Synthesis, Characterization, and Application of Oleophobic Fluorinated Copolymers

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SYNTHESIS, CHARACTERIZATION, AND APPLICATION OF OLEOPHOBIC FLUORINATED COPOLYMERS

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Materials Science and Engineering

by
Liying Wei
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Accepted by:
Dr. Igor Luzinov, Committee Chair
Dr. Philip J. Brown
Dr. O. Thompson Mefford
Dr. Olga Kuksenok
ABSTRACT

For decades, water and oil repellency of engineering thermoplastics has been achieved with the introduction of long-chain perfluoroalkyl substances and moieties \((C_nF_{2n+1}, n \geq 7)\). However, their bioaccumulative and toxicological impact is now widely recognized and; consequently; the substances have been phased out of industrial production and applications. To this end, the key goal of this dissertation is to develop safe and effective replacements for the long-chain perfluoroalkyl substances.

Namely, we report here on synthesis, characterization, and application of perfluoropolyether-based copolymers as low surface energy oligomeric additives to engineering thermoplastics. First, perfluoropolyether-based triblock polyester copolymers with different end-groups were obtained via polycondensation polymerization. Then, the materials were blended with thermoplastic polymers, such as polyethylene terephthalate (PET), nylon 6, and poly(methyl methacrylate) (PMMA), at various concentrations to obtain oleophobic polymer films. The morphology and surface properties of the films were studied. The results show that the fluorinated triblock copolymers with non-fluorinated middle block readily migrate to the film boundary. They can form brush-like structure on the polymer film surface, and in doing so impart significant water and oil repellency to the polymer films.

The final part of this work was focused on synthesis and characterization of perfluoropolyether-based polyurethane materials (oligomers and block copolymer) obtained via step-growth polymerization. We found that the synthesis of the fluorinated polyurethanes is less challenging than the one for fluorinated polyesters. The wettability
measurements indicated that addition of the polyurethanes to engineering thermoplastics offers somewhat higher water and oil repellency in comparison to the polyester based fluorinated block copolymers. However, the polyurethane materials have lower decomposition temperature.
DEDICATION

I dedicate this dissertation to my husband Yuqi Zeng and my family in China for their support, love, and encouragement throughout my PhD study and my life.
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CHAPTER ONE

INTRODUCTION

There is significant work has been carried out to develop effective replacements for low surface energy additives containing long-chain perfluoroalkyl substances and moieties (PFASs, \( C_nF_{2n+1}, n \geq 7 \)). The reason is that PFASs are found to be persistent and toxic to environment, humans, and wildlife. In this respect, perfluoropolyethers (PFPEs) are considered as the potential substitutes for PFASs. However, pure PFPE materials cannot serve as effective water/oil repellent additives for conventional thermoplastics due to their immiscibility and incompatibility with polymer matrices. In addition, pure PFPEs are liquids of very low viscosity, which leads to their exudation from the surface of the host polymer over short periods of time. Therefore, PFPE-based materials (not pure PFPEs) are suggested as replacements to PFASs. However, to date, limited research has been conducted to obtain effective hydrophobic/oleophobic PFPE-based additives to engineering thermoplastics. This work is aiming for filling this gap.

Specially, we focused on the synthesis, characterization, and application of PFPE-based oligomeric triblock copolymer (FOPB) additives, which are designed to produce surface modifications to conventional polymer materials. For this purpose, PFPE-based oligomers and triblock copolymers with different macromolecular architectures were synthesized and characterized. The materials contain short \( C_4F_9 \)– or \( C_6F_{13} \)– perfluoroalkyl segments and do not yield unsafe long-chain perfluoroalkyl carboxylic acid. They were used as effective low surface energy additives to limit surface wettability of thermoplastic polymers. The structure of this dissertation is as followed:
**Chapter 2** gives the literature review of materials and techniques used for fabrication and characterization of hydrophobic/oleophobic surfaces. It also describes the synthesis and characterization of PFPE-based materials and their practical applications as low surface energy additives.

**Chapter 3** introduces the materials, experimental analysis and techniques used in this research.

**Chapter 4** concentrates on the synthesis and characterization of PFPE-based polyester triblock copolymers with C₄ and C₆ end-groups. The results of structural and thermal analysis for the materials are also included in **Chapter 4**.

**Chapter 5** focuses on the fabrication and characterization of hydrophobic and oleophobic boundaries by blending PFPE-based polyester copolymers with thermoplastic polymers, such as poly(ethylene terephthalate) (PET), nylon 6, and poly(methyl methacrylate) (PMMA). **Chapter 5** also discusses the effect of annealing treatment at elevated temperature and storage time on the surface wettability of modified polymers. Furthermore, the formation of fluorinated copolymer surface layers and structural characterization of the layers are also described in **Chapter 5**.

**Chapter 6** details the synthesis and characterization of copolymer with poly (ethylene isophthalate-co-terephthalate) (PEI-co-PET) middle block. **Chapter 6** also focuses on alternating the surface wettability of PET films using this copolymer possessing PEI-co-PET.

**Chapter 7** describes the synthesis of PFPE-based polyurethane oligomers with different chemical structures and their characterization. The fabrication and
characterization of hydrophobic and oleophobic PET films by adding fluorinated polyurethanes into PET are also discussed in Chapter 7.

Chapter 8 details the synthesis of PFPE-based polyurethane triblock copolymer with C\textsubscript{4}F\textsubscript{9}-fluorinated ends. Then, the copolymer was blended with PET with different concentrations, and the wettability of the obtained films was determined.

Chapter 9 concludes and summarizes the results of this dissertation.

References


CHAPTER TWO
LITERATURE REVIEW

In general, hydrophobic/oleophobic substances are being used as low surface energy additives to polymeric materials. The low surface energy materials with limited wettability by water and oils have received significant attention for numerous applications, including textiles, membranes, and self-cleaning boundaries.\textsuperscript{1-4} To date, an extensive portfolio of materials possessing low water wettability is available for applications. In turn, the preparation of oleophobic surfaces is more challenging, since oils have much lower surface tension ($\sigma_{\text{oil}} = 23$–$40$ mN/m) than that of water ($\sigma_{\text{water}} = 72$ mN/m) (\textbf{Table 2.1}).\textsuperscript{5-10} With the above in mind, there are a number of reasons for the preferential employment of fluorinated oligomers/polymers as low surface energy additives, including (a) mechanical properties, (b) abrasion and solvent resistance, (c) absence of evaporation/sublimation, and (d) possibility of melt processing at high temperature.\textsuperscript{11-21}

The research in this dissertation concentrates on the synthesis and surface modification of thermoplastic surfaces with the addition of PFPE-based materials (PFPE-based polyesters and polyurethanes). Therefore, \textbf{Chapter 2} presents the overview of studies on the development of low surface energy coatings. Also, the synthesis and characterization of PFPE-based materials are reviewed. In addition, the challenges in formation and applications of water/oil repellent surfaces are also discussed.
Table 2.1. Surface tension of common liquids used to evaluate surface repellency.\textsuperscript{7-10}

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<tr>
<th>Liquid</th>
<th>Surface Tension (mN/m)</th>
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<tbody>
<tr>
<td>Water</td>
<td>71.99</td>
</tr>
<tr>
<td>Diiodomethane</td>
<td>50.80</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>47.70</td>
</tr>
<tr>
<td>Olive oil</td>
<td>32.03</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>27.05</td>
</tr>
<tr>
<td>Ethanol</td>
<td>22.10</td>
</tr>
<tr>
<td>Hexane</td>
<td>18.43</td>
</tr>
<tr>
<td>Silicone oils</td>
<td>16-20</td>
</tr>
<tr>
<td>Perfluorohexane (FC-72)</td>
<td>10</td>
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</tbody>
</table>

2.1. Modeling of Wetting

The study of wetting phenomena has attracted great interest from both theoretical and practical standpoints.\textsuperscript{22-24} Among these studies, contact angle (CA) measurements are believed to be the simplest testing method to perform.\textsuperscript{25} The concept of CA and its equilibrium state are important to determine the surface wettability. On the ideal flat surfaces, Young’s model can be applied.\textsuperscript{26} On the other hand, Wenzel and Cassie-Baxter models play a key role in understanding the surface wettability of a rough surface.\textsuperscript{27-28} In addition, re-entrant angle model and dynamic contact angle hysteresis model have also received a significant attention from both fundamental and applied points of view.\textsuperscript{5, 29-33}

2.1.1. Young’s Model

The equilibrium of forces at the three-phase (solid, liquid, vapor) contact points is explained by Young’s model.\textsuperscript{26} In this model, it is assumed that the surface is smooth and non-textured. The equilibrium contact angle ($\theta$) is defined as the Young’s angle, which is
formed at the intersection of the liquid-solid interface and the liquid-vapor interface, as shown in Equation 2.1 and Figure 2.1.

\[ \gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \]  

(2.1)

where \( \gamma_{SV}, \gamma_{LV}, \) and \( \gamma_{SL} \) represents the interfacial tension at solid-vapor, liquid-vapor, and solid-liquid boundaries, respectively.

**Figure 2.1.** Images of wetting phenomena on a smooth and homogeneous solid surface (Young’s model).

Therefore, the surface wettability is determined by the chemical makeup of the solid and liquid.\(^{29}\) It means when a liquid droplet is in contact with the solid and reaching the equilibrium state, a solid phase with low surface tension \( (\gamma_{SV}) \) would provide a large interfacial tension \( (\gamma_{SL}) \), resulting in a large static CA of the liquid phase through the model.\(^{29}\)
On the basis of Young’s equation, it is illustrated that as a liquid is placed on a smooth homogenous solid surface, it either spreads over the surface or forms a drop with a definite angle of contact between the liquid-solid phase. As shown in Figure 2.1, when the Young’s CA is 0°, the surface is completely wetted by the liquid. As the surface is partially wetted by the liquid, there is a defined angle formed on the surface. Specially, the surfaces have CA less than 90° are considered to be hydrophilic/oleophilic surfaces, while hydrophobic/oleophobic surfaces possess CA larger than 90°. When the CA equals to 180°, the surface is defined as non-wetting surface. It is necessary to note that the maximum water CA that has been reported on a smooth surface is about 130°.34-35 However, most solid surfaces are non-ideal. Namely, the surfaces are rough and/or complex. Therefore, Young’s model has significant limitations in explaining the surface wettability in practical.

2.1.2. Wenzel and Cassie-Baxter Models

The effect of roughness on surface wettability has been described by Wenzel and Cassie-Baxter models.27-28 It is demonstrated that both surface free energy and surface roughness are the critical factors for observed wettability. The schematic illustrations of Wenzel and Cassie-Baxter model is presented in Figure 2.2 and Figure 2.3, respectively.

In Wenzel’s theory, it is assumed that the rough surface demonstrates an apparent contact angle ($\theta_w$):

$$\cos \theta_w = r \cos \theta_Y$$

(2.2)

where $r$ is the surface roughness factor displayed as the ratio of the surface area in contact with liquid to the projected surface area, and $\theta_Y$ is the Young’s contact angle on the flat surface made from the same material (Figure 2.2).
According to Wenzel’s model, the liquid is completely in contact with the surface; thus, the surface roughness factor ($r$) is always larger than 1. As a result, in the case of hydrophobic/oleophobic surface ($\theta_Y > 90^\circ$), a higher apparent contact angle ($\theta_w$) is obtained as the contact area increases. On the other hand, when the surface is hydrophilic/oleophilic ($\theta_Y < 90^\circ$), the apparent contact angle ($\theta_w$) is lower than the one of the flat surface. However, the agreement of experimental results with Wenzel’s model is far from ideal. It has been proposed that only when the size of the liquid drop is larger than the roughness scale by two or three orders of magnitude, the Wenzel’s equation can be applied.

The Cassie-Baxter model suggests that, for hydrophobic surfaces, the liquid droplet is not completely in contact with the rough surface. Subsequently, air pockets are forming between the droplet and solid surface, resulting in a composite interface (Figure 2.3). In this model:

$$\cos \theta_{CB} = f_1 \cos \theta_{Y1} + f_2 \cos \theta_{Y2}$$ (2.3a)

where $\theta_{Y1}$, $\theta_{Y2}$ are Young’s contact angles, and $f_1, f_2$ are area fraction of the component surface. At this time, the apparent contact angle ($\theta_{CB}$) is displayed as the sum of the
contribution of the solid surface and the air contact, where $\theta_{12}$ equals to $180^\circ$. Therefore, the equation can be simplified to

$$\cos \theta_{cb} = f_1(1 + \cos \theta_{11}) - 1 \quad (2.3b)$$

where $f_1$ and $f_2 = 1 - f_1$ is a fraction of the liquid-solid interface and the liquid-air interface, respectively.

**Figure 2.3.** A schematic illustration of the Cassie-Baxter model. Redraw from Ref [102].

It is necessary to point out that the presence of the air pockets between the liquid and solid surface has a significant effect on the CA results.\(^{38-39}\) As contact area of the liquid and air ($f_2$) increasing, a higher apparent contact angle ($\theta_{cb}$) is obtained. Namely, the Cassie-Baxter model indicates that the amplification of the contact area between liquid and air trapped in small-scale surface feature can influence the surface wettability.\(^{28-29}\)

**Figure 2.4** presents the relationship of water contact angle on a smooth surface ($\theta_{flat}$) and contact angle on a rough surface ($\theta_{rough}$). The slope can be determined by the surface roughness factor ($r$) and the contact area surface fraction ($\phi_s$).\(^{29}\) The contact point of the two lines in the figure can be used to find the point of transformation from the Wenzel
state to the Cassie-Baxter state, and such transformation can be regulated through alternating of surface structures.\textsuperscript{40}

\textbf{Figure 2.4.} The Wenzel and Cassie-Baxter models in relation to the surface roughness and static contact angle. Adapted from Ref [29] with permission from Journal of Engineered Fibers and Fabrics.

\subsection*{2.1.3. Re-Entrant Angle Model}

It is obvious that Cassie-Baxter wetting model is desirable for obtaining the hydrophobic and oleophobic surfaces.\textsuperscript{28} However, the design of robust superhydrophobic and superoleophobic materials with static water and oil contact angle larger than 150° is even more challenging. These highly-repellent surfaces are needed to resist polluted water, alcohols, and various oil solvents (alkanes and octanes), whose surface tension is much lower than that of water. The surfaces with very limited wettability are important in numerous practical applications, such as in functional textiles, oil capture, fluid transport, fingerprint resistant surfaces, and anti-corrosion coatings.\textsuperscript{41-55}
Therefore, the geometry of surface structures needs to be optimized to further enhance the surface repellency.\textsuperscript{33, 56-60} As shown in Figure 2.5, there are two different types of surface textures having sharp edges. \textbf{Figure 2.5a} shows the concave structure, and the texture in \textbf{Figure 2.5b} is convex structure. They both have the same solid surface energy. In the concave structure, the surface protrusion’s geometric angle (\(\psi > 90^\circ\)) is larger than the contact angle (\(\theta\)) between the liquid and the protrusion. Consequently, the net traction on the liquid-vapor interface is downward due to capillary force, which results to the liquid fully wetting the solid and changing to the Wenzel state.\textsuperscript{29, 32, 58}

![Figure 2.5](image)

\textbf{Figure 2.5.} Re-Entrant Angle Models. a) concave and b) convex structure. Redraw from Ref [58].

In contrast, when \(\psi (\psi < 90^\circ)\) is smaller than \(\theta\), the texture is defined as convex structure, which can lead to the stable Cassie-Baxter state.\textsuperscript{3} It means the liquid does not proceed into the solid textures in convex structure. Thus, the droplet will not wet through the rough surface entirely and will leave air pockets. Numerous studies have been demonstrated that the highly oil-repellent surfaces can be effectively fabricated by alternating the micro/nano-scale protrusions to become convex structures.\textsuperscript{33, 61-65} However,
there are still many limitations in this approach since precisely geometrical parameters control for re-entrant structures is required.

### 2.1.4. Dynamic Contact Angle Model

Besides static contact angle, another important parameter characterizing the surface wettability is dynamic contact angles, including advancing and receding angles.\(^{66}\) Contact angle hysteresis (CAH) is defined as the difference between advancing and receding angle value of a droplet started on a solid surface.\(^{32,67-68}\) The criteria for superoleophobic surface is not only high static CA (> 150°), but also low CAH (< 5°).

\[
CAH = \theta_A - \theta_R
\]

where \(\theta_A\) and \(\theta_R\) is the value of advancing and receding angle, respectively.

Typically, dynamic contact angles and CAH can be measured using two methods: volume changing method (Figure 2.6a) and tilting cradle method (Figure 2.6b). For the volume changing method, a droplet is formed on the solid surface, a needle is placed close to the surface, and the volume of the droplet is increased gradually until CA reaches a constant value. This provides the advancing angle, while when volume of the droplet is gradually decreased, the receding angle is determined. On the other hand, in the tilting cradle method, the droplet is placed on substrate, which is gradually tilted. The advancing angle is determined at the front of the droplet before it begins to slide, while the receding angle is measured at the back of the droplet at the same time. Furthermore, this slippery behavior is also referred as the sliding angle (SA). The SA (\(\alpha\)) is defined as the lowest angle that a surface has to be titled in order to let the droplets sit on it; subsequently; start to slide due to the gravitational force (Figure 2.6b).\(^{69}\)
Figure 2.6. Illustration of dynamic contact angle and contact angle hysteresis measurement. a) volume changing and b) tilting cradle method.

2.2. Wetting Surfaces in Nature

Scientists and researchers have learnt how plants create and use the hydrophobic surfaces in nature, and have mimicked the properties of these natural surfaces to create man-made products. One of the most well-known hydrophobic surfaces created by nature is the surface of lotus leaf. It was found that the water droplets falling on the leaf exhibit high contact angle and a low hysteresis.\textsuperscript{5, 70} Therefore, the droplets can freely move along the leaf and remove the contaminants to keep the surface clean. This superhydrophobicity (water CA > 150°) and self-cleaning properties of the lotus leaves in air are often referred as “lotus effect”. The phenomena is observed because the upper side of the lotus leaves is
covered with micro-/nanoscale hierarchical papillae and epicuticular wax. The size of these three-dimensional wax crystals ranges from 0.5 to 20 μm, and the composition is various, including long chain hydrocarbon and their derivatives. Therefore, the combination of the structural roughness and hydrophobic wax results in the high water repellency. There are lots of other plants in nature that can repel water like lotus leaves, and their properties have been studied to create water repellent products. However, these hydrophobic examples in nature cannot repel oil using the same method. Oils are more likely to spread out on a surface because oils have much lower surface tension than water.

However, there are creatures in nature demonstrating superoleophobicity in different environments. Cheng et al. revealed the underwater superoleophobicity on the lower side of lotus leaves (Figure 2.7). They measured the underwater oil CA and the results show that the lower side of the leaves exhibited the value of 155.0 ± 1.5° for 1,2-dichloroethane oil CA. The oil droplets could also roll off easily from the surfaces (Figure 2.7a). The reason behind this is that the lower side of lotus leaves has no hierarchical papillae and is hydrophilic. In turn, the lower surface consists of various tabular and slightly convex papillae (Figure 2.7b), which are individually covered with nanogroove structures (Figure 2.7c). Furthermore, it is suggested that certain hydrophilic materials like ferns exist on the surface of lower side also can influence the oil repellency. As a result, the lower side of the lotus leaves is hydrophilic in air, but superoleophobic in water when floating. Another underwater oleophobic surface created by nature is the fish scales. They are composed of calcium phosphate (Ca₃(PO₄)₂), protein, and a thin layer of mucus, which resulted in hydrophilic surfaces. Furthermore, it was found that the scales are
also covered with oriented micropapillae. Thus, when immersed in water, it forms oil-water-solid interface since water taking place of the air, which preventing the oil from contacting the solid substrates. This oil-water-solid interface leads to the oil repellency of the fish scales underwater. Up to now, the design and development of underwater oleophobic surfaces inspired by fish scales have attracted increasing attention for the applications in anti-bioadhesion, microfluidics, and marine anti-biofouling coatings since they are fluoride-free.

**Figure 2.7.** Images of oil wettability of the lower side of a lotus leaf under water (a), environmental scanning electron microscope (ESEM) images of tabular and slightly convex papillae (b), and atomic force microscope (AFM) images of the tabular papillae coving with nanogroove structures (c). Reproduced from Ref [67] with permission from the Royal Society of Chemistry.
Natural surfaces exhibiting oleophobicity in air are quite rare. It was reported that some insect species can repel oil in air. For example, the wings of leafhoppers exhibit diiodomethane ($\sigma = 50.80$ mN/m) and ethylene glycol ($\sigma = 47.70$ mN/m) CAs around $148.2-156.0^\circ$ and $152.7-164.1^\circ$, respectively. Springtails are wingless insects live in temporarily rain-flooded habitat. When immersed in olive oil ($\sigma = 32.03$ mN/m), springtails can repel oil due to the formation of a plastron layer around their body. The reason behind the high oil repellency for both cases above is the re-entrant geometric surface texture. However, a nature surface which can repel oil with surface tension less than 30 mN/m in air has not been found yet.

2.3. Synthetically Oleophobic Surfaces

Up to now, significant effort has been made towards oleophobic surfaces preparation. Generally, there are three different concepts of oil repellent surfaces (Figure 2.8). One method is only based on surface chemistry, especially the use of fluorocarbon-based materials. This is because that -CF$_3$ and -CF$_2$ groups exhibit the lowest surface energy as monolayer films. The carbon-fluorine bond exhibits high electronegativity and low polarizability in the fluorocarbon substances, resulting in high stability and low intermolecular attractive forces.

The second method is introducing surface texture on substrates. The appropriate surface roughness can increase oil repellency by entrapping air bubbles in the asperities across solid-liquid interface during oil contact. To increase the oil repellency further, it is necessary to combine the surface chemistry with proper texture. In 1997, Tsujii et al. were first to develop an artificial superoleophobic surface by roughening aluminum
with anodic oxidation and depositing a perfluorinated monolayer.\textsuperscript{86} The third method to achieve oleophobic surfaces is to cover the porous solid substrates with a highly viscous lubricant. After it infused into the surface, the oil can freely roll on the lubricant and avoid interacting with the underlying surfaces.\textsuperscript{69, 87} Overall, these three approaches confirm that the oleophobic surfaces can be fabricated by controlling surface chemistry and surface texture, and also by introducing an intermediary liquid layer.

![Oleophobic Surfaces Diagram]

**Figure 2.8.** Different approaches to fabricate oil repellent surface. Redraw from Ref [65].

### 2.4. Surfaces Chemistry

Traditionally, different types of fluorocarbon-based materials are used in non-aqueous repellent coatings, such as perfluoro silanes, perfluoro acids, and fluorinated polymers.\textsuperscript{13, 17, 20, 88-100} Although perfluoro silanes have been developed and applied in various fields, the deposited monolayer on substrates may not efficient enough to bring the
necessary repellent functions to the surfaces. Since perfluoro silanes are quite substrate dependent, perfluoro acids have attracted significant interests.

2.4.2. Perfluoro Acids

Perfluoro acids can be both physically and chemically deposited on various substrates to obtain significant water and oil repellency. For decades, long chain perfluoro acids, such as perfluoroalkyl sulfonic acids (C\textsubscript{n}F\textsubscript{2n+1}SO\textsubscript{3}H, n ≥ 6, PFSAs) and perfluoroalkyl carboxylic acids (C\textsubscript{n}F\textsubscript{2n+1}COOH, n ≥ 7, PFCAs), have been practically exclusively used for the fabrication of water and oil repellent surfaces in numerous applications, including textiles, polymer films, and surfactants. However, it has been widely recognized that the long chain perfluoro acids and their byproduct have toxicological impact on environment, humans and wildlife. The long chain perfluoro acids are more toxic in laboratory tests rather than their short chain analogues. Therefore, they have been phased out of industrial production and applications. Furthermore, PFSAs and PFCAs have also been restricted in different applications. As a result, the replacements for long chain perfluoro acids have been developed in intensified research.

2.4.2. Fluorinated Polymers

The fluorinated polymers are considered as alternatives to long chain perfluoro acids to achieve water and oil repellent surfaces. According to the literature, fluorinated polymers can be categorized in three groups, as shown in Table 2.93
Table 2.2. Categorizations of fluorinated polymers. Reproduced from Ref [93] with permission from Integrated Environmental Assessment and Management.

<table>
<thead>
<tr>
<th>Fluorinated Polymers</th>
<th>Examples</th>
</tr>
</thead>
</table>
| **Fluoropolymers**: Carbon-only polymer backbone with F directly attached to backbone C atoms | -(CF₂CF₂)ₙ- PTFE  
- (CH₂CF₂)ₙ- PVDF  
- (CH₂CHF)ₙ- PVF |
| **Side-chain fluorinated polymers**: Non-fluorinated polymer backbone with fluorinated side chains, ending in -CₙF₂ₙ₊₁ | **Fluorinated acrylate and methacrylate polymers**  
Acrylate: backbone: -CH-C(O)O-X-CₙF₂ₙ₊₁  
Methacrylate: backbone: -C(CH₃)-C(O)O-X-CₙF₂ₙ₊₁  
where X is -CH₂CH₂N(R')SO₂⁻ with R' = -CₙH₂ₙ₊₁ (n=0,1,2,4) or -CH₂CH₂⁻  
**Fluorinated urethane polymers**  
Backbone: -NHC(O)O-X-CₙF₂ₙ₊₁  
where X is either –CH₂CH₂N(R')SO₂⁻ with R' = -CₙH₂ₙ₊₁ (n=0,1,2,4) or -CH₂CH₂⁻  
**Fluorinated oxetane polymers**  
Backbone: -CH₂OCH₂-R  
where R = -CF₃, -C₂F₅ or -CH₂C₄F₉ |
| **Perfluoropolyethers**: Ether polymer backbone with F atoms directly attached | F-(CₙF₂mO-)ₙCF₃  
HOCH₂O-[CₙF₂mO-]ₙCH₂OH  
where CₙF₂mO represents -CF₂O-, -CF₂CF₂O-, and -CF(CF₃)CF₂O- units |
The fluorinated polymers display a wide range of useful properties, including chemical resistance, thermal and photochemical stability, low-reflective index, and low surface energy/adhesion. Different types of fluorinated polymers, including polyesters, polyethers, polyurethanes, acrylates/methacrylates, tetrafluoroethylene- and vinylidenefluoride- based polymers, and polyamides have been synthesized and characterized.

**Fluoropolymers**

In 2011, Robert et al. defined fluoropolymers as the ones containing F bond to one or two olefinic C atoms, to form a perfluorinated C atoms only polymer backbone with F atoms directly attached to it. This type of materials includes, polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polyvinyl fluoride (PVF), and copolymers of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP). Some of them were manufactured by emulsion polymerization. During the processing, ammonium salt of perfluoroctanoic acid (PFOA, C$_7$F$_{15}$COOH) was used as emulsifier in order to obtain a fine particle size and distribution. Since the safety concerns about PFOA, most producers have discontinued the products or using more environmental acceptable alternatives. On the other hand, fluoropolymers like PTFE and PVDF are typically prepared by suspension polymerization without using fluorosurfactants.

PTFE was first discovered in 1938. It has been widely recognized because of its properties, such as high thermal stability and low friction. It was reported that the water and hexadecane contact angle for PTFE was 108° and 46°, respectively. However, PTFE usually exhibits relatively poor mechanical properties and low adhesion due to its
low surface energy. In addition, the higher cost of PTFE than others also prevents PTFE from wide spreading as bulk materials in industrial and practical applications.

**Side-chain Fluorinated Polymers**

In the opposite of fluoropolymers, side-chain fluorinated polymers possess various non-fluorinated polymer backbone with fluorinated side chains, ending in \(-C_nF_{2n+1}\). Examples of these materials are typically fluorinated acrylate/methacrylate polymers, fluorinated urethane polymers, polystyrenes, and fluorinated oxetane polymers. For polyacrylate/methacrylate, the fluorinated acrylate/methacrylate monomers are copolymerized with one or more non-fluorinated monomers and other possible monomers to give the final fluorinated side chain. They are useful as water- and grease-proofing finishes for textiles, leather, and paper surfaces. The fluorinated oxetane polymers are synthesized by reacting polyfluorinated alcohols with oxetanes bearing a CH₂Br in the side segments to form oxetane monomers. Subsequently, the ring opening polymerization is used to obtain side-chain polyfluorinated polymers. These polymers are offered in many forms and mainly used as fluorosurfactants and coating additives. In 1989, Kirhner demonstrated that side-chain fluorinated urethane polymer was obtained by reacting polyisocyanate homopolymers with fluortelomer alcohols (FTOHs) or perfluoroalkane sulfonaidoethanols (alkyl-FASEs). Furthermore, Ameduri et al. proposed that the fluorinated materials with fluorine-containing pendant groups were better than those with fluorinated groups in the main chain. To date, there are numerous studies that have focused on fluorinated polyurethane materials. The combination
of urethane and fluoro-containing segments provides many advantages to the resulting materials, such as low water absorptivity, excellent flexibility, and low surface energy.

*Perfluoropolyethers*

Perfluoropolyethers are macromolecules possessing in their backbone the units of \(-\text{CF}_2-, \text{-CF}_2\text{-CF}_2-,\) and \(-\text{CF}(\text{CF}_3)\text{-CF}_2-,\) which are separated by oxygen atoms.\(^{93}\) PFPEs are first reported in the early 1960s, and since then have proven to be a unique class of fluorinated polymers with low volatility, high chemical inertness and radiation resistance, nonflammability, low surface tension, good oxidative/thermal stability, and low coefficients of friction.\(^{20, 95, 98-99, 151-152}\) In addition, PFPEs possess good chain mobility and flexibility due to the oxygen atoms in the polymer main chains. Since the repeating units of these PFPEs contain only 2 or 3 perfluorinated C atoms per O atom, their degradation cannot result in the formation of long chain perfluoroalkyl carboxylic acids.\(^{93}\) Furthermore, the surface tension of linear PFPE is quite low (20-22 mN/m) and approaching the surface tension of PTFE/Teflon (\(\sigma_{\text{PTFE/Teflon}} = 18.5\) mN/m).\(^{20, 114}\) Owing to these properties, PFPE-based materials are considered as the potentially safer substitutes for PFSAs and PFCAs. Although PFPEs have numerous advantages, as pure materials, they cannot serve as effective water/oil repellent additives due to their immiscibility and incompatibility with other organic polymers.\(^{20, 153}\)

In this respect, there are three common methods to add pure PFPEs to other reactants in order to achieve an appreciable surface properties. One method is using PFPEs with reactive terminal groups like hydroxyl groups as co-monomer. However, this may be economically infeasible, since the chemical modification has to be done during synthesis,
and a fraction of unreacted PFPEs will remain at the end. In a different method, pure PFPEs are blended with other polymers. The enrichment of fluorinated content on the surface creates a high fluorine concentration by using less PFPEs. But the immiscibility between fluorinated and non-fluorinated counterparts can cause extensive phase separation, resulting in poor mechanical properties. A more versatile method is to prepare block copolymers containing fluorinated segments separately, then incorporate them into another polymers. In this case, compatibility may be controlled by the type and length of the non-fluorinated parts. Therefore, fluorinated block copolymers can provide more promising results.

With the above in mind, the addition of PFPE-based materials to polymers, which can migrate to the surface of the host materials to modify it and replenish it under wear/abrasion, is very important and a practical proven approach for obtaining water/oil-repellent surfaces. Several publications have reported on the formation of low surface energy coatings via the addition of PFPE-based polyesters. For instance, Wang et al. focused on the modification of polybutylene terephthalate with fluorinated multiblock polyester containing PFPE segments. Drysdale et al. concentrated on the blending of polytrimethylene terephthalate with blocky polyesters containing fluorinated isophthalic units with PFPE. Finally, Demir et al. reported on modifying the water and oil repellency of PET films with the PFPE-based polyesters. In this study, original PFPE-based polyester oligomers with different macromolecular structures were synthesized by polycondensation polymerization. It was demonstrated that the addition of the oligomeric PFPE-based polyesters to PET materials, even at low concentration, allows
reaching the level of oil repellency and surface energy comparable to that of PTFE.\textsuperscript{156} Therefore, the PFPE-based polyester oligomers can be considered as the potential replacements for additives containing long-chain perfluoroalkyl substances.

**2.5. Surfaces Texture**

It is well established that an effective hydrophobic/oleophobic surfaces are characterized by low surface energy, low wettability hysteresis, and high surface roughness.\textsuperscript{157} Therefore, appropriate surface texture is used to introduce the surface roughness in order to further enhance the oil repellency. During the last two decades, the intensive research both theoretical and experimental has been conducted by using top-down or bottom-up surface modification techniques.\textsuperscript{21, 69, 74, 158-163} In this section, we are focusing on the experimental techniques that have been reported in the scientific literatures.

**2.5.1. Top-down Fabrication Methods**

The top-down method is based on using nanofabrication tools to create nanoscale structures with desired properties. The process typically starts from samples with larger surface features and reduces them to smaller structures.\textsuperscript{158} There are numerous techniques that are considered as top-down methods, such as etching, lithography, and laser processing.\textsuperscript{74}

Etching is widely used to fabricate oleophobic surfaces. It is a convenient and relatively low cost method to introduce surface roughness. Song \textit{et al.} fabricated a superoleophobic surfaces with CA of 160.0 ± 2° for peanut oil using electrochemical etching to form micro/nano structures with the combination of perfluorooctanoic acid as low surface energy additive.\textsuperscript{164} One of the most common etching method is plasma etching.
In 2014, Ellinas et al. prepared the superhydrophobic and superamphiphobic polymeric surface in a two-step process: i) introduction of micro/nano texture, including random and ordered hierarchical structures, into the polymeric surface by ion-enhanced plasma etching, and ii) grafting of self-assembled perfluorododecyltrichlorosilane monolayers (SAMs). In general, etching treats the entire surface; however; the created surface layers are fragile, and the use of specialty conditions and chemicals may be expensive.

Using lithography is possible to prepare surface patterns with different shapes and sizes. This method allows precise control of the structures on surface, leading to various surface morphologies. Choi et al. prepared superamphiphobic surface with structures by reverse nanoimprint lithography. The CAs for the sample were 164°, 151°, and 114° for water, diiodomethane, and hexadecane, respectively. However, the lithography manufacture processing needs a long molding cycle and it can produce defects.

Laser processing is a relatively new technique to form special surface topography. The structures of the surface can be controlled by scanning speed, pulse number, and laser fluence. It was reported that the underwater superoleophobic surfaces were obtained using femtosecond laser micromachining of a flat Si surface through a line-by-line and serial processes. Although the value of water CA is 4 ± 1° in air, the CA for 1,2-dichloroethane oil is 159.4 ± 1° in water, and oil can easily roll on the textured surface. However, the mechanism of laser processing is still unclear. Thus, more studies are needed to improve the process.
2.5.2. Bottom-up Fabrication Methods

In bottom-up methods, the molecular and atomic components are built up into more complex multi-level structures.\textsuperscript{158} This method is promising because there is no waste or unused materials during the processing. Among the techniques, sol-gel is one of the most common method. It can be carried out at relatively low temperature. It is also simple and low cost. However, the process may take a long time to complete. Hayase \textit{et al.} prepared the first superamphiphobic monolith using the co-precursor system of vinyltrimethoxysilane (VTMS)-vinyl-methylidimethoxysilane (VMDMS), then the system was treated with 2-propanol solution containing 1H,1H,2H,2H-perfluorodecanethiol with azobisisobutyronitrile (AIBN).\textsuperscript{168} Consequently, the hexadecane CA for the sample was measured as 151°.

Electrospinning is another method to fabricate textured surfaces. This technique is straightforward, scalable, and inexpensive to produce nonwoven micro/nanofibers with high specific surface area and porosity in a direct and continuous manner.\textsuperscript{74} Ganesh \textit{et al.} prepared robust superamphiphobic self-cleaning coatings on glass substrate by introducing rice-shaped TiO\textsubscript{2} nanostructures through electrospinning and salinization.\textsuperscript{169} The water and ethylene glycol CA was 166° and 152.6°, respectively. Furthermore, it is necessary to point out that the coatings exhibited excellent thermal stability and mechanical properties with a high level of adherence to the glass substrate.

Furthermore, electrodeposition can also fabricate rough surfaces regardless of the size and shape of substrate.\textsuperscript{85} The only requirement for the electrodeposition is that the surface should be conductive and difficult to oxidize.\textsuperscript{74} Since long chain perfluoropolymers
are toxic and have limited applications, a series of superoleophobic surfaces were achieved by combining shorter fluorinated chains with electrodeposition. Darmanie et al. designed the oil repellent surfaces through electrodeposition of fluorinated 3,4-ethylenedioxythiophene (EDOT) derivatives containing an amide connector.\textsuperscript{170-173} It was found that the oil CA for the product with F-butyl tails was 150° for sunflower oil and 136° for hexadecane.

There are other bottom-up methods for superoleophobic surface fabrication have been demonstrated, such as dip coating, vapor deposition, template method, and layer-by-layer.\textsuperscript{85, 160, 162, 174-178}

2.6. Lubricated Porous/Textured Surfaces

The concept of lubricated porous surface was first proposed by Wong et al. under the name ‘slippery liquid-infused porous surface(s)’ (SLIPS).\textsuperscript{179} The surfaces are self-healing surfaces because of the redistribution of lubricant. The SLIPS was inspired by the natural mechanism of Nepenthes pitcher plant used for entrapping its pray.\textsuperscript{180} This approach demonstrates that oil-repellent surfaces fabrication is using liquid-liquid interfaces instead of the complex solid-liquid interfaces.\textsuperscript{69} For this, perfluorinated lubricant is needed to repel not only water, but also oils, alcohols, and other organic solvents. Because of capillarity, the imbibition of lubricant into the properly designed porous substrates can lead to a long lasting oil repellency. On the contrary to the textured superoleophobic surfaces, the lubricated surfaces are relatively smooth. The mechanism for their oil repellency is based on the interfacial forces between the lubricant and oil. In
general, they will exhibit lower static CA than superoleophobic surfaces; however, the sliding angle for the lubricated surfaces are typically less than 5°.

2.7. Step Growth Polymerization

According to the kinetics of polymer synthesis, step and chain growth polymerization are classified as two major polymerization processes.\textsuperscript{181-182} In the chain growth polymerization, high molecular weight polymer is formed early during synthesis, and the percentage of monomer converted to polymer (polymerization yield) is increased gradually within time. On the other hand, high molecular weight polymer is only obtained near the end of the step growth polymerization, where monomer conversion is typically higher than 98%. There are other specific features for the step growth polymerization. For instance, the same reaction mechanism is realized throughout the process, while in the chain growth polymerization, initiation, propagation, and termination are typically involved. In addition, polymerization rate in the step growth decreases steadily as the functional groups are consumed. However, the polymerization rate in chain growth decreases as initiator and monomer are reacted. In this work, step growth polymerization was mostly used to obtain low surface energy oligomers and polymers.

2.7.1. Molecular Weight in Step Growth Polymerization

During step growth polymerization, the regulation of molecular weight is one of the most important task during the synthesis. In the process, the molecular weight of a polymer is dependent on the extent of conversion ($p$) of the monomer. One way to characterize the molecular weight is using degree of polymerization ($\overline{DP}$ or $\overline{X_n}$), which represents the number of monomeric units in the polymer main chain.\textsuperscript{183} Carothers
described a simple method for predicting the molar mass of polymers prepared by the step
growth polymerization.\textsuperscript{184}

\[
\overline{DP} = \frac{1+r}{r+1-2rp} \quad (2.5)
\]

\[
r = \frac{N_A^0}{N_B^0} \leq 1 \quad (2.5a)
\]

\[
p = \frac{N_A^{\text{reacted}}}{N_A^0} \quad (2.5b)
\]

where \( r \) is stoichiometric ratio, \( N_A^0 \) and \( N_B^0 \) are the number of A and B functional groups
present initially, respectively. \( N_A^{\text{reacted}} \) is the number of A functional groups reacted with
B functional groups after polymerization a time of \( t \).

When \( r = 1 \),

\[
\overline{DP} = \frac{1}{1-p} \quad (2.6)
\]

if one functional group is completely used up during reaction, which means when \( p \approx 1 \),

\[
\overline{DP} = \frac{1+r}{1-r} \quad (2.7)
\]

According to \textbf{Equation 2.5}, it was found out that only very slight stoichiometric
imbalances can be tolerated to form high molecular weight polymer. Therefore, to control
\( r \) precisely, the monomer used in the linear step growth polymerization must has very high
purity. Additionally, the criteria for applying these equations are: i) A and B are linear
molecules; and ii) no side reactive groups, A can only react with B.\textsuperscript{183}
Another way to control polymer molecular weight is based on polymerization kinetics. They are classified into self-catalyzed and external-catalyzed polymerization.\textsuperscript{183} Some reactions can be proceed at reasonable rate as uncatalyzed reaction, while some reactions need external catalyst to obtain desired reaction rate. Often, polymerization process carried as uncatalyzed reaction to avoid side reactions.\textsuperscript{183}

In summary, the molecular weight of a product depends on many factors, such as monomer conversion, stoichiometric equivalence, monomer purity, reactant concentration, and the factors drives the reaction, like inert gas, reaction temperature and pressure.\textsuperscript{183}

\textbf{2.7.2. Condensation Polymerization}

The step growth polymerization is divided into two groups: condensation and non-condensation polymerization. Condensation polymerization involves the reactions where small molecules are eliminated during the synthesis.\textsuperscript{182} Examples of commercial polycondensation polymers are polyester, polyether, and polyamide (Figure 2.9).\textsuperscript{102, 185-187} Among these polymers, polyesters is one of the most widespread products. They can be produced by direct esterification of a diacid with a diol or self-condensation of a hydroxyl carboxylic acid.
Furthermore, the most important commercial polyester is poly(ethylene terephthalate). The production of PET involves two processes. One is based on dimethyl terephthalate (DMT) and the other is terephthalic acid (TA) process. The DMT process was first used to obtain commercial PET, since pure TA was not available at that time. DMT process contains two stages of ester interchange process. The first stage is a solution polymerization to produce bis(2-hydroxyethyl)terephthalate (BHTE) along with oligomers. The reaction is heated at increasing temperature from 150°C to 210°C, and the by-product of methanol is continuously distilled off to proceed the reaction. In this stage, catalyst such as manganese, zinc, calcium, and cobalt is used. Then, phosphate is added to terminate the first-stage catalysis. The second-step catalyst is antimony (III) oxide. The temperature is raised up to around 275°C during the second-stage melt polymerization, while the pressure is reduced to remove ethylene glycol. In order to obtain high yield and high molecular weight PET, the ethylene glycol is required to be removed completely during the process. On the other hand, TA process is a modification of the DMT process.
Terephthalic acid and an excess of ethylene glycol are used to produce BHTE, then polymerized as described above. For TA process, only one catalyst system is used and the by-product is H₂O.

### 2.7.3. Non-Condensation Polymerization

There are relatively few polymers prepared by non-condensation polymerization. The most well-known example of non-condensation polymerization is the synthesis of polyurethane (PU). It is prepared by the ionic addition of a diol to a diisocyanate (Figure 2.10). In contrast of polycondensation, there is no elimination of small molecules or by-product during PU synthesis. The other example of non-condensation polymerization is the polymerization of poly(2,6-dimethyl-1,4-phenylene oxide) (Figure 2.10). Although the elimination of small molecular is involved and high molecular weight polymer is only obtained at the end of this synthesis, the mechanism of this polymerization is free radical of the oxidative-coupling polymerization of 2,6-xylenol.

![Figure 2.10. Examples of non-condensation polymerization.](image)

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2.8. Conclusions

In conclusion, significant progress has been made in fabrication and applications of various oleophobic surfaces. It is well known that the addition of fluorinated materials to polymers, which can migrate to the surface of the host material to modify it and replenish under wear/abrasion, is very important and practical approach to achieve oil repellency. PFPE-based materials (not pure PFPEs) are one of the most promising alternatives to long chain perfluoro acids. Therefore, in the next chapters of this dissertation, PFPE-based copolymers with different macromolecular architectures are synthesized and used to fabricate oleophobic surfaces.

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CHAPTER THREE
EXPERIMENTAL

3.1. Chemical reagents used

**Methyl ethyl ketone:**
Company Identification: Alfa Aesar
MSDS Name: 2-Butanone, 99+%
CAS Number: 78-93-3

**Chloroform:**
Company Identification: VWR International LLC.
MSDS Name: Chloroform, ACS.
CAS Number: 67-66-3

**Chloroform-D:**
Company Identification: Acros Organics
MSDS Name: Chloroform-d, for NMR, 99.8% atom D
CAS Number: 865-49-6

**Sulfuric acid 98%:**
Company Identification: Millipore Sigma
MSDS Name: Sulfuric acid, reagent ACS
CAS Number: 7664-93-9

**Hydrogen peroxide 30%:**
Company Identification: EMD Millipore
MSDS Name: Hydrogen Peroxide (30% in Water) (Without Stabilizer), reagent ACS
CAS Number: 7722-84-1

**1,1,1,3,3,3-Hexafluoro-2-propanol:**

Company Identification: Oakwood Products Inc.

MSDS Name: 1,1,1,3,3,3-Hexafluoro-2-propanol, 99%

CAS Number: 920-66-1

3.2. Chemicals Used for the Synthesis

**Ethylene Glycol:**

![Ethylene Glycol structure](image)

**Isophthaloyl Chloride:**

![Isophthaloyl Chloride structure](image)

**Terephthaloyl Chloride:**

![Terephthaloyl Chloride structure](image)
1H,1H,11H,11H-Perfluoro-3,6,9-trioxaundecane-1,11-diol:

\[
\text{HO} \quad \text{F} \quad \text{F} \quad \text{O} \quad \text{F} \quad \text{F} \quad \text{O} \quad \text{F} \quad \text{F} \quad \text{OH}
\]

1H,1H,-Perfluoro-3,6,9-trioxatridecan-1-ol:

\[
\text{O} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{O} \quad \text{F} \quad \text{F} \quad \text{O} \quad \text{F} \quad \text{F} \quad \text{OH}
\]

1H,1H,-Perfluoro-1-Heptanol:

\[
\text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{O} \quad \text{F} \quad \text{F} \quad \text{OH}
\]

Hexamethylene Diisocyanate:

\[
\text{O} \quad \text{C} = \text{N} \quad \text{N} = \text{C} = \text{O}
\]

4,4'-Methylene Diphenyl Diisocyanate:

\[
\text{O} \quad \text{C} = \text{N} \quad \text{N} = \text{C} = \text{O}
\]
3.3. Structural Characterization Techniques of Materials

3.3.1. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR)

Fourier transform infrared spectroscopy, or FTIR, is an effective and highly versatile instrument to structurally characterize unknown samples. FTIR can be used on a wide variety of materials including solids, liquids, and gases. The basic premise of FTIR is irradiating a sample with IR light, and measuring how the intensity of IR beam at different wavelength is changed by passing through the sample. Chemical functional groups are excited at certain energies, which can be used to identify structural characteristics of a molecule via IR spectrum. There are two main sampling modes: transmission and reflection. Accessories can also be included to add further analysis options, such as IR microscopy.

In our work, ATR-FTIR spectroscopy is mainly used to determine the major functional groups presented in synthesized materials. This technique differs from transmission because sample preparation usually is not required. In ATR-FTIR, the IR beam is directed up into an IR transparent crystal, which is called ATR crystal. When an internal reflection occurs, and the sample is in intimate contact with the ATR crystal at the point of the internal reflection, an evanescent wave is formed in the sample. Figure 3.1 is
a representation of an ATR crystal and the evanescent wave forms on a sample if the critical angle of the system is exceeded.

![Diagram of ATR Crystal and Wave Forms](image)

**Figure 3.1.** Conceptual diagram of a beam path in ATR.

### 3.3.2. Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance spectroscopy is one of the most efficient techniques for polymer characterization. A number of molecular-level features can be determined using NMR spectra, including dynamics, polymer microstructure, and chain conformation. The most fundamental principle of NMR is that numerous nuclei have spin and all nuclei are charged electrically. When an external magnetic field is applied, an energy transfer between the base energy to a higher energy level is obtained (Figure 3.2). This energy transfer is based on the unique radio frequency energy. Consequently, NMR can identify the structures of the sample since each molecule is corresponding to one unique radio frequency.

For this work, fluorine ($^{19}$F) NMR was employed to identify the structure of fluorinated oligomers and triblock copolymers. The $^{19}$F NMR (300 MHz) spectra of the
samples were recorded on a Bruker Avance II Spectrometer. The dried sample were dissolved in deuterated chloroform for overnight before analysis. In addition, the trichlorofluoromethane was used as reference.

**Figure 3.2.** Principle of NMR analysis.\(^3\) Redraw from Ref [3].

### 3.3.3. Gel Permeation Chromatography (GPC)

Gel permeation chromatography is one of the most powerful analytical techniques to determine molecular weight and molecular weight distribution of polymers.\(^4\) GPC separates molecules in solution by their “effective size in solution.” Inside the GPC column, there is a continually flowing stream of solvent (mobile phase). The mobile phase flows through millions of highly porous, rigid particles (stationary phase) tightly packed together in a column. Molecules of various sizes elute from the column at different rates. The column retains low molecular weight material longer than the high molecular weight
material. The time it takes for a specific fraction to elute is called its “retention time” (Figure 3.3).

The molecular weight of the materials synthesized in this work was measured by GPC (Waters Breeze). Prior to the measurements, the samples were dissolved in chloroform and kept overnight. Then, the resulting solution was filtered through 0.2 μm PTFE filters. Polystyrene was employed as a standard for GPC calibration.

![Figure 3.3. Principle of GPC analysis. Redraw from Ref [4].](image)

3.4. Thermal Analysis Techniques of Materials

3.4.1. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is a technique in which the mass of a substance is measured as a function of time or temperature, while the substance is subjected to a
controlled temperature change.\textsuperscript{5} The basic principle of TGA is that as a sample is heated, its mass may change. This change can be used to determine the composition of a material and its thermal stability. TGA provides a quantitative measurement of any mass change in the material associated with a transition or thermal dehydration. The changes in mass are a result of the rupture or the formation of various chemical and physical bonds, such as dehydration, decomposition, evaporation, or oxidation of a sample with time and temperature. In general, the sample will lose weight during decomposition, reduction, or evaporation; however, a sample could also gain weight due to oxidation or absorption.\textsuperscript{5-6}

In this work, TGA analysis was conducted to determine the composition, evaporation, and decomposition temperature of the products. PerkinElmer TGA was used and a sample (~5 mg) was heated under a nitrogen atmosphere (gas flow = 20 mL/min) from room temperature to different temperatures depends on sample types. The heating rate was 20°C/min.

\textbf{3.4.2. Differential Scanning Calorimetry (DSC)}

Differential scanning calorimetry is another technique used for thermal analysis. DSC is used in various applications including polymer characterization, pharmaceuticals, quality control, oxidative stability, and general chemical analysis.\textsuperscript{5-6} The sample is compared to a reference with a well-defined heat capacity over the scanning temperature range. DSC identifies the energy required to keep the sample and the reference at the same temperature. DSC curves allow determine thermal events including glass transitions, melting, crystallization, enthalpy relaxation, and others (Figure 3.4).
For our materials, DSC 2920 (TA instruments) was used to identify thermal transitions, such as glass transition ($T_g$) and melting ($T_m$) temperatures. A sample (~5 mg) was heated under nitrogen atmosphere (gas flow = 20 mL/min) using different temperature ranges depending on TGA results. The heating rate was 20°C/min.

![DSC Curve Diagram](image)

**Figure 3.4.** An example of a typical DSC curve. Redraw from Ref [5].

### 3.5. General Experiment Procedures for Preparation of Polymer Films

#### 3.5.1. Cleaning of Silicon Wafers

In this work, Si wafer substrates had typical size of 1.5 x 4.5 mm$^2$. The Si wafers from WRS Materials were first cleaned in a ultrasonic bath (VWR Symphony) for 30 min with deionized water. Subsequently, the wafers were placed in a hot (~60 °C) “piranha” solution (3:1 concentrated sulfuric acid/30% hydrogen peroxide) for 1h in sonication. Then, the wafers were rinsed several times with high purity deionized water and stored in
deionized water. Before use, the substrates were dried under a stream of dry high purity nitrogen (National Specialty Gases).

### 3.5.2. Dip Coating

Dip coating was used to fabricate polymer films on Si wafer in our study. It has been reported that the thickness of polymer films prepared by dip-coating is mainly dependent on the withdraw speed control, fluid viscosity, surface tension, and fluid density. To obtain thin films, in this work, we deposited our films from 3 wt% polymer solution in HFIP at different concentrations using 320 mm/min withdraw speed. The dip coater (Mayer Fientechnik D-3400) was placed in a clean room to avoid contaminations during the film deposition.

### 3.6. Characterization of Polymer Films

#### 3.6.1. Film Thickness Measurement

Ellipsometry can be used to identify the optical properties and thickness of polymer films. It measures a relatively large change of polarization and compares it to a theoretical model. Ellipsometry can also be applied to characterize other material properties, such as roughness and composition. A schematic setup of an ellipsometry is presented in Figure 3.5.

In this study, ellipsometry was performed with a COMPEL automatic ellipsometer (InOmTech, Inc.) at an incidence angle of 70° and wavelength of 653 nm. The reflective index for polymer films was assumed to be 1.5.
3.6.2. Surface Morphology Characterization

Atomic force microscopy (AFM) is a type of the scanning probe microscopy. It is used to determine the surface morphology of polymer films with vertical resolution on the order of a nanometer. In general, there are two different AFM modes (Figure 3.6). One is contact (static) modes, and the other one is dynamic modes. The dynamic modes include non-contact and tapping mode, where the cantilever is oscillated or vibrated at a fixed frequency.9

Figure 3.5. Principal of an ellipsometry.

Figure 3.6. Schematic of AFM analysis.
In our work, AFM topographical and phase images were obtained using Dimension 3100 microscope (Digital Instrument, Inc.). Typically, a 10 µm x 10 µm film area was scanned in tapping mode using NSC16 tips at 1 Hz scan rate.

### 3.6.3. Surface Wettability Characterization

Numerous methods to identify the solid surface wettability have been reported.\(^{10-15}\) CA measurements based on Young’s model (Chapter 2) are considered as one of the most direct and simplest method to perform.\(^{16}\)

In this study, the static water contact angle (WCA) and hexadecane contact angle (HCA) were measured at room temperature using a sessile drop method. The equilibrating time for the measurement was 30 seconds. The CA results were recorded on a drop shape analysis instrument (DSA10, Kruss, Germany) with drop shape analysis (DSA) software. The CAs were measured 3-5 times for each sample and the average value was reported. In addition, the CA values were also used to estimate the surface energy of polymer films using Owens-Wendt method.\(^ {17}\) Furthermore, the effective surface coverage of the films by fluorinated chain segments was also calculated using the measured CAs based on Cassie-Baxter method.\(^ {18}\)

### 3.6.4. Surface Composition Analysis

X-ray photoelectron spectroscopy (XPS) is a spectroscopic technique to identify the composition, chemical state, and electronic state of the elements in the sample. During XPS analysis, the sample is irradiated with a beam of X-ray at specific energy, while the photoelectrons are emitted from the surface.\(^ {19}\) A representation of XPS is displayed in
**Figure 3.7.** In XPS, the kinetic energy of the emitted electrons was measured. Therefore, the binding energy can be determined to identify elements on the films’ surface.

In our study, XPS spectra were obtained using a Thermo K-Alpha XPS (Thermo Fisher Scientific, West Palm Beach, FL) with a monochromatic X-Rays (Al K\(\alpha\) at 15 kV) located in Georgia Institute of Technology. The samples were analyzed at an incident angle of 90°, where the detector line of sight is normal to the film.

![Figure 3.7. Principal of XPS analysis.](image)

### 3.7. References


CHAPTER FOUR
SYNTHESIS AND CHARACTERIZATION OF FLUORINATED POLYESTER
TRIBLOCK COPOLYMERS WITH DIFFERENT END-GROUPS

4.1. Introduction

Perfluoropolyethers were first reported in the early 1960s, and currently they have been considered as the potential safer substitutes for long-chain perfluoroalkyl substances, PFASs. Indeed, linear PFPEs are possessing low surface tension (20-22mN/m), low volatility, high chemical inertness, good thermal stability, and low toxicity. However, pure PFPEs cannot serve as effective additive alternatives due to their low viscosity and immiscibility with polymer matrices.

To this end, PFPE-based cross-linked materials and copolymers have been demonstrated to have the capability to function as hydrophobic/lyophobic materials and interfaces. These copolymers are also shown to be quite effective additives that offer long-lasting surface modifications to polymer materials. In this latter case, the compatibility between different segments can be controlled by the chemical composition and structure of non-fluorinated parts. For instance, Drysdale et al. reported on the blending of polytrimethylene terephthalate with blocky polyesters containing fluorinated isophthalic units with PFPE. Wang et al. described the modification of polybutylene terephthalate with fluorinated multi-block polyester containing PFPE segments. Demir et al. demonstrated the synthesis of PFPE-based oligomeric polyesters (FOPs) with different end-groups.
To obtain the next generation of more effective PFPE-based materials, we conducted the synthesis of PFPE-based polyester triblock copolymers (FOPBs). In the copolymers, two longer PFPE-based polyester oligomeric end-blocks are separated by a short non-fluorinated polyester block. The molecular weight of the materials was measured by gel permeation chromatography. Infrared spectroscopy was used to characterize the major structural elements presented in the synthesized materials. Thermalgravimetric analysis and differential scanning calorimetry analysis were conducted to determine thermal properties of the polymers. Furthermore, nuclear magnetic resonance spectroscopy was also employed to elucidate the structure of fluorinated polyester triblock copolymers.

4.2. Experimental Part

4.2.1 Materials

Telechelic polyethylene isophthalate (PEI) oligomer was synthesized by solution reaction of isophthaloyl chloride (IsoCl) with ethylene glycol (EG), which were both purchased from Sigma-Aldrich. Semi-telechelic PFPE-based polyester oligomers (FOPs) were synthesized through the reaction of IsoCl with fluorinated ether alcohols, such as 1H,1H-perfluoro-1-heptanol (C₆F₁₃-OH) from Matrix Scientific, 1H,1H-perfluoro-3,6,9-tiroxatridecan-1-ol (C₄F₉-PFPE-OH), and 1H, 1H, 11H, 11H-perfluoro-3,6,9-trioxaundecane-1,11-diol (PFPE-diol) from Synquest Laboratories. In these synthesis, methyl ethyl ketone (MEK) from Alfa Aesar, dried by molecular sieves, was used as a solvent. Triethylamine (Et₃N) used for the removal of HCl salt during the synthesis was from Sigma-Aldrich. FOPBs were synthesized through melt polymerization of PEI with FOPs having different end-groups.
4.2.2. Synthesis of Materials

Telechelic PEI oligomer was synthesized to serve as a middle block in the triblock copolymers. The chemical scheme of PEI synthesis is presented in Figure 4.1. To obtain the polyester, IsoCl was reacted with EG through Schotten-Baumann reaction between acid chloride and hydroxyl functionalities of the monomers.\textsuperscript{14-15} We employed a classical Carothers approach to regulate the molecular weight and chemical nature of the polyester end-groups during the polycondensation using stoichiometric imbalance.\textsuperscript{16-17} Specifically, the molar ratio between -COCl and -OH functionalities was set to be 2:1 in order to obtain the PEI oligomer terminated with -COCl reactive groups on both sides.

![Figure 4.1. General schematics for synthesis of PEI.](image)

Two semi-telechelic PFPE-based polyester oligomers terminated with (i) one hydroxyl and one C\text{4}F\text{9}-PFPE- end group (FOP-1), and (ii) one hydroxyl and one C\text{6}F\text{13}-end group (FOP-2) were synthesized. The general schematic for synthesis of FOP blocks is depicted in Figure 4.2. The same chemical procedures as for the synthesis of PEI
FOPB triblock copolymers were synthesized via Schotten-Baumann reaction. A scheme of the reaction is given in Figure 4.3. PEI oligomers were reacted with FOPs possessing different end-groups. Two different copolymers end-terminated with (i) C₄F₉-PFPE- end-groups (FOPB-1), and (ii) C₆F₁₃- end-groups (FOPB-2) in both sides were obtained. In the synthesis, the FOP/PEI molar ratio was 2/1 to ensure the formation of triblock copolymer having PEI middle block.
Figure 4.3. General schematics for synthesis of FOPBs.
**General Procedure of the Synthesis**

In a typical synthesis of PEI oligomer, IsoCl was dissolved in dry MEK and pre-heated at 70°C for 30 min. Then, EG and Et₃N in dry MEK were added to the IsoCl solution dropwise under vigorous stirring, and the solution was incubated at 70°C for 3h. After the formation of oligomers, the reaction mass was cooled down to room temperature and stirred overnight. Next, HCl salt trapped by Et₃N was removed by centrifugation at 5000 rpm for 1h. The remaining solution was transferred to a 100 mL three-necked flask, which was equipped with a mechanical stirrer. The oligomer was heated at 50°C for 4h and 70°C for 1h under a stream of nitrogen (N₂) to remove MEK. After MEK was removed, the reaction media was heated at 100°C, 120°C, and 150°C for 4h, 2h, and 7h, respectively under N₂ to obtain higher molecular weight macromolecules.

For FOP synthesis, fluorinated ether alcohols and Et₃N were dissolved in dry MEK and pre-heated at 70°C for 30 minutes with stirring. Then, the solution of IsoCl was added dropwise into the reaction media, and reaction was carried out at 70°C for 3h. Afterwards, the reaction was conducted by following the procedure described above. After the removal of HCl salt and MEK, the reaction media was heated at 150°C for 7h under N₂ to obtain the targeted oligomers.

To obtain FOPBs, telechelic PEI oligomer with reactive end-groups was reacted with semi-telechelic FOP oligomers in the melt state in a 100 mL three-necked flask to obtain fluorinated triblock copolymers. The reaction was carried out under N₂ at 200°C for 5h with vigorous stirring.
Synthesis of PEI

In the synthesis of PEI, 6.30 g (31.0 mmol) of IsoCl in 10 ml dry MEK was heated at 70°C. A solution of 0.962 g (15.5 mmol) of EG and 3.32 g (31.0 mmol) of triethylamine in MEK (10 ml) was added into the IsoCl solution dropwise. The reaction was proceeded following the above-written procedures. After the synthetic procedure described above was followed, the final product was dissolved in chloroform. Subsequently, it was dried with N₂, a dark green PEI (Figure 4.1) was obtained.

Synthesis of FOP-1 (Figure 4.4)

18 g (43.9 mmol) of PFPE-diol, 5.35 g (9.8 mmol) of C₄F₉-PFPE-OH, and 9.88 g (97.6 mmol) of Et₃N were dissolved in 20 ml MEK and pre-heated. Then, 9.92 g (48.8 mmol) of IsoCl in dry MEK (10 ml) was added dropwise into reactive solution to obtain the FOP-1 oligomer using the procedure described above. After drying, a yellow FOP-1 oligomer was obtained.

Figure 4.4. Chemical structure of FOP-1.

Synthesis of FOP-2 (Figure 4.5)

18 g (43.9 mmol) of PFPE-diol, 3.43 g (9.8 mmol) of C₆F₁₃-OH, and 9.88 g (97.6 mmol) of Et₃N were dissolved in 20 ml MEK and pre-heated. Subsequently, 9.92 g (48.8
mmol) of IsoCl in dry MEK (10 ml) was added into the solution dropwise to prepare the FOP-2 oligomer using the procedure described above. After drying, a yellow FOP-2 oligomer was obtained.

**Figure 4.5.** Chemical structure of FOP-2.

*Synthesis of FOPB-1 (Figure 4.6)*

In a typical procedure for the synthesis of FOPB-1, 1.5 g (0.316 mmol) FOP-1 terminated with C₄F₉-PFPE- end-groups and 0.25 g (0.158 mmol) PEI with -Cl reactive groups were reacted following the procedure detailed in previous sections. The final product was dissolved in chloroform. Subsequently, it was dried by N₂, and a slightly yellow FOPB-1 copolymer was obtained.

*Synthesis of FOPB-2 (Figure 4.7)*

For the synthesis of FOPB-2, 3 g (0.70 mmol) FOP-2 terminated with C₆F₁₃- end-groups and 0.55 g (0.35 mmol) PEI were added and reacted. The above-written procedure was followed. The final product was dissolved in chloroform. Afterwards, it was dried by N₂, and a slightly yellow FOPB-2 was obtained.
Figure 4.6. Chemical structure of FOPB-1.

Figure 4.7. Chemical structure of FOPB-2.
4.3. Results and Discussions

4.3.1. PEI Middle Block

The PEI synthesis was conducted by combination of solution and melt polymerization following the procedure previously used by us to obtain PFPE-based oligomeric polyesters. First, the solution polymerization is carried out to isolate significant amount of HCl produced at the initial stages of the polycondensation with Et₃N dissolved in MEK. This polymerization stage was carried out at 70°C to avoid boiling of MEK. Then, using TGA, it was determined that PEI oligomers obtained in the solution process can withstand 100°C (Figure 4.8). Therefore, the second stage of the polymerization was performed in melt at this temperature for 4h. Then, the reaction was proceeded at 120°C and 150°C for 2h and 7h, respectively to form higher molecular weight and more temperature stable oligomers.

Figure 4.8. TGA traces for PEI in course of polymerization: after consecutive polymerizations at 70°C for 1h (1), 100°C for 2h (2), 100°C for 2h (3), 120°C for 2h (4), and 150°C for 7h (5).
ATR-FTIR Analysis of PEI

ATR-FTIR analysis was performed to identify the structure of PEI. The results shown in Figure 4.9 were analyzed using readily available spectral databases for organic compounds.\textsuperscript{18} The IR spectrum clearly indicated that PEI oligomers were obtained by the employed synthetic procedure.

![ATR-FTIR spectrum of PEI](image)

**Figure 4.9.** ATR-FTIR spectrum of PEI: Mark on spectrum: (1) \(-\text{C-H stretching (aromatic)}\), 3080 cm\(^{-1}\), (2) \(-\text{C-H asymmetric stretching, 2961 cm}\(^{-1}\), (3) \(-\text{C=O stretching (acid chloride)}, 1793 \text{ cm}\(^{-1}\), (4) \(-\text{OC=O stretching, 1718 cm}\(^{-1}\), (5) \(-\text{C=C- ring stretching (aromatic)}, 1604 \text{ cm}\(^{-1}\), (6) \(-\text{C-O- asymmetrical stretching (ester)}, 1182 \text{ cm}\(^{-1}\), and (7) \(-\text{C-Cl stretching, 720-550 cm}\(^{-1}\).
Figure 4.9 reveals the presence of ester (-OC=O) stretching and -C-O-C stretching vibrations, where the peaks were seen at 1718 cm\(^{-1}\) and around 1182-1024 cm\(^{-1}\), respectively. This was the result of the reaction of acid chloride with alcohol. Furthermore, the spectrum for PEI possessed the -C=O stretching (acid chloride, 1793 cm\(^{-1}\) peak) and the -C-Cl stretching (peaks in the region 730-550 cm\(^{-1}\)). Therefore, IR spectra confirmed that the targeted PEI oligomers were obtained.

**GPC Analysis of PEI**

The molecular weight (MW) and polydispersity index (PDI) of PEI was determined using GPC. Polystyrene with different MWs were used as calibration standards. PEI was dissolved in chloroform and was filtered before GPC analysis. The GPC results are presented in Table 4.1. The results indicated that PEI oligomers with weight-average molecular weight of 1564 g/mol and PDI of 2.8 were obtained. We associate the relatively high PDI with the presence of lower MW oligomers in the samples (as it is found in the TGA measurements). The weight-average molecular weight was used to estimate the number of repeating units for the higher molecular weight PEI fraction. According to the chemical structure, the MW of a PEI repeating units is 192 g/mol and the MW of end-segment is 202 g/mol. Using these values, the number of repeating units for PEI is estimated as ~7. It means that the weight percentage of polyester repeating units in the oligomeric chain is 87%.

**Thermal Analysis of PEI**

TGA analysis was conducted to determine the thermal stability of PEI (Table 4.1 and Figure 4.8). It was found that the obtained oligomers have ~20% lower molecular
weight fraction mixtures, which are thermally stable until ~200°C. This result was reflected in the GPC measurement, where relatively high PDI was found for PEI. However, the major PEI fraction withstands higher temperature (> 300°C). The high MW fraction of the product displayed a decomposition temperature (Td) around 388°C.

Table 4.1. Major characteristics of PEI and FOPs.

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>M_n (g/mol)</th>
<th>M_w (g/mol)</th>
<th>PDI</th>
<th>T_g (°C)</th>
<th>T_m (°C)</th>
<th>T_d (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI</td>
<td>569</td>
<td>1564</td>
<td>2.8</td>
<td>-5</td>
<td>-</td>
<td>388</td>
</tr>
<tr>
<td>FOP-1</td>
<td>981</td>
<td>4752</td>
<td>4.8</td>
<td>-35</td>
<td>47</td>
<td>423</td>
</tr>
<tr>
<td>FOP-2</td>
<td>2338</td>
<td>4279</td>
<td>1.8</td>
<td>-22</td>
<td>47</td>
<td>415</td>
</tr>
</tbody>
</table>

Furthermore, we employed DSC analysis to identify the thermal transitions for PEI, such as T_g and T_m. According to the DSC results in Table 4.1 and Figure 4.10, the midpoint of T_g for PEI was found to be -5°C. It is known that for condensation polymers, such as polyesters, T_g(K)/T_m(K) ≈ 2/3.\textsuperscript{19} Therefore, we can estimate that, if the PEI oligomer were able to crystallize, T_m would be about 130°C. Though, DSC measurements revealed that PEI oligomer is amorphous, since it has no melting point below 200°C. The results indicate that PEI chains are possessing high chain mobility/diffusivity at and above room temperature.
4.3.2. FOP Blocks

For FOP synthesis, we used the same chemical procedures as for the synthesis of PEI oligomer. Specifically, the solution polycondensation in MEK for 3h at 70°C was followed by the melt polycondensation for 7h at 150°C to obtain high MW and temperature stable products.

**ATR-FTIR Analysis of FOPs**

The major structural elements in synthesized FOPs were determined using ATR-FTIR analysis (Figure 4.11). It was found that the -OH peaks around 3500 cm⁻¹ were not clearly observed. However, the IR spectra show that both oligomers have the -OC=O ester stretching and -O-C-O- stretching vibration peaks at 1743 cm⁻¹ and 1269 cm⁻¹, respectively due to the reaction of acid chloride and alcohols. Furthermore, the -CF₂ and -CF₃ stretching vibration peaks were also detected in the region of 1200-1100 cm⁻¹. In addition, C-H stretching and -CH bending were also identified, for both oligomers, at 1611 cm⁻¹ and 723
cm$^{-1}$, respectively. As a result, the IR spectra indicated that the targeted fluorinated polyester oligomers were obtained.

Figure 4.11. ATR-FTIR spectra of FOPs: a) FOP-1 and b) FOP-2. Mark on spectra (1) -OH stretching, 3500-3450 cm$^{-1}$, (2) =C-H stretching (aromatic), 3084 cm$^{-1}$, (3) C-H asymmetric stretching, 2978 cm$^{-1}$, (4) -OC=O stretching, 1743 cm$^{-1}$, (5) -C=C- stretching, 1611 cm$^{-1}$, (6) -OH bending (in plane), 1415 cm$^{-1}$, (7) -C-O-C symmetric stretching, 1269 cm$^{-1}$, (8) -CF$_2$ and -CF$_3$ stretching, 1186-1100 cm$^{-1}$, (9) -OH bending (out of plane), 952 cm$^{-1}$, and (10) C-H bending, 723 cm$^{-1}$.

GPC Analysis of FOPs

GPC was used to determine the MW and PDI of FOPs, and the results are presented in Table 4.1. $M_w$ for the oligomers was on the level of 4000-5000 g/mol. We suggest that
quite broad PDI (~2-5) for the materials is also connected to presence of lower MW oligomers in the samples. Furthermore, the number of repeating units for FOPs was also estimated using $M_w$. The MW of FOP repeating unit is 540 g/mol. The MW of a $C_4F_9$-PFPE- tail in FOP-1 is 547 g/mol, and the MW of a $C_6F_{13}$- tail in FOP-2 is 349 g/mol. Therefore, the estimated number of repeating units are ~8 for FOP-1 and ~7 for FOP-2. Consequently, the weight percent of the fluorinated end-segments is quite similar and is about 11% and 8% for FOP-1 and for FOP-2, respectively.

**Thermal Analysis of FOPs**

The thermal stability of synthesized FOPs was determined using TGA (Table 4.1 and Figure 4.12). The measurements indicated that the higher molecular weight oligomer fraction was ~82% and ~88% for FOP-1 and FOP-2, respectively. TGA results also show that higher molecular weight FOP fractions have a $T_d$ above 400°C. FOP-1 terminated with $C_4F_9$-PFPE- end-groups has a $T_d$ of 423°C, which is relatively higher than that of FOP-2, possessing $C_6F_{13}$- end segments ($T_d = 415°C$). It is reasonable to assume that the thermal stability for FOPs is somewhat end-group dependent.
DSC analysis revealed that FOPs are semi-crystalline materials having both $T_g$ and $T_m$ (Table 4.1 and Figure 4.13). $T_g$ for FOP-1 and FOP-2 is $-35^\circ$C and $-22^\circ$C, respectively. We attribute the difference in $T_g$ with the chemical composition of FOP end-groups.\textsuperscript{20} Owing to the oxygen atoms, the C$_4$F$_9$-PFPE- tails in FOP-1 are more flexible than C$_6$F$_{13}$-tails from FOP-2. Thus, $T_g$ for FOP-1 is lower than that of FOP-2. It is necessary to point out that both FOPs have the same melting temperature of 47°C, since the materials possess the same crystalizing repeating unit.
4.3.3. FOPB copolymers

Synthesis of the FOPBs was conducted in melt for 5h at 200°C. The reaction conditions were decided based on the Mₘ of PEI and FOP blocks from GPC and Tₐ of each reactants obtained from TGA (Table 4.1 and Figure 4.8 and 4.12). The FOP/PEI molar ratio was 2/1 to ensure formation of triblock copolymers having PEI middle block. Therefore, FOPB-1 copolymer was terminated with C₄F₉-PFPE- end-groups in both sides, while FOPB-2 possessed C₆F₁₁₃- end-groups.

ATR-FTIR Analysis of FOPBs

ATR-FTIR analysis supported the proposed structure of FOPBs, since the major functional groups of FOPBs are present in the IR spectra (Figure 4.14). For instance, the -CF₃ and -CF₂ stretching vibrations (1200 -1100 cm⁻¹), the -OC=O stretching (1749 cm⁻¹), and -C-O-C- stretching (1270 cm⁻¹) peaks were detected for both FOPB-1 and FOPB-2.
Figure 4.14. ATR-FTIR spectra of FOPBs: (a) FOPB-1, and (b) FOPB-2. Mark on spectra: (1) $\text{C-H}$ stretching (aromatic), 3087 cm$^{-1}$, (2) C-H asymmetric stretching, 2977 cm$^{-1}$, (3) $\text{OC=O}$ stretching, 1743 cm$^{-1}$, (4) -C=C- stretching, 1611-1414 cm$^{-1}$, (5) -C-O-C symmetric stretching, 1270 cm$^{-1}$, (6) -CF$_2$ and -CF$_3$ stretching, 1186-1099 cm$^{-1}$, (7) C-H bending (out of plane), 953 cm$^{-1}$, and (8) C-H bending, 723 cm$^{-1}$.

$^{19}$F NMR Analysis of FOPBs

$^{19}$F NMR spectroscopy was employed to further elucidate the chemical structure FOPB block copolymers (Figure 4.15 and 4.16). Generally, NMR results confirmed the synthesis of targeted FOPBs. For FOPB-1, we found the disappearance of the triplet peak at -80.72 to -80.80 ppm assigned to the fluorine atom in the -CF$_2$ group close to -OH end group in fluorinate polyester oligomers.$^{11,21}$ It confirms the formation of ester groups in
FOPB-1, which was a result of the reaction of -OH end groups in fluorinated block with chlorine groups (-Cl) in the PEI middle block. Therefore, the signal at -77.23 to -77.26 ppm (a) is connected with the -O-CF2-CH2-O-CO- formation (Figure 4.15) in FOPB-1. It also reveals the presence in the structure of the fluorine atom in the -CF2 groups bonded to the methyl ester in the repeating unit of fluorinated block. Distinctive multiple peaks at -88.74 to -88.95 ppm (b) are attributed to the fluorine atoms of the -CF2- groups located between ethers (-O-CF2CF2-O-) in the repeating units.

Three additional peaks (c, d, and e) belong to the fluorine atoms in the C4F9-PFPE-end segment. The two singlet peaks at -81.09 ppm (c) and -83.57 ppm (d) are corresponded to the fluorine atoms in the -CF3 group and the -CF2 group bonded to ether (CF3-CF2CF2-CF2-O). Another peak “e” at -126.67 belongs to the fluorine atoms of the -CF2 groups (CF3-CF2CF2-CF2-O) in the tail. As a result, FOPB-1 is confirmed to be terminated with C4F9-PFPE-tail, as it is targeted before synthesis.

Figure 4.15. $^{19}$F NMR spectrum of FOPB-1.
$^{19}$F NMR indicates the presence of “a” and “b” peaks in FOPB-2 chemical structure (Figure 4.16), since copolymer FOPB-2 possesses the same ester repeating units as FOPB-1. In addition, six additional peaks (c, e, f, g, h, and i), which belong to the fluorine atoms and originate from C$_6$F$_{13}$- end segments, are detected in FOPB-2. The peak “c” is attributed to the fluorine atom in the -CF$_3$ group in the tail. The peak at -126.17 ppm (e) is connected with the fluorine atoms of the -CF$_2$ group bonded to -CF$_3$ group (CF$_3$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$).\(^ {22}\) Another peak, “i” at -119.33 ppm, corresponds to fluorine atoms in -CF$_2$ group close to -CH$_2$ group (CF$_3$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$-CH$_2$-) at the end of the fluorinated tail.\(^ {22}\) Three additional singlet peaks at -122.17 ppm (f), -122.86 ppm (g), and -123.25 ppm (h) are attributed to the rest fluorine atoms of the -CF$_2$ groups (CF$_3$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$-CH$_2$-) in the tail, respectively in an increasing distance to -CF$_3$ group.\(^ {23}\) Therefore, the $^{19}$F NMR results confirm that FOPB-2 possesses C$_6$F$_{13}$- end groups.

![Figure 4.16. $^{19}$F NMR spectrum of FOPB-2.](image)
It has been reported that NMR spectroscopy has been utilized to determine the molecular weight of some polymers. \(^\text{24-25}\) It is a fairly accurate, fast, and simple method. The area under resonance peaks in NMR spectra is proportional to the molar concentration of the species in the samples. \(^\text{24, 26}\)

\[
\frac{a_x}{n_x m_x} = \frac{a_y}{n_y m_y}
\]  

(4.1a)

where \(a_x, a_y\) is the area of the \(^{19}\)F NMR peak of moiety x and y, respectively, \(n_x, n_y\) is the number of repeating units of moiety x and y, respectively, and \(m_x, m_y\) is the number of fluorine atoms of moiety x and y, respectively. Herein, by rearranging Equation 4.1a:

\[
n_x = \frac{a_x n_x m_y}{a_y m_x} = DP
\]  

(4.1b)

As a result, the number-average molecular weight can be calculated as follow:

\[
M_n = n M_0 + M_e
\]  

(4.2)

where \(n\) is the number of repeating units or equals to \(DP\), \(M_0\) is the molecular weight of one repeating unit, and \(M_e\) is the molecular weight of the end-groups. Based on this method, we estimated the number of repeating units for FOPB blocks and number-average molecular weight for FOPBs by using NMR spectra.

For FOPB-1 (Figure 4.15), the peak “c” area of -CF\(_3\) end-groups in the copolymer is 1, and the total peak “b” area corresponding to the -CF\(_2\) groups between ether (-OCF\(_2\)CF\(_2\)O-) is 14.9881. We assumed that the -CF\(_3\) group peak area is proportional to the peak area of -OCF\(_2\)CF\(_2\)O- moieties located in the end-groups; therefore; the peak area for -OCF\(_2\)CF\(_2\)O- in the tails equals to 4. Consequently, the peak area for -OCF\(_2\)CF\(_2\)O- in the
repeating units is 10.9881. Then, we substituted the area values into Equation 4.1b, and the number of repeating units was calculated to be ~4 for one FOP-1 block. Therefore, the number-average molecular weight for FOP-1 block was estimated to be 2707 g/mol (Table 4.2). Finally, based on the MW for one FOP block repeating unit and C4F9-PFPE- tail detailed in previous section as well as the number-average molecular weight for PEI (Mn = 569 g/mol from GPC), the number-average of molecular weight for FOPB-1 was estimated to be 5983 g/mol (Table 4.2). Based on the same method, the number of repeating unit is ~5 for one FOP-2 block, the Mn for FOP-2 block is 3049 g/mol (Table 4.2), and the calculated number-average molecular weight is 6667 g/mol for FOPB-2 copolymer (Table 4.2). However, NMR analysis is unable to determine the weight-average molecular weight and polydispersity of the polymers.

*GPC Analysis of FOPBs*

Apart from NMR, we employed GPC to determine the Mw and PDI for FOPB copolymers. The results reveal that the Mw is 10432 g/mol for FOPB-1 and 8260 g/mol for FOPB-2, the Mn is 3731 g/mol for FOPB-1 and 4859 g/mol for FOPB-2, and PDI is 2.8 and 1.7 for FOPB-1 and FOPB-2, respectively. Although GPC is the most commonly used method for measuring polymer molecular weight, it is a relative method based on hydrodynamic volume of polymer. Its data strongly depends on calibrants as well as solvent and analysis time. Therefore, we calculated the weight-average molecular weight for FOP blocks and FOPB copolymers using the PDI data obtained from GPC and number-average molecular weight from NMR. The estimated Mw is presented in (Table 4.2). It is on the level of 10000-17000 g/mol for FOPBs, while Mw for FOP block ranges from 5000
to 13000 g/mol. In addition, on the basis of the structure of end-groups, MW and the number of repeating unit for PEI, FOP-1, and FOP-2 blocks, we estimated that the atomic concentration of fluorine in the block copolymer chain is practically the same and is about 23% for both FOPB-1 and FOPB-2.

Table 4.2. Major characteristics of materials.

<table>
<thead>
<tr>
<th>FOPB</th>
<th>$M_n^a$ (g/mol)</th>
<th>$M_w^b$ (g/mol)</th>
<th>PDI$^c$</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_d$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOPB-1</td>
<td>5983</td>
<td>16752</td>
<td>2.8</td>
<td>-18</td>
<td>46</td>
<td>416</td>
</tr>
<tr>
<td>FOPB-2</td>
<td>6667</td>
<td>11334</td>
<td>1.7</td>
<td>-16</td>
<td>48</td>
<td>412</td>
</tr>
<tr>
<td>FOP-1</td>
<td>2707</td>
<td>12994</td>
<td>4.8</td>
<td>-35</td>
<td>47</td>
<td>423</td>
</tr>
<tr>
<td>FOP-2</td>
<td>3049</td>
<td>5488</td>
<td>1.8</td>
<td>-22</td>
<td>47</td>
<td>415</td>
</tr>
</tbody>
</table>

$^a$: data obtained from NMR, $^b$: data obtained by combining NMR and GPC, and $^c$: data obtained from GPC

Thermal Analysis of FOPBs

According to the TGA analysis (Figure 4.17), the major component (> 97%) of the obtained FOPBs corresponds to higher molecular weight product having $T_d$ above 400°C (Table 4.2). It indicates that both FOPB-1 and FOPB-2 have relatively significant thermal stability irrespectively of the end-groups. Namely, they can be co-extruded with industrial polyester, whose reported manufacture temperature is above 250°C.\textsuperscript{17}
Figure 4.17. TGA traces for FOPBs: (a) FOPB-1 and (b) FOPB-2.

The thermal transition temperatures ($T_m$ and $T_g$) for FOPBs were determined using DSC analysis (Figure 4.18). The results in Table 4.2 showed that FOPBs are semi-crystalline copolymers since both $T_g$ and $T_m$ were detected for FOPBs. The midpoint $T_g$ is -18°C and -16°C for FOPB-1 and FOPB-2, while $T_m$ is 46°C and 48°C, respectively. It is necessary to point out the obtained glass transition temperature is attributed to the
molecular motion of the entire FOPB copolymer chains, while the melting transition only belongs to the crystallizable fluorinated repeating units. The data also suggests that the influence of end-groups on the position of copolymer thermal transitions is not significant. In general, the glass transition temperature of copolymers is significantly higher than the one for the FOP blocks indicating significant influence of middle PEI block on the transition. However, the melting temperature is not influenced by the PEI block.

**Figure 4.18.** DSC traces for FOPBs: (a) FOPB-1 and (b) FOPB-2.
4.4. Conclusions

- Targeted telechelic non-fluorinated polyester oligomer PEI terminated with reactive -COCl end-groups and semi-telechelic PFPE-based polyester oligomers were obtained by polycondensation.
- PEI oligomer is low molecular weight, amorphous, and possesses high chain mobility/diffusivity at and above room temperature due to low $T_g$.
- TGA and DCS studies show that the end-groups for FOPs have effect on $T_d$ and $T_g$, while the effect on $T_m$ for FOPs is not pronounced.
- Targeted PFPE-based triblock copolymers with two longer FOP end-blocks (FOPB-1: $\text{C}_4\text{F}_9$-PFPE- and FOPB-2: $\text{C}_6\text{F}_{13}$-) and PEI as middle block were synthesized.
- The FOPBs can be co-extruded with industrial polyester due to the high thermal stability and low thermal transition temperatures.
- The thermal properties of FOPBs is independent on the end-groups. However, PEI middle block shows significant influence on $T_g$ for copolymers, while the effect on $T_m$ is not pronounced.

4.5. References


CHAPTER FIVE

FABRICATION AND CHARACTERIZATION OF WATER AND OIL REPELLENT THERMOPLASTIC FILMS

5.1. Introduction

In our preceding work, we have demonstrated that PFPE-based oligomeric polyesters can be employed as an effective low surface energy additives to engineering thermoplastic.\(^1\) In particular, FOP possessing only short C\(_4\)F\(_9\)-PFPE- tails (Figure 5.1a and c) allows PET material to reach the level of oil repellency and surface energy comparable to that of PTFE/Teflon. However, we also found that for FOP/PET blend to demonstrate surface energy close to that of PTFE quite a significant concentration (\(\sim 10\%-15\%)\) of FOP has to be used. We have associated this phenomenon with conformation of FOP macromolecule on the film surface (Figure 5.1b). For fluorinated materials, their surface is always preferentially occupied by the fragments of polymer chains with the lowest surface energy.\(^2\)-\(^5\) For FOP structural elements, the order in terms of surface energy is: CF\(_3\)- \(<\) -(CF\(_2\))\(_3\)- \(<\) -CF\(_2\)-CF\(_2\)-O- \(<\) non-fluorinated isophthalate (IPH) units. To reach the lowest surface energy, the surface has to be populated with C\(_4\)F\(_9\)- functional groups that possess lower surface energy than -CF\(_2\)-CF\(_2\)-O- and IPH chain segments. We suggest that FOP chains are spreading over the surface at relatively low concentrations and -CF\(_2\)-CF\(_2\)-O- and even IPH chain segments can interact with a contacting liquid attempting to wet the boundary (Figure 5.1b). Therefore, relatively high concentration of the fluorinated polyester is necessary to maximize the presence of C\(_4\)F\(_9\)- groups at the surface.
To this end, we used two FOPBs detailed in Chapter 4 as low surface energy additives to important thermoplastic polymers. We expected that the addition of non-fluorinated polyester middle block favorably changes the conformation of copolymer on the surface, providing enhanced water and oil repellency. To identify the surface morphology, wettability, and the composition of the obtained films, atomic force microscopy, contact angle measurements, and X-ray photoelectron spectroscopy was used, respectively.

Figure 5.1. General schematic of FOPs with two C₄F₉-PFPE- tails (a); a representation of FOP chains spread over the surface and interact with a contacting liquid attempting to wet the boundary (b); and chemical structure of FOP with two C₄F₉-PFPE- tails (c).
5.2. Experimental Part

5.2.1 Materials

The solvent for the polymer film fabrication, 1,1,1,3,3,3-hexafluoro-2-propanol from Oakwood Products, Inc., was used as received. Commercial grade PET and nylon 6 pellets from Unifi, PMMA pellets from Aldrich Chemical Company, Inc. were also used as received. The FOPBs described in Chapter 4 were used to fabricate polymer films.

5.2.2. Polymer Film Preparation

To prepare polymer films, PET, PMMA, or nylon 6 were solvent-blended with FOPBs in HFIP at different concentrations (1, 2, 5, and 10 wt%). Polymer blended films were fabricated on clean Si wafer substrate by dip-coating from 3 wt% polymer solution in HFIP using 320 mm/min withdrawal rate. Prior to film deposition, the wafers were first cleaned in an ultrasonic bath for 30 min, placed in a hot “piranha” solution (3:1 concentrated sulfuric acid/30% hydrogen peroxide) for 1h, and then rinsed several times with high purity deionized water. After being rinsed, the substrates were dried under a stream of dry nitrogen. After fabrication, the films were kept at room temperature and stored at ambient conditions for 16h to allow solvent evaporation. For selected experiments, the films were annealed at 140°C for 3h in a vacuum oven.

5.3. Results and Discussions

5.3.1. Fabrication of FOPB/PET Films

It is well known that PET is nearly completely wettable with oil, and partially wettable with water. Therefore, FOPB-1 (Figure 4.7) and FOPB-2 (Figure 4.8) with different end-groups were employed as low surface additives to PET in order to increase
its water and oil repellency. In practical applications, only films with a low concentration of fluorine species can be used; thus, we prepared polymer films containing 1, 2, 5 and 10 wt% of FOPBs. HFIP was selected for the film formation, since it is a good solvent for FOPBs and PET used here. The annealing temperature was selected to be above the FOPBs’ thermal transition and the $T_g$ of PET (70-80°C$^6$-$^7$), yet below the $T_m$ of PET (250-260°C$^6$-$^7$). The thickness of films was on the level of 300-350 nm as measured by ellipsometry before and after annealing. On the macroscopic level, all films were even and uniform without visual defects.

5.3.2. Characterization of FOPB/PET Films

Polymer blended films consisting FOPB-1 and FOPB-2 copolymer at different concentrations in PET matrix were fabricated. In addition, pure PET and FOPB films were also prepared to identify their water and oil repellency. The films were divided into two groups: (i) the films from the first group were just dried at ambient conditions (no annealing); and (ii) the films from the second group were first dried and then annealed at 140°C for 3h under vacuum.

Surface Morphology of FOPB/PET Films

AFM topography imaging was used to investigate the micro/nanoscale morphology of the films before (Figure 5.2) and after the annealing treatment (Figure 5.3) for FOPB/PET films possessing different amounts of the fluorinated copolymer. In this study, all AFM images were dimensionally 10 μm x 10 μm. The root-mean-square (RMS) roughness was obtained using AFM imaging analysis software. Figure 5.2 shows that the smooth polymer films were fabricated by dip-coating from FOPB/PET solutions without
visible crystal formation. It is apparent that PET and FOPBs are to some extent immiscible and phase-separated (dark) domains of FOPBs are clearly seen in a (bright) PET matrix on the AFM images. It was also found that an increase of FOPB concentration in blends resulted in an increased extent of phase separation.

On the other hand, Figure 5.3 shows that the annealing treatment has a significant effect on the film surface morphology, since the crystalline structures are formed within FOPB/PET films. It was expected because intensive PET crystallization occurs at the temperature of 140°C.6-7 PET polymer chains rearranged and reoriented themselves to form crystals during the thermal treatment. We also noted that the phase separation of FOPBs was not clearly observed for the annealed films on AFM topographical images. Thus, it is possible that as a result of the annealing FOPB dissolves in PET matrix. In an alternative scenario, FOPB (as a lower surface energy component) can spread over the PET surface forming a continuous layer owing to the thermodynamical condition of the reduction of the film surface energy.8
Figure 5.2. AFM (10 µm x 10 µm) topographical images of polymer films before annealing (a-l). (a) Pure PET (RMS = 0.3 nm), (b) 1% FOPB-1/PET (RMS = 1.0 nm), (c) 2% FOPB-1/PET (RMS = 1.0 nm), (d) 5% FOPB-1/PET (RMS = 2.0 nm), (e) 10% FOPB-1/PET (RMS = 2.5 nm), (f) 1% FOPB-2/PET (RMS = 1.0 nm), (g) 2% FOPB-2/PET (RMS = 9.5 nm), (h) 5% FOPB-2/PET (RMS = 1.0 nm), and (i) 10% FOPB-2/PET (RMS = 32.5 nm).
Figure 5.3. AFM (10 µm x 10 µm) topographical images of polymer films after annealing (a-l). (a) Pure PET (RMS = 8.0 nm), (b) 1% FOPB-1/PET (RMS = 10 nm), (c) 2% FOPB-1/PET (RMS = 7.0 nm), (d) 5% FOPB-1/PET (RMS = 11.0 nm), (e) 10% FOPB-1/PET (RMS = 7.0 nm), (f) 1% FOPB-2/PET (RMS = 4.0 nm), (g) 2% FOPB-2/PET (RMS = 9.0 nm), (h) 5% FOPB-2/PET (RMS = 7.5 nm), and (i) 10% FOPB-2/PET (RMS = 20.0 nm).
To clarify this matter, we have determined thermal transitions of the annealed (at 140°C for 3h) FOPB/PET blends (Figure 5.4). The transitions were compared to the ones observed for pure PET and FOPB materials processed under the same conditions. The major focus was to understand if FOPBs have some level of miscibility with the PET matrix. To this end, we followed the PET melting transition, which does not overlap with \( T_g \) and \( T_m \) of FOPBs. If at least the partial miscibility of PET and FOPB is present, it has to significantly decrease the melting temperatures of PET.9

Figure 5.4. DSC traces for annealed PET and FOPB/PET blends at different concentrations: (a) FOPB-1/PET and (b) FOPB-2/PET.
However, data for the FOPB/PET blends (Table 5.1) shows that there is no significant and systematic decrease in $T_m$ of PET matrix with addition of FOPBs. For the blends containing 80% of FOPBs, it was found that $T_m$ for the fluorinated block copolymer is not influenced by the presence of PET phase as well. Therefore, the polymer materials are practically immiscible. Since the copolymers cannot be accommodated in the PET matrix and have the lower surface energy, we suggest that FOPBs spread over the boundary of the film and form continuous layer upon the annealing.

Table 5.1. Melting temperature of annealed PET and FOPB/PET blends.

<table>
<thead>
<tr>
<th>Polymer Blend</th>
<th>FOPB Content (wt%)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>0</td>
<td>238</td>
</tr>
<tr>
<td>FOPB-1/PET</td>
<td>1</td>
<td>238</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>235</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>236</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>232</td>
</tr>
<tr>
<td>FOPB-2/PET</td>
<td>1</td>
<td>236</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>238</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>237</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>234</td>
</tr>
</tbody>
</table>

In fact, AFM phase images (Figures 5.5), which are particularly sensitive to heterogeneity of surface composition\textsuperscript{10}, do not show that the surface layer is discontinuous and partially covering the film surface. Therefore, based on the AFM and DSC results, we assumed that after the annealing step practically all the surface of the FOPB/PET films is covered with the nanoscale copolymer layers.
Figure 5.5. AFM (10 µm x 10 µm) phase images of annealed polymer films (a-l). Pure PET (a), FOPB-1/PET (b-e), and FOPB-2/PET (f-i). Concentration of FOPB: (b, f) 1%; (c, g) 2%; (d, h) 5%; and (e, i) 10%.
**Surface Wettability of FOPB/PET Films**

**Wettability of Solvent-Casted FOPB/PET Films**

To examine the level of hydrophobicity and oleophobicity of solvent-casted FOPB/PET films (no annealing), we measured the static water and hexadecane contact angle. It was shown experimentally that liquids with bulky molecules like hexadecane are suitable for contact angle measurements to characterize energetics of fluorinated polymer surfaces.\(^{11\text{-}12}\) Prior to the CA measurements, we performed solubility test for FOPBs, and determined that the copolymers were not soluble in water and hexadecane. The CA results are presented in **Figure 5.6**. It can be clearly seen that pure PET films are nearly completely wettable with hexadecane (HCA < 5°), and partially wettable with water (WCA ≈ 58°).

![Contact Angle Graph](attachment:image.png)

**Figure 5.6.** WCA and HCA for FOPB/PET films of different FOPB contents before annealing.
Figure 5.6 also illustrates that addition of the FOPBs into PET leads to a significant increase in values of both WCA and HCA. The films containing 1-2% of FOPBs have 70-80° WCA and 30-50° HCA. Furthermore, the repellency of the films increases with FOPB content as more fluorinated copolymer is presented on the film surface. At the concentration of 10%, the WCA and HCA for blended films are 80-90° and 55-65°, respectively.

Wettability of Annealed FOPB/PET Films

It is obvious that, for practical applications, annealing treatment for the films is necessary. In an industrial setting, the thermoplastic materials are fabricated at elevated temperature via melting processing. Therefore, to investigate the influence of annealing treatment on surface wettability, we also conducted CA measurements for the annealed FOPB/PET films. For comparison, annealed pure PET and FOPB films were also prepared at the same condition. The measured CAs are shown in Figure 5.7.

It is evident that the WCA and HCA for the polymer films increased significantly after the annealing in comparison with the solvent casted ones (Figure 5.6). It means that fluorinated copolymer chains became mobile at elevated temperature, which supported the migration of the FOPB over the area on the film surface occupied by the PET matrix. We also connect the CA improvement with the intensive crystallization of PET at 140°C, as it is evident from the AFM imaging (Figure 5.3). The densification (shrinkage) of PET phase caused by PET crystallization increased the surface exposure of FOPB phase. Therefore, more FOPB macromolecules could enrich to the film surface.
Furthermore, as shown in Figure 5.7, there is a significant dependence of CAs on concentration of the fluorinated copolymers in the blends. The WCA for FOPB-1/PET films increased from 81° to 107° as FOPB-1 content increased from 1 to 10%, and HCA of the films was also increased from 50° to 62°. For FOPB-2/PET films, a similar trend was observed, where WCA increased from 77° to 101° as FOPB-2 concentration increased from 1% to 10%. The HCA was also increased from 53° to the level of 63°. It is necessary to highlight that, at 10% load, the wettability of the FOPB/PET films is virtually as same as wettability of pure (100%) FOPBs. It indicates that practically all surface of the film is occupied with the copolymers.
We also benchmarked the wettability of polytetrafluoroethylene films against that of FOPB/PET films. The wettability of PTFE was measured using the same method as the one for FOPB/PET films. The WCA and HCA for PTFE we measured was 118° and 51°, respectively. They correlated well with the values reported in the scientific literature.13-14 Figure 5.7 reveals that the highest WCA for annealed FOPB/PET films was reached at 5% copolymer content and was on the level of 100°, which was relatively lower than that of PTFE. However, with addition of just 1% of FOPB, oil repellency of PET films was on the same level as demonstrated by PTFE. The oil repellency of FOPB/PET films was better than the one of PTFE when 2% of FOPB-1 or 5% of FOPB-2 was added to the PET matrix. In addition, it appears that there was no clear difference in wettability of FOPB-1/PET and FOPB-2/PET possessing different end-groups. On the other hand, it is necessary to point out that, for practically important concentration (≤ 5%), the water and oil repellency of the C₄ material (FOPB-1 with C₄F₉-PFPE- tails) is on the level of the C₆ material (FOPB-2 with C₆F₁₃- tails).

Surface Energy of FOPB/PET Films

Surface energy is an important parameter in characterizing the level of surface modification. To this end, the WCA and HCA data was used to estimate surface energy of the FOPB/PET films using Owens-Wendt method.15 This method is one of the most used to determine surface energy of polymer surfaces and is based on principal assumption that the surface energy is a sum of two components: dispersion and polar.
\[ \gamma_{11}(1 + \cos \theta_1) = 2\sqrt{\gamma_s^d \gamma_{11}^d} + 2\sqrt{\gamma_s^p \gamma_{11}^p} \]  
(5.1 a)

\[ \gamma_{12}(1 + \cos \theta_2) = 2\sqrt{\gamma_s^d \gamma_{12}^d} + 2\sqrt{\gamma_s^p \gamma_{12}^p} \]  
(5.1 b)

\[ \gamma_s = \gamma_s^d + \gamma_s^p \]  
(5.1 c)

where \( \gamma_s \) and \( \gamma_l \) is the surface tension of the solid and liquid, respectively. The subscript \( d \) and \( p \) corresponds to dispersion and polar components of the surface tension, respectively.

Surface free energy (\( \gamma_s \)) and its polar (\( \gamma_s^p \)) and dispersion (\( \gamma_s^d \)) components of the FOPB/PET surfaces were determined using known surface tension components for water and hexadecane (Table 5.2).\(^{16}\)

**Table 5.2.** The \( \gamma_l^p \) and \( \gamma_l^d \) components of liquids.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>( \gamma_l^d ) (mN/m)</th>
<th>( \gamma_l^p ) (mN/m)</th>
<th>( \gamma_l ) (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexadecane</td>
<td>26.35</td>
<td>0</td>
<td>26.35</td>
</tr>
<tr>
<td>Water</td>
<td>21.8</td>
<td>51</td>
<td>72.8</td>
</tr>
</tbody>
</table>

The estimated surface energy (\( \sigma \)) for films before and after the annealing are presented in Figure 5.8 and Figure 5.9, respectively. It can be seen that pure PET films have a quite high surface energy around 46 mN/m. However, as shown in Figure 5.8, the addition of a small amount of FOPB into PET reduces the surface energy of the blended films significantly. For instance, at 1% concertation, the surface energy of FOPB/PET films is 33 mN/m and 38 mN/m for FOPB-1 and FOPB-2, respectively. As the FOPB content increased further, the surface energy decreased. For the films with 10% FOPB, \( \sigma_{\text{FOPB-1}} \) is
20 mN/m and $\sigma_{\text{FOPB-2}}$ is 24 mN/m. The surface energy of 10% films is lower than that of PTFE ($\sigma_{\text{PTFE}} = 18.5$ mN/m).

![Graph showing surface energy vs concentration of FOPB](image)

**Figure 5.8.** Surface energy of FOPB/PET films before annealing. Surface energy for PET, PTFE, and pure FOPBs are given for comparison.

**Figure 5.9** shows that the surface energy of annealed FOPB/PET films is significantly lower than the energy of the unannealed films (**Figure 5.8**). Specially, at the concentration of 5%, all films have surface energy practically equal to $\sigma_{\text{PTFE}}$. For the films with 10% FOPB, $\sigma_{\text{FOPB-1}}$ and $\sigma_{\text{FOPB-2}}$ are 15 mN/m and 17 mN/m, respectively. Namely, both FOPB-1/PET and FOPB-2/PET with 10% load have lower surface energy than that of PTFE. In addition, it is apparent that C$_4$ material (FOPB-1) has a surface energy value quite similar to C$_6$ polymer (FOPB-2) at all concentrations.
Figure 5.9. Surface energy of FOPB/PET films after annealing at 140°C for 3h. Surface energy for PET, PTFE, and pure FOPBs are given for comparison.

The Effect of Storage Time on Wettability

Our preceding studies on wettability of PET films containing PFPE-based oligomeric polyester indicated that the solvent cast films are not at equilibrium and the enrichment of the film surface with the oligomeric polyesters was continuing for several days. Therefore, we investigated if the level of FOPB copolymer migration to the surface increases with the storage time. For this purpose, we determined the WCA and HCA for the films with 5% FOPB as a function of time. The results are displayed in Figure 5.10.
Figure 5.10. WCA and HCA for 5 wt% FOPB/PET films as a function of storage time.

The migration of FOPB to/over the film boundary continues for up to 6-7 days as indicated by significant change in WCA that increased by ~10° after 7 days of storage. We also noted that HCA practically does not change with the storage time. The results suggest that the size of the wetting liquid plays a critical role in the wettability. Indeed, based on molecular weight and chemical structure, the size of water molecule is about order of magnitude smaller than that of hexadecane. Specifically, the molecular volumes for water and hexadecane at 20°C are 30 and 458 Å³, respectively. Therefore, WCA is more sensitive to the density (or thickness) of the fluorinated monolayer covering the PET phase. It means water can penetrate to a greater degree through the layer of fluorinated oligomer and contact the PET matrix when compared to hexadecane. We suggest that significant amount of time is needed for films to reach the equilibrium state and higher levels of
hydrophobicity and oleophobicity. Furthermore, it was found that the values of CA after 7 days storage (Figure 5.10) are smaller than those of annealed films (Figure 5.7). Consequently, it is concluded that annealing treatment is necessary for practical applications to prompt CAs to saturation limit over a relatively short time.

5.3.3 Thermodynamics of FOPB Layer Formation

The study of FOPB/PET film morphology indicates that FOPB is immiscible with PET and presumably forms a nanoscale layer covering the exterior of the film. Furthermore, we also assumed that films’ surface is practically covered with nanoscale copolymer layer after annealing. Therefore, we have foreseen that FOPBs (Figure 5.11a) will support formation of FOP brush on the surface, where fluorinated end-groups are concentrating on the exterior of the film. To this end, we evaluated the capability of FOPB layer to possess brush-like structure, where PEI block segregated to the PET surface (Figure 5.11b) based on thermodynamical condition of surface energy minimization.

The lowest free energy \( (G) \) of layer formation between the two oligomeric blocks (FOPs and PEI) and our model substrate, PET were defined. We performed a simple thermodynamic approximation to predict which oligomer component would have a favorable interaction with the surface, assuming homo-oligomer chains of FOPs, PEI and the PET substrate surface. The thermodynamic favorable conditions are governed by the surface tensions (i.e. reversible increase in the Gibbs \( (G) \) free energy upon creation of a unit surface area) of the individual components of the oligomers, PET, and the interfacial tension interactions for the different combinations between the component materials.
Figure 5.11. General schematic of FOPBs. a) FOPBs with two FOP end-blocks and PEI middle block. b) a representation of FOPBs structure and formation of FOP brush on the surface.

The individual surface tensions, $\gamma$, for FOP-1, FOP-2, PEI, and PET were calculated using Biscerano algorithms (Polymer Design Tools, Version 1.1, DTW Associates, Inc) and taken as: FOP-1: $\gamma_{FOP-1} = 32.8$ mN/m, FOP-2: $\gamma_{FOP-2} = 34.5$ mN/m, PEI: $\gamma_{PEI} = 51.0$ mN/m, and PET: $\gamma_{PET} = 47.1$ mN/m. First, to approximate the favorable layer formation by the lowest Gibbs free energy of the layers, the interfacial tensions between the two
materials were estimated by using the harmonic mean equation (Equation 5.2 \(T = 298\text{K}\))\textsuperscript{18-19}.

\[
\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d\gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p\gamma_2^p}{\gamma_1^p + \gamma_2^p}
\]

(5.2)

In order to predict the polar \( (\gamma_p) \) and dispersive \( (\gamma_d) \) components of FOPs, PEI, and PET.

Equation 5.3 was utilized to estimate the polar component of the surface tension\textsuperscript{18}:

\[
\frac{\gamma_p}{\gamma_T} = \left(\frac{\delta_p}{\delta_T}\right)^2
\]

(5.3)

where \( \gamma_T \) is the overall surface tension. \( \delta_p \) and \( \delta_T \) are the polar and total solubility parameters, respectively. The dispersive component of the surface tension, \( \gamma_d \), could then be found utilizing the additive nature of the surface tension relationship:

\[
\gamma_T = \gamma_p + \gamma_d
\]

(5.4)

The polar component of the solubility parameter for FOPs, PEI, and PET was estimated by first calculating the dispersive component of the solubility parameter, \( \delta_d \), from Equation 5.5:

\[
\delta_d = \frac{F_d}{V_m}
\]

(5.5)

where \( F_d \) is defined as the dispersion component of the molar attraction\textsuperscript{20} and \( V_m \) is the molar volume of the monomer unit. From the estimated values of the overall solubility parameter, \( \delta_T \), and \( \delta_d \), the polar component can be found using the relationship\textsuperscript{21}:

\[
\delta_T = \sqrt{\delta_d^2 + \delta_p^2}
\]

(5.6)
Table 5.3 presents all values for the solubility parameters, surface tension, and interfacial tensions calculated for the possible combinations of the polymer layers in a “stacked” arrangement. To determine the favorable FOPB layer formation on PET surface, we estimated the total change in the Gibbs energy for the system by utilizing the following relationship:

\[
dG = \left( \frac{\partial G}{\partial A} \right) dA_A + \left( \frac{\partial G}{\partial A_B} \right) dA_B + \left( \frac{\partial G}{\partial A_{AB}} \right) dA_{AB} + \left( \frac{\partial G}{\partial A_{PET}} \right) dA_{PET} + \left( \frac{\partial G}{\partial A_{PETO}} \right) dA_{PETO}
\]

(5.7)

where \( dA_B = -dA_A = dA_{AB} \) and \( \frac{\partial G}{\partial A_A} = \gamma_A \) for component A, B, and AB. In this model, a negative coefficient was employed when a surface disappears; conversely, a positive coefficient was used when a new surface is formed.
Table 5.3. Calculated surface energy, solubility parameter values, and interfacial energy in the system.

<table>
<thead>
<tr>
<th>Individual Material</th>
<th>$\gamma_T$ (mN/m)</th>
<th>$\gamma_d$ (mN/m)</th>
<th>$\gamma_p$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOP-1</td>
<td>32.80</td>
<td>22.00</td>
<td>10.80</td>
</tr>
<tr>
<td>FOP-2</td>
<td>34.50</td>
<td>22.97</td>
<td>11.53</td>
</tr>
<tr>
<td>PEI</td>
<td>51.00</td>
<td>27.96</td>
<td>23.04</td>
</tr>
<tr>
<td>PET</td>
<td>47.10</td>
<td>29.92</td>
<td>17.18</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Individual Material</th>
<th>$\delta_T$ (J/cm$^3$)$^{1/2}$</th>
<th>$\delta_d$ (J/cm$^3$)$^{1/2}$</th>
<th>$\delta_p$ (J/cm$^3$)$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOP-1</td>
<td>19.30</td>
<td>15.81</td>
<td>11.07</td>
</tr>
<tr>
<td>FOP-2</td>
<td>19.60</td>
<td>15.99</td>
<td>11.33</td>
</tr>
<tr>
<td>PEI</td>
<td>24.40</td>
<td>18.07</td>
<td>16.40</td>
</tr>
<tr>
<td>PET</td>
<td>22.50</td>
<td>17.93</td>
<td>13.59</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material Interface</th>
<th>$\gamma_T$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOP-1/PEI</td>
<td>5.14</td>
</tr>
<tr>
<td>FOP-2/PEI</td>
<td>4.32</td>
</tr>
<tr>
<td>FOP-1/PET</td>
<td>2.66</td>
</tr>
<tr>
<td>FOP-2/PET</td>
<td>2.02</td>
</tr>
<tr>
<td>PEI/PET</td>
<td>0.92</td>
</tr>
</tbody>
</table>
We then considered two border situations (A and B) for the FOPBs layer arrangement on the PET surface. In the case A, the layer has PEI blocks exposed to the layer exterior whereas FOP blocks are segregated to the PET boundary (Figure 5.12a). In scenario B (FOPB brush formation), FOP chains are located on the surface while PEI is in contact with the PET surface (Figure 5.12b). For the first arrangement, the change in the Gibbs energy can be approximated using Equation 5.8:

\[ dG_1 = -\gamma_{FOP} + \gamma_{PEI} + \gamma_{FOP-PEI} - \gamma_{PET} + \gamma_{PET-FOP} \]  

(5.8)

where \( \gamma_{FOP} \) is the surface energy of FOP, \( \gamma_{PEI} \) is the surface energy of PEI, \( \gamma_{FOP-PEI} \) is the interfacial tension for FOP-PEI, \( \gamma_{PET} \) is the surface energy of PET substrates, and \( \gamma_{PET-FOP} \) is the interfacial tension between PET substrates and FOP. For the second arrangement, the change in Gibbs energy equation can be estimated Equation 5.9:

\[ dG_2 = -\gamma_{PEI} + \gamma_{FOP} + \gamma_{FOP-PEI} - \gamma_{PET} + \gamma_{PET-PEI} \]  

(5.9)

where \( \gamma_{PET-PEI} \) is the interfacial tension value for PET substrates and PEI. Using the data from Table 5.3, the change in Gibbs free energy of the layer arrangements were calculated to be -21.10 mN/m (FOPB-1) or -24.26 mN/m (FOPB-2) for arrangement A, respectively and -59.24 mN/m (FOPB-1) or -59.28 mN/m (FOPB-2) for arrangement B, respectively. It is evident that the lowest free energy layer formation is given by arrangement B, where PEI is segregated to the PET surface and FOP blocks are positioned at the external interface. Therefore, from the thermodynamic point of view, the formation of the FOPB brush-like layer on the PET surface is favorable. This is the preferential arrangement for the applications targeted here, where fluorine entities are needed at the polymer air interface to minimize the surface tension.
Figure 5.12. Schematic illustration of the two border situations for the FOPB monolayer arrangement on the PET surface: (a) PEI exposes to the exterior while FOP locates on the PET surfaces; (b) PEI is in contact with PET whereas FOP exposes to exterior.

Surface Coverage of Annealed FOPB/PET Films

Our thermodynamic estimations indicate that for equilibrated FOPB/PET films, all of the surface has to be covered with the layer of fluorinated copolymer. The AFM phase imaging and contact angle measurements (especially HCA) also clearly indicate that the surface of the film is occupied with the fluorinated copolymers. Therefore, the value of the contact angles is controlled by the thickness of the layer and ability of the FOPB macromolecules to screen the PET phase from the probing liquids. We estimated the effective surface area of PET shielded from the wetting liquids by the fluorinated
copolymers using classical Cassie-Baxter model. The model describes the apparent contact angle of liquid (\( \theta_{\text{FOPB/PET}} \)) on a composite surface when the surface is not completely wetted by the liquid droplet:

\[
\cos \theta_{\text{FOPB/PET}} = f_{\text{FOPB}} \cos \theta_{\text{FOPB}} + f_{\text{PET}} \cos \theta_{\text{PET}} \tag{5.10}
\]

where \( \theta_{\text{FOPB}} \) and \( \theta_{\text{PET}} \) are experimentally determined Young’s contact angles of a liquid on pure (100\%) FOPB and PET surfaces, respectively. \( f_{\text{FOPB}} \) and \( f_{\text{PET}} \) are surface area fractions of the component surfaces. From experimentally measured contact angles for annealed FOPB/PET films (\( \theta_{\text{FOPB/PET}} \)), we calculated the surface fraction of the PET surface screened from the wetting liquids with FOPBs using Equation 5.10. The results are displayed in Table 5.4.

<table>
<thead>
<tr>
<th>Polymer Film</th>
<th>FOPB Content (wt%)</th>
<th>( f_{\text{FOPB}} ) from WCA</th>
<th>( f_{\text{FOPB}} ) from HCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOPB-1/PET</td>
<td>1</td>
<td>0.49</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.55</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.89</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>FOPB-2/PET</td>
<td>1</td>
<td>0.39</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.68</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.91</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.92</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Table 5.4. Apparent surface area of the annealed FOPB/PET films (\( f_{\text{FOPB}} \)) that is screened effectively by fluorinated chain segments.
The results indicate that FOPBs readily segregated to the surface and effectively shielded it from the probing liquids. We noted that FOPB-1 is better for shielding surfaces from hexadecane than from water, especially with low (1% and 2%) concentration in PET films. The same phenomenon is observed with PET films with addition of 1% FOPB-2. We reiterate here that the reason behind this observation is the difference in the size of the probe liquid molecules, where water molecules are much smaller. Therefore, more dense FOPB layer on the surface are needed to screen the PET surface from water. On the other side, the difference disappeared at higher concentrations of FOPBs. With 10% load, the surface was practically fully screened with FOPBs.

**XPS Analysis of Annealed FOPB/PET Films**

To further investigate the FOPBs localization on the boundary of the FOPB/PET film, XPS analysis was conducted for the annealed films with different copolymer concentrations (1, 2, and 5 wt%). In this work, samples were analyzed at incident angle of 90°, where the detector line of sight is normal to the film. Therefore, the corresponding sampling depth from the air/film boundary is around 10 nm.\(^{24-25}\) XPS survey spectra of the top 10 nm layer of FOPB/PET films primarily possess three characteristic peaks: F1s, O1s, and C1s. The F1s signal was from the fluorinated copolymer. The O1s and C1s peaks were from both FOPBs and PET polymers. The XPS data is displayed in Table 5.5 and Table 5.6. The atomic concentration of fluorinated triblock copolymer segments in the topmost 10 nm layer was calculated using the experimental $F/O$ ratio from the survey spectra and not $F/C$ ratio to avoid possible carbon-based contaminates. The following equations were applied:\(^{26-27}\)
\[
\left( \frac{F}{O} \right)_{XPS} = \frac{X_{FOPB} F_{FOPB}}{X_{FOPB} O_{FOPB} + (1 - X_{FOPB}) O_{PET}} \quad (5.11a)
\]

\[X_{FOPB} + X_{PET} = 1 \quad (5.11b)\]

where \(X_{FOPB}\) and \(X_{PET}\) are the atomic concentration of FOPBs and PET within the top layer, respectively. \(F_{FOPB}\) and \(O_{FOPB}\) is the fluorine and oxygen atomic concentrations in the fluorinated copolymers obtained from spectra of 100% FOPB films (Table 5.5 and Table 5.6). \(O_{PET}\) is the oxygen atomic concentrations in PET polymer. Since hydrogen atoms are not detectable in our XPS experiment, \(O_{PET}\) was calculated using only carbon and oxygen present in the PET structure.
### Table 5.5. Atomic concentration percentage of F, O and C for FOPB-1/PET films.

<table>
<thead>
<tr>
<th>Angle</th>
<th>1% of FOPB-1 in the Films</th>
<th>2% of FOPB-1 in the Films</th>
<th>5% of FOPB-1 in the Films</th>
<th>100% of FOPB-1 in the Films</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atomic Concentration %</td>
<td>Atomic Concentration %</td>
<td>Atomic Concentration %</td>
<td>Atomic Concentration %</td>
</tr>
<tr>
<td>F 1s</td>
<td>16.01</td>
<td>17.81</td>
<td>28.66</td>
<td>36.13</td>
</tr>
<tr>
<td>O 1s</td>
<td>26.26</td>
<td>23.89</td>
<td>27.22</td>
<td>21.06</td>
</tr>
<tr>
<td>C 1s</td>
<td>57.73</td>
<td>58.30</td>
<td>44.12</td>
<td>42.81</td>
</tr>
</tbody>
</table>

### Table 5.6. Atomic concentration percentage of F, O and C for FOPB-2/PET films.

<table>
<thead>
<tr>
<th>Angle</th>
<th>1% of FOPB-2 in the Films</th>
<th>2% of FOPB-2 in the Films</th>
<th>5% of FOPB-2 in the Films</th>
<th>100% of FOPB-2 in the Films</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atomic Concentration %</td>
<td>Atomic Concentration %</td>
<td>Atomic Concentration %</td>
<td>Atomic Concentration %</td>
</tr>
<tr>
<td>F 1s</td>
<td>13.55</td>
<td>20.92</td>
<td>24.59</td>
<td>38.12</td>
</tr>
<tr>
<td>O 1s</td>
<td>26.59</td>
<td>29.34</td>
<td>22.13</td>
<td>18.41</td>
</tr>
<tr>
<td>C 1s</td>
<td>59.86</td>
<td>49.74</td>
<td>53.28</td>
<td>43.47</td>
</tr>
</tbody>
</table>
The concentration of the fluorinated copolymer within 10 nm layer from the air/film interface is calculated by Equation 5.11 and showed in Figure 5.13a. It is seen that the FOPB content in the topmost layer is increasing with FOPB concentration and is more than an order of magnitude higher than that in the “as-prepared” film bulk. It appears that the exterior of the FOPB/PET films are extensively enriched with the fluorinated copolymers.

As a first approximation, the coarse grain model was used to describe the top 10 nm of the film exterior as two layered system, where the FOPB layer is positioned on the top of the PET one (Arrangement B in Figure 5.12b). Within this model, we determined the effective thickness of the FOPB layers by considering the thickness of the layer to be directly proportional to the atomic concentration of FOPB within 10 nm of the surface. Results in Figure 5.13b reveal that the thickness of the layer is on the level of 3-7 nm depending on FOPB concentrations.
Figure 5.13. Atomic concentration of FOPB within 10 nm top layer (a) and the effective thickness of FOPB layer on the surface (b) of the annealed FOPB/PET film as a function of FOPB concentration in the blends.

Structural Characterization of FOPB Layer

We compared the FOPB layer thickness with dimensions of the FOPB macromolecules. To this end, we estimated the root-mean-square end-to-end distance ($R$) of the macromolecular chain. We calculated the upper border $R$ value size by assuming the same scaling relationships as for oligomeric PET, which is less flexible than FOPB using Equation 5.12:

$$R = 0.04 (M_n)^{0.57}$$  \hspace{1cm} (5.12)

where $M_n$ is the number-average molecular weight of FOPB estimated using NMR data.

Then, the lower border end-to-end distance was also estimated using Equation 5.13 for perfluoropolyethers, which are more flexible than FOPBs:

$$R = 0.056 (M_n)^{0.5}$$  \hspace{1cm} (5.13)
Our estimations indicated that $R$ value is 4-6 nm for both FOPB-1 and FOPB-2. Therefore, the thickness of copolymer layers is $\sim$1 FOPB monolayer for the films with 1% of FOPB.

Our thermodynamic estimations point out that the macromolecules in the layer have to be organized in a brush-like structure, whereas PEI blocks are segregated to the PET surface. In this structure, FOP blocks are anchored by the one end to the surface, while another $\text{C}_4\text{F}_9$-PFPE-$\text{/C}_6\text{F}_{13}$- fluorinated end is exposed to the air (Figure 5.12b). We estimated parameters of the brush layer using relationships developed for polymer grafted layers. Specifically, we calculated the chain density of FOP brushes, the surface coverage of FOP brush, and the average distance ($L$) between FOP chains in the brush layer (Table 5.7). The chain density of FOP brushes, $\Sigma$ (chain/nm$^2$) was estimated with Equation 5.14$^{30}$:

$$\Sigma = \Gamma N_A \times 10^{-21} / M_n = (6.023 \Gamma \times 100) / M_n$$

(5.14)

where $\Gamma$ (mg/m$^2$) is the surface coverage of FOP brush, $N_A$ is Avogadro’s number, and $M_n$ is the number-average molecular weight of FOP block estimated from NMR analysis. The surface coverage of FOP brush was first calculated from Equation 5.15$^{30}$:

$$\Gamma = h \rho$$

(5.15)

where $h$ and $\rho$ are the dry thickness and density of attached macromolecules, respectively. In our calculation, the density value of 1.5 g/cm$^3$ was selected for FOP based on known values of PET$^6$ (amorphous 1.34 g/cm$^3$, crystalline 1.52 g/cm$^3$) and PFPE$^{31}$ (1.8-1.9 g/cm$^3$) densities. The dry thickness was estimated using XPS analysis (Figure 5.13b). We also estimated the average distance ($L$) between FOP chains in the brush layer using Equation 5.16$^{30}$:

$$L = (4/\pi \Sigma)^{0.5}$$

(5.16)
Table 5.5. Calculated parameters for the FOPB layers.

<table>
<thead>
<tr>
<th>FOPB layer</th>
<th>FOPB Content (wt%)</th>
<th>Chain Density $\Sigma$, (chain/nm$^2$)</th>
<th>Surface Coverage $\Gamma$, (mg/m$^2$)</th>
<th>Average Distance between Chains $L$, (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOPB-1</td>
<td>1</td>
<td>1.44</td>
<td>6.45</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.70</td>
<td>7.65</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.30</td>
<td>10.35</td>
<td>0.66</td>
</tr>
<tr>
<td>FOPB-2</td>
<td>1</td>
<td>1.01</td>
<td>5.10</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.33</td>
<td>6.75</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.93</td>
<td>9.75</td>
<td>0.72</td>
</tr>
</tbody>
</table>

To better understand how the parameters are related to the size of FOP blocks, we determined (using Equation 5.13) that the end-to-end distance for FOP-1 and FOP-2 is practically the same and is between 3 and 4 nm. From $R$ and $L$, it is possible to evaluate degree of the overlap between FOP chains in the brush-like layer using straightforward geometrical model described elsewhere (Figure 5.14).$^{32-34}$ It is apparent that the higher degree of the overlap is directly related to the higher capability of the FOP layer to screen the PET matrix from the probing liquids.
Figure 5.14. A geometric 2D model of surface coverage by FOP chain. (a) The radius of the disc is equal to the radius of gyration of the FOP brushes. (b) A mathematical demonstration of three different regimes for FOP surface coverage.

There are three different regimes to be considered for the surface shielding within the geometrical model. In Regime I \((L > R)\), FOP chains are spaced out, do not overlap, and do not screen the surface effectively. However, when FOP chain density is increased, the chains start to overlap and transition to Regime II \((R \geq L > R/2^{1/2})\). In Regime II, the chain density is not sufficient to cover the whole surface area. In Regime III \((L \leq R/2^{1/2})\), the chain density is sufficient to screen the surface completely. Namely, there is no open surface in this case of Regime III. A comparison of \(R\) (~3.5 nm) and \(R/2^{1/2}\) (~2.5 nm), values for FOPs with \(L\) values presented in Table 5.7, it is evident that all copolymer layers
studied here follow Regime III. However, even the surface is fully covered with FOP chains only, values of FOP blocks chain density $\Sigma$ on the level of 1 chain/nm$^2$ (1% FOPB/PET films) are effectively screening the surface from water and hexadecane. At these values of $\Sigma$, thickness of the FOPB layer is somewhat higher than the end-to-end distance of FOP blocks. Therefore, the FOP blocks stretch away from the surface and populate the surface with low energy $\text{C}_4\text{F}_9$-PFPE- and $\text{C}_6\text{F}_{13}$- end-segments.

5.3.4 Addition of FOPB to Other Thermoplastic Materials

To demonstrate the applicability of our surface modification approach utilizing FOPBs to other than PET engineering thermoplastics, we prepared FOPB/nylon 6 and FOPB/PMMA films. The FOPB content in the films was 5%. The films were annealed at 140° for 3h prior to the CA measurements. The obtained wettability and surface energy results are presented in Table 5.8.

It is necessary to point out that both pure nylon 6 and PMMA are partially wettable with water and nearly completely wettable by hexadecane. The incorporation of FOPB in the thermoplastics dramatically increased HCA of the surface. We noted that the HCA for FOPB-1/nylon 6 and FOPB-1/PMMA increased from 1-5° to 72° and 88°, respectively. For FOPB-2, the same trend was observed as the HCA increased from 1-5° to 68° for nylon 6, and to 70° for PMMA. The WCA was also significantly increased with FOPB addition. The surface energy for annealed films was also estimated. Table 5.8 shows that both pristine nylon-6 and PMMA have a quite similar and relatively high surface energy at (37 and 35 mN/m, respectively). Conversely, at 5% FOPB/nylon 6 films, the surface energy is 24 and 23 mN/m for FOPB-1 and FOPB-2, respectively. For the films blended with
PMMA, the surface energy for both FOPB-1 (9 mN/m) and FOPB-2 (13 mN/m) becomes much lower than that of PTFE (18.5 mN/m). Without an additional study, we cannot offer a comprehensive explanation why FOPB/PMMA films have much lower surface energy than the FOPB/PET and FOPB/nylon 6 ones. However, we can conclude that the addition of FOPBs can decrease surface energy of various engineering thermoplastics and not only PET.
Table 5.6. CAs and surface energies for annealed 5% FOPB/thermoplastic films.

<table>
<thead>
<tr>
<th>Material</th>
<th>Pure Thermoplastic Films</th>
<th>5% of FOPB-1 in the Films</th>
<th>5% of FOPB-2 in the Films</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WCA (degree)</td>
<td>HCA (degree)</td>
<td>Surface Energy (mN/m)</td>
</tr>
<tr>
<td>Nylon 6</td>
<td>72±0.4</td>
<td>1-5</td>
<td>37±0.1</td>
</tr>
<tr>
<td>PMMA</td>
<td>77±2</td>
<td>1-5</td>
<td>35±1.1</td>
</tr>
</tbody>
</table>
5.4. Conclusions

- The addition of fluorinated polyester triblock copolymers to PET allows increasing the level of water and oil repellency, even at relatively low FOPB concentrations.
- Annealing treatment has significant effect on the surface morphology and wettability of FOPB/PET films.
- Annealing supported the surface migration of FOPB over the film and prompted CAs to saturation values.
- The surface wettability and energy is not end-group dependent. C4 material (FOPB-1 with C4F9-PFPE- tails) is on the comparable level of the C6 material (FOPB-2 with C6F13- tails).
- FOPB brush-like layer on the PET surface is a thermodynamically favorable arrangement, where PEI is segregated to the PET surface and fluorinated segments are positioned at the top.
- FOPBs are also capable to be used as low surface energy additives to engineering thermoplastic other than PET, such as nylon 6 and PMMA.
- FOPB copolymers can be considered as the next generation of more effective low surface energy additives to important engineering thermoplastics.

5.5. References


32. Burtovyy, O., Synthesis and characterization of macromolecular layers grafted to polymer surfaces. **2008**.


CHAPTER SIX
FLUORINATED POLYESTER TRIBLOCK WITH POLY(ETHYLENE ISOPHTHALATE-CO-TEREPHTHALATE) COPOLYMER AS A MIDDLE BLOCK

6.1. Introduction

In Chapter 5, we showed that the hydrophobic and oleophobic PET films can be fabricated by the addition of FOPBs. We have also found that, for practically important concentration (≤ 5%), the water and oil repellency of the C₄ material (FOPB-1: C₄F₉-PFPE-tails) is on the comparable level of the C₆ material (FOPB-2: C₆F₁₃-tails). Therefore, the study reported in this chapter is focused on C₄-based materials only, since they have shorter CₙF₂n₊₁- fragment. We have also reported that the formation of the fluorinated polymer brushes on PET substrate is supported by segregation of the PEI non-fluorinated middle block to the higher surface energy thermoplastic surface. The chemical structure and surface energy of PEI are similar to PET material; thus, PEI can segregate to PET substrate, while fluorinated segments are exposed on the film surface. Therefore, the question comes to mind whether the water and oil repellency of C₄ materials could be further enhanced with changing composition of the middle block.

To this end, we synthesized the non-fluorinated polyester middle block with certain amount of PET units to replace PEI sequences. Since PET substrate also possesses terephthalate segments, the affinity between PET surface and the middle block might increase and result in the alternating of surface wettability. Specially, we synthesized copolymer middle block with PET and PEI units in 1:1 molar ratio. Then, the middle block
was reacted with fluorinated oligomer containing C₄F₉-PFPE- tail through reactive end-groups to form fluorinated polyester triblock copolymer. Subsequently, the triblock copolymer was blended with PET to prepare water and oil repellent polyester films. The morphology of the polymer blended films was determined using AFM. The WCA and HCA were measured to determine the level of wettability of film surfaces.

6.2. Experimental Part

6.2.1 Materials

Telechelic non-fluorinated polyester oligomer was synthesized via condensation reaction of EG with mixture of IsoCl and terephthaloyl chloride (TereCl), which was purchased from Sigma-Aldrich and used as received. The FOPB copolymer was prepared in melt through reaction between non-fluorinated polyester oligomer and semi-telechelic FOP-1 terminated with C₄F₉-PFPE- end-groups (reported in Chapter 4, Figure 4.4).

6.2.2. Synthesis of Poly(ethylene isophthalate-co-terephthalate) (PEI-co-PET)

Telechelic PEI-co-PET oligomer was synthesized to serve as middle block in FOPB copolymer. The chemical scheme of the synthesis is presented in Figure 6.1. The reaction was proceeded following the detailed procedures in Chapter 4. In this synthesis, 50 mol% of IsoCl was replaced with TereCl to react with EG to obtain oligomer with terephthalate segments in the macromolecular chains. A final product of dark green PEI-co-PET oligomer was obtained (Figure 6.1).
6.2.3. Synthesis of Fluorinated Polyester Triblock Copolymer (FOPB-3)

The fluorinated triblock copolymer, FOPB-3 (Figure 6.2), was synthesized, where two FOP-1 blocks were separated by short PEI-co-PET block. The synthesis details are presented in Chapter 4. The final product was terminated with C₄F₉-PFPE- end-groups in both sides.

6.2.4. Polymer Film Preparation

The synthesized FOPB-3 copolymer with PEI-co-PET middle block was blended with PET at different concentrations (1, 2, 5, and 10 wt%). The polymer films were fabricated following the details in Chapter 5. Then, after being stored for 16h at ambient conditions, the films were annealed at 140°C for 3h under vacuum.
Figure 6.2. Chemical structure of FOPB-3.
6.3. Results and Discussions

6.3.1. Characterization of PEI-co-PET Middle Block

ATR-FTIR Analysis

To begin, ATR-FTIR analysis was employed to characterize the major functional groups in PEI-co-PET oligomer. The results shown in Figure 6.3 were analyzed using readily available spectral databases for organic compounds.¹

Figure 6.3. ATR-FTIR spectrum of PEI-co-PET oligomer. Mark on spectrum: (1) C-H stretching (aromatic), 3080 cm⁻¹, (2) C-H asymmetric stretching, 2962 cm⁻¹, (3) -C=O stretching (acid chloride), 1793 cm⁻¹, (4) -OC=O stretching (ester), 1718 cm⁻¹, (5) ring -C=C- stretching (aromatic), 1605-1400 cm⁻¹, (6) C-O stretching (connected to benzene ring), 1262 cm⁻¹, (7) -C-O-C- stretching (ester), 1195-1033 cm⁻¹, and (8) -C-Cl stretching, 730-550 cm⁻¹.
IR spectrum for polyester oligomer possessed the ester stretching (\(-\text{OC}=\text{O}\), at 1718 cm\(^{-1}\)) and -C-O stretching (connected to aromatic ring, at 1262 cm\(^{-1}\)) vibration peaks, which were formed as a result of acid chloride reaction with alcohol. Furthermore, the -C-Cl stretching peaks appeared in the region of 730-550 cm\(^{-1}\) and -C=O stretching peaks (acid chloride) at 1793 cm\(^{-1}\) were also detected. In general, the IR results indicate the formation of PEI-co-PET oligomer by using the employed synthetic procedure.

**GPC Analysis**

GPC analysis was performed to determine the molecular weight and polydispersity index for PEI-co-PET oligomer. In the analysis, polystyrenes with different MWs were used as calibration standards. The sample was completely dissolved in chloroform and filtered before the analysis. The data obtained from GPC analysis is presented in **Table 6.1**. It was found that PEI-co-PET oligomer with M\(_w\) of 2209 g/mol and PDI of 3.1 was obtained. The broad PDI value indicated the presence of lower MW fraction in the samples. The number of repeating units for higher M\(_w\) PEI-co-PET fractions was estimated as ~10.

**Table 6.1.** Major characterization of materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>(M_n) (g/mol)</th>
<th>(M_w) (g/mol)</th>
<th>PDI</th>
<th>(T_g) (°C)</th>
<th>(T_m) (°C)</th>
<th>(T_d) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI-co-PET</td>
<td>709</td>
<td>2209</td>
<td>3.1</td>
<td>28</td>
<td>-</td>
<td>391</td>
</tr>
<tr>
<td>FOPB-3</td>
<td>2364</td>
<td>4882</td>
<td>2.1</td>
<td>-20</td>
<td>49</td>
<td>398</td>
</tr>
</tbody>
</table>

**Thermal Analysis**

We employed the TGA analysis (**Figure 6.4**) to identify the thermal properties of PEI-co-PET oligomer. The results are tabulated in **Table 6.1**. As can be seen in **Figure 6.4**,
there is ~11% lower MW fractions presented in PEI-co-PET oligomers, which are thermally stable until ~210°C. It is correlated well with the broad PDI value observed in the GPC analysis. The TGA measurement also indicated that the major fractions of PEI-co-PET oligomer (~77%) possess a relatively high thermal stability, where the $T_d$ is around 390°C. It is comparable to the $T_d$ of PEI oligomer (Table 4.1 in Chapter 4). The results indicate that the thermal stability is not significantly dependent on the chemical structure of the non-fluorinated polyester oligomer.

![Figure 6.4. TGA trace of PEI-co-PET.](image)

The value of glass transition temperature and melting temperature for the PET-co-PEI oligomer were investigated using DSC (Figure 6.5). Results are presented in Table 6.1. It is apparent that DSC measurement did not indicate crystallinity for PEI-co-PET. Therefore, the oligomer is amorphous with the midpoint $T_g$ of 28°C. Although the glass transition temperature is slightly higher than room temperature, PEI-co-PET oligomeric chains should possess high chain mobility/diffusivity at room temperature.
6.3.2. Characterization of FOPB-3

ATR-FTIR Analysis

The major structural elements presented in FOPB-3 copolymer were identified using ATR-FTIR analysis. The spectrum is displayed in Figure 6.6. In general, the IR spectrum indicated that the targeted FOPB-3 triblock copolymer was obtained using the outlined synthetic procedures above. For instance, the -CF₃ and -CF₂ stretching vibrations (1200 -1100 cm⁻¹), the -OC=O stretching peaks at 1743 cm⁻¹, and -C-O-C- stretching peaks at 1270 cm⁻¹ were detected for FOPB-3 copolymer.
**Figure 6.6.** ATR-FTIR spectrum of FOPB-3 copolymer. Mark on spectrum: (1) C-H stretching (aromatic), 3087 cm$^{-1}$, (2) C-H asymmetric stretching, 2973 cm$^{-1}$, (3) -C=O stretching (ester), 1743 cm$^{-1}$, (4) -C=C- stretching (aromatic), 1611-1414 cm$^{-1}$, (5) -C-O- C stretching (ester), 1270 cm$^{-1}$, (6) -CF$_2$ and -CF$_3$ stretching, 1186-1098 cm$^{-1}$, (7) C-H bending (in-plane), 953 cm$^{-1}$, and (8) C-H bending (out of plane), 723 cm$^{-1}$.

**GPC Analysis**

The GPC data (Table 6.1) reveals that the FOPB-3 copolymer with $M_w$ of 5000 g/mol and PDI of 2 was synthesized. We also estimated the atomic concentration of fluorine in FOPB-3 chain using the method described in Chapter 4. As a result, the fluorine concentration is about 24% in FOPB-3 copolymer.
Thermal Analysis

The thermal stability of FOPB-3 was determined using TGA analysis. The TGA trace and data is presented in Figure 6.7 and Table 6.1, respectively. It appears that the major high MW fraction (> 97%) of FOPB-3 possesses a decomposition temperature around 400°C, which indicated that FOPB-3 has relatively good thermal stability.

![Figure 6.7. TGA trace for FOPB-3.](image)

We performed DSC analysis to identify the thermal transitions for FOPB-3 copolymer, such as $T_g$ and $T_m$. In Figure 6.8, the DSC trace reveals that FOPB-3 is a semi-crystalline material since FOPB-3 has both $T_g$ and $T_m$. The data in Table 6.1 shows that the midpoint of glass transition for FOPB-3 is around -19°C, while $T_m$ is 49°C.
6.3.3. Fabrication of FOPB-3/PET Films

A series of polymer films were prepared on clean Si wafer by dip-coating from 3 wt% PET blended with FOPB-3 at various concentrations (1, 2, 5, 10 wt%) in HFIP solution. The films were annealed at 140°C for 3h under vacuum after being dried and stored at ambient conditions for 16h.

6.3.4. Characterization of FOPB-3/PET Films

Surface Morphology Analysis

AFM analysis was employed to analyze the surface morphology of FOPB-3 blended films. Figure 6.9 displays the AFM topographical images of FOPB-3/PET films before (top row) and after the annealing (bottom row), respectively.
Figure 6.9. AFM (10 µm x 10 µm) topographical images of polymer films before (a, c-f) and after (b, g-k) annealing. Before annealing: (a) Pure PET (RMS = 0.3 nm), (c) 1% FOPB-3/PET (RMS = 5.0 nm), (d) 2% FOPB-3/PET (RMS = 6.0 nm), (e) 5% FOPB-3/PET (RMS = 2.0 nm), and (f) 10% FOPB-3/PET (RMS = 1.5 nm). After annealing: (b) Pure PET (RMS = 8 nm), (g) 1% FOPB-3/PET (RMS = 9.5 nm), (h) 2% FOPB-3/PET (RMS = 7.5 nm), (i) 5% FOPB-3/PET (RMS = 5.0 nm), and (j) 10% FOPB-3/PET (RMS = 7.0 nm).
For films without annealing, it was found that there is no visible phase separation for the films containing 1-2% of FOPB-3. It means that FOPB-3 and PET are to some extent miscible at relatively low concentrations (≤ 2%). This could happen because that the middle block of FOPB-3 has terephthalate segments, which can improve the compatibility of FOPB-3 with PET matrix. As FOPB-3 content increased to 5-10%, the small number of phase-separated domains (dark) of FOPB-3 are clearly seen in the PET matrix (light). In addition, the crystalline structures were not observed on the films before annealing. Consequently, we assumed that the structure of middle block has effect on the surface morphology of unannealed polymer films, where much less phase separation is observed in contrast to FOPB-1/PET films.

Figure 6.9 also shows that the annealing treatment significantly changes the surface morphology of FOPB-3/PET films. The PET crystals can be clearly seen on the AFM topographical images. This was expected since the intensive crystallization of PET polymer chains occurred at the elevated temperature of 140°C.\textsuperscript{2-3} The phase separation of FOPB-3 is not apparent for annealed films on AFM topographical images. Therefore, the AFM phase images for annealed films were scanned and presented in Figure 6.10. We expected that the surface of FOPB-3/PET films are covered with a continuous fluorinated copolymer layer during the heat treatment as it has lower surface energy.
Figure 6.10. AFM (10 µm x 10 µm) phase images of annealed polymer films (a-e). Pure PET (a), and FOPB-3/PET (b-e). Concentration of FOPB-3: (b) 1%; (c) 2%; (d) 5%; and (e) 10%.

Surface Wettability of FOPB-3/PET Films

Contact Angle Measurements

Figure 6.11 and Figure 6.12 shows the results of WCA and HCA measurements for FOPB-3/PET films at different concentrations before and after the annealing, respectively. As shown in the figures, the WCA and HCA for FOPB-3/PET films steadily increased with the increasing fluorinated content in the blends before annealing. For instance, at the concentration of 1%, WCA and HCA for FOPB-3/PET is 71° and 52°, respectively. As the concentration increased up to 10%, the WCA and HCA increased to
89° and 62°, respectively. The CA results clearly indicated that FOPB-3 occupies the surface of the polymer films.

**Figure 6.11.** WCA for FOPB-3/PET films of different concentrations before (solid) and after (mesh) annealing at 140°C for 3h.

We also investigated the effect of annealing treatment on surface wettability of FOPB-3/PET films (**Figure 6.11** and **Figure 6.12**). The results show that the influence of annealing on HCA is less pronounced than WCA for FOPB-3. For instance, at 5% load, the WCA for films increased from 83° to 101° after annealing, while HCA did not change meaningfully. The same trend was observed for films with other concentrations. We once again have connect the variance with the different molecular sizes of wetting liquids.
Figure 6.12. HCA for FOPB-3/PET films of different concentrations before (solid) and after (mesh) annealing at 140°C for 3h.

Surface Energy Estimation

Apart from the CA measurements, the surface energy (σ) of annealed FOPB-3/PET films was estimated using Owen-Wendt method⁴ (Equation 5.1 in Chapter 5). The data is presented in Figure 6.13. We found out that the FOPB-3/PET polymer surfaces possess much lower surface energy than pure PET films, even at low FOPB-3 concentrations. Specifically, at the concentration of 5%, the surface energy for FOPB-3 films is 18 mN/m. It is on the same surface energy level of PTFE (σ_{PTFE} =18.5 mN/m), a fully perfluorinated polymer. At 10% concentration, the film surface energy (σ =15 mN/m) becomes lower than σ of PTFE.
Figure 6.13. Surface energy of annealed FOPB-3/PET films at different concentrations.

Surface energy for PET and PTFE are given for comparison.

We also compared the major characteristics of FOPB-3 with those of FOPB-1 copolymer (Table 6.2). Although the molecular weight and miscibility with PET for FOPB-1 and FOPB-3 are different, both copolymers have the similar thermal stability and transition temperatures. We also found that FOPB-3 containing copolymer (PEI-co-PET) as middle block demonstrates comparable level of water and oil repellency to FOPB-1 possessing PEI as middle block after the annealing despite the difference between the molecular weight of FOPBs.
Table 6.2. Comparison of FOPB-3 with FOPB-1 copolymer.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>FOPB-3</th>
<th>FOPB-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Middle block</td>
<td>PEI-co-PET</td>
<td>PEI</td>
</tr>
<tr>
<td>Miscibility with PET</td>
<td>to some extent</td>
<td>low</td>
</tr>
<tr>
<td>$M_w^a$</td>
<td>4882</td>
<td>10432</td>
</tr>
<tr>
<td>$M_n^a$</td>
<td>2364</td>
<td>3731</td>
</tr>
<tr>
<td>$T_g$</td>
<td>-20</td>
<td>-18</td>
</tr>
<tr>
<td>$T_m$</td>
<td>49</td>
<td>46</td>
</tr>
<tr>
<td>$T_d$</td>
<td>398</td>
<td>416</td>
</tr>
<tr>
<td>WCA at 1%</td>
<td>84</td>
<td>81</td>
</tr>
<tr>
<td>HCA at 1%</td>
<td>56</td>
<td>50</td>
</tr>
<tr>
<td>WCA at 5%</td>
<td>101</td>
<td>99</td>
</tr>
<tr>
<td>HCA at 5%</td>
<td>57</td>
<td>57</td>
</tr>
<tr>
<td>$\sigma$ at 1%</td>
<td>25</td>
<td>28</td>
</tr>
<tr>
<td>$\sigma$ at 5%</td>
<td>18</td>
<td>19</td>
</tr>
</tbody>
</table>

$a$: data from GPC

6.4. Conclusions

- Telechelic non-fluorinated polyester oligomer PEI-co-PET was obtained by employed condensation polymerization.
- PEI-co-PET is amorphous and possesses high chain mobility/diffusivity above room temperature.
- Fluorinated polyester triblock copolymer, FOPB-3 with C₄F₉-PFPE- end-groups and PEI-co-PET middle block was synthesized in melt polymerization.
- FOPB-3 containing copolymer as middle block demonstrates comparable level of water and oil repellency to FOPB-1 with PEI middle block.
• The miscibility of middle block with PET does not have significant effect on hydrophobicity and oleophobicity.

6.5. References


CHAPTER SEVEN
PFPE-BASED POLYURETHANE OLIGOMERS

7.1. Introduction

The synthesis and characterization of original fluorinated polyester materials, such as fluorinated oligomers and triblock copolymers have been reported in Chapter 4. Then, the copolymers were used as low surface energy additives to PET to fabricate hydrophobic/oleophobic films (Chapter 5). Extensive scientific literatures have reported that fluorinated polyurethanes have been considered as a relatively new class of functional materials.\textsuperscript{1-5} They can combine the advantages of polyurethanes and fluorinated polymers, such as low water absorptivity, excellent flexibility, and low surface energy. Furthermore, for fluorinated polyurethanes, the fluorine segments in the polymer chains are capable to enrich to the outmost surface, while the polyurethane segments prefer to remain in bulk. Consequently, the polymer surface tension is minimized due to the segregation of fluorinated segments. It was also found that the synthesis of fluorinated polyurethanes is less challenging than that of fluorinated polyesters.\textsuperscript{1,6}

With the above in mind, we synthesized and characterized PFPE-based polyurethane oligomers (FOPUs) possessing different chemical structures. ATR-FTIR was employed to identify the major structural elements in the FOPUs. Thermal properties of the oligomers were determined using TGA and DSC analysis. Then, FOPU oligomers were used to prepare PET polymer blended films. The surface properties, such as wettability and morphology, were studied by contact angle measurements and AFM, respectively.
7.2. Experimental Part

7.2.1 Materials

Semi-telechelic PFPE-based polyurethane oligomers were synthesized by solution reaction of fluorinated ether alcohol(s) (PFPE-diol and/or C₄F₉-PFPE-OH) with 1, 6 hexamethylene diisocyanate (HDI) or 4, 4'-methylenebis(phenyl isocyanate) (MDI). HDI and MDI monomers were both purchased from Sigma-Aldrich and used as received. In the synthesis of the oligomers, dry MEK was used as solvent. Dibutyltin dilaurate (DBTDL) from Sigma-Aldrich was used as catalyst. PET pellets from Unifi and 1,1,1,3,3,3-hexafluoro-2-propanol were used to prepare polymer films.

7.2.2 Synthesis of FOPUs

A series of PFPE-based polyurethane oligomers was synthesized via step growth polymerization in solution using the reaction of perfluoro ether alcohol(s) with diisocyanate. The general scheme of reaction is presented in Figure 7.1.

In this study, four FOPUs with different chemical structures were synthesized. Table 7.1 shows the molar ratios of monomers and reaction temperature for the synthesis. When only the PFPE-diol monomer reacted with HDI or MDI using equimolar amount, HFOPU-1 and MFOPU-1 oligomers were obtained, respectively. HFOPU-1 oligomer possessed aliphatic urethane linkage in-chain segments, isocyanate (-NCO) and hydroxyl (-OH) end-groups. For MFOPU-1 oligomer, it was also terminated with -NCO and -OH end-groups; in turn; it possessed aromatic urethane linkage in-chain segments.
For the other two oligomers, 10 mol% PFPE-diol was replaced with fluorinated mono alcohol (C₄F₉-PFPE-OH) to terminate oligomers with C₄F₉-PFPE- end-groups on one side. As a result, HFOPU-2 oligomer with aliphatic segments and MFOPU-2 oligomer with aromatic structures were prepared, respectively. In addition, the molar ratio between -NCO and -OH functionalities was also set to be 1:1 in the reactions.

**Figure 7.1.** General procedure of synthesis of FOPUs.
Table 7.1. Reaction conditions of the synthesis of FOPUs.

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>PFPE-diol:HDl or MDI</th>
<th>C₄F₉-PFPE-OH:HDl or MDI</th>
<th>OH:NCO</th>
<th>T_solution polymerization/Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFOPU-1</td>
<td>1:1</td>
<td>-</td>
<td>1:1</td>
<td>75°C/2h</td>
</tr>
<tr>
<td>HFOPU-2</td>
<td>0.9:1</td>
<td>0.2:1</td>
<td>1:1</td>
<td>75°C/2h</td>
</tr>
<tr>
<td>MFOPU-1</td>
<td>1:1</td>
<td>-</td>
<td>1:1</td>
<td>75°C/2h</td>
</tr>
<tr>
<td>MFOPU-2</td>
<td>0.9:1</td>
<td>0.2:1</td>
<td>1:1</td>
<td>75°C/2h</td>
</tr>
</tbody>
</table>

General Procedure of the Synthesis of FOPUs

To obtain FOPU oligomers with different end-groups, the synthesis was divided into two groups. HDI or MDI in MEK solution were added dropwise to the solution of i) PFPE-diol alcohol in dry MEK, and ii) PFPE-diol and C₄F₉-PFPE-OH alcohol solution in MEK. The solution was placed in a 100 mL three-necked flask, which was equipped with a mechanical stirrer. For all synthesis, DBTDL was used as catalyst and added to the reaction solution at room temperature. Subsequently, the solution was heated at 75°C for 2h with vigorous stirring under nitrogen stream. The concentration of the catalyst was 0.2-0.3% by weight of the reactants, and the concentration of the reactants in the solution was 30-35% (w/v).

Synthesis of HFOPU-1 (Figure 7.2)

1.8 g (4.39 mmol) of PFPE-diol was dissolved in 3 ml MEK. Then, a solution of 0.74 g (4.39 mmol) of HDI in dry MEK (5 ml) was added into the PFPE-diol solution dropwise. The reaction was conducted following the above-written procedure. The final product was dissolved in chloroform, and then dried with N₂. As a result, a light yellow HFOPU-1 oligomer was obtained.
Synthesis of HFOPU-2 (Figure 7.3)

To obtain HFOPU-2 oligomer, a solution of 3.6 g (8.78 mmol) of PFPE-diol and 1.07 g (1.95 mmol) of C₄F₉-PFPE-OH were dissolved in 10 ml MEK. Then, 1.8 g (4.39 mmol) of PFPE-diol was dissolved in 3 ml MEK. Subsequently, 1.64 g (9.75 mmol) of HDI in dry MEK (10 ml) was added dropwise into the PFPE-based alcohols solution to prepare HFOPU-2 using procedure described above. After drying, a final product of light yellow HFOPU-2 was obtained.

Synthesis of MFOPU-1 Oligomer (Figure 7.4)

For the synthesis of MFOPU-1 oligomer, 1.8 g (4.39 mmol) of PFPE-diol was dissolved in 3 ml MEK. Then, a solution of 1.10 g (4.39 mmol) of MDI in dry MEK (5 ml) was added to PFPE-diol solution dropwise. Consequently, the reaction was carried out following the above-written procedure. The final product was dissolved in MEK, and then dried with N₂ to be stored. A light yellow MFOPU-1 oligomer was obtained.
Synthesis of MFOPU-2 Oligomer (Figure 7.5)

To obtain MFOPU-2 oligomer, 2.44 g (9.75 mmol) of MDI in 10 ml dry MEK was added dropwise into a solution of 3.6 g (8.78 mmol) of PFPE-diol and 1.07 g (1.95 mmol) of C4F9-PFPE-OH in 10 ml MEK. Then, the reaction was conducted following the procedure above. After drying, a final product of light yellow MFOPU-2 oligomer was obtained (Figure 7.5).

7.2.3 Polymer Film Preparation

PET was blended with the synthesized fluorinated polyurethane oligomers at 5 wt% concentration in HFIP solution, respectively. The polymer films were fabricated following the details described in Chapter 5. After the fabrication, the films were stored at ambient conditions for 16h. Then, they were annealed at 140°C for 3h under vacuum.
7.3. Results and Discussions

7.3.1 Characterization of FOPUs

*ATR-FTIR Analysis*

To confirm the oligomers’ synthesis, ATR-FTIR analysis was performed to identify the major functional groups presented in the obtained FOPUs. The IR spectra are displayed in *Figure 7.6*. The results were analyzed using readily available spectra databases for organic compounds and presented in *Table 7.2*.7

![Figure 7.6. ATR-FTIR spectra of FOPUs: (a) HFOPU-1, (b) HFOPU-2, (c) MFOPU-1, and (d) MFOPU-2. Mark on spectra: (1) -OH stretching, 3500-3450 cm⁻¹, (2) -NH stretching, 3335 cm⁻¹, (3) -CH stretching (aromatic), 3100-3000 cm⁻¹, (4) -CH stretching (aliphatic), 2938-2861 cm⁻¹, (5) -OC=O stretching, 1701 cm⁻¹, (6) -C=C- stretching (aromatic), 1598 cm⁻¹, (7) -NH bending, 1533 cm⁻¹, (8) -CH₂ scissoring, 1283 cm⁻¹, (9) -C-O-C symmetric stretching, 1283 cm⁻¹, (10) -CF₂ and -CF₃ stretching, 1139-100 cm⁻¹.]}
Table 7.2. IR absorption bands of FOPUs.

<table>
<thead>
<tr>
<th>Absorbing group and type of vibration</th>
<th>HFOPU-1 wavenumber (cm(^{-1}))</th>
<th>HFOPU-2 wavenumber (cm(^{-1}))</th>
<th>MFOPU-1 wavenumber (cm(^{-1}))</th>
<th>MFOPU-2 wavenumber (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OH stretching</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-NH stretching</td>
<td>3344</td>
<td>3335</td>
<td>3336</td>
<td>3334</td>
</tr>
<tr>
<td>-CH aliphatic stretching</td>
<td>2938-2861</td>
<td>2938-2861</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-NH bending</td>
<td>1533</td>
<td>1533</td>
<td>1537</td>
<td>1538</td>
</tr>
<tr>
<td>-CH(_2) scissoring</td>
<td>1415 (weak)</td>
<td>1415 (weak)</td>
<td>1415 (strong)</td>
<td>1415 (strong)</td>
</tr>
<tr>
<td>=C-H bending (out of plane)</td>
<td>964</td>
<td>974</td>
<td>984</td>
<td>984</td>
</tr>
<tr>
<td>-OC=O stretching</td>
<td>1701</td>
<td>1701</td>
<td>1721</td>
<td>1721</td>
</tr>
<tr>
<td>C=C aromatic stretching</td>
<td>-</td>
<td>-</td>
<td>1598</td>
<td>1598</td>
</tr>
<tr>
<td>-CF(_2) and -CF(_3) stretching</td>
<td>1139-100</td>
<td>1140-100</td>
<td>1167-100</td>
<td>1169-100</td>
</tr>
<tr>
<td>=C-H bending (out of plane)</td>
<td>964</td>
<td>974</td>
<td>984</td>
<td>984</td>
</tr>
</tbody>
</table>

The results revealed that all four oligomers possessed the -NH stretching and -NH bending vibration peaks around 3340 cm\(^{-1}\) and 1535 cm\(^{-1}\), respectively. These peaks were formed as a result of isocyanate reaction with alcohol. Furthermore, -OC=O stretching peaks around 1700 cm\(^{-1}\) and -C-O-C- stretching vibration peaks at 1283 cm\(^{-1}\) were also
detected. All four oligomers possessed -CF$_2$ and -CF$_3$ stretching vibrations in the region of 1200-1100 cm$^{-1}$. In general, it confirms that FOPU oligomers were obtained by the employed synthetic procedure.

For the HFOPU oligomers, the -CH aliphatic stretching peaks were detected in the region of 2938-2861 cm$^{-1}$. On the other hand, the -CH aromatic stretching peaks were found between 3100 cm$^{-1}$ and 3000 cm$^{-1}$ for MFOPU oligomers. In addition, the -CH$_2$ scissoring peak at 1415 cm$^{-1}$ in the MFOPUs was much stronger than it in HFOPUs because of the connection of -CH$_2$ group with the two aromatic rings in MDI monomers.

$^{19}$F NMR Analysis

$^{19}$F NMR analysis was conducted to further investigate the structure of FOPUs. However, the MFOPU oligomers could not be dissolved in the deuterated solvent; therefore; only NMR result for HFOPU-1 and HFOPU-2 is presented in Figure 7.7 and Figure 7.8, respectively.

![Figure 7.7. $^{19}$F NMR spectrum of HFOPU-1.](image-url)
In general, NMR data confirmed the synthesis of targeted HFOPUs. For both HFOPU-1 and HFOPU-2 oligomers, the signals at -77.40 to -77.87 ppm (a) are present, which are attributed to the fluorine atom in the CF$_2$ groups bonded to methyl ester (-O-CF$_2$-CH$_2$-O-CO-) in repeat units. The distinctive multiple peaks at -88.76-89.58 ppm (b) correspond to the fluorine atoms of the -CF$_2$- groups located between ethers (-O-CF$_2$CF$_2$-O-) in the repeating units. Furthermore, the triplet peaks at -80.38 to -80.55 ppm (f) belong to the fluorine atom in the CF$_2$ group, which is close to the -OH end groups (-O-CF$_2$-CH$_2$-OH). It confirms that both HFOPU oligomers possessed -OH end-groups.

Furthermore, for HFOPU-2 oligomer (Figure 7.8), three additional peaks (c, d, and e) that belong to the fluorine atoms in C$_4$F$_9$-PFPE- end segment are detected. The two singlet peaks at -81.09 ppm (c) and -83.57 ppm (d) are attributed to the fluorine atoms in the -CF$_3$ group and -CF$_2$ group bonded to ether (CF$_3$-CF$_2$-CF$_2$-O). Another peak “e”
at -126.67 belongs to the fluorine atoms of the -CF₂ groups (CF₃-CF₂CF₂-CF₂-O) on the tail. The results revealed that HFOPU-2 oligomer was terminated with C₄F₉-PFPE- end-groups on one side.

**GPC Analysis**

The MW and PDI for FOPUs were determined by GPC analysis. Chloroform and polystyrenes was used as solvent and calibration standards for the samples, respectively. HFOPU oligomers can be completely dissolved in chloroform, while MFOPUs can only be partially dissolved. The data obtained from GPC analysis in Table 7.3 revealed that HFOPU oligomers with M_w between 2800-4010 g/mol and PDI around ~1.8 were obtained. On the other hand, dissolved fraction of MFOPU oligomers possessed M_w and PDI around 2500 g/mol and 1.2, respectively.

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>M_n (g/mol)</th>
<th>M_w (g/mol)</th>
<th>PDI</th>
<th>T_g (°C)</th>
<th>T_m (°C)</th>
<th>Crystallinity (%)</th>
<th>T_d (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFOPU-1</td>
<td>1588</td>
<td>2879</td>
<td>1.67</td>
<td>-32</td>
<td>60</td>
<td>27.8</td>
<td>230 (62%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>305 (38%)</td>
</tr>
<tr>
<td>HFOPU-2</td>
<td>2257</td>
<td>4009</td>
<td>1.78</td>
<td>-28</td>
<td>64</td>
<td>31.1</td>
<td>170 (15%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>320 (48%)</td>
</tr>
<tr>
<td>MFOPU-1</td>
<td>2320*</td>
<td>2682*</td>
<td>1.16</td>
<td>45</td>
<td>125</td>
<td>35.6</td>
<td>160 (44%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>320 (48%)</td>
</tr>
<tr>
<td>MFOPU-2</td>
<td>2258*</td>
<td>2556*</td>
<td>1.13</td>
<td>47</td>
<td>123</td>
<td>34.7</td>
<td>160 (10%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>310 (81%)</td>
</tr>
</tbody>
</table>

*: molecular weight for oligomer can be dissolved in chloroform obtained from GPC
Thermal Analysis

TGA analysis was performed to determine the composition and $T_d$ for FOPUs. As seen in Figure 7.9, the TGA shows that the lower molecular weight (LMW) fraction was presented in all FOPUs.

**Figure 7.9.** TGA traces for FOPUs: (a) HFOPU-1, (b) HFOPU-2, (c) MFOPU-1, and (d) MFOPU-2.

We also used DSC to identify the $T_g$ and $T_m$ for FOPUs. The DSC trace and data is presented in Figure 7.10 and Table 7.3, respectively. The results indicate that all FOPUs are semi-crystalline materials. The midpoint of $T_g$ for FOPUs ranges from -32 °C to 47°C,
while $T_m$ (at maximum) ranges from 60°C for 125°C. We connect the differences with the chemical structure of oligomers. HFOPUs is possessing more flexible aliphatic urethane segments in the backbone, while the presence of the rigid phenyl rings in MFOPU oligomers increases their the thermal transition temperatures.

**Figure 7.10.** DSC traces for FOPUs: (a) HFOPU-1, (b) HFOPU-2, (c) MFOPU-1, and (d) MFOPU-2.

Apart from thermal transition temperatures, the degree (percentage) of crystallinity for FOPUs was estimated using DSC data and presented in Table 7.3. The percentage was calculated based on the heat of fusion ($\Delta H_f$) by following equation:
The heat of fusion ($\Delta H_f$) for FOPUs was obtained from DSC results and presented in Table 7.4. Neither of the oligomer has the heat of the additional crystallization ($\Delta H_c$); hence; the $\Delta H_c$ was considered as 0 J/g. Furthermore, the heat of fusion for 100% crystalline material ($\Delta H_{f\text{crys}}$) for FOPUs was determined from the tabulated molar contributions of the chemical groups constituting repeating units (Table 7.4). We determined the degree of crystallinity is on the level of 28-36%. In conclusion, the thermal properties of FOPUs are highly dependent on the molecular structure of the oligomeric chains.

Table 7.4. Tentative values of group contributions to the heat of fusion for FOPUs.

<table>
<thead>
<tr>
<th></th>
<th>HFOPU-1</th>
<th>HFOPU-2</th>
<th>MFOPU-1</th>
<th>MFOPU-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 CH$_2$ = 8x4</td>
<td>8 CH$_2$ = 8x4</td>
<td>3 CH$_2$ = 3x4</td>
<td>3 CH$_2$ = 3x4</td>
<td></td>
</tr>
<tr>
<td>= 32 kJ/mol</td>
<td>= 32 kJ/mol</td>
<td>= 12 kJ/mol</td>
<td>= 12 kJ/mol</td>
<td></td>
</tr>
<tr>
<td>6 CF$_2$ = 6x4</td>
<td>6 CF$_2$ = 6x4</td>
<td>6 CF$_2$ = 6x4</td>
<td>6 CF$_2$ = 6x4</td>
<td></td>
</tr>
<tr>
<td>= 24 kJ/mol</td>
<td>= 24 kJ/mol</td>
<td>= 24 kJ/mol</td>
<td>= 24 kJ/mol</td>
<td></td>
</tr>
<tr>
<td>5 O = 5x1</td>
<td>5 O = 5x1</td>
<td>5 O = 5x1</td>
<td>5 O = 5x1</td>
<td></td>
</tr>
<tr>
<td>= 5 kJ/mol</td>
<td>= 5 kJ/mol</td>
<td>= 5 kJ/mol</td>
<td>= 5 kJ/mol</td>
<td></td>
</tr>
<tr>
<td>1 CONH = 1x2</td>
<td>2 CONH = 2x2</td>
<td>1 CONH = 1x2</td>
<td>2 CONH = 2x2</td>
<td></td>
</tr>
<tr>
<td>= 2 kJ/mol</td>
<td>= 4 kJ/mol</td>
<td>= 2 kJ/mol</td>
<td>= 4 kJ/mol</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>2 -C$_6$H$_4$ = 2x5</td>
<td>2 -C$_6$H$_4$ = 2x5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>= 10 kJ/mol</td>
<td>= 10 kJ/mol</td>
<td></td>
</tr>
<tr>
<td>Total = 63 kJ/mol</td>
<td>Total = 65 kJ/mol</td>
<td>Total = 53 kJ/mol</td>
<td>Total = 55 kJ/mol</td>
<td></td>
</tr>
<tr>
<td>$\text{MW } \text{repeat units} = $ 535 g/mol</td>
<td>$\text{MW } \text{repeat units} = $ 578 g/mol</td>
<td>$\text{MW } \text{repeat units} = $ 617 g/mol</td>
<td>$\text{MW } \text{repeat units} = $ 660 g/mol</td>
<td></td>
</tr>
<tr>
<td>$\Delta H_{f\text{crys}} = 117.8$ J/g</td>
<td>$\Delta H_{f\text{crys}} = 112.5$ J/g</td>
<td>$\Delta H_{f\text{crys}} = 85.9$ J/g</td>
<td>$\Delta H_{f\text{crys}} = 83.3$ J/g</td>
<td></td>
</tr>
<tr>
<td>$\Delta H_f = 32.7$ J/g</td>
<td>$\Delta H_f = 35.0$ J/g</td>
<td>$\Delta H_f = 30.6$ J/g</td>
<td>$\Delta H_f = 28.9$ J/g</td>
<td></td>
</tr>
</tbody>
</table>
7.3.2. Fabrication of FOPU/PET Films

A series of polymer films was prepared on clean Si wafer by dip coating from 3 wt% PET blended with FOPUs at 5 wt% concentration in HFIP solution. After the deposition, the films were dried at room temperature overnight. For selected experiment, films were annealed at 140°C for 3h under vacuum after being dried and stored at ambient conditions for 16h.

7.3.3. Characterization of FOPU/PET Films

Surface Morphology Analysis

The micro/nanoscale morphology of the blended films before and after the annealing (Figure 7.11) was scanned using AFM imaging. Figure 7.11 reveals that films as fabricated from FOPU/PET solution are without visible crystal formation. It is apparent that PET and FOPU oligomers are to some extent immiscible and appear to be phase-separated on the AFM topographical images. However, the surface morphology of FOPU/PET blended films is significantly influenced by the annealing treatment. PET crystalline structures are formed in all FOPU/PET films after they were annealed at 140°C. We also noted that, for the annealed fluorinated polyurethane blended films, phase separation is not clearly observed on the topographical images. To this end, AFM phase images for the annealed FOPU/PET films are presented in Figure 7.12. The figures do not show that the surface layer discontinuous. It is possible that FOPU dissolves in the PET matrix as a result of annealing. In an alternative scenario, FOPU spreads over the PET surface forming a continuous layer as a lower surface energy component for thermodynamical reasons.11
Figure 7.11. AFM (10 µm x 10 µm) topographical images of polymer films before (a, c-f) and after (b, g-k) annealing. Pure PET (a, b), and 5% FOPU/PET films (c-k). Before annealing: (a) Pure PET (RMS = 0.3 nm), (c) HFOPU-1/PET (RMS = 13.5 nm), (d) HFOPU-2/PET (RMS = 15.0 nm), (e) MFOPU-1/PET (RMS = 8.0 nm), and (f) MFOPU-2/PET (RMS = 17.0 nm). After annealing: (b) Pure PET (RMS = 8.0 nm), (g) HFOPU-1/PET (RMS = 9.0 nm), (h) HFOPU-2/PET (RMS = 16.0 nm), (i) MFOPU-1/PET (RMS = 8.5 nm), and (j) MFOPU-2/PET (RMS = 11.0 nm).
Figure 7.12. AFM (10 µm x 10 µm) phase images of annealed polymer films (a-e). Pure PET (a), and 5% FOPU/PET films (b-e) (a) Pure PET, (b) HFOPU-1; (c) HFOPU-2; (d) MFOPU-1; and (e) MFOPU-2.

Surface Wettability of FOPU/PET Films

Contact Angle Measurements

We determined the contact angle of water and hexadecane for FOPU/PET blended films to investigate the effect of PFPE-based polyurethane oligomers on surface wettability of the polyester. The values of WCA and HCA for 5% FOPU/PET films are presented in Figure 7.13 and Figure 7.14, respectively.
For water repellency (Figure 7.13), it is obvious that the addition of 5% of FOPU into the PET results in a significant increase in the CA values of PET before annealing. Specially, for the two oligomers terminated with C₄F₉-PFPE- end-groups (HFOPU-2 and MFOPU-2), the WCA increased from 58° (pure PET) to the level of 88°. On the other hand, the WCA for oligomers without fluorinated ends (HFOPU-1 and MFOPU-1) was on the level of 78°. This was expected since the surface of the films is always preferentially occupied by the fragments of the molecular chains with the lowest surface energy. Indeed, -CF₃ groups possesses the lowest surface energy (6 mN/m at 20°C). Therefore, the oligomers with fluorinated end-groups showed a higher value of WCA.

\[ 
\text{Figure 7.13. WCA for 5% FOPU/PET blended films before (solid) and after (mesh) annealing at 140°C for 3h.} 
\]

In terms of oil repellency, Figure 7.14 reveals that the highest HCA for 5% films before annealing is 68° for HFOPU-2/PET films, while the HCA is 47° for HFOPU-1/PET and MFOPU-2/PET films. However, it can be clearly seen that the unannealed MFOPU-
1/PET films are nearly completely wettable with hexadecane (< 5°). This could happen because MFOPU-1 oligomers have bulky aromatic structures and higher affinity to PET matrix, which caused the reduction of surface migration of fluorine moieties. Additionally, there was no -CF₃ end-groups in MFOPU-1 oligomeric chains. The lower values of CA indicates the majority of the fluorinated content remains in the bulk after the deposition.

**Figure 7.14.** HCA for 5% FOPU/PET blended films before (solid) and after (mesh) annealing at 140°C for 3h.

Furthermore, we studied how the annealing treatment influences WCA and HCA for 5% FOPU/PET films (Figure 7.13 and Figure 7.14). In general, the thermal treatment significantly increased WCA and HCA in comparison with unannealed ones except HFOPU-2/PET films. In fact, there was no meaningful changes for HFOPU-2 films in terms of water and oil repellency. Since HFOPU-2 has long and flexible aliphatic segments, it is reasonable to assume that practically all fluorine species in HFOPU-2 are enriched.
over the area on the film surface, and the films approached the CA saturation values after the solvent-based deposition. Conversely, for HFOPU-1/PET films, the WCA and HCA increased from 78° to 90° and 48° to 55°, respectively. On the other hand, it is necessary to point out that the films containing MFOPU-1 became partially repelling oil after annealing with the HCA value reaching 53°. For films with MFOPU-2, the highest HCA, 72°, was achieved after annealing. For WCA, the value increased to the level of ~110°. It appears that the thermal treatment has prompted the migration of oligomers to practically screen all of the surface and approach the saturation limit. It is concluded that FOPU oligomers addition can significantly improve the hydrophobicity and oleophobicity of PET. We also noted the surface wettability of FOPU/PET blended films has a strong dependence on the chemical structure of fluorinated polyurethane oligomers.

**Surface Energy Estimation**

Apart from CA measurements, we used the Owens-Wendt method\textsuperscript{12} detailed in Chapter 5 to estimate the surface energy (σ) of FOPU/PET films using WCA and HCA values. The data is presented in Figure 7.15. It is obvious that, after incorporation of 5% FOPU into PET, the surface energy of the polyester films was significantly reduced. For instance, the surface energy is 21 and 24 mN/m for HFOPU-2 and MFOPU-2, respectively before annealing. However, it is apparent that the surface energy for each unannealed films is higher than that of PTFE (18.5 mN/m).

For the annealed samples, we observed significant decrease in the surface energy. The surface energy for HFOPU-1/PET films decreased from 30 to 22 mN/m after the annealing. It is necessary to highlight that, for films containing MFOPU-1, the surface
energy was reduced significantly from 35 to 19 mN/m, which practically equals to the value of $\sigma_{\text{PTFE}}$. Furthermore, for annealed MFOPU-2/PET films, the surface energy was just 12 mN/m. Namely, $\sigma_{\text{MFOPU-2}}$ became 35% lower than that of PTFE after the annealing. However, for HFOPU-2, the surface energy did not change meaningfully with the thermal treatment. This was expected since the CAs for the films were on the similar level before and after the annealing.

**Figure 7.15.** Surface energy of 5% FOPU/PET films before (□) and after (○) annealing at 140°C for 3h. Surface energy for PET and PTFE are given for comparison.

*Surface Coverage of Annealed FOPU/PET Films*

The annealed films are covered with nanoscale FOPU layer (AFM phase images in Figure 7.12) and the contact angles are approaching high values after the annealing. Therefore, we roughly calculated the effective surface area of PET shielded from the wetting liquids by the FOPU oligomers using the Cassie-Baxter model. The details of the
model have been described in **Chapter 5**. In this case, we measured the WCA and HCA for annealed pure FOPU films. (HFOPU-1: WCA = 92° and HCA = 58°; HFOPU-2: WCA = 99° and HCA = 68°; MFOPU-1: WCA = 114° and HCA = 65°; and MFOPU-2: WCA = 120° and HCA = 75°). According to **Equation 5.1**, the effective surface coverage by fluorinated chain segments was estimated and presented in **Table 7.5**.

**Table 7.5.** Apparent surface area of the annealed FOPU/PET films ($f_\text{FOPU}$) that is screened effectively by fluorinated chain segments.

<table>
<thead>
<tr>
<th>5% FOPU/PET Film</th>
<th>$f_{\text{FOPU}}$ from WCA</th>
<th>$f_{\text{FOPU}}$ from HCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFOPU-1/PET</td>
<td>0.94</td>
<td>0.91</td>
</tr>
<tr>
<td>HFOPU-2/PET</td>
<td>0.73</td>
<td>0.97</td>
</tr>
<tr>
<td>MFOPU-1/PET</td>
<td>0.75</td>
<td>0.69</td>
</tr>
<tr>
<td>MFOPU-2/PET</td>
<td>0.94</td>
<td>0.93</td>
</tr>
</tbody>
</table>

The results indicate that the FOPU oligomers occupied between 70-97% of the films’ surface. We noted that HFOPU-1 and MFOPU-1 with in-chain fluorinated segments are better for shielding surface from water than from hexadecane; in turn; HFOPU-2 with in-chain aliphatic segments and fluorinated end-groups are better in shielding hexadecane. In addition, MFOPU-2 with aromatic structures and C$_4$F$_9$-PFPE- end-groups displays practically the same screening ability from the wetting liquids. We associated this observation with the type of oligomers, including the chemical structure and number of -CF$_2$ and -CF$_3$ groups possessing in FOPU oligometric chains.

Furthermore, we also compared the major features of FOPUs with those of FOPB-1 polyester copolymer (**Table 7.5**). In general, polyurethane oligomers have higher melting
point, while lower decomposition temperature than polyester copolymer (FOPB-1). For
surface wettability, HFOPU-1 and HFOPU-2 show lower WCA than that of FOPB-1
polyester; however; HFOPU-2 has slightly higher HCA than FOPB-1. MFOPU-2 with
aromatic-urethane segments and one C₄F₉- end-group has the highest water and oil
repellency among the materials. Also, it has the lowest surface energy.

Table 7.6. Comparison of FOPUs with FOPB-1 copolymer.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>HFOPU-1</th>
<th>HFOPU-2</th>
<th>MFOPU-1</th>
<th>MFOPU-2</th>
<th>FOPB-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Miscibility with PET</td>
<td>low</td>
<td>low</td>
<td>low</td>
<td>low</td>
<td>low</td>
</tr>
<tr>
<td>Mₐᵃ</td>
<td>1588</td>
<td>2257</td>
<td>2320*</td>
<td>2258*</td>
<td>3731</td>
</tr>
<tr>
<td>Mₘᵃ</td>
<td>2879</td>
<td>4009</td>
<td>2682*</td>
<td>2556*</td>
<td>10432</td>
</tr>
<tr>
<td>T₉</td>
<td>-32</td>
<td>-28</td>
<td>45</td>
<td>47</td>
<td>-18</td>
</tr>
<tr>
<td>Tₘ</td>
<td>60</td>
<td>64</td>
<td>125</td>
<td>123</td>
<td>46</td>
</tr>
<tr>
<td>Tₜ</td>
<td>230/305</td>
<td>170/320</td>
<td>160/320</td>
<td>160/310</td>
<td>416</td>
</tr>
<tr>
<td>WCA at 5%</td>
<td>90</td>
<td>88</td>
<td>100</td>
<td>116</td>
<td>99</td>
</tr>
<tr>
<td>HCA at 5%</td>
<td>55</td>
<td>67</td>
<td>53</td>
<td>72</td>
<td>57</td>
</tr>
<tr>
<td>σ at 5%</td>
<td>22</td>
<td>21</td>
<td>19</td>
<td>12</td>
<td>19</td>
</tr>
</tbody>
</table>

ᵃ: data from GPC and *: molecular weight for oligomer can be dissolved in chloroform

7.4. Conclusions

- Four fluorinated polyurethane oligomers with different chemical structures were
  synthesized by step growth polymerization.
- The chemical structure of FOPUs has influences on the thermal properties of oligomers.
- The hydrophobic/oleophobic PET films are achieved by the blending of PET with the
  FOPU having different macromolecular architectures.
• The surface properties of FOPU/PET blended films are dependent on: i) the chemical structure of FOPUs (aliphatic and aromatic urethane segments), ii) The number of -CF\(_2\) and -CF\(_3\) groups in the oligomeric chains, and iii) annealing treatment.

• Fluorinated polyester copolymer (FOPB-1) shows higher thermal stability than fluorinated polyurethane oligomers. FOPUs demonstrates comparable surface wettability to FOPB-1. Specially, MFOPU-2, containing in-chain aromatic-urethane segments and one C\(_4\)F\(_9\)- end-groups has the highest water/oil repellency, while the lowest surface energy.

### 7.5. Reference


8. Wu, J.; Zhou, X.; Harris, F. W., Bis(perfluoro-2-n-propoxyethyl)diacyl peroxide initiated homopolymerization of vinylidene fluoride (VDF) and copolymerization with perfluoro-n-propylvinylether (PPVE). Polymer 2014, 55 (16), 3557-3563.


CHAPTER EIGHT

FLUORINATED POLYURETHANE TRIBLOCK COPOLYMER

8.1. Introduction

We have established that hydrophobic/oleophobic PET films can be obtained by blending PET with fluorinated polyurethane oligomers FOPUs (Chapter 7). Furthermore, we have also found that fluorinated triblock copolymer structure can further support the migration of fluorinated content over the surface and formation of brush-like structures. Therefore, in this chapter, we reported on synthesis and characterization of fluorinated polyurethane triblock copolymer (FOPB-4). We characterized FOPB-4 using ATR-FTIR and NMR. We also identified the thermal properties of FOPB-4 using TGA and DSC analysis. Furthermore, we reported on how the chemical structure of fluorinated copolymers influences the surface wettability of PET films in this chapter. For this purpose, we measured the contact angle of water and hexadecane for FOPB-4/PET blended films. In addition, we also determined the surface morphology and film composition by using AFM and XPS. For synthesis of FOPB-4, we selected HFOPU-2 oligomer (Figure 7.3 in Chapter 7). The reason behind this choice was the flexibility and resemblance of FOP-1 (Figure 4.4 in Chapter 4). Specially, we targeted comparison between polyurethane and polyester triblock copolymers, having similar thermal properties. In this respect, MFOPU-2 oligomer containing aromatic fragments (Figure 7.5 in Chapter 7) is not suited for this study, since it has very high melting point.
8.2. Experimental Part

8.2.1 Materials

Fluorinated polyurethane triblock copolymer, FOPB-4, was synthesized through melt condensation of PEI (Figure 4.1 in Chapter 4) with HFOPU-2 possessing aliphatic urethane in-chain segments and C₄F₉-PFPE-end-groups (Figure 7.3 in Chapter 7). Commercial grade PET pellets from Unifi were used as received. HFIP was used as solvent for the polymer film fabrication.

8.2.2. Synthesis of FOPB-4

In the synthesis of FOPB-4 (Figure 8.1), telechelic PEI oligomer and semi-telechelic HFOPU-2 oligomer were reacted in a 100 mL three-necked flask at 100°C, 150°C, 180°C, and 200°C for 2h at each temperature. The reaction media was carried under N₂ atmosphere with vigorous stirring. The final product was terminated with C₄F₉-PFPE-end-groups on both sides and PEI serving as the middle block.

8.2.3. Polymer Film Preparation

The synthesized FOPB-4 copolymer was solvent-blended with PET at different concentrations (1, 2, 5, and 10 wt%) in HFIP solution. The details of the fabrication of polymer films are described in Chapter 5. For the selected experiment, the films were annealed at 140°C for 3h under vacuum after being dried at ambient conditions for 16h.
Figure 8.1. Chemical structure of FOPB-4.
8.3. Results and Discussions

8.3.1. Characterization of FOPB-4

ATR-FTIR Analysis

We performed ATR-FTIR analysis to identify the major structural elements presented in FOPB-4 copolymer. The results are displayed in Figure 8.2. The -NH stretching vibrations (3335 cm\(^{-1}\)) and the -NH bending peaks at 1533 cm\(^{-1}\) were detected for FOPB-4. Furthermore, the -C=C- stretching vibration peaks in the region of 1611-1414 cm\(^{-1}\) and C-H bending peaks at 953 cm\(^{-1}\) were also presented in the IR spectrum due to the incorporation of PEI block into the copolymer. In addition, the -CF\(_3\) and -CF\(_2\) stretching vibrations (1200-1100 cm\(^{-1}\)), the -OC=O stretching peaks (1701 cm\(^{-1}\)), and -C-O-C- stretching peaks (1283 cm\(^{-1}\)) were identified for FOPB-4. Overall, the analysis supports the proposed chemical structure of FOPB-4 copolymer.
Figure 8.2. ATR-FTIR spectrum of FOPB-4. Mark on spectrum: (1) -NH stretching (aromatic), 3335 cm$^{-1}$, (2) -CH stretching (aliphatic), 2938-2861 cm$^{-1}$, (3) -OC=O stretching, 1701 cm$^{-1}$, (4) -C=C- stretching (aromatic), 1611-1414 cm$^{-1}$, (5) -NH bending, 1533 cm$^{-1}$, (6) -C-O-C symmetric stretching, 1283 cm$^{-1}$, (7) -CF$_2$ and -CF$_3$ stretching, 1200-1099 cm$^{-1}$, and (8) C-H bending (in-plane), 953 cm$^{-1}$.

$^{19}$F NMR Analysis

We also conducted $^{19}$F NMR analysis to further examine the structure of FOPB-4 (Figure 8.3). The three main peaks (c, d, and e) belonging to the fluorine atoms in the C$_4$F$_9$-PFPE- end segment were found in the structure. Two singlet peaks at -81.09 ppm (c) and -83.57 ppm (d) are attributed to the fluorine atoms in the -CF$_3$ group and -CF$_2$ group bonded to ether (CF$_3$-CF$_2$CF$_2$-CF$_2$-O).$^1$ Another peak “e” at -126.67 ppm belongs to the fluorine atoms of the -CF$_2$ groups (CF$_3$-CF$_2$CF$_2$-CF$_2$-O) on the tail.$^1$ FOPB-4 also showed signals at -77.40 to -77.87 ppm (a) corresponding to the fluorine atom in the CF$_2$ groups bonded to methyl ester (-O-CF$_2$-CH$_2$-O-CO-) in repeat units.

The distinctive multiple peaks at -88.76 to -89.58 ppm (b) were also detected, which are attributed to the fluorine atoms of the -CF$_2$- groups located between ethers (-O-CF$_2$CF$_2$-O-) in the repeating units. Interestingly, peak “j” belongs to the fluorine atom in the CF$_2$ group, which is close to the -OH end groups (-O-CF$_2$-CH$_2$-OH) $^{2-3}$ was also detected, although the intensity of the peak has been decreased compared to that of HFOPU-2 oligomer (Figure 7.8 in Chapter 7). It means that some of the polyurethane oligomer terminated with -OH end-groups were not reacted with -Cl end-groups in PEI.
Apart from chemical structure of FOPB-4, we also estimated the number of repeating units and the number-average molecular weight for FOPB-4 using the method described in Chapter 4 based on NMR analysis. As a result, the calculated number of repeating units for one HFOPU-2 block is ~7 and $M_n$ for FOPB-4 copolymer is 9755 g/mol (Table 8.1).

**GPC Analysis**

The GPC analysis reveals that the weight-average molecular weight, number-average molecular weight, and polydispersity index for FOPB-4 was 9444 g/mol, 4891 g/mol, and 1.9, respectively. Consequently, using PDI from GPC and $M_n$ from NMR, the $M_w$ for FOPB-4 was calculated to be 18353 g/mol (Table 8.1). The results indicate that FOPB-4 has practically the same $M_w$ as FOPB-1. However, the PDI for FOPB-4 (~2) is somewhat narrower than that of FOPB-1 (~3). We also estimated the atomic concentration...
of fluorine in FOPB-4 using the method described in Chapter 4. According to the chemical structure, the fluorine concentration in FOPB-4 polyurethane is 20%, which is slightly lower than the fluorine concentration in FOPB-1 polyester (~23%).

Table 8.1. Major characterization of fluorinated triblock copolymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n^a$ (g/mol)</th>
<th>$M_w^b$ (g/mol)</th>
<th>PDI$^c$</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_d$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOPB-4</td>
<td>9755</td>
<td>18353</td>
<td>1.9</td>
<td>-10</td>
<td>53</td>
<td>260</td>
</tr>
<tr>
<td>FOPB-1</td>
<td>5983</td>
<td>16752</td>
<td>2.8</td>
<td>-18</td>
<td>46</td>
<td>401</td>
</tr>
</tbody>
</table>

$^a$: data from NMR, $^b$: data obtained by combining NMR and GPC, and $^c$: data from GPC

Thermal Analysis

TGA analysis was employed to identify the composition of FOPB-4 and decomposition temperatures of the components obtained during the reaction process. The TGA traces are presented in Figure 8.4. It is found that the majority of product obtained at 100°C (~80%) have LMW fraction mixtures, which are thermally sable until ~250°C. However, ~14% of the resulting oligomer can withstand higher temperature (> 300°C). Then, the reaction was proceeded for 2h at 150°C, 180°C, and 200°C, respectively to form higher molecular weight and more temperature stable oligomers. However, as seen in Figure 8.4, the major fraction of final product is LMW having $T_d$ around 260°C, while ~10% fraction is HMW and stable until 380°C. Though, the thermal stability of FOPB-4 is higher than the initial HFOPU-2 block; however, it is still lower than that of FOPB-1. This could happen because the presence of long aliphatic urethane segments in FOPB-4 polymer chains. Therefore, it is reasonable to assume that the thermal stability of the fluorinated copolymer is dependent on the molecular structure of the copolymer.
DSC was used to determine the glass transition and melting temperature for FOPB-4 copolymer. The results (Table 8.1) reveal that FOPB-4 is semi-crystalline material since both $T_g$ and $T_m$ were detected. The DSC trace (Figure 8.5) also reveals that, for FOPB-4, the midpoint of $T_g$ was $-10^\circ$C, while $T_m$ was $53^\circ$C. Both thermal transition temperatures for FOPB-4 are relatively higher than those of FOPB-1 (Table 8.1). We connect the variance in the thermal transition temperatures with their different macromolecular structures. FOPB-4 possesses the urethane units containing polar group and hydrogen bonding, while rigid aromatic rings are presented in FOPB-1 polyester copolymer.
8.3.3. Fabrication of FOPB-4/PET Films

A series of polymer films containing 1, 2, 5, 10% FOPB-4 copolymer in PET matrix was prepared using HFIP solution by dip-coating. After the film fabrication, the films were stored overnight at ambient conditions to dry. Subsequently, they were annealed at 140°C for 3h under vacuum. In this work, the surface wettability and morphology of FOPB-4/PET blended films were determined.

8.3.4. Characterization of FOPB-4/PET Films

Surface Morphology Analysis

Figure 8.6 shows the AFM topographical images of the films before and after the annealing treatment for FOPB-4/PET films possessing different amounts (1-10%) of the fluorinated copolymer. The size for the images is 10 μm x 10 μm. The smooth films were obtained without the formation of crystalline structures before the annealing. It appears
that FOPB-4 polyurethane and PET are to some extent immiscible. The clear phase separation was observed from the surface of polymer films. On the other hand, the phase separation did not change meaningfully with an increase of FOPB-4 content in the blends until the concentration of FOPB-4 is 10%.

**Figure 8.6.** AFM (10 µm x 10 µm) topographical images of polymer films before (a, c-f) and after (b, g-k) annealing. Pure PET (a, b), and FOPB-4/PET films (c-k). Before annealing: (a) Pure PET (RMS = 0.3 nm), (c) 1% FOPB-4/PET (RMS = 10.5 nm), (d) 2% FOPB-4/PET (RMS = 13.0 nm), (e) 5% FOPB-4/PET (RMS = 8.5 nm), and (f) 5% FOPB-4/PET (RMS = 21.5 nm). After annealing: (b) Pure PET (RMS = 8.0 nm), (g) 1% FOPB-4/PET (RMS = 10.0 nm), (h) 2% FOPB-4/PET (RMS = 8.0 nm), (i) 5% FOPB-4/PET (RMS = 11.0 nm), and (j) 10% FOPB-4/PET (RMS = 16.0 nm).
The surface morphology changed significantly for the films after the annealing (Figure 8.6). One can see that crystals are formed on the films due to the rearrangement and reorientation of PET polymer chains during the thermal treatment. The shrinkage of the PET phase might support the surface migration of FOPB-4, since FOPB-4 has much lower thermal transition temperatures than those of PET polymer. Furthermore, it was also found out that the phase separation is not clearly seen on AFM topographical images for the annealed samples. The AFM phase images (Figure 8.7) for annealed films show that FOPB-4 layer is not discontinuous and covering evenly the PET matrix.

**Figure 8.7.** AFM (10 µm x10 µm) phase images of annealed polymer films (a-e). Pure PET (a), and FOPB-4/PET (b-e). Concentration of FOPB-4: (b) 1%; (c) 2%; (d) 5%; and (e) 10%.
Surface Wettability of FOPB-4/PET Films

Contact Angle Measurements

The WCA and HCA were measured to determine the level of hydrophobicity and oleophobicity of PET films containing different concentrations of FOPB-4 polyurethane copolymers. The results are shown in Figure 8.8 and Figure 8.9, respectively.

It is evident that small amount of FOPB-4 copolymer incorporated into polyester results in a strong increase in the WCA and HCA values. For instance, the WCA on unannealed pure PET films is 58°. However, it increased to 75° when blended with 1% FOPB-4. Furthermore, it was found that there is a significant dependence of CAs on concentration of FOPB-4 in PET films before the annealing. The WCA for FOPB-4/PET films increased from 75° to 94° as FOPB-4 content increased from 1 to 10%, and the HCA of the films was also increased from 32° to 71° with the FOPB-4 concentration.

The effect of annealing treatment on surfaces wettability was also investigated using CA measurements. We observed a significant change in the values of CA for the FOPB-4/PET films upon annealing. At 1% load, the HCA increased from 32° to 51°, while WCA did not change meaningfully. However, for the films with 10% FOPB-4, the WCA increased from 94° to 107°, while the effect of annealing on HCA was less pronounced. In addition, at 2% FOPB-4 concentration, the WCA and HCA increased from 81° to 88° and from 41° to 56°, respectively. The same trend was realized for 5% films, where WCA increased from 87° to 96°, and HCA increased from 58° to 66°. It is apparent that annealing supports the surface enrichment of FOPB-4 over the PET matrix.
**Figure 8.8.** WCA for (red) FOPB-1/PET and (blue) FOPB-4/PET films of different concentrations before (solid) and after (mesh) annealing at 140°C for 3h.

**Figure 8.9.** HCA for (red) FOPB-1/PET and (blue) FOPB-4/PET films of different concentrations before (solid) and after (mesh) annealing at 140°C for 3h.
Furthermore, we compared the wettability of FOPB-4/PET films with that of FOPB-1/PET films measured by us using the same method (Chapter 5). It is found that when the films possess 5-10% FOPB-4, the oil repellency of the FOPB-4/PET films is better than the one of FOPB-1/PET films at the same conditions. Thus, it is possible that FOPB-4 polymer chains can cover PET surface to a higher extent, since FOPB-4 has more flexible aliphatic urethane segments than FOPB-1, which has aromatic ester units. It is reasonable to assume more fluorine moieties from FOPB-4 could migrate to the surface of the films. Furthermore, it appears that the surface energy change in FOPB-4 molecular chains are more gradually than that in FOPB-1 chains, since pure polyurethane typically has lower surface energy than polyester. Therefore, we again associate the variance in CA with the chemical structure of fluorinated copolymers.

**Surface Energy Estimation**

We calculated the surface energy for annealed FOPB-4/PET films using CA according to Owen-Wendt method\(^4\) (details in Chapter 5). We also compared the surface energy of FOPB-4/PET films to that of FOPB-1/PET films. The results are shown in Figure 8.10. For the films with 1% FOPB-4, \(\sigma_{\text{FOPB-4}} = 32\) mN/m, which was higher than that of 1% FOPB-1/PET films (28 mN/m). However, surface energy of the films is on the similar level of when 2 or 5% fluorinated copolymer (FOPB-1 or FOPB-4) was added to the PET matrix. Furthermore, as the fluorinated content increased up to 10%, the surface energy for annealed FOPB-4/PET films decreased to 13 mN/m. It is necessary to highlight that \(\sigma_{\text{FOPB-4}}\) for films containing 10% FOPB-4 is 13% lower than \(\sigma_{\text{FOPB-1}}\) (15 mN/m) and 30% lower than \(\sigma\) of PTFE (18.5 mN/m).
Figure 8.10. Surface energy of annealed FOPB/PET films at different concentrations.

Surface energy for PET and PTFE are given for comparison.

Effect of Storage Time on Surface Wettability of FOPB-4/PET Films

We have found out that the FOPB-1 polyester is not equilibrium for several days without annealing. Therefore, to investigate if the surface migration of FOPB-4 increases during storage, we conducted CA measurement for 5% FOPB-4/PET films as a function of storage time. The measured WCA and HCA are presented in Figure 8.11. One can see that the migration of FOPB-4 over the PET surface was continues for 2 days. In addition, the increase of WCA is relatively stronger than that of HCA. For instance, the change in WCA increased by ~13° after 2 days of storage. However, HCA practically did not change within time. This was expected since we have established that WCA is more sensitive to
the thickness of fluorine layer covering the PET, because the size of water molecule is smaller than that of hexadecane.

![Figure 8.11. WCA and HCA for 5 wt% FOPB-4/PET films as a function of storage time.](image)

**Surface Coverage of Annealed FOPB-4/PET Films**

The CA measurements indicated that the surface of FOPB-4/PET films is occupied to a great extend with fluorinated polyurethane copolymer after the annealing. Therefore, the Cassie-Baxter model\(^5\) was employed to estimate the effective surface area of annealed FOPB-4/PET films screened by FOPB-4 fluorinated chain segments. The data in **Table 8.2** reveals that FOPB-4 readily enriches to the surface and effectively screens it from wetting liquids of water and hexadecane. However, we noted that FOPB-1 is better shielding the surface from both water and hexadecane than FOPB-4 at the same concentration in general. Therefore, it is necessary to point out that the gradually surface energy changed polymer chains influences the surface energy more predominantly than the surface migration of fluorinated chain segments.
Table 8.2. Apparent surface area of the annealed FOPB/PET films ($f_{FOPB}$) that is screened effectively by fluorinated chain segments.

<table>
<thead>
<tr>
<th>Polymer Films</th>
<th>FOPB Content (wt%)</th>
<th>$f_{FOPB}$ from WCA</th>
<th>$f_{FOPB}$ from HCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOPB-4/PET</td>
<td>1</td>
<td>0.25</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.54</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.66</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.85</td>
<td>1</td>
</tr>
<tr>
<td>FOPB-1/PET</td>
<td>1</td>
<td>0.49</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.55</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.89</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

*XPS Analysis of Annealed FOPB-4/PET Films*

To further elucidate the FOPB-4 localization on the surface of FOPB-4/PET films, we performed XPS analysis for annealed films with different FOPB-4 contents (1, 2, and 5%). For the analysis, the incident angle for samples was 90°, where the detector line of sight is normal to the film. Consequently, the corresponding sampling depth from the air/film boundary was around 10 nm. The XPS data is displayed in Table 8.3. It is clearly seen that the XPS survey spectra of the top 10 nm layer of FOPB-4/PET films mainly possess four characterization peaks: F1s, O1s, C1s, and N1s. The F1s and N1s peaks were from FOPB-4. The O1s and C1s signals were from both PET and FOPB-4.
Table 8.3. Atomic concentration percentage of F, O, N and C for FOPB-4/PET films.

<table>
<thead>
<tr>
<th>Angle</th>
<th>1% of FOPB-4 in the Films</th>
<th>2% of FOPB-4 in the Films</th>
<th>5% of FOPB-4 in the Films</th>
<th>100% of FOPB-4 in the Films</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atomic Concentration %</td>
<td>Atomic Concentration %</td>
<td>Atomic Concentration %</td>
<td>Atomic Concentration %</td>
</tr>
<tr>
<td></td>
<td>F 1s</td>
<td>O 1s</td>
<td>C 1s</td>
<td>N 1s</td>
</tr>
<tr>
<td>90°</td>
<td>10.53</td>
<td>28.89</td>
<td>58.76</td>
<td>1.81</td>
</tr>
</tbody>
</table>
We calculated the molar concentration of FOPB-4 copolymer segments in the topmost 10 nm layer (Equation 5.11 in Chapter 5). The results are showed in Figure 8.12. For the sake of comparison, we also displayed the results for FOPB-1 in Figure 8.12. It appears that the atomic concentration of fluorinated content on the top surface is practically the same with the addition of 2 and 5% FOPBs. However, at the concentration of 1%, the PET surface area is covered with more fluorinated chain segments from FOPB-1 polyester than FOPB-4 polyurethane. Herein, we reiterate that the effect of surface energy change in polymer chains on surface wettability of PET blended films is more pronounced than chain flexibility.

![Figure 8.12](image)

**Figure 8.12.** Atomic concentration of FOPB within 10 nm top layer (a) and the effective thickness of FOPB layer on the surface (b) of the annealed FOPB/PET film as a function of FOPB concentration in the blends.
8.4. Conclusions

- The fluorinated polyurethane triblock copolymer, FOPB-4, terminated with C₄F₉-PFPE-end-groups in both sides was synthesized via melt condensation.
- FOPB-4 polyurethane has relatively lower thermal stability than FOPB-1 polyester.
- The hydrophobic/oleophobic PET blended films were obtained by FOPB-4 polyurethane copolymer, even at low concentrations.
- The FOPB-4 polyurethane shows better oil repellency than FOPB-1 at high concentration (≥ 5%) due to the presence of gradually surface energy change segments in FOPB-4 chains.

8.5. References


2. Wu, J.; Zhou, X.; Harris, F. W., Bis(perfluoro-2-n-propoxyethyl)diacyl peroxide initiated homopolymerization of vinylidene fluoride (VDF) and copolymerization with perfluoro-n-propylvinylether (PPVE). *Polymer* 2014, 55 (16), 3557-3563.


CHAPTER NINE
SUMMARY AND FUTURE WORK

9.1. Summary

Fluorocarbon containing compounds are used to fabricate water and oil repellent surfaces for numerous applications due to their low surface energy. It is important for fluorinated low surface energy additives offer long-lasting hydrophobic/oleophobic properties when added to different materials, but also to be friendly to the environment, humans, and wildlife in nature. To this end, PFPE-based materials are considered as safer replacement for additives containing PFASs.

This work has presented the synthesis of PFPE-based triblock polyester copolymers (FOPBs) containing C₄F₉-PFPE- or C₆F₁₃- low surface energy end-groups in Chapter 4. Furthermore, we compared the efficiency of these FOPBs as water/oil repellent additives to that of thermoplastic materials (PET, nylon 6, or PMMA) in Chapter 5. It was found out that FOPB molecular brush is formed on thermoplastic surface to minimize the surface energy. We also found out that the surface wettability of polymer films containing C₄ (FOPB-1 with C₄F₉-PFPE- tails) is on the level of that of the films having C₆ material (FOPB-2 with C₆F₁₃- tails). In Chapter 6, we reported the synthesis of FOPB-3 with PEI-co-PET copolymer as the middle block and two C₄F₉-PFPE- as end-blocks. The results show that FOPB-3 has comparable level of water and oil repellency despite the molecular weight difference. The synthesis and characterization of fluorinated polyurethane oligomers (FOPUs) with different chemical structures was detailed in Chapter 7. The
synthesis of fluorinated polyurethanes was less challenging than that of polyesters. MFOPU-2 polyurethane oligomer possessing one C₄F₉-PFPE- end-group and aromatic urethane linkages, achieved the highest values of WCA and HCA for polyester blends. The work in Chapter 8 presents the synthesis of FOPB-4 polyurethane triblock copolymer (with C₄F₉-PFPE-tails and aliphatic urethane linkage). According to CA measurements, we suggest that FOPB-4/PET might achieve lower water/oil wettability than FOPB-1/PET due to more gradually surface energy change segments in FOPB-4. Selected parameters of synthesized fluorinated polyesters and polyurethanes is summarized in Table 9.1. The surface properties of pure PET (WCA = 58°, HCA < 5°, σₚₑᵗ = 46 mN/m) and PTFE (WCA = 118°, HCA = 51°, σₚₑᵗₑ = 18.5 mN/m) are given for comparison.

In summary, original PFPE-based polyesters and polyurethanes of different macromolecular architectures were synthesized. Specially, the ones with four perfluorinated carbon atoms, can be considered as safer replacements to long-chain perfluoroalkyl substances. In fact, it was found that the materials synthesized here, when added to industrial polymer films, readily migrate to the film surface and bring significant water and oil repellency to the films. These films reach the level of oil repellency and surface energy comparable to those of PTFE, a fully perfluorinated polymer. The superiority of the synthesized macromolecules in achieving high water and oil repellency is associated with their ability to form brush-like structures on polymer film surfaces.
Table 9.1. Major characteristics of synthesized PFPE-based fluorinated materials.

<table>
<thead>
<tr>
<th></th>
<th>FOPB-1</th>
<th>FOPB-2</th>
<th>FOPB-3</th>
<th>HFOPU-1</th>
<th>HFOPU-2</th>
<th>MFOPU-1</th>
<th>MFOPU-2</th>
<th>FOPB-4</th>
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<td>6667&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>3427&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>11334&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>2879&lt;sup&gt;c&lt;/sup&gt;</td>
<td>6100&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>2556&lt;sup&gt;*&lt;/sup&gt;</td>
<td>18535&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>160/320</td>
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<td>101</td>
<td>101</td>
<td>90</td>
<td>88</td>
<td>100</td>
<td>116</td>
<td>96</td>
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<tr>
<td>HCA at 5%</td>
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<td>60</td>
<td>57</td>
<td>55</td>
<td>67</td>
<td>53</td>
<td>72</td>
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<td>18</td>
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<td>22</td>
<td>21</td>
<td>19</td>
<td>12</td>
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</table>

<sup>a</sup>: data from NMR,  <sup>b</sup>: data obtained by combining GPC and NMR,  <sup>c</sup>: data from GPC, and  <sup>*</sup>: molecular weight for oligomer can be dissolved in chloroform obtained from GPC
9.2. Future Work

We found out that C₄ materials can be considered as the effective alternatives to long-chain PFASs. For future work, the PFPE-based acrylate monomer terminated with C₄F₉-PFPE- end-groups will be synthesized and characterized. Once obtained the monomer, we will also polymerize the fluorinated monomers or react them with glycidyl methacrylate (GMA) via free radical polymerization to form molecular brushes. Specially, thermally cross-linked poly(glycidyl methacrylate) (PGMA) can be formed, which can support the fluorinated additives to form a stable permanent network layer on the substrate. As a result, a long-lasting surface modifications to polymer materials can be prepared.

It is obvious that non-toxic and environmental friendly low surface energy additives are essential for many practical applications. Therefore, I would recommend that the blending of C₄-based fluorinated copolymers to offer effective and safe surface modifications to important thermoplastic polymers.