose their protein repulsive properties above 35 °C.\textsuperscript{36} The potential of our PFPE/PEG blends as alternative non-fouling coating
materials was explored. Fibrinogen adsorption on the optically transparent 1 kg/mol PFPE/PEG thin films was determined by an ELISA method. A gold surface with covalently banded OEG SAMs was set up as the negative control and a bare glass substrate as the positive control. The enzyme-induced color change in the protein solution was recorded at 450 nm as absorbance, which is proportional to the amount of antibody bound to the surfaces. To better compare the amount of fibrinogen on each surface, the absorbance on the glass substrate was set as 100% for the relative adsorption. As shown in Figure 3-13, both of the 1 kg/mol and 4 kg/mol homo-polymer PFPE surfaces demonstrated a certain level of resistance characteristic to fibrinogen with an average relative adsorption of approximately 30%, which was higher than that on OEG SAMs (2%). However, the relative adsorption was significantly reduced by incorporating PEG into the PFPE networks. For example, the relative protein adsorption decreased from 31% to 7% in going from the 1 kg/mol PFPE-DMA surface to the 70/30 1k PFPE/550 PEG blend surface. Insignificant difference in fibrinogen adsorption was found between the three 1k PFPE/550 PEG blend samples, which indicates that a high content of the PEG in the PFPE network is not necessary to maintain the protein resistant capability of these amphiphilic blends. According to the literature, as long as a surface is completely covered by ethylene glycol groups, the PEG chain length does not have a strong influence on protein adsorption activity.37 The effect of the PEG chain length on the protein adsorption is not clear here. A 70/30 PFPE/750 PEG sample was studied and found to have a relative adsorption of approximately 4.9%, which is comparable to all of the three 1k PFPE/550 PEG samples.
Figure 3-13. Amount of adsorbed fibrinogen from 1 mg/mL solution measured by ELISA. The data at the top of each of the columns is the relative adsorption values (mean ± SD %).

3.4 Conclusions

We studied the compatibility and miscibility behavior between fluorophilic PFPE’s and hydrophilic PEG’s. Clear liquid blends were achieved between the low molar mass 1 kg/mol PFPE-DMA and the 550 g/mol PEG-DMA in all composition ratios. The liquid blends of the 1 kg/mol PFPE-DMA with the higher molecular weight 750 g/mol PEG-DMA turned from slightly hazy to clear with decreasing content of the 750 g/mol PEG-DMA. Optically opaque blends were obtained when the higher molecular weight 4 kg/mol PFPE-DMA was mixed with either of the 550 or 750 g/mol PEG-DMAs. All of these liquid blends with dimethacrylate functional endgroups were easily cured in one step to form optically transparent or opaque free-standing elastomeric films. The complex morphologies given by DMTA, DSC, and microscopy methods are consistent. It was indicated that nanophase
separation occurs for the clear to hazy 1 kg/mol PFPE/PEG blends while macrophase separation with domain sizes of 1 - 100 µm was consistently observed for the opaque 4k PFPE/PEG blends. Compared with the cured PEG-DMA homo-polymers, both mechanical strength and water resistance properties have been optimized by incorporating durable hydrophobic PFPE into a hydrophilic PEG matrix. Chemical compositions by XPS revealed the highly asymmetric interfaces with PFPE-enrichment at the air interface and PEG-enrichment at the substrate interface of the blends. Preliminary results show that the 1 kg/mol PFPE/PEG amphiphilic surfaces were able to reduce the fibrinogen adsorption to a level comparable with that on an OEG SAM surface and a high incorporation of PEG into the blend is not necessary to keep a relatively low fibrinogen adsorption on the blend surfaces. With the combination of the high durability of the PFPE and the non-fouling properties of the PEG, the amphiphilic PFPE/PEG networks show good potential to be used as non-fouling coating materials.
3.5 References


Chapter 4

Miscibility and Phase Separation of Crosslinked Perfluoropolyether Copolymer Networks
4.1 Introduction

Polymeric fouling-release coatings are environmentally friendly alternatives to toxic, anti-fouling coatings. According to Baier and Brady’s research, polymeric materials with low surface tension and low modulus are apt to provide surfaces with low adhesion force to attached fouling species.\textsuperscript{1,2} Though the mechanisms controlling fouling-release behavior are not fully understood,\textsuperscript{3} the low surface tension and modulus design criteria has been widely accepted in the biofouling community since this observation has been supported by numerous related studies.\textsuperscript{4-9} The low surface tension of non-polar materials is thought to reduce ionic and polar chemical interactions between adhesives and coatings,\textsuperscript{10} while having a low modulus serves to minimize mechanical locking and facilitates the breaking of adhesive joints.\textsuperscript{11,12} Therefore, polymeric materials combining these two factors are favored as promising candidates for fouling-release applications. One example is poly(dimethylsiloxane) (PDMS), which possesses a low surface tension of ~ 25 mN/m and low modulus (2.4 MPa for fully cured Sylgard 184\textsuperscript{®}).\textsuperscript{1,13-15} With even lower surface tensions compared to PDMS, fluorinated polymers have recently drawn a lot of attention as fouling-release coating materials.\textsuperscript{16,17} Additionally, fluorinated polymers exhibit exceptionally high chemical and thermal stabilities imparted by the strong C-F and C-C bonds,\textsuperscript{18} which prevents swelling and loss of mass caused by degradation upon long-term water exposure. Though polymer-based soft coating materials may provide better fouling-release, there is a trade-off between fouling-release properties and mechanical durability. Softer materials normally have less durability than the harder ones.\textsuperscript{19} For example, an epoxy-siloxane fouling-release coating was shown to have improved impact resistance to prevent scratching and other physical damage after being toughened by 10 wt % of oxetane.\textsuperscript{20} Thus there is a great need for
improving the mechanical durability of these low surface tension materials in order to alleviate current problems with cutting, tearing and puncturing.$^{21-23}$

Previously discussed perfluoropolyether (PFPE) elastomeric materials were photochemically crosslinked from a series of difunctional macromonomers with various endgroups and molecular weights. These materials possess low surface tension and high flexibility. Furthermore, it was found that the modulus of these elastomers is tunable by varying the crosslink density using PFPE macromonomers of various molecular weights. The highest Young’s modulus achieved was only 90 MPa for a dimethacrylate-modified PFPE material ($M_n = 1$ kg/mol). A higher Young’s modulus is thought to be necessary to achieve better mechanical durability for a long-term fouling-release coating application.$^{24}$ As such, it is of practical importance to develop a novel strategy to increase the modulus, while maintaining the low surface tension of the current photochemically crosslinked systems. According to the literature, various inorganic nanoparticles such as titanium oxide, silica, and carbon nanotubes are widely used as reinforcing fillers to increase the mechanical strength of crosslinked systems.$^{25-27}$ While the addition of nanoparticles works well for a lot of hydrocarbon-based polymers, however, due to the high interfacial energy between perfluorinated polymer matrixes with inorganic nanoparticles, it is difficult for these nanoparticles to homogeneously disperse into these matrixes. To this end, difunctional organic small molecules were incorporated to overcome phase immiscibility problems associated with inorganic nanoparticles.$^{28}$ These compounds can dissolve and mix well in prepolymer systems and then crosslink together to form rigid materials with enhanced mechanical strength. Additionally, multifunctional macromonomers with large
functionalities (i.e. $f > 4$) can be incorporated to generate densely packed networks after crosslinking.\textsuperscript{29}

In this chapter, a commercially available perfluoropolyether tetrol oligomer was modified to form a tetramethacrylate-modified perfluoropolyether (PFPE-TMA) macromonomer with functionality equal to 4. This macromonomer was then photochemically crosslinked to form a mechanically strong fluorinated network material. Meanwhile, a short chain crosslinker, 1H,1H,6H,6H-perfluorohexyl diacrylate (PFHDA), was applied as an additive and copolymerized with the PFPE-TMA macromonomer to further increase the mechanical strength upon UV irradiation. One advantage of the PFHDA additive is that the perfluorinated molecule appears to be miscible with the PFPE-TMA macromolecule matrix to yield a homogeneous solution at room temperature or with slight heating. The liquid binary system was then photochemically crosslinked via UV light to form optically transparent films. The phase separation and morphologies of these cured samples were studied by a variety of techniques including DMTA, SAXS, and AFM. This study will help to understand the miscibility and compatibility behavior between the two fluorinated monomers and optimize the design of perfluorinated systems to obtain enhanced mechanically durable materials as long-term fouling-release coating materials.

### 4.2 Experimental Section

#### 4.2.1 Materials

The solvent 1,1,1,3,3-pentafluorobutane (Solkane 365 MFC) was purchased from Micro-Care. The 1H,1H,6H,6H-perfluoro-1,6-hexyl diacrylate additive was purchased from
Oakwood Products, Inc. The Fomblin® Z03 (M_n = 4000 g/mol) was purchased from Solvay Solexis. Poly(tetrafluoroethylene oxide-co-difluoromethylene oxide) α,ω-bis(2,3-dihydroxypropylether) (PFPE tetrol, M_n = 2000 g/mol), tetrabutyltin diacetate (DBTDA), α-hydroxycyclohexyl phenylketone (HCPK) and 2-isocyanatoethyl methacrylate (IEM) were purchased from Aldrich-Sigma. All of the chemicals were used as received.

4.2.2 Synthesis of Tetramethacrylate-modified Perfluoropolyether Macromonomer (PFPE-TMA)

The tetramethacrylate-modified perfluoropolyether (PFPE-TMA) macromonomer was synthesized by the following procedure: In a typical synthesis, 10 grams of the PFPE tetrol (5 mmols) was added to 50 mL of 1,1,1,3,3-pentafluorobutane to form a slightly cloudy liquid mixture, which was followed by the addition of 3.1 grams of 2-isocyanatoethyl methacrylate (IEM, 20 mmols) and 0.1 mL of tetrabutyltin diacetate (DBTDA) as a catalyst. The solution was kept under a nitrogen purge and upon mild stirring and heating to 45 °C, the initially turbid solution became clear after about 5 min. After 8 h, the reaction solution was passed through a chromatographic column filled with alumina (2 x 10 cm) followed by evaporation of the solvent to yield a clear, colorless, viscous oil.

4.2.3 Photocuring of PFHDA-PFPETMA samples.

The clear PFPE-TMA precursor with 0.2 wt % of α-hydroxycyclohexyl phenylketone (HCPK) was cast on a clean silicon wafer, then photochemically crosslinked to form an optically transparent elastomer film via UV irradiation (Electronlite UV curing chamber model No. 81432-ELC-500, λ = 365 nm) under nitrogen purge for 5 min (~38,000 mJ/cm²). The poly(perfluorohexyl diacrylate-co-tetramethacrylate perfluoropolyether) p(PFHDA-PFPETMA) elastomeric network material was obtained by photochemically crosslinking the
liquid binary system consisting of the PFPE-TMA macromonomer and 1H,1H,6H,6H-perfluoro-1,6-hexyl diacrylate (PFHDA) in a desired weight composition ratio in a similar manner. Due to the partial immiscibility of the two components, while the crosslinked p(PFHDA\textsubscript{0.2}-PFPETMA\textsubscript{0.8}) and p(PFHDA\textsubscript{0.4}-PFPETMA\textsubscript{0.6}) samples were optically transparent, the p(PFHDA\textsubscript{0.6}-PFPETMA\textsubscript{0.4}) and p(PFHDA\textsubscript{0.8}-PFPETMA\textsubscript{0.2}) samples were cloudy upon UV curing at room temperature. However, optically transparent samples of p(PFHDA\textsubscript{0.6}-PFPETMA\textsubscript{0.4}) and p(PFHDA\textsubscript{0.8}-PFPETMA\textsubscript{0.2}) can be obtained by warming the samples during curing. To do this, a heating plate with a precisely controlled temperature was placed inside the UV chamber and a piece of silicon wafer was then put atop the heating plate followed by pouring the cloudy liquid mixture onto the silicon wafer. Heating the system to a temperature slightly higher than the cloud-point, 65 °C for p(PFHDA\textsubscript{0.6}-PFPETMA\textsubscript{0.4}) and 85 °C for p(PFHDA\textsubscript{0.8}-PFPETMA\textsubscript{0.2}), the cloudy mixtures turned to a clear homogeneous solution. The solution was then crosslinked by UV curing. Both the cured p(PFHDA\textsubscript{0.6}-PFPETMA\textsubscript{0.4}) and p(PFHDA\textsubscript{0.8}-PFPETMA\textsubscript{0.2}) samples were optically transparent that were obtained in this manner and remained so even after cooling to room temperature.

4.3 Characterization

Nuclear magnetic resonance (NMR) spectra were taken using a Bruker 400 MHz DRX spectrometer. Fourier Transform Infrared spectrometry (FTIR) was carried out on a Tensor 27 FTIR instrument (Bruker) with a 4 cm\textsuperscript{-1} resolution and 32 scans. Atomic force microscopy (AFM) was carried out on an Asylum MFP-3D scanning probe microscope at ambient conditions using Tap300Al-G (tapping mode) cantilevers (Budget Sensors).
AFM phase contrast images were taken on the cross section of samples cut by a Reichert Supernova ultramicrotome. Differential scanning calorimetric (DSC) measurements were conducted using a Seiko DSC 220. The samples were first heated to 150 °C and then cooled down to -150 °C at a rate of 80 °C/min. Thermographs were then recorded from -150 to 120 °C at a heating rate of 10 °C/min. Dynamic mechanical thermal analysis (DMTA) measurements were performed in a PerkinElmer Pyris Diamond DMA 6100, operating at a fixed frequency (1 Hz) in tension mode. The temperature was varied from -150 °C to 150 °C with a heating rate of 2 °C/min. The cloud-point temperature curves of the PFHDA-PFPETMA binary system was determined by cooling the liquid mixture of a known composition ratio from 120 °C in a temperature-controlled oil bath to the temperature at which the clear liquid solution was observed to become cloudy. Small angle X-ray scattering (SAXS) instrument (Anton Paar) was utilized to probe the microstructure in the fully cured p(PFHDA-PFPETMA) samples. The film was placed in a copper sample holder and scattering was measured at room temperature for 5 min, operating at 40 KV and 50 mA. The scattering signal was integrated into a 1D plot of intensity versus the scattering vector, q. Stress-strain measurements were performed on rectangular samples (1 x 10 x 15 mm) at room temperature on an Instron model 5566 system using a 10 kN load cell at a crosshead speed of 5 mm/min.

4.4 Results and Discussion

4.4.1 Synthesis of Tetramethacrylate-modified Perfluoropolyether Macromonomer (PFPE-TMA)
The PFPE tetrol oligomer ($M_n = 2000$ g/mol) is partially soluble in $1,1,1,3,3$-pentafluorobutane to form a slightly cloudy mixture at room temperature. With dibutyltin diacetate (DBTDA) as a catalyst, isocyanatoethyl methacrylate quickly reacts with the hydroxyl endgroups in the tetrol precursor to yield the PFPE-TMA macromonomer (Scheme 4-1). The cloudy reaction system was observed to become clear about 5 min after the reaction was initiated due to the formation of multifunctional PFPE macromonomer.

Scheme 4-1. Synthesis of PFPE-TMA macromonomer.

The $^1$H-NMR spectrum of the final product PFPE-TMA macromonomer is shown in Figure 4-1. A triplet peak at 3.87 ppm ($H_a$) corresponds to the PFPE methylene protons next to the ether linkage (2H, -CF$_2$-CH$_2$-O-) and the multiplet peaks at 4.30 ppm correspond the protons in the ether linkage group (3H, -O-CH$_2$-CH(O)-CH$_2$-O-) and multiplet peaks at 3.75 ppm for the protons (2H, -O-CH$_2$-CH(O)-CH$_2$-O-). The singlet peak at 5.09 ppm was assigned to the proton in the urethane group (1H, -NH-). The ethylene protons between the
urethane and the methacrylate endgroup appeared at 4.22 ppm (2H, -NHCH₂-CH₂O-) and 3.50 ppm (2H, -NHCH₂CH₂O-). The vinyl protons appeared at 5.59 and 6.11 ppm (vinyl, =CH₂). The very sharp singlet peak at 1.94 ppm corresponds to the protons in the methyl group (3H, -CH₃).

Figure 4-1. ¹H-NMR spectrum of PFPE-TMA macromonomer.

The hydrocarbon endgroups containing the urethane units tend to strongly self-associate through intermolecular interactions induced by hydrogen bonds between the urethane amide (-NH-) and the carbonyl groups present in both the urethane and methacrylate groups. These strong intermolecular interactions result in an extremely viscous PFPE-TMA macromonomer compared to the difunctional linear PFPE’s discussed in Chapter
2. The FTIR spectrum of the PFPE-TMA macromonomer is plotted in Figure 4-2. A stretching peak is observed near 3360 cm\(^{-1}\) corresponding to the hydrogen-bonded N-H stretching vibration.\(^{30}\) Accordingly, the deformation stretch of the urethane group was found at 1540 cm\(^{-1}\). As reported for a related system, the bond absorbing at around 3500 cm\(^{-1}\) for the free (non hydrogen-bonded) N-H stretching is not very pronounced.\(^{31}\) This indicates that most of the amide groups in the PFPE-TMA chains are involved with hydrogen bonding. The hydrogen-bonded and non-bonded carbonyl groups in the urethane units are indistinguishable by FTIR spectroscopy.\(^{32,33}\) Coleman et al. reported that in an amorphous polyurethane-polyether blend system, no stretching was found dominant either at 1700 cm\(^{-1}\) for the hydrogen-bonded carbonyl or at ~ 1740 cm\(^{-1}\) for the free carbonyl group.\(^{34}\) As seen in Figure 4-2, the broad stretching peak of the carbonyl groups found at 1720 cm\(^{-1}\) indicates that both free and hydrogen-bonded carbonyl groups coexist in the system.

![FTIR spectrum of PFPE-TMA macromonomer](image)

**Figure 4-2.** FTIR spectrum of PFPE-TMA macromonomer.
4.4.2 Cloud-point Temperature

In order to further increase the mechanical strength of the crosslinked PFPE material, a short chain crosslinker was incorporated into the PFPE-TMA matrix to enhance the degree of crosslinking. As previously mentioned, PFPE-TMA is able to strongly self-associate through intermolecular hydrogen bonding and so in order to achieve an intimately mixed system, it is suggested that the second component have a strong association with the PFPE-TMA macromonomer.\textsuperscript{34} To this end, 1H,1H,6H,6H-perfluorohexyl diacrylate (PFHDA) was studied as a crosslinker to mix with the PFPE-TMA macromonomer because the fluorinated nature of PFHDA will help to achieve a better miscibility with PFPE-TMA than most normally used hydrocarbon crosslinkers such as poly(ethylene glycol) triacrylate.\textsuperscript{35} Additionally, it is also important to use a fluorinated crosslinker additive to preserve the fluorinated nature of the resulting network materials and keep the surface tension at a minimum. It was found that after vortexing the liquid mixture at room temperature for 2 min, a homogeneous solution was consistently formed when less than 40 wt % of PFHDA was incorporated but the liquid binary system of PFHDA\textsubscript{0.4}-PFPE\textsubscript{0.6} appeared to be slightly cloudy at room temperature. Interestingly, the cloudiness of this sample disappeared to form a homogeneous single phase solution simply by warming to 36.5 °C and the solution remained clear even after cooling to room temperature. A similar phenomenon has been previously reported by Rábai \textit{et al.} for a fluorinated binary system.\textsuperscript{36}

A less compatible binary system was found when the content of PFHDA was further increased to 50 wt %. In this case, mixing of the two components yielded a cloudy and thermodynamically unstable emulsion, which readily separated into two phases within 2 h. It is well known in certain cases that two organic liquids with poor miscibility can reversibly
form a clear one phase solution above certain cloud-point temperature.\textsuperscript{37,38} Figure 4-3 shows the cloud-point temperatures of the PFHDA-PFPETMA liquid binary systems. With a decreasing fraction of the PFPE-TMA macromonomer in the system, the cloud-point temperature increases from 3 °C at 80 wt % to 110 °C at 10 wt %.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4-3.png}
\caption{Cloud-point temperatures of PFHDA-PFPETMA liquid binary systems.}
\end{figure}

The partial compatibility of PFPE-TMA with PFHDA was suspected to be caused by the immiscibility either between PFHDA and the methacrylate endgroups of the PFPE-TMA macromonomer or between PFHDA and the perfluorinated repeat units (-CF$_2$CF$_2$O- and -CF$_2$O-) in the PFPE-TMA macromonomer. To understand the nature of the incompatibility and immiscibility behavior, a simple solubility experiment was designed by first mixing PFHDA with isocyanatoethyl methacrylate (IEM). IEM is the compound that is reacted with the PFPE tetrol to add the urethane ether methacrylate functional groups to the PFPE-TMA macromonomer; therefore, it is very similar in chemical structure to the endgroups of the
macromonomer. It was observed that a homogeneous solution could be formed between the PFHDA and IEM over all composition ratios at room temperature. This observation indicates that the two compounds are fully miscible. The PFHDA was then mixed with a non-functional PFPE oligomer (Fomblin® Z03, CF₃-O-(CF₂CF₂O⁻/⁻CF₂O)ₙ-CF₃). The oligomer has similar perfluorinated repeat units to the PFPE-TMA macromonomer but has –CF₃ endgroups instead of methacrylate urethane endgroups. The non-functional -CF₃ endgroups on both ends fully exclude the effect of the hydrocarbon endgroups on the miscibility. The miscibility test unexpectedly showed that the PFHDA is incompatible with the non-functional PFPE. A dispersion was initially formed by vortexing the two-component mixture that then quickly separated into two phases. Based on these studies, it is hypothesized that the incompatibility of the PFPE-TMA macromonomer with PFHDA is mainly caused by the immiscibility of PFHDA with the perfluorinated repeat segments in the PFPE backbone.

This hypothesis agrees with the cloud-point temperature curve shown in Figure 4-3. Because of the good miscibility of PFHDA with the methacrylate endgroups in the PFPE-TMA macromonomer, the small PFHDA molecules can diffuse into the self-associated PFPE matrix and disrupt with the hydrogen-bonded system to form new associations between PFHDA and the PFPE-TMA macromonomer. These new associations can be accomplished either by hydrogen bonds between the urethane groups and the carbonyl groups in PFHDA, or by dispersive interactions between the methacrylate/acrylate endgroups. As a result, these two components show good miscibility up to a certain weight ratio. For example, the PFHDA₀.₂-PFPETMA₀.₈ liquid binary system appeared clear at room temperature and only turned cloudy when cooled to 3 °C. However, the resulting cloudiness of this sample may be
caused by the crystallization of PFHDA, which will be discussed in the following section. When the content of PFHDA was increased to 40 wt %, the intermolecular interactions of PFHDA with the methacrylate endgroups of the PFPE-TMA macromonomer were increased and the PFHDA self-aggregated. The self-aggregation may result in swelling the domains to a larger size. Once the domains become large enough, they can scatter the light inside the solution making it appear cloudy. In this case, the system was found to possess a cloud-point temperature of 28 °C. With such a low cloud-point temperature, the cloudy PFHDA_{0.2}\text{-PFPETMA}_{0.8} mixture can easily be turned into a homogeneous single phase solution simply by hand warming for about 2 min. The small amount of energy provided by warming to slightly above room temperature is thought to disrupt the self-aggregation of the PFHDA molecules and facilitate their efficient diffusion into the PFPE-TMA matrix to form a homogeneous system. However, when the concentration of PFHDA is further increased, the self-aggregation of the PFHDA molecules dominates the interactions with the methacrylate endgroups in the PFPE-TMA macromonomers. Therefore, as the PFHDA concentration is increased further, more energy is needed to disrupt this self-association to form a homogeneous solution, resulting in a system with an increased cloud-point temperature.

### 4.4.3 Glass Transition Temperatures

Phase separation occurred for the liquid PFHDA-PFPETMA binary systems due to the partial incompatibility of these two components. The glass transition temperatures (T_g) of these binary systems were determined by DSC measurements. As seen in Figure 4-4, a single T_g was observed for all of the liquid binary systems at around -100 °C, corresponding to the chain mobilization inside the fluorocarbon domains. The T_g was slightly lower at -114
°C for the liquid PFPE-TMA macromonomer, which was determined by dynamic differential scanning calorimetry (DDSC) (Table 4-1).

**Figure 4-4.** DSC spectra of liquid PFHDA-PFPETMA binary systems.

<table>
<thead>
<tr>
<th></th>
<th>( T_g (^\circ\text{C}) )</th>
<th>( T_c (^\circ\text{C}) )</th>
<th>( T_m (^\circ\text{C}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFHDA(<em>{0.2})-PFPETMA(</em>{0.8})</td>
<td>-98</td>
<td>-9.5</td>
<td>4.4</td>
</tr>
<tr>
<td>PFHDA(<em>{0.4})-PFPETMA(</em>{0.6})</td>
<td>-100</td>
<td>-12.1</td>
<td>5.6</td>
</tr>
<tr>
<td>PFHDA(<em>{0.6})-PFPETMA(</em>{0.4})</td>
<td>-100</td>
<td>-60.2</td>
<td>6.1</td>
</tr>
<tr>
<td>PFHDA(<em>{0.8})-PFPETMA(</em>{0.2})</td>
<td>-100</td>
<td>-63.6</td>
<td>7.2</td>
</tr>
<tr>
<td>PFPE-TMA</td>
<td>-114</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

**Table 4-1.** Glass transition temperatures of PFHDA-PFPETMA liquid binary systems determined by DSC.
It is interesting to find a crystallization-melting process involved at low temperature for all of the binary systems. When 20 wt % of PFHDA was added, a small amount of crystallinity was observed at -9.5 °C, which then quickly melted at 4.4 °C. The crystallization of PFHDA may be responsible for the cloudiness of this solution at about 3 °C. As the PFHDA content in the system was increased, the crystallization became more pronounced. The crystallization temperature was also found to shift from -9.5 °C for the PFHDA0.2-PFPETMA0.8 sample to -63.6 °C for the PFHDA0.8-PFPETMA0.2 sample. Meanwhile, the melting temperature of the crystallinity was only slightly increased from 4.4 to 7.2 °C. The crystallization-melting process is thought to be involved with the alignment of small PFHDA molecules, not related to the PFPE-TMA macromonomer, since no crystallization and melting was found in the thermograph of the neat PFPE-TMA sample. Unlike the PFHDA0.2-PFPETMA0.8 sample, the cloudiness at room temperature of the binary systems with a higher PFHDA content was not associated with the crystallization process, because PFHDA crystals completely melted before room temperature. The cloudiness of these samples is therefore mainly attributed to phase separation.

By adding 0.2 wt % of HCPK as a photoinitiator, all of the liquid binary samples can be easily photochemically crosslinked to form fluorinated films under UV irradiation. At room temperature, a homogeneous PFHDA0.2-PFPETMA0.8 solution was cured to yield an optically transparent sample. Because the cloud-point temperature of PFHDA0.4-PFPETMA0.6 was only 28 °C, the heating generated by the UV irradiation was sufficient to interrupt the self-associations of the PFHDA molecules and thus form a clear system before the crosslinking was initiated. Curing of this homogeneous solution resulted in an optically transparent film. Only the PFHDA0.6-PFPETMA0.4 and PFHDA0.8-PFPETMA0.2 systems
were cured to yield cloudy samples at room temperature because of the partial incompatibility of these two components. However, the cloud-point temperature curve in Figure 4-3 indicates that the two-phase cloudy mixture can be made to be a homogeneous single phase when the temperature is higher than its cloud point. This provided a strategy to yield optically transparent network samples from these cloudy liquid mixtures by controlling the cure temperature. As a result, optically transparent p(PFHDA_{0.6}-PFPETMA_{0.4}) and p(PFHDA_{0.8}-PFPETMA_{0.2}) samples were obtained when cured at 65 and 85 °C, respectively (Figure 4-5).

![Figure 4-5](image-url)

**Figure 4-5.** Photograph of cured p(PFHDA-PFPETMA) samples. Optically transparent p(PFHDA_{0.6}-PFPETMA_{0.4}) and p(PFHDA_{0.8}-PFPETMA_{0.2}) samples were obtained when cured at 65 and 85 °C, respectively.

All of the crosslinked network samples appeared to be amorphous. No crystallization peak was found for these samples by DSC, but neither was the T_g information of these crosslinked samples detectable by DSC. The T_g’s were therefore studied by the loss factor (tan δ) determined by DMTA. The DMTA data is also useful for understanding the morphology and miscibility of the two fluorinated components in this system. Similar to the PFPE networks discussed in Chapter 2, two pronounced relaxation peaks were observed for the PFPE-TMA network sample, as seen in Figure 4-6.
The relaxation peak with a maximum at -123 °C was assigned to the fluorocarbon domains from the PFPE segments. Compared to the cured difunctional PFPE materials (PFPE-DMA), the relaxation temperature of the fluorocarbon domains for the cured PFPE-TMA sample was slightly higher than that of the 4 kg/mol PFPE-DMA (-130 °C) and lower than the 1 kg/mol PFPE-DMA (-80 °C). It is hypothesized that the PFPE segments with longer chains are more flexible and easier to relax and mobilize inside of the fluorinated domains. Unlike the PFPE-DMA samples, the relaxation peaks from the hydrocarbon domains of the crosslinked methacrylate endgroups appear to be very broad. For the PFPE-TMA sample, the relaxation peak ranges from -25 to 140 °C, which indicates a highly microheterogeneous morphology. From the plot, the maximum of the relaxation peak for the hydrocarbon domains from the polymerized methacrylate endgroups was determined to be approximately 104 °C, which is close to the previously reported crosslinked poly(methyl methacrylate) system (T_g = 135 °C).39

A shoulder at about -63 °C was observed for the cured PFPE-TMA sample. The shoulder is referred to as a β-maximum, generally found in polyurethanes and thought to be related to hydrogen bonds between contiguous chains.40 For both the clear p(PFHDA_0.2-PFPETMA_0.8) and p(PFHDA_0.4-PFPETMA_0.6) samples, a very broad relaxation peak for the copolymerized methacrylate/acrylate domains was observed which suggests an intermediate degree of miscibility between two components.41 The β-maximum was not observed for the p(PFHDA-PFPETMA) samples probably because hydrogen bonds associated with the urethane groups of the PFPE-TMA macromonomer are disrupted by the self-aggregation of PFHDA. As the fraction of PFHDA increased in the blend matrix, the samples cured at high temperature still appeared to be optically transparent; however, the loss factor values (tan δ)
of both relaxation peaks for each sample were gradually decreased. The decrease in the factor values probably indicates that the chains in both domains (hydrocarbon and fluorocarbon) were less free to mobilize in the blend systems. This could be caused by an increase in the crosslink density through incorporating numerous small PFHDA molecules into the system.\textsuperscript{41} Additionally, the DMTA spectrum of the cured, clear p(PFHDA$_{0.8}$-PFPETMA$_{0.2}$) sample was compared with the cloudy one of the same composition ratio. For the cloudy sample, the relaxation peak for the PFPE segments at \textasciitilde 120 °C became undetectable and the intensity of the relaxation peak in the high temperature region was slightly higher than that of the clear sample. Overall, the difference in the spectra for these two samples is insignificant due to both of them sharing very similar crosslink densities.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4-6.png}
\caption{DMTA spectra of cured p(PFHDA-PFPETMA) samples.}
\end{figure}
4.4.4 Morphologies

Two separated relaxation peaks in the DMTA spectra indicate phase separated systems.\textsuperscript{42} The clear appearance can only be explained that these systems are micro-heterogeneous with micro-scale domain sizes smaller than the wavelength of visible light, < 400 nm. SAXS experiments were performed to determine the average domain size of the cured, clear samples with variable composition weight ratios as seen in Figure 4-7. The cloudy samples were not included in this study because the domain size is beyond the detection limit (> 80 nm) of SAXS. A single broad peak was observed for both the PFPE-TMA and p(PFHDA\textsubscript{0.2}-PFPETMA\textsubscript{0.8}) samples. From the position of the peak in scattering intensity, a principal size (D) of the PFPE-TMA sample associated with the domains formed by the polymerized methacrylate endgroups of about 5.7 nm was calculated using \( D = \frac{2\pi}{q} \), where q is the principal scattering vector. The peak in scattering intensity shifted to a lower value of q when 20 wt % of PFHDA was incorporated, indicating a larger domain size of 6.4 nm. The slightly increased domain size is likely due to the domain swelling upon the addition of PFHDA. As discussed previously, the partial compatibility of PFHDA with the methacrylate endgroups helps to achieve a well-mixed system in the liquid state when a small amount of PFHDA was added (e.g. 20 wt %). In contrast, instead of a pronounced peak, an upturn was found for all of the other p(PFHDA-PFPETMA) samples with the PFHDA content greater than 40 wt %. It is postulated that the enhanced scattering intensity at \( 0.2 < q < 1 \) (ca. 6 – 30 nm length scales) suggests compositional heterogeneities over a range of larger length scales. As discussed in the cloud-point temperature measurements, the larger domain size in these cases results from the self-aggregation of the PFHDA molecules dominating the intermolecular interactons between PFHDA and PFPE-TMA. Due to the relatively small
length scale (less than 50 nm) of the system heterogeneities, the microphase separation does not cause the samples to be visibly cloudy.

**Figure 4-7.** 1D SAXS data for cured p(PFHDA-PFPETMA) clear samples.

The bulk morphologies of the cured p(PFHDA-PFPETMA) samples were investigated by AFM. The phase contrast images were taken on the cross sections of these samples and the results were found to be generally consistent with the SAXS data. As seen in Figure 4-8a, the cross section of the neat PFPE-TMA sample looks highly disordered. The small domains of 3 – 5 nm from the polymerized methacrylate endgroups are randomly distributed in the continuous PFPE matrix. When 20 wt % of PFHDA was added into the PFPE-TMA, the domain size was slightly increased to 6 – 10 nm (Figure 4-8b). Further increasing the content of PFHDA to 40 wt % resulted in a more heterogeneous cross section and also increased the domain size from less than 10 nm to 10 – 30 nm as shown in Figure 4-8c. The increased domain size is a result of the self-aggregation of PFHDA beginning to
dominate the interactions of PFHDA with the methacrylate endgroups of the PFPE-TMA chains. When PFHDA became the major component of the blend system some domains as large as 50 nm formed (see Figure 4-8d for the cured p(PFHDA\textsubscript{0.6}-PFPETMA\textsubscript{0.4}) clear sample).

As the PFHDA content was increased to 60 wt %, the amount of the domains from the copolymerized methacrylate/acrylate was increased and the boundary between these isolated domains and the continuous PFPE matrix appears sharper compared to that in Figure 4-8c for the p(PFHDA\textsubscript{0.6}-PFPETMA\textsubscript{0.4}) clear sample. The changes on the morphology presumably indicate a decreased compatibility of these two components in the copolymerized system. When the PFHDA content was increased to 80 wt %, some isolated domains were observed with a domain size of 30 – 50 nm and many domains began to aggregate with each other to form a strip-like morphology of 10 – 30 nm in thickness and 50 – 200 nm in length as shown in Figure 4-8e. In this case, a co-continuous biphasic morphology began to form. The neat p(PFHDA) sample gives a very homogeneous cross section without any noticeable domains observed (Figure 4-8f). The AFM phase contrast images show a transition in the bulk morphologies of the materials as the PFHDA content is increased thus indicating that as more PFPE is added a less miscible system is obtained. These results corroborate the observation by SAXS.

Additionally, the AFM phase contrast images were compared for two pairs of clear and cloudy samples in the composition ratios of 60 wt % and 80 wt %. Not surprisingly, it was observed that the morphologies of the two cloudy samples in Figure 4-7g and 4-7h were very different from those of the corresponding clear samples in Figure 4-7d and 4-7e. The cloudy samples possess a more heterogeneous cross sections with some large domains of
several hundred nanometers in size resulting in the cloudy appearance of the samples. In contrast, the optically transparent samples are only microphase separated and thus do not scatter visible light.

Figure 4-8. AFM phase contrast images in tapping mode on cross sections of cured samples. (a) PFPE-TMA, (b) clear p(PFHDA0.2-PFPETMA0.8), (c) clear p(PFHDA0.4-PFPETMA0.6), (d) clear p(PFHDA0.6-PFPETMA0.4), (e) clear p(PFHDA0.8-PFPETMA0.2), (f) p(PFHDA), (g) cloudy p(PFHDA0.6-PFPETMA0.4), and (h) cloudy p(PFHDA0.8-PFPETMA0.2).
4.4.5 Mechanical Properties

Compared to the previously studied PFPE elastomer materials crosslinked from difunctional linear macromonomers, the crosslinked tetramethacrylate-modified PFPE material with \( f = 4 \) is supposed to possess a higher degree of crosslinking. The modulus of PFPE-TMA (\( M_n = 2,000 \text{ g/mol} \)) was measured by the stress-strain curve to be 155 ± 6 MPa. This is much higher than that of the 4 kg/mol PFPE-DMA (7 MPa) and the 1 kg/mol PFPE-DMA (90 MPa) because of the enhanced crosslink density in the PFPE-TMA network induced by both chemical crosslinking and physical crosslinking (hydrogen bonds). It is expected that the Young’s modulus of the blend system can be further increased by copolymerizing with the short chain crosslinker PFHDA. When 20 wt % of PFHDA was added, the modulus was increased to 267 ± 11 MPa and when 80 wt % of PFHDA was added a very rigid material with a modulus of 458 ± 47 MPa was achieved. Compared with the difunctional elastomer materials, this material showed less flexibility with a short elongation (~ 1 %) and is therefore expected to provide enough mechanical durability for long term applications.

![Stress-Strain curves of cured p(PFHDA-PFPETMA) samples by Instron.](image)

**Figure 4-9.** Stress-Strain curves of cured p(PFHDA-PFPETMA) samples by Instron.


4.4.6 Surface Tensions

In adding the difunctional PFHDA as filler into PFPE matrix the mechanical strength is enhanced while simultaneously preserving the fluorinated nature of the resulting PFPE network materials, which served to keep the surface tension for these materials at a minimum. Surface tensions of the p(PFHDA-PFPETMA) materials were calculated based on the Owens-Wendt-Kaelble method (OWK). As discussed in Chapter 2, this method can distinguish the contributions of dispersive and polar components to the overall surface tension. The static contact angles of water and n-hexadecane were measured at air interfaces of crosslinked samples cured at room temperature. As summarized in Table 4-2, the surface tension of the neat PFPE-TMA sample is 14.6 mN/m, which is comparable to that of a crosslinked difunctional PFPE-DMA surface (13-16 mN/m). When incorporating 20 wt % of PFHDA into the crosslinked PFPE system, the surface tension remained low (14.3 mN/m). Further increasing the PFHDA content slightly decreased both the water and hexadecane contact angles, resulting in slightly increased contributions from the dispersive and polar components to the overall surface tension. When 80 wt % of PFHDA was incorporated, the overall surface tension was increased to 17.5 mN/m. Furthermore, the surface tension of a homogeneous p(PFHDA) sample was measured (23.6 mN/m). A large contribution of dispersive component was observed that contributed to a relatively higher overall surface tension for this material. Compared to other samples, the increased dispersive component was mainly attributed to the less hydrophobic nature of the PFHDA crosslinker. Along with the low surface tension, the greater mechanical durability of these PFPE materials would be advantageous since one of limiting factors in soft silicone-based fouling-release performance
such as silicone is its softness which makes it prone to physical damages in long term ocean trials.

<table>
<thead>
<tr>
<th></th>
<th>Static Contact Angle (degree)</th>
<th>Surface Tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water</td>
<td>Hexadecane</td>
</tr>
<tr>
<td>PFPE-TMA</td>
<td>104.8 ± 1.7</td>
<td>70.5 ± 0.6</td>
</tr>
<tr>
<td>p(PFHDA&lt;sub&gt;0.2&lt;/sub&gt;-PFPETMA&lt;sub&gt;0.8&lt;/sub&gt;)</td>
<td>105.5 ± 2.1</td>
<td>70.8 ± 1.0</td>
</tr>
<tr>
<td>p(PFHDA&lt;sub&gt;0.4&lt;/sub&gt;-PFPETMA&lt;sub&gt;0.6&lt;/sub&gt;)</td>
<td>103.5 ± 1.3</td>
<td>69.3 ± 0.5</td>
</tr>
<tr>
<td>p(PFHDA&lt;sub&gt;0.6&lt;/sub&gt;-PFPETMA&lt;sub&gt;0.4&lt;/sub&gt;)</td>
<td>102.0 ± 2.6</td>
<td>69.0 ± 0.8</td>
</tr>
<tr>
<td>p(PFHDA&lt;sub&gt;0.8&lt;/sub&gt;-PFPETMA&lt;sub&gt;0.2&lt;/sub&gt;)</td>
<td>98.3 ± 3.0</td>
<td>65.8 ± 2.2</td>
</tr>
<tr>
<td>p(PFHDA)</td>
<td>96.1 ± 1.8</td>
<td>41.0 ± 2.1</td>
</tr>
</tbody>
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Table 4-2. Surface tensions of PFPE materials determined by Owens-Wends-Kaelble method.

4.5 Conclusions

In this work, we were able to synthesize tetramethacrylate-modified perfluoropolyethers which can be photochemically crosslinked by UV irradiation in one step to yield a fluorinated network with improved mechanical strength. With hydrogen bonds and dispersive interactions between the urethane ether methacrylate and fluorinated acrylate groups, PFHDA shows partial miscibility with the PFPE-TMA macromonomer. As a small amount of PFHDA (< 40 wt %) is mixed with the PFPE-TMA macromonomer, a homogeneous solution can be formed at room temperature. However, when the PFHDA becomes the major component of the liquid binary system, the self-aggregation of the PFHDA begins to dominate the intermolecular interactions between these two components and results in an incompatible system. The cloud-point temperature data indicates that as the
content of the PFHDA in the binary system is increased, the miscibility between the two components is decreased, and a homogeneous clear solution becomes more difficult to achieve. Because of the partial immiscibility of these two components, only optically transparent materials with a PFHDA content of less than 40 wt % can be obtained via UV curing at room temperature. However, optically transparent samples with a PFHDA content larger than 40 wt % can be achieved by controlling the cure temperature above the corresponding cloud-point temperature of the system. The DMTA spectra indicate that the partial immiscibility of the two components results in microphase separation even in the cured clear samples. The domain size of these microheterogeneous domains was revealed to vary from < 10 nm to 30 nm by SAXS. AFM contrast images further confirmed the microphase separation morphology of these optically transparent materials.

The Young’s moduli of these materials (155 – 458 MPa) are much higher than those reported for PDMS (2.5 MPa) and other fluorinated elastomer materials (1 – 90 MPa). Along with the low surface tensions (14.3 – 17.5 mN/m), these materials should provide enhanced mechanical strength for fouling-release coating applications. Studies on these two-component systems will help to fundamentally understand the miscibility issues associated with fluorinated monomers and lead to an optimized design for more compatible fluorinated materials with better mechanical durability.
4.6 References

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