Wettability of polymer surfaces : effects of chemistry and topography.

Jeffrey P. Youngblood

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WETTABILITY OF POLYMER SURFACES: EFFECTS OF CHEMISTRY AND TOPOGRAPHY

A Dissertation Presented

by

JEFFREY P. YOUNGBLOOD

Submitted to the Graduate School of the University of Massachusetts in partial fulfillment of the degree requirements for the degree of

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Polymer Science and Engineering
WETTABILTY OF POLYMER SURFACES: EFFECTS OF CHEMISTRY AND TOPOGRAPHY

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Polymer Science and Engineering
Many have contributed to the development of myself, and this dissertation, and as such both are certainly collective works. The faculty have been delightful to learn from and, in particular, my advisor Prof Tom McCarthy, who never failed to let me put my foot in my mouth, has been a wonderful boss. Deserving of mention also is Prof Tom Russell, who was always there to offer advice and say, “when will you cut that hair?”

I would also like to thank my colleagues: group members, classmates, sports people, and lunchroom companions. I will always remember fondly the conversations in the labs and halls on topics that would make the layman go insane. Particularly unforgettable are my labmates – the Frisbee duo, Meng and Chris – of whom I would always beat at “Name That Song”. Thanks everybody for all the fun.

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From this Cajun’s heart out to all of you – thanks for a lifetime of memories!
ABSTRACT

WETTABILITY OF POLYMER SURFACES: EFFECTS OF CHEMISTRY AND TOPOGRAPHY

SEPTEMBER 2001

JEFFREY P. YOUNGBLOOD, B.S., LOUISIANA STATE UNIVERSITY
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Directed by: Professor Thomas J. McCarthy

Various methods for modification of polymer surfaces were studied with the objective of controlling changes in wetting behavior. Random copolymers and block copolymers were synthesized by free radical polymerization and atom transfer radical polymerization, respectively, of methacryloxyethyl- or methacryloxypropyltris(trimethylsiloxy)silane and methyl methacrylate. These polymers spontaneously rearrange to concentrate the low energy, non-wettable siloxane at the surface. The nanoporous nature of the surfaces of these polymers was confirmed using X-ray photoelectron spectroscopy (XPS) analysis and dynamic contact angle analysis. Another method for wettability modification that was studied was the selective modification of polymer surfaces using 3-aminopropyltriethoxysilane (APTES); this provided surfaces with silica-like reactivity. This surface chemistry had been reported for poly(ethylene terephthalate); this thesis work expands the reaction to many other polymers (ostensibly all that are H-bond acceptors). Variations in temperature, concentration, and solvent were studied as well as reagent mixtures with tetraethoxysilane. Our experiments led us to propose a new pathway for the reaction. Subsequently, polymers were hydrophobized by fluorination with a monochlorosilane.
Argon plasma sputtering of polymers was investigated and a new mechanistic scheme was developed for non-classical polymer sputtering in which the polymer depolymerizes yielding gas-phase monomer which then re-polymerizes. This new understanding of the sputtering process was used to create ultrahydrophobic surfaces, which water drops were unstable on. Polymer surfaces were simultaneously roughened and hydrophobized to test the effect of roughness and topography on surface wettability. A new phenomenological model for wettability was developed with this knowledge in which wettability is treated as a one-dimensional contact line issue. For droplet motion to occur, an energy barrier to three phase contact line motion must be overcome, which can be accomplished by: 1) surface structures becoming smaller to lower barriers to motion and/or 2) contortion of the contact line to raise its ground state energy.
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CHAPTER 1

OVERVIEW

Wetting phenomena have long been researched as a means to increase (or decrease) adhesion, improve coatings, and create repellency. It is known how the surface energetics play a role in these examples. What has been missing, however, is a detailed understanding of the topographical effects on wetting at the both the macroscopic (micron) and the atomic (angstrom) levels. Additionally, there has been little work done to understand the “ultrahydrophobic” effect. Materials with this property have promising use in drag reduction, among other things. Although previous work has been done relating roughness and chemical changes to wetting behavior, this work seeks to present a thorough investigation of how we can influence surface properties to better understand ultrahydrophobic materials. This dissertation describes research that is done in order to obtain an in-depth understanding of wettability and how to influence the factors involved to create ultrahydrophobic and ultralyophobic materials. Two approaches are used: 1) influencing surface chemistry and 2) influencing surface topography. The chemical method is further divided into bulk synthesis and surface modification.

Chapter two is a general introduction to this research and will serve as an introduction to the later sections as well. The theory and background of wettability and its influencing factors will be explored. Ultrahydrophobicity and ultralyophobicity will be defined and discussed. In addition, certain surface characterization techniques that appear throughout this research will be described.
Chapter three describes the synthesis of materials for controlled surface energy and hydrophobicity. These syntheses are accomplished through the copolymerization of methyl methacrylate and a methacrylate monomer containing a low surface energy, highly hydrophobic side-group. This side-group, tris(trimethylsiloxy)silane, has previously been shown to produce monolayers that are nearly ideal in these areas. After spin-casting and annealing, this low surface energy group will reorganize to the surface creating a highly non-wettable, uniform surface. Both random and block structures are investigated. The surface structure is characterized by probe fluid size-dependent contact angle analysis as well as the general techniques mentioned previously.

The fourth chapter describes a different approach to changing the wetting behavior of materials using known chemical techniques. Instead of synthesizing new materials, surface modification is carried out on existing polymer films. A general method of surface modification that allows subsequent silane monolayer chemistry for PET is known. This method has been extended to other substrates, such as other polyesters and polycarbonate. Significant work is put forth in understanding this reaction. After the various polymers are activated towards further modification, silane monolayers have been applied to affect changes in wetting behavior. Overall, this method is an applied approach to control of the surface properties of a variety of materials.

The final chapter of this dissertation deals with the controlled roughening of polypropylene (PP) to affect changes in wetting behavior. This phase of research is composed of two sections. The first is the investigation of the plasma ablation and sputtering processes, an understanding of which is crucial to this research (due to the
The method of roughening). The second is the actual wetting studies and the creation of ultrahydrophobic materials. In the former, various polymers are studied so as to apply our knowledge of sputtering to the synthesis of ultrahydrophobic materials. This work appears in Thin Solid Films¹ (2001). In the latter, knowledge of the ultrahydrophobic effect is garnered through control of surface topography and has been published in Macromolecules² (October 1999).

Included in the appendix section of this dissertation are two projects that were worked on in addition to the main dissertation research. The first is the plasma polymerization of mixed monomer gases to create ultrahydrophobic powder coatings. It had been previously found that plasma polymerization of highly reactive fluorinated acrylates produces powders of controlled size with some showing ultrahydrophobicity. My work has expanded this method to include mixtures of powder-forming monomers and fluorinated monomers to produce similar results. Another project area in the appendix is an attempt, albeit unsuccessful, to control and improve the self-healing performance of oil-filled capacitor dielectrics. The method is to use polymer thin films to control the local electrical, thermal, and material properties to influence the performance.
CHAPTER 2

INTRODUCTION

2.1. Wettability

The term wettability is a very vague term referring the general wetting behavior of a surface. One could think that this behavior could be broken up into two aspects: 1) the energetic part which has to do with only thermodynamics and the 2) dynamic aspect where droplets are moving onto and off of surfaces. The latter has more to do with repellency than the former, since usually one is more interested in having droplets slide or be shaken off easily than with the static shape of the drop. For this reason, the dynamic aspect of wetting behavior will be defined as hydrophobicity (or lyophobicity). The thermodynamic part will be referred to as surface energy. One should note that there are many possible definitions of hydrophobicity, and that this particular definition is chosen to further our arguments and not disparage any other. One should also note that this term is a comparative one and not an absolute measure.

2.1.1. Surface Energetics

It has long been common principle that energy is required to form new surface area (Griffith’s criteria). This is an indication of the fact that every material has an energy associated with its surface. When a droplet is in contact with a surface, the energies of the three-phase contact line balance to a minimum. This causes the tangent
of the droplet surface to form a distinct angle of contact with the other surface and is described by Young's equation which is shown diagramitically in Figure 2.1.

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

**Figure 2.1** Representation of the contact angle along with Young's equation.

Throughout this text this behavior will be termed "contact angle." From the equation one can see that a fluid will wet a surface if its surface energy is lower than the difference between the solid-vapor interfacial energy and the solid-liquid interfacial energy (this value is known as the critical surface tension). Conversely, the further in energy the solid is below the fluid, the higher the contact angle will be.

**Table 2.1** Critical surface tension values for common surfaces and liquid surface tensions for some fluids.\(^4,\!^5\)

<table>
<thead>
<tr>
<th>Surface</th>
<th>(\gamma_s) (dynes/cm)</th>
<th>Liquid</th>
<th>(\gamma_{LV}) (dynes/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CF(_3) (densely packed monolayer)</td>
<td>6</td>
<td>n-Hexadecane</td>
<td>28</td>
</tr>
<tr>
<td>Poly(tetrafluoroethylene)</td>
<td>18</td>
<td>Ethylene Glycol</td>
<td>47</td>
</tr>
<tr>
<td>-CH(_3) (densely packed monolayer)</td>
<td>22</td>
<td>Methylene iodide</td>
<td>67</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>31</td>
<td>Water</td>
<td>72</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO(_2) (silicon wafer)</td>
<td>73</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
This is the reason that water wets glass but beads on Teflon™ coated cookware. A table of selected critical surface tensions, commonly assumed to be equivalent to the surface energy of the material, is given in Table 2.1.

Although the contact angle gives, in theory, a thermodynamic value of surface energetics, in reality it is far from it. Any non-uniformity (physical or chemical) causes the actual value to differ.\(^5\) One can use this to gather more accurate data about a surface. A dynamic contact angle (as opposed to a sessile contact angle) where the three-phase contact line is in motion can be used for this. An advancing line’s contact angle will be raised above the thermodynamic one while the receding line’s angle will be depressed. The contact angle hysteresis (the difference between the two) then gives a measure of the degree of non-uniformity. Much information can be gleaned when using this technique with a variety of probe fluids. In this research, the dynamic contact angle is measured by adding fluid to a drop on a surface to advance the contact line. The drop is then receded by withdrawing fluid from it.

2.1.2. Chemical Non-uniformity and Roughness Effects

It had been previously said that heterogeneity could have an effect on the nature of the surface and its contact angle behavior. In the case of chemical non-uniformity, one must define what the term means. If something is molecularly mixed then, although it may be heterogeneous, it is uniform. If the mixing is patchy then it is both heterogeneous and non-uniform. For the molecularly mixed uniform surface the surface energy is expressed by the Israelachvili equation.\(^6\)
\[(1 + \cos \theta)^2 = \sum f_n(1 + \cos \theta_n)^2 \quad ; \quad \sum f_n = 1\]

Although the surface is mixed and heterogeneous, since it is uniform the contact angle hysteresis is unaffected. In the case of the patchy surface, both the energy (and thereby the contact angle) and the hysteresis are affected. Cassie\(^7\) derived an equation for this behavior by geometrically averaging the constituents.

\[\cos \theta = \sum f_n \cos \theta_n \quad ; \quad \sum f_n = 1\]

Although there is no equation for contact angle hysteresis, one can assume that it goes up with degree of non-uniformity.

Surface roughness can also have a large effect upon the contact angle. In the simplest case, a rough surface has more surface area underneath the liquid and therefore more surface energy. Wenzel\(^9\) put this idea in mathematical form

\[\cos \theta_A = r \cos \theta_T\]

where \(\theta_A\) is the actual (perceived) contact angle, \(\theta_T\) is the thermodynamic angle, and \(r\) is the roughness. This last value is the true surface area divided by the geometric area of integration. Unfortunately, as roughness increases, this approach loses its effectiveness. This is due to the fluid failing to penetrate the asperities. At high roughness the surface obtains a porous-like structure with the droplet resting on both solid and air. This is akin
to a mixed surface and is termed a “composite” surface. Cassie and Baxter\(^8\) derived an equation for this behavior:

\[
\cos \theta_A = f_1 \cos \theta_T - f_2
\]

where \(\theta_A\) and \(\theta_T\) are again the actual and thermodynamic angles, \(f_1\) is the fractional area of contact with surface, and \(f_2\) is the fractional contact area with air underneath the drop. Another model was put forward by Johnson and Dettre\(^{10}\) involving metastable states. This model is phenomenologically correct to the observed behavior that is seen as the roughness ratio increases from unity to higher values. It also predicts a sharp transition region between the two. Although not a thermodynamic equation, it explains the dynamic contact angle and the hysteresis between advancing and receding angles. Figure 2.3 shows a graph taken from Johnson and Dettre’s paper with plots of contact angle versus roughness for various equations. A are the maximum and minimum values of \(\theta\) that are obtained from geometrical considerations. B shows Wenzel’s equation and Cassie and Baxter’s equation intercepting just before a roughness of 2.0. The dotted lines C and D show Johnson’s and Dettre work for both the advancing and receding angles on a surface of sinusoidal roughness.
2.1.3. Hydrophobicity and Lyophobicity

In the discussion of wettability above, hydrophobicity was defined as the ease with which water drops move on surfaces. Lyophobicity would then be the ease with which any fluid moves. With these definitions, the easier it is to move a drop off of a surface, then the more hydrophobic (lyophobic) the material. Although seemingly inconsequential, the difference between these terms becomes apparent when one considers the relatively high surface tension of water. Since surface effects become more pronounced as the surface tension of the fluid increases, it is then just a matter of degree.
To move a drop across a surface requires overcoming an opposing force. This force is proportional to the contact angle hysteresis\textsuperscript{11} and is given by the equation

\[ F \sim \gamma_{LV} (\cos \theta_{\text{rec}} - \cos \theta_{\text{adv}}) \]

As one can see the keys to hydrophobicity and lyophobicity are in reducing the hysteresis and not in the actual surface energies. Along these lines, our group has postulated\textsuperscript{1} that a surface with \( \theta_{\text{adv}} \) and \( \theta_{\text{rec}} \) of 36\(^\circ\) and 36\(^\circ\) is more lyophobic than one with \( \theta_{\text{adv}} \) and \( \theta_{\text{rec}} \) of 170\(^\circ\) and 70\(^\circ\). In fact both of these surfaces have been prepared and the former has drops that move easily when only slightly tilted while the latter has drops that pin (unable to remove them). Surfaces that exhibit near-zero hysteresis (that have drops that move readily) are termed ultrahydrophobic\textsuperscript{12} if the fluid is water. For surfaces that exhibit this behavior with all fluids, the term ultralysophobic\textsuperscript{12} is used. Looking again at the previous equation, the inclusion of the fluid energy term dictates that an ultrahydrophobic material may not necessarily be ultralysophobic.

Roughness effects can also have a profound influence on the hydrophobicity as was mentioned before. Glancing at the plot of Johnson and Dettre of water contact angle as a function of roughness, one notices that the surface transitions to a low hysteretic region after a critical value (that appears around two). This region is the ultrahydrophobic region. A droplet would have almost no energetic barrier to motion and would move spontaneously. There have been numerous recent reports,\textsuperscript{13-22} from a variety of research fields, of surfaces exhibiting very high water contact angles, due to surface topography.
2.2. Surface Characterization Methods

Owing to the fact that this work is overwhelmingly surface oriented, a thorough knowledge of surface characterization techniques is needed. Primarily, two techniques are used to characterize our surfaces. Therefore it seems appropriate that these are discussed in detail so as to gain better insight into the nature of the work. If and when other techniques are used, a short but concise description of them will be included.

2.2.1. Dynamic Contact Angle Analysis

Since much of the previous introduction has related to surface energetics, the foundation of understanding the contact angle has been laid. The actual measurement of the value is a very hands-on technique. In our case, a droplet of fluid is suspended from a 24-gauge flat tipped needle on a Gilmont syringe. The droplet is allowed to touch the surface and fluid is either added or withdrawn by the syringe to obtain advancing and receding angles. A Rame-Hart telescopic goniometer is used to view the drop and the angle is measured by eye with a protractor included in the eyepiece. Typically, water and hexadecane are used as the probe fluids for this gives a good range of surface tensions, although others may be used. This technique is extremely powerful for characterization of the outer few angstroms of a surface.
2.2.2. X-Ray Photoelectron Spectroscopy

The other technique routinely used in this research is x-ray photoelectron spectroscopy (XPS).\(^3\) As x-rays impinge on a material, core electrons are ejected with energy equal to the photon energy minus the binding energy of the electron. An electron’s binding energy is dependant upon the atom it is ejected from, the atomic orbital it is in, and the oxidation state of the atom. Thus, if the photon energy is known, one can determine what composition the material has based on the atom concentration and the chemical shift.

XPS is a surface sensitive technique. This is due to the fact that an electron will only travel a certain distance before striking another atom. This may be expressed statistically as an average and is called the “mean free path.” This value is dependent on the energy of the electron and the material that it is traveling through. As one may readily ascertain, the further the electron has to travel through material before being detected, the lower the amount that will be detected. This basic expression for XPS is

\[
N = N_0 e^{-h/(\lambda \sin \theta)}
\]

Where \( h \) is the depth of the signal of interest, \( \lambda \) is the mean free path, and \( \theta \) is the angle of view that the detector makes with the surface (known as the take-off angle). This angular dependence dictates that the lower angles are more surface sensitive than higher angles. Typical carbon 1s electron mean free path values for polymers are on the order of 10-45 Å.
SYNTHESIS OF TRIS(TRIMETHYLSILOXY)SILYL-CONTAINING POLYMERS FOR CONTROLLED WETTABILITY

3.1. Tris(trimethylsiloxy)silane

It has been established by previous work\textsuperscript{23} in our group that the tris(trimethylsiloxy)silyl group (Tris) can lead to ultralyophobic surfaces with water contact angle hysteresis of $5^\circ$ and less than $1^\circ$ for hexadecane. The mechanism for this behavior is not known, but it is believed that the molecular motion of the bulky Tris group can affect the three-phase contact line perimeter in such a way as to lower the energy barrier to motion. This is much like trying to stand on an arrangement of rotating disks; one cannot gain stable footing. A pictorial representation of a Tris surface is given in Figure 3.1 along with the chemical structure. Notice the nano-porous structure. This
has a major effect upon the wettability and shows probe fluid size-dependent hysteresis. At low molar volumes the hysteresis is high, presumably because the fluid is able to fit into the holes and "see" the underlying groups. At high molar volumes the hysteresis is low, since the probe fluid cannot fit into the holes and it "sees" a uniform surface of Tris groups. There is a sharp transition between the two regimes. It is at or below this molar volume, and therefore size, that the holes are penetrated.

3.2. Random Copolymers

The drawback of the previous research is that it was done by coupling silane monolayers onto perfectly smooth silicon wafers. One could wonder if the low hysteresis is only seen upon these smooth surfaces or if it is possible to observe this effect upon polymer samples. Thus, we created polymer surfaces of controlled wettability (both surface energy and hysteresis) by synthesizing polymers with various amounts of the Tris group on the chain. This synthesis could have been accomplished in two principle ways: (1) grafting of Tris onto a polymer chain or (2) synthesizing a polymer from a Tris containing monomer. Fortunately, methacrylate based Tris monomers are used both academically and commercially in contact lens applications. Owing to their availability, methacryloxyethyltrimethylsiloxysilane (MMT) and methacryloxypropyltrimethylsiloxysilane (MPT) (Figure 3.2) were chosen as monomers for the synthesis of Tris polymers. Notice that the two differ in the spacer length between the methacrylate and Tris groups. Previous work has indicated that spacer length between Tris and silica is important for the wettability of Tris monolayers.
To simplify the system, methyl methacrylate (MMA) was chosen as the comonomer for this work. We then spin-coated these polymers onto silicon wafers and annealed them so as to reconstruct the surface to bring the Tris to the surface (being the lowest energy constituent). The kinetics of this reorganization are unknown, so a variety of annealing temperatures and times were employed to determine the best conditions. This was done under vacuum to prevent thermal degradation of the samples. These surfaces were then analyzed using the aforementioned techniques. A homologous series of poly(ethylene glycol)s was used for the larger molar volume probe fluids owing to the solubility of the Tris polymers solubility in aliphatic fluids.

**Figure 3.2** Structures of (a) methacryloxyethyltris(trimethylsiloxy)silane (MMT) and (b) methacryloxypropyltris(trimethylsiloxy)silane (MPT)
3.2.1. Materials and Methods

Methyl methacrylate (MMA), bis(triphenylphosphine)nickel(II) bromide, ethyl 2-bromoiso-butyrurate (2-EiB), benzene, toluene, methanol, silica gel, hexanes, tetrahydrofuran, formamide, hexadecane, ethylene glycol (as well as the di-, tri-, tetra-, penta-, hexamers), and 2,2′-azobis(isobutyronitrile) (AIBN) were obtained from Sigma-Aldrich. Methacryloxy methyltris(trimethylsiloxy)silane (MMT) and methacryloxypropyltris(trimethylsiloxy)silane (MPT) were purchased from Gelest Inc. Monomers were distilled prior to use.

Copolymers of MMT and MPT with MMA were prepared using standard free radical polymerization techniques. In a typical random polymerization, all reagents and the reaction flask were first purged with nitrogen. Various ratios of MMA to Tris monomers (100/0, 90/10, 75/25, 50/50, 25/75, 10/90, 0/100) for a total volume of 1 mL were syringed through a septum into a 10 mL round-bottomed flask with a stopcock top and Teflon stir bar. For 100/0, 90/10, 75/25, and 50/50 (MMA/Tris monomer) 1.5 mL toluene was then added. For the others 0.588 mL toluene was added. 0.13 mL of AIBN initiator dissolved in toluene (0.5 wt% AIBN solution) was then added and the solution was mixed. The vessel was placed in an oil bath and heated at 85 °C for four hours. The polymer was then precipitated in methanol, filtered, and collected.

Various feed ratios were used resulting in number average molecular weights around 100,000 and polydispersity indeces between 1.5 and 2.0. A few interesting observations of the polymerizations and products deserve note: (1) The Tris containing polymers are surface active and form soap-like bubbles in solvents (THF, toluene) under
relatively dilute conditions (<2mg/mL). This is not surprising owing to the low surface energy of the Tris group, but the intensity of the effect was unexpected. (2) The higher the Tris concentration of the polymer, the more difficult it is to remove the toluene solvent. This presented problems upon workup as the polymers precipitated into gummy deposits swollen with solvent. (3) The yields of the reaction were inverse with MMT or MPT feed concentration. In order to increase yields of high Tris incorporations, monomer concentration was increased (added toluene diluent was decreased from 1.5 mL to 0.588 mL). (4) Tris is a very effective solubilizing agent. Higher incorporations are soluble in a variety of non-solvents for PMMA.

3.2.2. Characterization

Samples were spin-coated onto silicon wafers at 3000 rpm with 2.5 % solutions in toluene. All annealing was performed in vacuo for 24 hours at 150 °C. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer - Physical Electronics 5100 spectrometer with Al Kα excitation (15 kV, 400 W) at a take-off angle of 75° (between the plane of the sample surface and the entrance lens of the detector optics). Atomic concentration data were determined using sensitivity factors obtained from samples of known composition: C₁s, 0.200; O₁s, 0.501; N₁s, 0.352; F₁s, 1.00. Contact angle measurements were made with a Ramé-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Dynamic advancing (θA) and receding angles (θR) were recorded while the probe fluid was added to and withdrawn from the drop, respectively. Molecular weight distribution was analyzed by gel permeation
chromatography using Polymer Laboratories PL gel columns (10^4, 10^3, 10^2 Å), a Polymer Laboratories LC 1120 HPLC pump with THF as the mobile phase, and a Waters differential refractometer as the detector. The instrument was calibrated using polystyrene standards. NMR was performed on a Bruker Spectrospin (300MHz) in deuterated chloroform. To determine the actual percentage of Tris monomer in the copolymer, proton NMR was used. Sample spectra are given in Figure 3.3. Using the Si-CH₃ groups as an indicator for Tris, the percentage incorporation of Tris monomer was determined by comparing integration values (Table 3.1) to the values of the C-CH₃ of the backbone methacrylate. This was plotted versus the feed percentage (Figure 3.3).

**Figure 3.3** ¹H-NMR spectra of (a) PMMA, (b) PMMT, and (c) PMPT
Table 3.1  $^1$H-NMR peak integration values for MMT and MPT random copolymers with MMA

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>O-CH$_3$, O-CH$_2$</th>
<th>C-CH$_3$</th>
<th>Si-CH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>1.0000</td>
<td>0.9463</td>
<td>--</td>
</tr>
<tr>
<td>90/10 MMA/MPT</td>
<td>1.0000</td>
<td>0.9748</td>
<td>0.1810</td>
</tr>
<tr>
<td>75/25 MMA/MPT</td>
<td>1.0000</td>
<td>0.9798</td>
<td>0.5543</td>
</tr>
<tr>
<td>50/50 MMA/MPT</td>
<td>1.0000</td>
<td>1.0290</td>
<td>1.4749</td>
</tr>
<tr>
<td>25/75 MMA/MPT</td>
<td>0.9899</td>
<td>1.0959</td>
<td>4.1080</td>
</tr>
<tr>
<td>10/90 MMA/MPT</td>
<td>1.0000</td>
<td>1.2530</td>
<td>8.2363</td>
</tr>
<tr>
<td>PMPT</td>
<td>1.0000</td>
<td>1.7330</td>
<td>19.097</td>
</tr>
<tr>
<td>90/10 MMA/MMT</td>
<td>1.0000</td>
<td>0.9601</td>
<td>0.1412</td>
</tr>
<tr>
<td>75/25 MMA/MMT</td>
<td>1.0000</td>
<td>1.0152</td>
<td>0.4833</td>
</tr>
<tr>
<td>50/50 MMA/MMT</td>
<td>1.0000</td>
<td>1.0499</td>
<td>1.3250</td>
</tr>
<tr>
<td>25/75 MMA/MMT</td>
<td>1.0000</td>
<td>0.9255</td>
<td>3.1310</td>
</tr>
<tr>
<td>10/90 MMA/MMT</td>
<td>1.0000</td>
<td>1.1985</td>
<td>6.4084</td>
</tr>
<tr>
<td>PMMT</td>
<td>1.0000</td>
<td>1.4110</td>
<td>13.361</td>
</tr>
</tbody>
</table>

Although the Tris incorporation is very close to the feed percentage (Figure 3.4), one does notice an inhibited uptake of Tris monomer into the copolymer. This is likely due to the steric interference of the Tris group, since substitution at the ester group is too far away from the reaction center to influence the electron density enough to significantly change the chemistry. Using these data, it is possible to calculate reactivity ratios for this reaction. They are not in any way meant to be rigorous statistical quantities, but only for representative purposes. Mathematical definitions of reactivity ratios are given by:
\[ r_1 = \frac{k_{11}}{k_{12}} ; r_2 = \frac{k_{22}}{k_{21}} \]

\( r_1 \) and \( r_2 \) are the reactivity ratios for monomers 1 and 2 respectively and \( k_{xy} \) is the rate of the reaction in which an x chain end reacts with y monomer. If the product \( r_1 r_2 \) is unity, then the copolymer is statistically random. The analysis was performed by a method described by Kelen and Tudos. The reactivity ratios for the MMT reaction were calculated to be 0.73 and 1.7 for MMT and MMA respectively. For the MPT synthesis similar values of 0.80 and 1.6 for MPT and MMA were calculated. We can easily see that the polymer has an inhibited uptake of the Tris monomer, yet the polymerization does indeed have a tendency towards randomness with \( r_1 r_2 \) values of 1.2.

**Figure 3.4** Tris monomer incorporation as a function of feed percentage as determined by NMR for free-radical polymerization in toluene (MMA comonomer)
3.2.3. Surface Reorganization

After purification, the polymers were dissolved in toluene (2.5%) and spin-coated (3000 rpm) onto single crystal silicon wafers (110 crystal plane). This gives an approximate thickness of 1000 Å. Subsequent to coating, the samples were annealed in vacuo at 150 °C for 24 hours. XPS was performed (Figure 3.5) to determine surface enrichment and reconstruction of Tris upon annealing. The angle-dependent silicon concentration is apparent for all samples. This is indicative of greater Tris aggregation at the surface due to its lower surface energy. What should also be noticed is that the degree of enrichment at the surface lessens as the bulk percentage of Tris is increased. This is a consequence of the higher bulk percentage driving the high angle values up. Similar behavior was observed without annealing, although the effect was slightly less. Annealing at higher temperatures or longer times showed no improvement.
Figure 3.5  XPS take-off angle dependence of silicon atomic concentration for various Tris monomer incorporations of (a) MMT and (b) MPT random copolymers after spin-coating and annealing; Lines are merely to aid the eye.
Dynamic contact angle analysis was performed upon the annealed samples with a variety of probe fluids to analyze wettability. Figure 3.6 shows the water contact angle data. As is obvious, only very modest amounts of Tris in the random copolymer are needed to elicit a drastic change in the surface energy of the sample. Just 1.6% Tris is needed to raise the advancing angle 20° (from 72° to 92°). At 13% the surface is nearing the homopolymer value of 107°. Although these data are only shown for MMT polymers, MPT polymers show similar behavior with the following caveat – high percentage (>13%) MPT polymers did not spin sufficiently well to obtain good data. The surfaces were rough and had visible defects that were unavoidable.

![Graph](image)

**Figure 3.6** Dynamic water contact angle of MMT random copolymers as a function of Tris incorporation after spin-coating and annealing.
3.2.4. Probe Fluid Size-Dependent Contact Angle

Contact angle hysteresis plotted versus the molar volume (density/molecular weight) of the probe fluids is shown in Figure 3.7. Many fluids (i.e. aliphatics) could not be used due to the solubility of Tris-containing polymers in these fluids. Instead a homologous series of glycols (from ethylene glycol to hexaethylene glycol) was used as a range of fluids with various molar volumes. Upon addition of Tris to the polymers, the hysteresis gains two transitions (at low and at high molar volume) as opposed to the flat high hysteresis PMMA. All Tris polymers except for PMMT start out at \( \sim 15^\circ \) hysteresis (the same value as PMMA) and drop to an intermediate value at about 80 cm\(^3\)/mole. The hysteresis then seems to drop at about 250 cm\(^3\)/mole, although this becomes less prominent as Tris incorporations increase, because of the lower intermediate value of the hysteresis. The Tris homopolymer undergoes only the first transition.

![Figure 3.7](image)

**Figure 3.7** Probe fluid size-dependent contact angle for various Tris monomer incorporations of random copolymers after spin-coating and annealing: (a) PMMA, (b) 1.6\% MPT, (c) 5.1\% MPT, (d) 13.0\% MPT, (e) 1.6\% MMT, (f) 5.0\% MMT, (g) 13.3\% MMT, (h) 35.7\% MMT, (i) 56.5\% MMT, (j) PMMT (100\%)
Figure 3.7 Continued

Continued next page
3.3. Block Copolymers

The previously described work with random copolymers indicated that pure Tris polymers have the lowest overall contact angle hysteresis. In an effort to create surfaces with this behavior (and without the solubility problems inherent in high Tris polymers) block copolymers of MMT and MMA were synthesized. Due to the siloxane moiety (end-capping of the anion), traditional synthesis by anionic polymerization cannot be done. This leaves more cutting edge techniques such as living free radical and group transfer polymerizations (GTP).\(^3\) Although much effort has been devoted to it, there has been no successful polymerization of methacrylates by nitroxide mediated free radical reactions. Atom transfer radical polymerization (ATRP)\(^{32,36}\) does work, however. This technique was chosen over GTP because of the ease of use and typical product molecular weights (although both are low, GTP is typically more so).
3.3.1. Atom Transfer Radical Polymerization (ATRP)

The synthetic technique chosen to prepare these block copolymers was by a living radical polymerization known as atom transfer radical polymerization (ATRP). Here, a radical is produced by thermal homolysis of the initiator. In this case it is a carbon-halogen bond. A metal “catalyst” is added to complex the halide radical, thus extending the lifetime of the initiating radical. Otherwise, the bond will exist primarily as the covalent bond and the radical concentration will be so low that it does not start the polymerization. Even so, the radical concentration is so low that there is very little chain termination or chain transfer. Multiple reaction systems are known, but a nickel catalyst system without any Lewis acid was chosen because of the ease of use. Figure 3.8 shows a schematic of the reaction. The actual mechanism of metal-halide complexation is unknown.

![Reaction pathway schematic for ATRP](image.png)
3.3.2. Materials and Methods

Methyl methacrylate (MMA), bis(triphenylphosphine)nickel(II) bromide, ethyl 2-bromoiso-butyrate (2-EiB), benzene, toluene, methanol, silica gel, hexanes, tetrahydrofuran, formamide, hexadecane, ethylene glycol (as well as the di-, tri-, tetra-, penta-, and hexamers), and 2,2'-azobis(isobutyronitrile) (AIBN) were obtained from Sigma-Aldrich. Methacryloxymethyltris(trimethylsiloxy)silane (MMT) and methacryloxypropyltris(trimethylsiloxy)silane (MPT) were purchased from Gelest Inc. Monomers were distilled prior to use.

The block copolymers were synthesized using the same glassware that were used for the random copolymer polymerizations. The Tris-containing monomer was syringed into a purged vessel. Diluent benzene was then added. Nickel bromide catalyst (2.0 wt% in benzene) was then syringed in followed by an equal amount of 2.0 wt% ethyl 2-bromoiso-butyrate initiator dissolved in benzene. The mixture was then placed in an oil bath at 85 °C for 5 days at which point an aliquot was taken for GPC. MMA was added along with another charge of catalyst solution equal to the first. The MMA was allowed to react overnight. The solution was precipitated in methanol, filtered, and collected. The exact concentrations of monomers were experimented with to attain the desired polymers. Successful block polymerizations were at the following amounts: for the 96/4 MMA/MMT copolymer 0.5 mL MMT, 0.5 mL initiator and catalyst solutions, 0 mL benzene, and 5.0 mL MMA; for the 75/25 MMA/MMT copolymer 1 mL MMT, 0.36 mL initiator and catalyst solutions, 0 mL benzene, and 1mL MMA; for the 55/44...
MMA/MMT copolymer 1mL MMT, 0.09 mL initiator and catalyst solutions, 0.22 mL benzene, and 1.5 mL MMA.

A few notes on the polymerization are warranted. The copolymers were prepared by sequential monomer addition, as the molecular weights are too high to use a halogenated polymer as the initiator. Also, it was found that PMMA is not soluble in the Tris monomer and thus cannot be the first polymer block synthesized. Tris monomer was added first and after sufficient conversion (as determined by GPC), MMA was added. The reaction kinetics were determined and are plotted in Figure 3.9; these indicate that the rate of MMA polymerization is much faster than the MMT polymerization and both are faster than MPT polymerization. Although the chain termination is small, it is present. Therefore, slow reaction rates dictated that MMT homopolymer was present in large quantities in these samples and had to be removed. The MPT block copolymer synthesis was not successful due to the chain termination. From the kinetics data, it was decided to allow MMT to react for 5 days before MMA was added and the reaction was quenched 1 day later.
Figure 3.9  Reaction kinetics of MMA, MMT, and MPT polymerizations by NiBr$_2$(PPh$_3$)$_2$ catalyzed ATRP; reaction temperature = 85°, NiBr$_2$(PPh$_3$)$_2$ = 0.2%, 2-EiB= 0.2%, $M_c$ = 60% in benzene

3.3.3. Purification

As was mentioned previously, there are significant quantities of homopolymer in the samples that have to be removed. This presents difficulties since the Tris group is an effective solubilizer. Very little of the Tris moiety is needed in the polymer to render the same solvent/non-solvent behavior as pure Tris homopolymer. Only the 96/4 di-block had enough differences to be purified by solubility. It was dissolved in THF, precipitated in acetic acid, filtered, and recovered. The other two samples were purified by flash chromatography on a 300A silica gel column with hexane as the eluent. Figure 3.10
shows GPC traces of as prepared di-block and the purified di-block. Three copolymers were prepared: 95/5, 75/25, 56/44 (MMA/MMT) by NMR (integrations are given in Table 3.2). Molecular weights were determined by GPC (relative to styrene) and are: (M_n) 92K, 54K, and 91K for the 96/4, 75/25, 56/44 copolymers. Polydispersities were around 1.5 after purification.

Figure 3.10  GPC's of block copolymers before (top) and after (bottom) purification for (a) 96/4 MMA/MMT, (b) 75/25 MMA/MMT, and (c) 56/44 MMA/MMT
Table 3.2  $^1$H-NMR peak integration tables for MMT block copolymers with MMA

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>O-CH$_3$, O-CH$_2$</th>
<th>C-CH$_3$</th>
<th>Si-CH$_3$</th>
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</thead>
<tbody>
<tr>
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<td>0.9688</td>
<td>0.3936</td>
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<tr>
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<td>1.0000</td>
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<td>1.0000</td>
<td>1.1700</td>
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</tbody>
</table>

3.3.4. Characterization

Samples were spin-coated onto silicon wafers at 3000 rpm with 2.5% solutions in toluene. All annealing was performed in vacuo for 24 hours at 150 °C. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer - Physical Electronics 5100 spectrometer with Al K$_{\alpha}$ excitation (15 kV, 400 W) at a take-off angle of 75° (between the plane of the sample surface and the entrance lens of the detector optics). Atomic concentration data were determined using sensitivity factors obtained from samples of known composition: C$_{1s}$, 0.200; O$_{1s}$, 0.501; N$_{1s}$, 0.352; F$_{1s}$, 1.00. Contact angle measurements were made with a Ramé-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Dynamic advancing ($\theta_A$) and receding angles ($\theta_R$) were recorded while the probe fluid was added to and withdrawn from the drop, respectively. Molecular weight distribution was analyzed using a gel permeation chromatograph equipped with Polymer Laboratories PL gel columns (10$^4$, 10$^3$, 10$^2$ Å), a Polymer Laboratories LC 1120 HPLC pump with THF as the mobile phase, and a Waters differential refractometer as the detector. The instrument was calibrated using polystyrene standards. NMR was performed on a Bruker Spectrospin (300MHz) in
deuterated chloroform. Atomic force microscopy (AFM) was performed in air using a Digital Instruments Nanoscope IIIa AFM in tapping mode on cryo-microtomend polymer samples embedded in epoxy. This was necessary as the pure block copolymers are too brittle to cut by themselves.

3.3.5. Morphology

As with any block copolymer, these materials likely have a nano-phase separated structure. In an attempt to characterize this aspect of these copolymers, atomic force microscopy (AFM) was performed. In many cases the phase structure is visible in this way. Figure 3.11 shows the AFM micrographs. Height images appear on the left and phase images on the right. The contrast of the structures is very low and so the tapping was varied to maximize contrast. This is the origin of the streaking in the pictures shown. In general, very little information is visible in the phase images. The height images possibly have some interesting features. Due to the low contrast, confidence is low in any statements made based on these data, but on the first set of images (96/4 copolymer), one can see what appear to be pits in the surface. The phase image has a corresponding peak indicating a modulus difference. These “pits” are the right size for spherical domains. This is not surprising as the 96:4 ratio copolymer should exhibit a spherical morphology. The next pictures correspond to the 75/25 copolymer. These pictures have very little visible. The last pictures (56/44 copolymer) have what can be called “worm-like” structures in the height image (nothing appears in the phase image). These features could possibly be cylinders or lamellae. Typically a 56/44 copolymer should be
considered lamellar, although this is dependent upon interfacial energies, compressibilities, and polymer stiffness’. It is unknown how these factors contribute to the Tris copolymers. There is, however, a large difference in the surface energies between PMMA and PMMT. TEM was performed to confirm the results, but satisfactory images were not attainable due to the brittleness of the polymers.

Figure 3.11 AFM of MMT block copolymers after spin-coating and annealing: (a) 96/4, (b) 75/25, and (c) 56/44. Images on the left are height and on the right are phase
3.3.6. Surface Reorganization

Surface properties of the MMT di-blocks were examined as in the random copolymer work and were prepared as before by spin-coating and vacuum annealing. Additional samples were prepared by blending the di-blocks with PMMA (di-block/PMMA: 10/90) in order to stabilize the samples toward solvents of Tris. XPS was performed on the surfaces and data are plotted versus take-off angle in Figure 3.12. One should immediately notice the difference between this graph and the previous XPS data (Figure 3.5). At high Tris block length there is almost no angular dependence, much as in the pure MMT homopolymer. As the effective Tris amount decreases, there is a rise in angular dependence indicating greater surface segregation. All curves seem to have about the same intercept at zero. The reason for these facts is quite obvious when one remembers the blocky nature of the samples. If the MMT block is at the surface (as is likely the case due to the lower surface energy), then as the block size decreases this layer
will be thinner and fewer photoelectrons will be coming from it. Blending has a similar effect in that more PMMA enables fewer di-block chains to occupy the surface and thus decreases the PMMT layer.

![Graph showing XPS take-off angle dependence of silicon atomic concentration for block copolymers and block copolymer/PMMA blends (10/90); Lines are merely to aid the eye.](image)

**Figure 3.12** XPS take-off angle dependence of silicon atomic concentration for block copolymers and block copolymer/PMMA blends (10/90); Lines are merely to aid the eye.

3.3.7. Probe Fluid Size Dependant Contact Angle

Contact angle measurements were performed on the di-blocks as well as their blends. In all cases except the 96/4 blend, advancing water contact angles had the same value as pure MMT homopolymer (107°), but the receding angles were less (97°) resulting in overall greater hysteresis. The 96/4 blend showed contact angle values of 103/91 (adv/rec). These lower values are probably due to insufficient Tris in the sample.
to cover the surface. Plots were made of the hysteresis versus the molar volume as before, and shapes nearly identical to pure PMMT were obtained for all samples other than the 96/4 blend. The overall hysteresis is higher, however and is probably due to a greater roughness of the samples. Graphs are given in Figure 3.13. The 96/4 blend showed anomalous behavior as it had a high hysteresis for all molar volumes and has high point dispersity. An aliphatic contact angle probe fluid (hexadecane) was attempted on all samples (it dissolved the 56/44 di-block sample) and is included as the last point on the graphs. Low hysteresis was not attained, due to a strong interaction with the Tris polymer surface.

![Graphs showing hysteresis versus molar volume](image)

**Figure 3.13** Probe fluid size dependant contact angles for block copolymers (left) and block copolymer/PMMA (10/90) blend (right): (a) 95/5 MMA/MMT, (b) 75/25 MMA/MMT, and (c) 56/44 MMA/MMT; Open circles are hexadecane data

Continued next page
3.4. **Explanation**

A short discussion is warranted to describe the molar volume-dependent hysteresis shown. As previously stated, a possible reason for molar volume-dependent contact angle behavior is nanoporosity of certain surfaces. This allows for a fluid to
“see” different surfaces depending on the fluid size. As is known, heterogeneity creates higher hysteresis.\textsuperscript{3,5,37-38} In our case, this can also be true. Instead of a Tris monolayer on silica however, we have a complex system of many possible components at the surface. Looking at the molar volume vs. hysteresis plots for the random copolymer (Figure 3.7), one notices that there seems to be two transitions and not one as in the Tris on silica case. Thinking again in terms of nanoporosity, an explanation can be given. Just as in Tris on a silicon wafer,\textsuperscript{23} the Tris layer must have holes due to exclusion. Our data suggests that the holes are larger (~250 cm\textsuperscript{3}/mole as opposed to ~175 cm\textsuperscript{3}/mole), possibly due to connectivity constraints. The interior of these holes should follow the same rules for surface energetics as any surfaces do. This means that the holes will try to fill with the lowest energy groups that will fit. In our case these are methyl groups. These methyl units are the origin of the low molar volume transition. Any group small enough to fit in between them will be “seeing” a ternary system that has high heterogeneity and thus high hysteresis. This is much like the Tris nanoporous surfaces filled with trimethylsilane previously reported (Figure 3.14).\textsuperscript{23} In fact, both have their transitions at approximately the same molar volume (<100 cm\textsuperscript{3}/mole). In our case we also have a loss of the high molar volume transition as the incorporation of Tris is increased. This could be due to a loss of heterogeneity. There are many methyl groups in the sample, but only those that are different from the Tris methyls (those that contribute to heterogeneity) will contribute to hysteresis. As more Tris is incorporated, the likelihood of the underlying methyls being from Tris increases, and so the difference between intermediate and low hysteresis decreases. The block copolymers also act in this
way. The blocky nature dictates that the surface act as a MMT homopolymer surface, which has only one transition region (<100 cm$^3$/mole) due to aforementioned reasons.

Figure 3.14 Pictorial representation of the copolymer surface

3.5. Summary

Copolymers of methacryloxyethyltris(trimethylsiloxy)silane (MMT) or methacryloxypropyltris(trimethylsiloxy)silane (MPT) and MMA were prepared by radical polymerization and ATRP. Reactivity ratios were calculated for the radical polymerization indicating randomness and slightly inhibited uptake of the Tris monomer. Slow reaction kinetics for the ATRP reactions prevented MPT block copolymerization, although MMT was successful yielding high polymer ($M_n = 50,000-90,000$). Further purification was necessary due to chain termination and was carried out. Significant surface-active rearrangement (Tris at surface) that decreases with Tris incorporation for
all polymers is observed. Low amounts of Tris hydrophobized the random copolymer surfaces, but only at high incorporation was hysteresis reduced. Molar volume-dependent contact angle analysis indicates two transitions in the hysteresis indicating nanoporosity of two different sizes. The second transition (high molar volume) decreases in intensity and eventually disappears as Tris incorporation increases, presumably due to a loss in heterogeneity. Contact angle data for the block copolymers were similar to MMT homopolymer, although the 96/4 di-block blended with PMMA showed high hysteresis, energy, and dispersity.
CHAPTER 4

SURFACE MODIFICATION OF POLYMERS WITH 3-AMINOPROPYLTRIETHOXYSILANE FOR CONTROLLED WETTABILITY

4.1. 3-Aminopropyltriethoxysilane (APTES)

A number of synthetic routes to chemically modified polymer surfaces have previously been developed. The approach has, in general, been to introduce covalently attached functional groups (e.g. alcohol) that can then be derivatized through well-controlled chemical reactions. Chemically resistant polymers such as poly(tetrafluoroethylene), polypropylene, poly(chlorotrifluoroethylene), and poly(ether ether ketone) have a number of advantages for doing surface chemistry, in particular, they act as inert supports for harsh chemical reactions.

Similar modifications on more reactive polymers is of interest, but is often more difficult as conditions that only affect the desired functionality, not the rest of the polymer chain are desired. Our group has previous experience in modifying poly(ethylene terephthalate) (PET) to improve the low surface energy that limits its use in many applications. PET glycolysis and reduction (Figure 4.1) were done to prepare surfaces with alcohol functionality. Both of these methods have inherent problems that limit their usefulness. The most limiting aspect of these methods is that they both cause chain cleavage such that functionalization must be balanced versus polymer degradation.
Other methods of modifying PET using ester chemistry have been reported of late including plasma treatment,\textsuperscript{50} graft polymerization,\textsuperscript{51} and activation with $p$-toluenesulfonyl chloride.\textsuperscript{52,53} The most interesting of these (in the context of our work) is that Thompson et al.\textsuperscript{54} who showed that the reaction of PET with 3-aminopropyltriethoxysilane (APTES) proceeds to a cross-linked siloxane network with a thickness larger than the X-ray photoelectron sampling depth. Unlike previous attempts to selectively modify its surface, the PET showed no degradation. Thompson suggested that the method of modification that happens is the formation of an amide bond between the PET and APTES. The insertion of APTES into the PET chain (Figure 4.2) was proposed where nucleophilic attack of the APTES amine on the carbonyl breaks the ester bond forming the amide with the resultant alcohol reacting with the silicon-oxygen bond.
Based on Thompson’s work, Fadeev and McCarthy\textsuperscript{55} furthered understanding of the reaction mechanism. Based on XPS data they proposed a similar insertion mechanism, but instead, argued intuitively that PET chain loops would be reacting with two APTES molecules (Figure 4.3). Using this method, surfaces with silica-like reactivity were prepared. Reactive silanol functionality was introduced to the surface of PET by subsequently hydrolyzing the APTES modified film. This silanol surface was shown to be reactive to various chlorosilanes while polycondensation of tetraethoxysilane (TEOS) on these silanol surfaces produced ultrathin silica films. These surfaces, as well, were reactive towards chlorosilanes. Thus, they produced a general method for surface modification of PET with the techniques demonstrated for silica surfaces.

**Figure 4.2** Thompson’s reaction scheme of APTES with an ester surface\textsuperscript{54}

**Figure 4.3** Resultant polymers by the modified chain insertion mechanism from McCarthy and Fadeev\textsuperscript{55}
4.2. APTES Surface Chemistry

As much as this chemistry on PET is laudable, it would be advantageous for many other substrates to have corresponding surface-selective chemical modification to help ease their use in a variety of fields. Such polymers as poly(butylene terephthalate), poly(ethylene naphthalenate), and poly(1,4-cyclohexanedicarboxylate-co-ethylene terephthalate), which is known as Kodak film and Kodel fiber, are either used or are thought to be heavily favored for industrial use. These polymers, being esters analogous to PET, are prime candidates for APTES modification. Modification of other polymers such as poly(methyl methacrylate) and poly(bisphenol-A carbonate) would also be valuable, but may not be able to undergo APTES modification for surface selective chemistry due to their structural differences from PET.

4.2.1. Materials and Methods

PET film (Mylar) was obtained from DuPont and was cleaned by rinsing with toluene and distilled water. Toluene, hexane, chloroform, ethanol, tetrahydrofuran, formamide, 1-octanol, carbon tetrachloride, dichloroacetic acid, and diethyl ether were all purchased from Aldrich and were anhydrous grade solvents (used as received). Polymers were also purchased from Sigma-Aldrich and were granular or pelletized. Poly(ethylene terephthalate), poly(ethylene naphthalenate), poly(butylene terephthalate), poly(1,4-cyclohexanedicarboxylate-co-ethylene terephthalate), poly(bisphenol-A carbonate), poly(methyl methacrylate), polystyrene, cellulose acetate, poly(vinyl
alcohol), poly(allyl amine) and nylon 6,6 were purchased (Aldrich) and used. Kapton polyimide was obtained from Dupont. Polytetrafluoroethylene was obtained from Berghoff America. Reagents used were 3-aminopropyltriethoxysilane (APTES), 3-aminopropylmethyldiethoxysilane (APMDS), and 3-aminopropyldimethylethoxysilane (APDES). They were also purchased from Sigma-Aldrich and used as received.

Samples were spin-coated onto silicon wafers at 2000 rpm using 2.5% solutions. All annealing was performed in vacuo for 24 hours at 150 °C. Solutions were prepared in dichloroacetic acid for polyesters and nylon 6,6, chloroform for poly(bisphenol-A carbonate), toluene for polystyrene and poly(methyl methacrylate), and in water for poly(vinyl alcohol) and cellulose acetate. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer - Physical Electronics 5100 spectrometer with Al Kα excitation (15 kV, 400 W) at a take-off angle of 75° (between the plane of the sample surface and the entrance lens of the detector optics). Atomic concentration data were determined using sensitivity factors obtained from samples of known composition: C_{1s}, 0.200; O_{1s}, 0.501; N_{1s}, 0.352; F_{1s}, 1.00. Contact angle measurements were made with a Ramé-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Dynamic advancing (θ_A) and receding angles (θ_R) were recorded while the probe fluid was added to and withdrawn from the drop, respectively.

APTES, APDES, or APMDS (0.3 mL unless otherwise indicated) was syringed into a flask containing 30 mL of toluene (or other solvent such as hexane). The flask was previously purged with nitrogen and all transfers were done under nitrogen. The flask contained up to seven samples in a custom holder and a Teflon stirbar. The reaction mixture was heated (75 °C unless noted otherwise) in an oil bath for the specified time
(72 hours unless noted otherwise) and then taken out. The samples were washed with copious amounts of flowing toluene and then dried at reduced pressure. Samples to be hydrolyzed were immersed in 30 mL of H₂O with a catalytic amount of HCl for 24 hours, washed with copious amounts of flowing water and dried at reduced pressure.

4.2.2. Effects of Temperature and Concentration on APTES reactions

Before looking at the reactive behavior of polymer surfaces with APTES, optimizing the reaction conditions with PET was carried out. Using the known reaction of PET with APTES in toluene, the variability of reaction with temperature and APTES concentration were studied. Figure 4.4 shows the increase of silicon and nitrogen atomic concentration on the surface as reaction temperature increases from −20 °C to 75 °C. There seems to be a linear relationship between the APTES modification and temperature. As 75 °C was the temperature of the previous work by Fadeev and McCarthy, it was chosen as the standard for our reactions. Unless noted otherwise, all further APTES modifications were carried out at this temperature
The effect of concentration is profound in this reaction. Looking at Figures 4.5 and 4.6, one notices the increase concentration in both the silicon and nitrogen atomic concentrations with APTES concentration. This is, of course, expected and differs little from most reactions. At 1%, however, there is a maximum and the amount of APTES on the surface decreases above this concentration. This is unexpected, but easily explained. The first possible reason is that as the amount of APTES increases, there is not enough water in the mixture to promote siloxy-bond formation at the surface. Water is required for the reaction, so dehydration of the surface by the APTES is detrimental to the reaction. Another explanation is that as the amount of APTES increases beyond 1%, it
becomes a greater portion of the solvent and in this fashion may have a deleterious effect. After 10%, the two curves diverge with silicon increasing and nitrogen decreasing to the control sample (0.00%). Reasons for this behavior are not clear, but may have to do with polymer degradation by the APTES. Amines are known to degrade PET. This could provide for a surface enrichment of the silica filler (thereby raising silicon concentration) without any APTES reaction with the surface (near-zero nitrogen concentration).

![Figure 4.5](image-url)

**Figure 4.5** 75° take-off angle silicon and nitrogen atomic concentration XPS results of the effect of reagent concentration on APTES surface modification of PET; reaction temperature = 75 °C, 72h in toluene
4.2.3. Effects of Substrate and Solvent on APTES Reactions

As the stated purpose of this work is to expand this technique to other ester substrates, APTES surface modification was performed on a variety of substrates. The spincoated samples were reacted at 75 °C and 1.0% concentration in toluene for 72 hours, unless noted otherwise. Table 4.1 gives XPS results for all substrates tested. Initially, only main-chain and side chain polyesters were tested: PET, poly(ethylene naphthalenate), poly(butyleneterephthalate), poly(1,4-cyclohexanediyl terephthalate-co-ethylene terephthalate), poly(methyl methacrylate), and cellulose...
acetate. As poly(methyl methacrylate) is soluble in toluene, the alternative medium of hexane was used. The use of alternative solvents is explored more in depth later in this section. From the amount of silicon and nitrogen observed on the surfaces, all were reactive towards APTES modification. Samples all have approximately 10-12% silicon atomic concentration and 9-11% nitrogen concentration with little difference between 15° and 75° take-off angle data. This indicates a thick multilayer of tens of Å or more. There seems to be no difference between the main-chain and side-chain esters. This is surprising as the McCarthy and Fadeev\textsuperscript{55} reaction scheme dictates this would form a C-O-Si bond for cellulose acetate, which is easily cleaved by water.

Substrates containing ester-analogs were also investigated, such as carbonate, acid, amide, and imide. Poly(bisphenol-A carbonate), poly(methacrylic acid), nylon 6,6, and Kapton polyimide were analyzed after attempted APTES surface modification. Looking at Table 4.1, notice that these polymers were successfully modified. The silicon and nitrogen atomic concentrations fall within the same range that the esters do. Although success with poly(methacrylic acid) is not unexpected, it is very surprising for all three of the others to be successfully modified as their reactions are equal to or uphill in energy with respect to their current states. For example, imides are notoriously stable materials. For this material to revert to the amic acid in order to form an amide with the APTES molecule is unheard of. This means either the experiment is flawed or that the reaction mechanism proposed by Thompson and subsequently by Fadeev and McCarthy is suspect. To confirm the experimental protocol, controls were performed with substrates that should have no possible mode of interaction. Poly(styrene) and poly(tetrafluoroethylene) were analyzed for APTES modification and, in fact, do not
have any interaction with APTES. Silicon and nitrogen atomic concentrations of less than 1% were observed after reaction (Table 4.1).

The last substrates tested were poly(vinyl alcohol) and poly(allyl amine). These polymers are dissimilar from those with ester functionality, other than being polar. They, too, were successfully modified, as evidenced by the silicon and nitrogen atomic concentrations observed. The ability of these various polymer substrates to enable APTES surface modification is curious and provides evidence that the reaction schemes of Thompson$^{54}$ and Fadeev-McCarthy$^{55}$ are suspect.

Samples were hydrolyzed in water with catalytic HCl for 24 hours after reaction to introduce silanol functionality that is reactive toward chlorosilanes. After hydrolysis, water contact angles on all successfully modified ester samples and nylon 66 were approximately 57/0 (advancing / receding) (except poly(1,4-cyclohexanedimethylene terephthalate-co-ethylene terephthalate) which was 77/0) indicating a relatively large amount of silanol functionality and similar surfaces on all samples. Poly(methyl methacrylate) and poly(bisphenol-A carbonate) had contact angles somewhat higher (75/30) possibly due to hexane being a poorer solvent than toluene for this reaction. Hydrolysis of non-reactive substrates leaves them marginally changed and hydrolysis of poly(methacrylic acid), poly(vinyl alcohol), cellulose acetate, and poly(allyl amine) were not done, as they are soluble in water.
Table 4.1  75° take-off angle silicon and nitrogen atomic concentration XPS results of APTES reaction on various polymer surfaces; reaction temperature = 75° (or refluxing), APTES = 1.0%, 72h

<table>
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<th>Polymer</th>
<th>Solvent</th>
<th>%Si</th>
<th>%N</th>
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</tbody>
</table>

APTES modifications of PET were carried out in alternative reaction media to determine if these changes would have any effect on the reaction. Results are given in Table 4.2. As with reactions in toluene, APTES modifications in other non-polar solvents such as hexane and carbon tetrachloride work well as evidenced by the silicon and nitrogen atomic concentrations. Even with ether solvents such as tetrahydrofuran
and diethyl ether, the surface modifications work well. However, formamide and ethyl alcohol inhibit surface reaction. The silicon and nitrogen atomic concentrations were lower relative to the other solvents and only showed from 1.5% to 4% on the surface. It is not likely that the hindered reaction is resulting from just solvent quality and polarity changes as reactions carried out in 1-octanol are similarly inhibited.

Table 4.2 75° take-off angle silicon and nitrogen atomic concentration XPS results of APTES reaction in various solvents; reaction temperature = 75° (or refluxing), APTES = 1.0%, t = 72h

<table>
<thead>
<tr>
<th>Solvent</th>
<th>%Si</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>11.6</td>
<td>11.1</td>
</tr>
<tr>
<td>hexane</td>
<td>11.5</td>
<td>9.8</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>11.4</td>
<td>10.1</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>12.5</td>
<td>9.0</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>10.4</td>
<td>9.9</td>
</tr>
<tr>
<td>formamide</td>
<td>2.9</td>
<td>3.9</td>
</tr>
<tr>
<td>ethanol</td>
<td>2.8</td>
<td>2.6</td>
</tr>
<tr>
<td>1-octanol</td>
<td>3.3</td>
<td>1.6</td>
</tr>
</tbody>
</table>

4.2.4. Reactions of 3-Aminopropylmethyldiethoxysilane (APMDS) and 3-Aminopropyltrimethylethoxysilane (APDES) with PET

With the intention of gathering more evidence to disprove the currently held hypotheses, surface modifications of PET were performed with reagents where the reactive ethoxy functionality of the APTES molecule was replaced with non-reactive
methyl groups. Although the ethoxy group is a required element of previous reaction schemes, only one ethoxy is required for the reaction to proceed. Removing excess ethoxy groups from APTES should have little effect until all of them are replaced, as even one ethoxy group should allow the reaction to continue. What actually occurs, however, is completely different (Table 4.3). Replacing just one of the ethoxy groups as in APDMS nearly shuts the reaction down. Silicon and nitrogen atomic concentrations between 2% and 3% were seen. Replacing two ethoxy groups (APDES) results in surfaces nearly the same as those that are unmodified, no reaction occurred as supported by the less than 1% silicon and nitrogen seen by XPS. Again, this is strong evidence that the currently held ideas of APTES modification are incorrect: Amidation is likely not an important feature of the reaction (or the reaction is competitively disfavored).

Table 4.3 75° take-off angle silicon and nitrogen atomic concentration XPS results of PET modified with 3-aminopropyltriethoxysilane (APTES), 3-aminopropyldimethylethoxysilane (APDES); reaction temperature = 75 °C, APTES = 1.0%, 72h in toluene

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Functionality</th>
<th>%Si</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>APTES</td>
<td>(-OEt)_3</td>
<td>11.6</td>
<td>11.1</td>
</tr>
<tr>
<td>APMDS</td>
<td>Me/(-OEt)_2</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>APDES</td>
<td>Me_2/(-OEt)</td>
<td>0.8</td>
<td>0.5</td>
</tr>
</tbody>
</table>
4.2.5. Explanation of Behavior

An explanation of the nature of the APTES surface modification that is consistent with the currently held view of the chain-insertion and amidation of PET cannot be given. Rather, a new scheme is proposed (Figure 4.7). Here, we propose that APTES adsorbs to, and then crosslinks on PET forming a multi-layer siloxane much as in self-assembled monolayers (SAM) of silanes on silica. The first step in this process (a) is the adsorption of APTES to the polymer surface through a hydrogen-bonding interaction to some H-bond acceptor on the surface. What happens next is siloxane bond formation through the ethoxy groups with neighbors H-bonded to the surface as in b, or with free APTES molecules in solution as shown in c. The second step is exactly the same as in SAM's. Notice that perfect registry between the donor amine and the acceptor groups is not required. The inter-APTES reaction to form siloxane cross-links then becomes the driving force of the reaction. Most likely, very few of the APTES molecules are actually H-bonded to the surface. However, the lateral bonds ensure that the layer will not come off. After (or concurrently with) the lateral cross-linking occurs, the layer builds up in thickness to form a thin multilayer as evidenced by the lack of angle dependence of the XPS atomic concentrations.
Figure 4.7  Proposed mechanism of APTES surface modification: a) initial adsorption via hydrogen-bonding, b) and c) subsequent lateral bond formation to the nearest neighbors, and d) multilayer formation

Using this model of APTES modification, previous results can readily be explained. It becomes clear why all of the polymers except polystyrene and poly(tetrafluoroethylene) were heavily modified. All except those two have polar, H-bond accepting groups. This allows for the initial adsorption event of the chain reaction.
Lacking groups such as these, polystyrene and poly(tetrafluoroethylene) did not support the reaction. Solvent may also inhibit the initial interaction. Polar protic solvents such as the three with negative results (formamide, ethanol, and 1-octanol) would interfere with H-bonding and prevent APTES modification. Barring this, varying the medium of reaction should have little effect. Exactly this is observed. The effects of replacing the reagent ethoxy groups are also congruent with our model of the reaction. Lateral bond formation is a necessary event. Interfering with this process would have negative consequences on the reaction. With just two possible linking points, APMDS can at most form linear chains. These would not be as effective as cross-linked networks at anchoring the layer on the surface. When two ethoxy groups are replaced, the APDES layer cannot maintain its integrity at all due to its ability to form only dimers. In short, all of the evidence is inconsistent with the previous held notions of the reaction, but it is consistent with our SAM-like H-bonding / cross-linking model.

4.3. Silane Modification

In order to test the usefulness of the APTES modification technique towards control of the wetting behavior of these various polymer surfaces, covalent attachment of a monochlorosilane on these surfaces was performed. (Tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane was used as it provides an efficient XPS label for subsequent analysis and also provides a highly non-wettable surface. Although better hydrophobization could no doubt be achieved through the use of trichlorosilanes, by using monochlorosilanes one can get an idea of the number and accessibility of silanols
with silica-like reactivity. No other silanes are used as our intent is to characterize the APTES pretreatment and prove its general utility in subsequent modification, not to duplicate previous silanizations with the technique.

4.3.1. Materials and Methods

The flask (previously purged with nitrogen) was loaded with up to seven samples in a custom holder and a Teflon stirbar. Ethyldisopropylamine (0.3 mL) was syringed into a flask containing 20 mL of toluene. Subsequently, 0.5 mL of (tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane was added to the reaction mixture. The reaction was heated for 72 hours at 75 °C in an oil bath and then removed. The samples were washed by immersion in the following order: toluene, toluene/ethanol, ethanol, ethanol/water, water. They were then dried at reduced pressure and characterized. All materials were purchased from Aldrich in the anhydrous form, with the exception of the silane, which was purchased from Gelest.

4.3.2. Results of Modification

After hydrophobization, the polymers were analyzed by XPS. Table 4.4 gives 75° XPS fluorine and nitrogen atomic concentration. It is readily seen that effective fluorination of the surfaces modified with APTES occurs. Esters modified in toluene as well as the nylon 6,6 samples have fluorination values approaching that of the silicon wafer (>40%) while displaying little nitrogen. This indicates all of the APTES has been
covered by the fluorinated silane. Both water and hexadecane contact angles of these esters are also high and approach those of, but are not quite as high as, the modified silicon. APTES treated polyvinyl alcohol was also silanated with mixed results. It must be mentioned first, however, that the sample could not be hydrolyzed as the polymer layer is removed by the water. Although the sample is spectroscopically similar (by XPS) to the afore-mentioned esters, contact the results are different. This is expected with water as the polymer has a specific interaction with the water. For hexadecane, the fluid may be penetrating the surface layer, thereby reaching the polymer underneath and wetting it. This would provide for the lack of dewetting of the hexadecane observed. The other two polymers, poly(methyl methacrylate) and poly(bisphenol-A carbonate), were silanized in hexane due to their solubilities in toluene. The hexane used was an inferior medium for silanization, possibly due to greater amounts of water present. Macroscopic “snowing” was observed in the reaction mixture indicating something amiss. There was fluorination on the surface, however it was much less than on the previous samples. More nitrogen was also observed. Water contact angle shows much higher hysteresis indicating an incomplete layer of silane. Hexadecane also shows higher hysteresis along with lower angles. Again this is indicative of poor surface coverage. This being said, there was a hydrophobization of the surface, although not to the degree of the other surfaces.
Table 4.4 75° take-off angle fluorine and nitrogen atomic concentration XPS results, water contact angle, and hexadecane contact angle of APTES pretreated polymer surfaces silanized with (tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane; ¹non-hydrolyzed, ²APTES modification and silanization done in hexane

<table>
<thead>
<tr>
<th>Polymer</th>
<th>%F</th>
<th>%N</th>
<th>$\theta_A(\circ)/\theta_R(\circ)^{\text{H}_2\text{O}}$</th>
<th>$\theta_A(\circ)/\theta_R(\circ)^{\text{Hex}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(ethylene terephthalate)</td>
<td>40.2</td>
<td>2.1</td>
<td>120 / 86</td>
<td>79 / 47</td>
</tr>
<tr>
<td>poly(ethylene naphthalenate)</td>
<td>43.8</td>
<td>1.2</td>
<td>120 / 90</td>
<td>75 / 44</td>
</tr>
<tr>
<td>poly(butylene terephthalate)</td>
<td>42.7</td>
<td>0.9</td>
<td>120 / 90</td>
<td>74 / 44</td>
</tr>
<tr>
<td>poly(1,4-cyclohexane dimethylene terephthalate-co-ethylene terephthalate)</td>
<td>38.9</td>
<td>1.5</td>
<td>117 / 80</td>
<td>75 / 43</td>
</tr>
<tr>
<td>nylon 6,6</td>
<td>46.7</td>
<td>0.8</td>
<td>122 / 89</td>
<td>74 / 34</td>
</tr>
<tr>
<td>poly(vinyl alcohol)¹</td>
<td>39.3</td>
<td>2.3</td>
<td>140 / 60</td>
<td>71 / 0</td>
</tr>
<tr>
<td>poly(methyl methacrylate)²</td>
<td>19.0</td>
<td>2.9</td>
<td>132 / 77</td>
<td>59 / 0</td>
</tr>
<tr>
<td>poly(bisphenol-A carbonate)²</td>
<td>25.1</td>
<td>3.9</td>
<td>130 / 76</td>
<td>70 / 26</td>
</tr>
<tr>
<td>Silicon</td>
<td>43.2</td>
<td>--</td>
<td>119 / 92</td>
<td>80 / 50</td>
</tr>
</tbody>
</table>

4.4. APTES Polymer Modification With Added Tetraethoxysilane (TEOS)

In an effort to increase the amount of reactive silica-like layer on the substrate surface, mixtures of APTES and tetraethoxysilane (TEOS) were used to modify PET film. Under standard conditions (1% silane, 75° C, 72 hours in toluene), the surfaces were reacted with varying ratios of APTES and TEOS. XPS results of these reactions are given in Figure 4.8. As can be expected, very little silicon and nitrogen are present on the pure TEOS samples, indicating no reaction with the surface. As the amount of APTES in the mixture increases, nitrogen at the surface has a corresponding rise. There seems to be
a slight enrichment of APTES reacted with the surface as opposed to the feed percentage, as seen by the slight upward curvature of the nitrogen data points. This is not surprising as the APTES has a specific interaction with the surface and the TEOS does not. The silicon data however are odd. As the feed of APTES is increased, the amount of silicon in the atomic concentration of the surface increases to a maximum and then drops down to the pure APTES amount. One would assume that the TEOS is providing for greater incorporation due to its not having an aminopropyl group diluting the silicon atomic percentage.

![Figure 4.8](image_url)

**Figure 4.8** 75° take-off angle silicon and nitrogen atomic concentration XPS results of mixed TEOS and APTES surface modification of PET; reaction temperature = 75 °C, APTES = 1.0%, 72h in toluene
To examine the amount of reactive silica on the surface, XPS was done after hydrolysis of the ethoxy groups (Figure 4.9). It is first evident that as the TEOS concentration increases, more silane modifier is cleaved by the hydrolysis conditions (as seen from the silicon atomic concentration). Upon looking at the nitrogen atomic concentration, one notices the initial flat profile at very low amounts indicating very little APTES left on the surface. As APTES is increased in the feed, the after-hydrolysis nitrogen atomic concentration shoots up. The behavior of these plots suggests that one possible explanation is that there is not enough APTES in the multilayer to stabilize it from removal due to H-bond interference. This would cause removal of large chunks of multilayer, drastically decreasing both silicon and nitrogen atomic concentrations. Regardless, APTES somehow stabilizes the multilayer against removal by hydrolysis.
Figure 4.9 75° take-off angle silicon and nitrogen atomic concentration XPS results of mixed TEOS and APTES surface modification of PET after hydrolysis; reaction temperature = 75°C, APTES = 1.0%, 72h in toluene

4.5. Summary

The utility of the modification of polymer surfaces with 3-aminopropyltriethoxysilane (APTES) was tested with a variety of polymer surfaces. Poly(ethylene terephthalate), poly(ethylene naphthalenate), poly(butylene terephthalate), poly(1,4-cyclcohexanedicarboxylic acid) (Kodak film or Kodel fiber), poly(bisphenol-A carbonate), poly(methyl methacrylate), polystyrene, cellulose acetate, poly(vinyl alcohol), poly(allyl amine), nylon 6.6, Kapton polyimide,
and polytetrafluoroethylene were tested and all polymers but polystyrene and poly(tetrafluoroethylene) were successfully modified by the evidence of 10%-12% silicon and 9%-11% nitrogen atomic concentrations by 75° take-off angle XPS. Water contact angle analysis also confirms the modification. The ability of some of these polymers to undergo reaction with APTES was found to be inconsistent with the chain-insertion model of reaction currently held. For this reason, a new model was proposed, analogous to SAM formation of silanes on silica, whereby initial H-bonding of the APTES followed by lateral bond formation occurs. Substrate reactivity and the inability of the reaction to proceed in polar protic solvents support the new model. An experiment was performed where the ethoxy groups were substituted for unreactive methyl groups of the APTES reagent and modifications were carried out with these. The reduction of reagent at the surface with one ethoxy substituted and the complete shutdown of the reaction with two substituted are further arguments for the new model.

Hydrophobization of the APTES modified surfaces was also carried out using (tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane after hydrolysis of the APTES layers. Effective hydrophobization was observed with water contact angles of 120/86 (adv/rec) and hexadecane angles of 79/47 (adv/rec) observed for PET film. Fluorine atomic concentrations are approaching those of, but are not quite as high as, similarly treated silicon wafers. The effects of temperature, concentration, and mixture with tetraethoxysilane (TEOS) on the APTES reaction were also investigated.
CHAPTER 5
INFLUENCING WETTABILITY USING CONTROLLED ROUGHNESS OF POLYPROPYLENE

5.1. Plasma Modification

Plasma techniques, in particular radio frequency (RF) sputtering of polymers, have been widely studied\textsuperscript{56-59} for use in the electronics industry. The ability to produce pinhole-free conformal coatings of otherwise insoluble, difficult-to-process polymers is of great interest. Typically, the polymers used are those with high thermal stability, high dielectric strength, and low dielectric loss. Because of this, there is a significant literature on sputtering fluoropolymers such as poly(tetrafluoroethylene) (PTFE),\textsuperscript{60-63} but few reports on other polymers. Classically, sputtering is a momentum transfer process in which excited particles collide with the target dislodging atoms and fragments from the surface. These gaseous species then travel to the substrate, collide and adhere. This can only occur in a line-of-sight geometry and the process is highly dependent on the mean free path of the dislodged atoms and fragments. This process requires that the pressure of the system be very low and that target-substrate spacing be extremely close (to prevent unwanted collisions with the carrier gas). This process is carried out with electron beams, ion beams, and RF plasmas. In the case of RF plasmas, excited gas molecules collide with the target.

In most cases, sputtering of polymers gives a structure that chemically resembles neither the target polymer nor the polymer prepared by plasma polymerization of the monomer. This is not surprising since any mass that is transferred is likely to be highly
reactive atoms and small polymer fragments and not long intact chains. These fragments likely do not resemble the monomer and therefore, the sputtered polymer will not resemble the plasma polymerized monomer film. It has been found,\textsuperscript{64,65} however, that PTFE is anomalous; the sputtered polymer resembles the plasma polymer of tetrafluoroethylene (TFE), although neither resemble virgin (conventional) PTFE. This suggests that the mechanisms that form plasma sputtered PTFE and plasma polymerized PTFE are similar.\textsuperscript{64,65} It has been shown that TFE is the principal product of the plasma ablation of PTFE,\textsuperscript{57,66} as well as the principal thermal degradation product.\textsuperscript{67} This suggests that sputtering of PTFE occurs by depolymerization to the monomer followed by plasma polymerization of TFE.

Plasma roughening of a surface can be considered nearly the same as reactive ion etching. The excited gas molecules degrade the surface at different rates depending upon the morphology of the substrate. Crystalline regions etch slower than amorphous regions. Different gases also affect the etch-rate of the polymer. Whereas in most cases argon gas etches relatively slowly, oxygen and tetrafluoromethane etch rapidly. It is believed that this is due to the added chemical etching nature of the latter two. Unfortunately, the chemical etching nature of these gases typically induces more surface functionalization than does argon. It is also believed that chemical nature of the polymer has a large effect upon the ablation rate. The more oxygenated polymers do, in fact, etch faster. Some research uses these facts to obtain micro-patterned surfaces by differential ablation of heterogeneous materials. In our case we have roughened semi-crystalline polypropylene (PP) using the differential etch rates of amorphous and crystalline regions.
We are interested in solvent-free coating processes and have carried out the work reported here to examine whether the non-classical sputtering observed with PTFE is a more general phenomenon than the literature indicates. We report the tendencies of various polymers to sputter under these conditions and comparisons between sputtered polymer films and films prepared by plasma polymerization of the monomers are made when applicable. We also studied the ablation rates of the polymers in order to gain an understanding of the factors involved in their sputtering behavior. This knowledge of sputtering behavior was then applied to a system to controllably roughen and hydrophobize a surface. This was used to gain insight into factors influencing wettability.

5.2. **Understanding Plasma Sputtering**

In order to prepare non-wettable surfaces, one must ensure that the surface energy of the substrate does not become too high. Unfortunately, even with argon as the etchant of PP, the residual surface radicals will still react upon exposure to air and give a high energy, oxidized surface. Fluoropolymers, however, escape this worry due to the high bond strength of the C-F bond. This prohibits the build-up of oxidized surface material and the surface retains its fluoropolymer properties. In addition, C-F bonds are stronger than C-O bonds which limits defluorination.

In order to better control surface energy in our system, we need to improve our understanding of the sputtering process. We have examined a system such that no sputtering by classical means can take place due to line-of-sight and mean free path
restrictions. We will report the various abilities of polymers to sputter under these conditions and a comparison will be made with the plasma polymer when applicable. Results will be in terms of XPS, contact angle, and infrared spectroscopy.

We have also undertaken a study of the various ablation rates of the polymers. This is to gain an understanding of the factors involved in their sputtering behavior. This knowledge will be compared to the individual properties of each.

5.2.1. Materials and Methods

Plasma modification reactions were carried out in a home-built inductively coupled Pyrex reactor (~3 L volume) in which flow rate, power (13.56 MHz - supplied by an Astron RS-35A power supply and a Yaesu FT-840 HF transceiver), and pressure can be controlled (Figure 5.1). The inner diameter of the reactor is 85 mm and 15 turns of \( \frac{3}{16} \)" soft copper tubing act as the electrode. X-ray photoelectron spectra (XPS) were recorded using a Perkin-Elmer - Physical Electronics 5100 spectrometer with Al K\( _\alpha \) excitation (15 kV, 400 W) at a take-off angle of 75° (between the plane of the sample surface and the entrance lens of the detector optics). Atomic concentration data were determined using sensitivity factors obtained from samples of known composition: C\(_{1s}\), 0.200; O\(_{1s}\), 0.501; N\(_{1s}\), 0.352; F\(_{1s}\), 1.00; Cl\(_{2p}\), 0.73; Au\(_{3d}\), 4.95. Contact angle measurements were obtained using a Ramé-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Dynamic advancing (\( \theta_A \)) and receding angles (\( \theta_R \)) were recorded while the probe fluid (water, purified using a Millipore Milli-Q\textsuperscript{®} system that involves reverse osmosis followed by ion-exchange and filtration steps) was
added to and withdrawn from the drop, respectively. Attenuated total reflectance infrared (ATR IR) spectra were recorded with a Bio-Rad FTS 175C spectrometer. Germanium crystals cut at 45 degrees were used for internal reflection elements. Ablation rate studies were carried out gravimetrically using a Cahn 29 electrobalance.

The polymers studied were obtained in powder or pellet form from the following suppliers: poly(tetrafluoroethylene) (PTFE) - Berghoff-America, poly(chlorotrifluoroethylene) (PCTFE) - 3M, poly(methyl methacrylate) (PMMA) - Scientific Polymer Products, high density polyethylene (HDPE) - Dow Chemical Company, polyisobutylene (PIB), poly(ethyl methacrylate) (PEMA), poly(butyl

Figure 5.1  Diagram of plasma reactor used for these experiments
methacrylate) (PBMA), poly(tetrahydrofuran) (PTHF), poly(oxymethylene) (POM), poly(ethylene oxide) (PEO), poly(α-methyl styrene) (PoMS)- Aldrich Chemical Company. The polymers were melt-pressed into plaques and cut to the desired size. For sputtering, 2 x 10 in samples were prepared and 2 or 3 plaques were used per reaction. For ablation rate studies, 1 in square plaques were used.

The substrate that was used for the sputtering experiments was gold evaporated onto aluminum-coated poly(ethylene terephthalate). This provided excellent contact with the internal reflection elements used for ATR IR spectroscopy. The substrate was placed about 5 cm (~250 mean free paths) from the target polymer, with both the substrate and the target polymer facing the same direction (no line of sight), in the full glow region of the reactor. The reactor was then sealed and evacuated to 5-10 mT. The chamber was then flooded with argon (Merriam Graves) to a pressure of 5 T. Then the system was pumped to a final steady state condition of 200 mT and 1.8 sccm. These conditions were maintained for 30 min prior to reaction to ensure stability. The RF coil was then activated at 100 W and the reaction was initiated (if needed) with an anti-static gun. To determine ablation rates, three plaques were placed at various areas in the full glow region after being tared. Various reaction times up to 60 min at were carried out under the same conditions used for sputtering and final masses were measured. Any mass loss that may have occurred due to evacuation was taken into account by measuring mass loss in samples treated under the same conditions without an RF field (no plasma). These control data were subtracted statistically from the ablation data and the results are reported as ablation rates (Å/min).
5.2.2. Sputtering

In an effort to better elucidate the mechanism of non-classical sputtering and to determine conditions to test other polymers, an experiment was designed to limit classical sputtering. The substrate was placed in a geometry in which there was no line of sight to the target and at a large distance relative to the mean free path of ablated fragments. Under these conditions, sputtering that occurs by the classical momentum transfer process will not transport mass to the substrate. If, however, the reaction can proceed by polymer degradation to monomer (depolymerization) and subsequent repolymerization from the gas-phase (plasma polymerization), then material will be deposited on the substrate. After 2 hours of exposure to argon plasma, PTFE sputtering onto the substrate was visibly detectable. Diffraction colors were observed on the glass throughout the reactor and the reactor walls were hydrophobized. These results are predicted from the proposed depolymerization/repolymerization pathway of PTFE sputtering, and our experiments support this hypothesis and indicate that the reactor geometry is appropriate for this study.

Various polymers were studied to determine their propensity to sputter under these conditions (non-classically). Halogenated, oxygenated, glassy, and semicrystalline polymers with a range of ceiling temperatures were chosen to see what effects, if any, these properties would have on the sputtering behavior. The vast majority of polymers did not show sputtering as determined from contact angle, XPS, and the presence of visible deposits on the substrate. Immediately after sputtering, the substrate was introduced into the XPS to limit chemistry that occurs with air. ATR IR and contact
angle measurements were also done as quickly as possible (on separate samples). For target polymers that showed no sputtering, contact angles were close to those of unmodified gold ($\theta_A/\theta_R = 45^\circ/0^\circ$) and large concentrations of gold were observed in XPS spectra. Contact angle and XPS data are shown in Table 5.1. Of the polymers that exhibit sputtering, PαMS does not leave a visible deposit on the substrate or the plasma reactor and only a weak ATR IR spectrum of this polymer was observed due to low signal. These observations indicate that PαMS does not sputter as efficiently as the others (PTFE, PCTFE, PIB) that sputter.

Table 5.1  Polymer sputtering results; XPS and water contact angle data

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\theta_A(\degree) / \theta_R(\degree)$</th>
<th>% C</th>
<th>% O</th>
<th>% N</th>
<th>% Au</th>
<th>% F</th>
<th>% Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>polytetrafluoroethylene</td>
<td>114 / 87</td>
<td>33.0</td>
<td>2.7</td>
<td>0.9</td>
<td>0</td>
<td>63.4</td>
<td></td>
</tr>
<tr>
<td>polyethylene</td>
<td>45 / 0</td>
<td>49.8</td>
<td>5.0</td>
<td>4.5</td>
<td>40.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>polystyrene</td>
<td>49 / 0</td>
<td>70.1</td>
<td>12.3</td>
<td>0</td>
<td>17.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>polyoxymethylene</td>
<td>50 / 0</td>
<td>32.0</td>
<td>46.1</td>
<td>0</td>
<td>21.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>polyisobutylene</td>
<td>75 / 22</td>
<td>83.8</td>
<td>7.7</td>
<td>8.5</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>polytetrahydrofuran</td>
<td>49 / 0</td>
<td>43.3</td>
<td>14.5</td>
<td>0</td>
<td>42.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>poly(chlorotrifluoroethylene)</td>
<td>95 / 6</td>
<td>20.5</td>
<td>26.4</td>
<td>5.5</td>
<td>0.5</td>
<td>41.3</td>
<td>5.9</td>
</tr>
<tr>
<td>poly(methylmethacrylate)</td>
<td>50 / 0</td>
<td>43.3</td>
<td>19.5</td>
<td>0</td>
<td>37.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>poly(α-methylstyrrene)</td>
<td>16 / 0</td>
<td>64.3</td>
<td>14.4</td>
<td>21.1</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>gold</td>
<td>45 / 0</td>
<td>69.8</td>
<td>9.9</td>
<td>0</td>
<td>19.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.2.3. Ablation Behavior

In an effort to understand this process and the influencing factors (for example, the fact that no oxygen-containing polymers sputter), ablation rates were determined for these as well as other polymers and are given in Table 5.2. Overall, the most important result is that the rate of ablation has no bearing upon the sputtering behavior of polymers (compare Tables 5.1 and 5.2). The material with the lowest ablation rate (PTFE) sputters well, thus all of the polymers produce enough mass of material in the gas phase to successfully sputter. This indicates that polymer sputtering requires more than just sufficient material in the gas phase. Polyethers and polymethacrylates failed to sputter even though they exhibited the highest ablation rates. Fragmentation of these polymers or gaseous fragments results in a mixed monomer system containing both oxygen and hydrocarbon. It has been shown that the rate of plasma polymerization is adversely affected by oxygen, so this effect may be at play here as well. These experiments do not distinguish whether degradation of the oxygen-containing polymers to fragments that do not sputter occurs in the solid-state target or in the gas phase or whether sputtered material is removed from the substrate by oxygen species.
### Table 5.2  Ablation rates of various polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>[%O]</th>
<th>Ablation Rate (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>polyisobutylene</td>
<td></td>
<td>15.8</td>
</tr>
<tr>
<td>polyethylene</td>
<td></td>
<td>4.3</td>
</tr>
<tr>
<td>poly(α–methylstyrene)</td>
<td></td>
<td>4.1</td>
</tr>
<tr>
<td>polystyrene</td>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>poly(chlorotrifluoroethylene)</td>
<td></td>
<td>10.4</td>
</tr>
<tr>
<td>polytetrafluoroethylene</td>
<td></td>
<td>2.1</td>
</tr>
<tr>
<td>polytetrahydrofuran</td>
<td>[22%]</td>
<td>67.2</td>
</tr>
<tr>
<td>poly(ethyleneoxide)</td>
<td>[36%]</td>
<td>63.2</td>
</tr>
<tr>
<td>polyoxymethylene</td>
<td>[53%]</td>
<td>50.0</td>
</tr>
<tr>
<td>poly(methylmethacrylate)</td>
<td>[32%]</td>
<td>23.1</td>
</tr>
<tr>
<td>poly(ethylmethacrylate)</td>
<td>[28%]</td>
<td>29.9</td>
</tr>
<tr>
<td>poly(butylmethacrylate)</td>
<td>[23%]</td>
<td>26.9</td>
</tr>
</tbody>
</table>

As previously reported, the chemical and physical structure of the polymer plays the dominant role in determining the etching rate. Oxygen-containing polymers etch faster than other polymers, but oxygen content is not the determining factor for these polymers, as oxygen content increases and ablation rate decreases for the polyethers studied. Among polymethacrylates, both PEMA and PBMA etch faster and contain less oxygen than PMMA. Overall, the polyethers etched faster than the polymethacrylates, which in turn etched faster than the other polymers (hydrocarbons and halocarbons). The main effect of physical state is that there is a narrower distribution of ablation rates among analogous glassy polymers than in analogous semicrystalline polymers. It is
known that crystalline regions frustrate the ablation process, so it is likely that the crystallinity affects etching rate - this is not an issue for the glassy polymers. The rates of PS and PαMS (both are amorphous) are essentially the same and the range of ablation rates for the glassy polymethacrylates is small. The semicrystalline polyethers (POM, PEO, and PTFE), hydrocarbons (PE and PIB) and halocarbons (PTFE and PCTFE) show much larger percentage differences in ablation rates.

Comparisons of the repeat unit structures of the polymers, their chemical composition and their thermal behavior suggest a few relations. PE, PIB, PS, and PαMS are all hydrocarbons, but they have very different ceiling temperatures: PE (T_c = 400 °C), PIB (T_c = 50 °C), PS (T_c = 310 °C), PαMS (T_c = 60 °C). The two polymers with low ceiling temperatures sputter, while those with high ceiling temperatures do not. It is certain that at least some C-C main chains in the polymers are cleaved homolytically by excited argon or by fragmentation of other radicals. This provides depropagating species that can produce monomer. The relative rates of depropagation and competitive plasma-induced chemistry determine the amount of monomer produced. The polymers with low ceiling temperatures have higher depropagation rates (relative to plasma degradation) than the high ceiling temperature polymers. This increased monomer in the gas phase leads to sputtering. PTFE has a very high ceiling temperature (T_c = 510 °C), which is inconsistent with the analysis made above. The depolymerization proceeds cleanly however and is due to the high strength of the C-F bonds (116 kcal/mol), which disfavors competitive degradation reactions. With little degradation, the monomer is free to plasma polymerize in typical fashion. PCTFE is similar in its behavior. Overall, it has stronger bonds and fewer degradative side reactions than hydrocarbons. This means its higher
ceiling temperature does not inhibit monomer formation, although the reduced strength of the C-Cl bond (81 kcal/mol) relative to the C-F bonds of PTFE results in greater degradation (relative to PTFE) and therefore less sputtering.

5.2.4. Spectral Comparisons

Figures 5.2 and 5.3 show infrared spectra of sputtered PIB and PαMS, respectively along with spectra of plasma polymerized monomers and conventional polymers for comparison. Looking at the PIB spectra first, it is apparent that the sputtered polymer structure is similar to the plasma polymer, but that both are significantly different than the conventional polymer structure. This supports the mechanism of depolymerization followed by plasma polymerization during sputtering. The C-H stretching regions (3000-2800 cm\(^{-1}\)) are similar for all 3 polymers, but the C-H bending regions differ significantly. The well-defined gem-dimethyl bending (doublet) at 1375 cm\(^{-1}\) in the conventional polymer is absent in spectra of the sputtered and plasma polymers. Carbonyl groups (1700 cm\(^{-1}\)) due to oxidation (either by oxygen impurities in the reactor or subsequent reactions in air) are apparent in both the sputtered and plasma polymer spectra, but are absent in the conventional polymer. Nitriles and/or isonitriles are apparent in the plasma polymer; this is likely due to nitrogen contamination in the reactor. XPS (table 3) confirms the presence of nitrogen. The PαMS spectra (Figure 5.3) also suggest that depolymerization followed by repolymerization is operative. Both the plasma polymer and sputtered polymer show no aromatic C-H stretching (3100-3000 cm\(^{-1}\)), while the conventional polymer exhibits sharp peaks in this region. ATR IR spectra
and XPS data for PCTFE polymers are shown in Figure 5.4 and Table 5.3. Again the plasma polymer and the sputtered polymer resemble one another and are very different than the conventional polymer. Oxidation (~1700 cm\(^{-1}\)) and hydrocarbon contamination (~3000 cm\(^{-1}\)) are evident. XPS indicates that the sputtered polymer contains less chlorine than the plasma polymer indicating that C-Cl bond cleavage competes with depolymerization in the sputtering process (in the solid state target and/or the gas phase). The comparisons made in Figures 5.2 and 5.3 have been reported for PTFE,\(^{64,65}\) and our experiments reproduce these results indicating a depolymerization and subsequent repolymerization mechanism.

![Figure 5.2 ATR IR spectra for (a) conventional PIB, (b) plasma polymerized isobutylene, and (c) sputtered PIB](image)

Figure 5.2 ATR IR spectra for (a) conventional PIB, (b) plasma polymerized isobutylene, and (c) sputtered PIB
Figure 5.3  ATR IR spectra for (a) conventional PnMS, (b) plasma polymerized a-methylstyrene, and (c) sputtered PnMS

Figure 5.4  ATR IR spectra for (a) conventional PCTFE, (b) plasma polymerized chlorotrifluoroethylene, and (c) sputtered PCTFE
Table 5.3  Virgin, sputtered, and plasma polymerized polymer XPS Data

<table>
<thead>
<tr>
<th>Polymer</th>
<th>%C</th>
<th>%O</th>
<th>%N</th>
<th>%F</th>
<th>%Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>polytetrafluoroethylene</td>
<td>35.3</td>
<td>3.0</td>
<td>0.0</td>
<td>61.7</td>
<td></td>
</tr>
<tr>
<td>plasma sputtered</td>
<td>41.2</td>
<td>3.3</td>
<td>0.0</td>
<td>55.5</td>
<td></td>
</tr>
<tr>
<td>polyisobutylene</td>
<td>94.6</td>
<td>5.4</td>
<td>0.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>plasma polymerized</td>
<td>85.3</td>
<td>3.1</td>
<td>11.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>plasma sputtered</td>
<td>83.6</td>
<td>7.7</td>
<td>8.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>poly(α–methylstyrene)</td>
<td>80.8</td>
<td>13.2</td>
<td>6.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>plasma polymerized</td>
<td>78.4</td>
<td>19.6</td>
<td>2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>plasma sputtered</td>
<td>64.3</td>
<td>14.4</td>
<td>21.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>poly(chlorotrifluoroethylene)</td>
<td>38.8</td>
<td>3.8</td>
<td>0.0</td>
<td>46.6</td>
<td>10.8</td>
</tr>
<tr>
<td>plasma polymerized</td>
<td>40.5</td>
<td>2.7</td>
<td>1.0</td>
<td>46.5</td>
<td>9.2</td>
</tr>
<tr>
<td>plasma sputtered</td>
<td>20.5</td>
<td>26.4</td>
<td>5.5</td>
<td>41.3</td>
<td>5.9</td>
</tr>
</tbody>
</table>

An analysis of the XPS C\textsubscript{1s} peak shapes may indicate more concerning the chemistry that is occurring. Unfortunately, materials consisting of entirely carbon (as is the case of PIB and PoMS) give C\textsubscript{1s} spectra that do not contain much useful information. Line shapes for the plasma polymerized and sputtered polymers are identical in both cases and are broadened relative to their virgin materials indicating cross-linked and oxidized polymers (Figures 5.5 and 5.6). In the case of PCTFE we can learn more. Notice that in Figure 5.7 virgin PCTFE has one peak that contains all halogenated carbons. Upon plasma polymerization or sputtering, peaks at high binding energy appear indicating a significant rearrangement of structure. More detail than this is difficult with the amount of peaks present, although results are consistent with ATR IR. A lower
binding peak is present in both sputtered and plasma polymerized samples indicating non-halogenated material.

Figure 5.5  XPS Cls spectra for (a) conventional PIB, (b) plasma polymerized isobutylene, and (c) sputtered PIB
Figure 5.6  XPS C1s spectra for (a) conventional PaMS, (b) plasma polymerized \( \alpha \)-methylstyrene, and (c) sputtered PaMS

Figure 5.7  XPS C1s spectra for (a) conventional PCTFE, (b) plasma polymerized chlorotrifluoroethylene, and (c) sputtered PCTFE
5.3. **Simultaneous Ablation and Plasma Sputtering**

If argon can etch a surface to give a controllably rough surface and it can sputter PTFE unto a surface, can one do these things simultaneously to create a controllably rough, non-wetting surface? In trying to do just this, four cases can be imagined: 1) if sputtering is faster than ablation, then the surface will have material placed upon it faster than can be eroded away. Thus the surface is fluorinated, but no roughening occurs. 2) If etching is faster than sputtering, then material will be ablated faster than the sputtering can remove material and the surface will roughen but not fluorinate. 3) The surface can etch first and then sputter. This would create a rough and fluorinated surface, but little control could be obtained. 4) The two could be truly independent phenomena and could occur simultaneously. This would dictate that the surface roughens underneath the sputtered coating. This research attempts the simultaneous sputtering of PTFE and roughening of bi-axially oriented PP.

Plasma techniques have previously been reported to prepare non-wetting surfaces. Washo\textsuperscript{69} reports contact angles of 165-170° for plasma-polymerized tetrafluoroethylene films, deposited in the powder region. Schreiber et al.\textsuperscript{70} prepared plasma-polymerized hexamethyldisiloxane films using low temperature plasma deposition and measured water contact angles “as high as 180°.” Garbassi et al.\textsuperscript{71} examined the wettability of oxygen plasma - treated PTFE and report contact angles of $\theta_A/\theta_R = 170°/160°$. This treatment of PTFE gives a rough, porous surface due to the difference in plasma susceptibility of crystalline and amorphous polymer.\textsuperscript{72,73}
5.3.1. Materials and Methods

Plasma modification reactions were carried out in a previously described\textsuperscript{31} home-built inductively coupled Pyrex reactor in which flow rate, power (13.56 MHz - supplied by an Astron RS-35A power supply and a Yaesu FT-840 HF transceiver), and pressure can be controlled. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer -Physical Electronics 5100 spectrometer with Al K\textsubscript{\alpha} excitation (15 kV, 400 W) at take-off angles of 15° and 75° (between the plane of the sample and the entrance lens of the detector optics). Atomic concentration data were determined using sensitivity factors obtained from samples of known composition: \(C_{1s}, 0.200; O_{1s}, 0.501, N_{1s}, 0.352, F_{1s}, 1.00\). Contact angle measurements were made with a Ramé-Hart telescopic goniometer and a Gilmont syringe and a 24-gauge flat-tipped needle. Dynamic advancing and receding angles were recorded as the probe fluid (either water, purified using a Millipore Milli-Q system that involves reverse osmosis followed by ion-exchange and filtration steps or hexadecane, purified by vacuum distillation) was added to and withdrawn from the drop, respectively. Atomic force microscopy (AFM) was performed in air using a Digital Instruments Nanoscope IIIa AFM in tapping mode. Scanning electron microscopy (SEM) micrographs were obtained with a JEOL-35CF microscope using an acceleration voltage of 20 kV.

Biaxially oriented capacitor grade polypropylene (6 \(\mu\)m thick) was obtained from Aerovox, Inc. PTFE film (4 mil) was obtained from Berghoff America. The polypropylene was cut into 1 in\(^2\) samples and placed into the full glow region of the plasma reactor on top of PTFE film (~90 in\(^2\)). The reactor was then sealed and evacuated
to < 0.01 mm. The chamber was then filled with argon (Merriam Graves) to a pressure of 5 mm and then pumped to a steady state condition of 0.2 mm and 1.0 sccm. These conditions were held steady state for 30 min to ensure stability. The radio coil was then charged and the plasma was ignited (if needed) with an anti-static gun. Various times of reaction were studied at a power of 100 W. Analyses were carried out on the exposed side of the polypropylene.

5.3.2. Surface Chemistry

Polypropylene and PTFE (in surface area excess of ~90 over polypropylene) film samples were simultaneously exposed to an argon plasma under conditions described in the experimental section. Both films are etched by the plasma; the etching of the PTFE produces a reactive fluorocarbon plasma that fluorinates the polypropylene surface in competition with its ablation. Figure 5.8 shows the atomic concentration of fluorine present in the surface region of polypropylene, determined by XPS, as a function of treatment time. Data for two take-off angles are included. The 15° take-off angle data indicate the composition of the outermost ~10 Å and the 75° take-off angle data represent the composition of the outermost ~40 Å. In addition to carbon and fluorine, oxygen and nitrogen are also present in variable low atomic concentration in all samples. The 15° fluorine concentration plateaus above 40 atom% after 6 min and rises to above 50 atom% after 2 hours (F:C ratios are ~1.4:1). The 75° data show a similar trend, but concentration plateaus above 50 atom% fluorine after 20 min and rises to ~60 atom% after 2 hours (F:C ratios are ~1.6:1). Several points concerning these data warrant comment: (1) The
surfaces are highly fluorinated even at low reaction times and the surface composition of the polypropylene remains approximately the same after ~20 min reaction. This indicates that solid PTFE is an excellent fluorinating agent in an argon plasma. (2) The 15° data (fluorine concentration) are higher than the 75° data at low reaction times and plateau earlier than the 75° data. This take-off angle dependence and the reaching of plateau values indicate that samples treated for less than ~20 min contain fluorinated polypropylene surface layers that are less than 40 Å thick and that samples treated for longer times have modified layers at least 40 Å thick. (3) The take-off angle dependence for samples treated for times longer than 20 min is unusual, indicating that reaction is more extensive in the region beneath ~10 Å deep than in the near-surface region. We ascribe this to reaction of radicals with oxygen after exposure of the sample to air. This is followed by elimination of HF, reducing the fluorine content at the surface.
Contact angle is normally a useful technique for assessing changes in surface chemistry and conversion of a hydrocarbon surface to a fluorocarbon surface should be straightforward to follow using this method. Analysis of data from this system is complicated, however, because in addition to chemical changes, significant topographical changes occur (we chose this system for this reason). Topography is discussed in detail below. Figure 5.9 shows advancing and receding contact angle data (water) for polypropylene treated with argon/PTFE plasma for various durations. After short reaction times (less than 6 min), contact angles decrease from $\theta_A/\theta_A = 103^\circ/89^\circ$ to $\sim 58^\circ/\sim 11^\circ$. There is not sufficient fluorination of the sample after this treatment duration.

Figure 5.8  XPS atomic concentration of fluorine in polypropylene as a function of argon/PTFE plasma reaction time at 15° and 75° take-off angle.
(Figure 5.8) to hydrophobize the material; the decrease is likely due to two factors: (1) the presence of oxygen and nitrogen functionality (that is indicated by XPS) and (2) roughening. Wenzel’s equation predicts a decrease in $\theta_{\text{rough}}$ with increasing roughness if the contact angle is less than $90^\circ$ ($\cos \theta$ is positive). After 20-30 min reaction time, the advancing contact angle is higher ($\theta_A = \sim120^\circ$) than the initial value for polypropylene ($\theta_A = 103^\circ$) and it continues to rise to $\sim170^\circ$ with longer treatments. The receding contact angle rises with longer treatment time, but remains lower than the initial polypropylene value unless reaction times greater than 60 min are used; $\theta_R$ values converge on $\theta_A$ values after 3 hours of reaction. The highest contact angles observed are $\theta_A/\theta_A = 172^\circ/169^\circ$. Advancing hexadecane contact angles increase with reaction time (other than the initial drop as described above) to a plateau of $\sim105^\circ$, but receding contact angles were $0^\circ$ for all surfaces (Figure 5.9).
Figure 5.9  Advancing and receding water (top) and hexadecane (bottom) contact angles of roughened and fluorinated polypropylene as a function of argon/PTFE plasma reaction time
5.3.3. Surface Topography

Figure 5.10 shows a series of SEM micrographs of polypropylene samples that were treated with argon/PTFE plasma for different reaction times. Each has the same magnification. The surfaces become rougher with reaction time with the features becoming smaller, closer together and more contorted. We have not examined the cause of this roughening (in terms of the initial polypropylene morphology) and rationalize it as based on the different etching rates of crystalline and amorphous material. The same features are observed in argon plasma treated polypropylene samples (without PTFE present). The etching rate is slower than with PTFE present, but the resulting samples are indistinguishable, using SEM, from those prepared with argon/PTFE plasma treatments. The morphologies are quite reproducible, but occasionally a very different morphology was observed. These samples exhibited hemisphere-shaped asperities; we ascribe this to melting and recrystallization of the polypropylene during treatment, but have not examined the process in any detail or deliberately tried to make samples with this topography. Data from samples that exhibited these ball-like features were discarded.
Atomic force microscopy was performed on these samples to quantify the topography changes. The images, topographies, and dimensions of the features are qualitatively similar those observed using SEM, but the quality of the data is poorer, due to polymer transfer to the probe tip. Images are given in Figure 5.11. AFM data was used to calculate two types of roughness, an average peak to valley distance and a ratio of
surface area to geometric area (Wenzel’s roughness factor - r). The latter was determined by squaring the ratio of the contour length to the straight-line length (20 μm) of a 20 μm X-Z slice of the data. The effects of reaction time on these roughness values are plotted in Figure 5.12. The roughness increases gradually with reaction time. Pits in samples also get deeper with time initially and then reach a constant depth beyond which longer reaction time has no effect. Only data for samples reacted for 120 min or less are included; there was excessive error in samples reacted for longer times, likely due to fluoropolymer buildup on the AFM tip as streaking is evident on the 180 min micrograph.

Figure 5.11  AFM micrographs of polypropylene as a function of argon/PTFE plasma reaction time: a) 0 min, b) 30 min, c) 60 min, d) 90 min, e) 120 min, and f) 180 min
AFM pictures were further analyzed by calculating lateral correlation lengths. The autocorrelation functions of the pictures were calculated via a specialty computer analysis program. This autocorrelation function can be generally characterized by the equation:

\[ C(r) = \sigma^2 e^{(-r/\xi)^2c} \]

where \( C(r) \) is the autocorrelation function, \( \sigma \) is the height, \( c \) is the roughness exponent and \( \xi \) is the lateral correlation length. These lateral correlation lengths are a measure of the lateral length scales of the roughness. The lateral correlation lengths of the plasma-
modified polypropylene were plotted as a function of time and are presented in Figure 5.13. As can be readily seen, correlation length increases with time of reaction and between 60 min and 90 min reaction time there is a precipitous drop. After this point it remains approximately constant with time. The data seems to qualitatively fit well with trends that may be observed considering just the roughness value and average depth data. At short times, the low roughness is not greatly altered, but the features are getting deeper. This is indicative of features becoming larger. As the modification continues, the surfaces have greatly increased roughness with feature depth constant. This necessitates a reduction in feature size.

![Graph](image)

**Figure 5.13** Lateral correlation lengths of polypropylene as a function of argon/PTFE plasma reaction time
5.4. Relevance of Chemistry and Topography to Hydrophobicity

Comparisons of Figures 5.8 and 5.9 indicate that surface chemistry (fluorine content) is not responsible for the differences in wettability - contact angle and hysteresis - between samples treated with argon/PTFE plasma for 60 min or less and samples treated for 90 min or more. There is a striking difference in wettability between these two sets of surfaces that roughness is responsible for and we focus on two samples, those treated for 60 and 90 min. Water droplets stay pinned on 60 minute-treated samples, even when the samples are tilted significantly from the horizontal. Water droplets, however, move spontaneously on horizontal surfaces of 90 minute-treated samples and do not come to rest, but roll off of the samples.

When the dynamic water contact angle is plotted against the calculated Wenzel’s roughness values (Figure 5.14), the contact angle behavior is exactly what is predicted (with the exception of the initial decrease in \( \theta_a \) due to polar functionality) by Johnson and Dettre\(^6\) for a hydrophobic surface becoming rougher with reaction time. Surfaces that have been treated for 60 min or less have low roughness values and exhibit high advancing contact angles and low receding contact angles (water drops are pinned on these surfaces), thus water penetrates at least a significant percent of the valleys of the rough surface. We describe the rugosity of surfaces with this behavior as being in the Wenzel regime. Surfaces with high roughness value (treated for 90 min or longer) exhibit both high advancing and receding contact angles. Water does not penetrate a significant percent of the valleys on these surfaces and contacts only the ridges (air is trapped in the valleys); water drops roll easily on horizontal surfaces. We describe these
surfaces as *ultrahydrophobic*\textsuperscript{12} and term their rugosity as being in the Cassie regime.

Also in Figure 5.14 the water contact angle hysteresis is plotted versus Wenzel’s roughness value; a maximum is observed at \( \sim 1.5 \) (60 min reaction time) and a sharp decrease occurs with further reaction. The roughness changes during this reaction period (60-90 min) are responsible for the transition from the Wenzel to the Cassie regime.

None of the surfaces prepared by this method are *ultralyophobic*\textsuperscript{12} as hexadecane drops remain pinned on them. The surface can not roughen enough to force the hexadecane droplet into the Cassie regime as \( \theta_T < 90^\circ \).

---

**Figure 5.14** (a) Contact angle and (b) contact angle hysteresis (\( \theta_A - \theta_R \)) of roughened and fluorinated polypropylene as a function of Wenzel’s roughness factor (\( r \)); Lines are merely to aid the eye

Continued next page
When hysteresis is plotted versus lateral correlation length as in Figure 5.15, one notices the tendency of contact angle hysteresis to scale with lateral spacing. Contrasting the dependence of hysteresis upon $r$ (Wenzel’s roughness factor) and $x$ (lateral spacing), other commonly used measures of roughness show no influence on the wettability of these surfaces. Measures such as $R_{\text{rms}}$, $R_a$, and $z$ (height) are useless in the confines of this research. The importance of $r$ and $x$ to wettability arguments do have basis in literature. Johnson and Dettre’s metastable state model\(^6\) predicts that $z$ and $z/x$ are the critical factors for a sinusoidal surface. On any surface of constant topology (shape) $r$ is dependent on $z/x$. 

Figure 5.14 Continued
Figure 5.15  Contact angle hysteresis ($\theta_A - \theta_R$) of roughened and fluorinated polypropylene as a function of lateral correlation length; Line is merely to aid the eye.

5.5. Phenomenological Model

In order for a droplet of water, in contact with a solid surface, to move across that surface (spontaneously or due to an external force), it has to both advance and recede. The force required to start a drop moving on a surface is related to the difference between the advancing and receding contact angles.$^{11}$

$$ F \sim \gamma_L (\cos \theta_R - \cos \theta_A) $$
This implies that water droplets on surfaces that exhibit no water contact angle hysteresis will not be stable and will easily slide or roll, regardless of the magnitude of the contact angle. Thus a surface with water contact angles of $\theta_A/\theta_R = 99^\circ/99^\circ$ should be considered more hydrophobic than a surface exhibiting contact angles of $\theta_A/\theta_R = 170^\circ/100^\circ$.

When a droplet moves on a surface, the entire contact perimeter (3-phase liquid/solid/vapor contact line) must move. More important to the argument that we are about to make, is that for small movements, or for each of many small incremental movements, the only liquid-solid interfacial water molecules that need to move are those that cover bare surface (upon advancing) and those that de-wet the surface (upon receding). The other interfacial water molecules need not move. So the actions of wetting and de-wetting or the actions of a droplet moving on a surface involve only contact line events and need not (and presumably do not) involve the vast majority of the liquid-solid interface. Consider the origin of hysteresis. When a drop deforms on a tilted surface prior to moving, the contact angles of the “downhill” 180° of the contact line increase and those on the “uphill” portion decrease (normally this is viewed in 2 dimensions with only two angles considered). There are energy barriers for both advancing and receding, and they may be (and most often will be) different. If the drop advances (at any point on or at all of the downhill contact line), before it recedes, this will induce an instability in the drop (increase in surface area at constant volume) that will cause recession. If the drop recedes first, this will introduce a different instability (a drop shape change due to gravity that will increase the advancing angle) that will cause advancement. When the drop is moving, both events must occur concertedly or in rapid succession, so whichever event, advancement or recession, has a higher energy barrier is
not an important issue - neither is rate limiting. We point out that instabilities at any point on the contact line (not just the advancing and receding “points”) will contribute to the momentum of a moving droplet. These energy barriers that give rise to contact angle hysteresis are generally considered to arise from three sources: chemical heterogeneity, strong interaction between the water and the surface, surface roughness. We are concerned here only with roughness and are considering only chemically homogeneous non-interacting surfaces.

Figure 5.16 describes a surface of one model roughness. The ellipses in the center of the figure describe plateaus that the water droplet rests on. We assume that water does not intrude into the valleys. This is a valid assumption because water will not intrude into micron scale pores of a hydrophobic surface at atmospheric pressures. The following equation,\(^7\) where \(\Delta P\) is the hydrostatic pressure that must be exceeded

\[
\Delta P = -p\gamma_L \cos \theta_A / A
\]

before water will penetrate pores, \(p\) is the perimeter of the pores, \(\gamma_L\) is the surface tension of water, \(\theta_A\) is the advancing contact angle of water on the surface and \(A\) is the area of the pore, is the governing expression; this equation predicts that pressures greater than 300 cm of water are necessary to cause intrusion into pores of micron size. The 3-phase contact line of a drop on this surface will be in a position that maximizes its contact with the plateaus. This metastable state is indicated by line A in Figure 5.16. In order for this drop to advance to metastable state B, a large energy barrier has to be overcome. Although there may be noise in the system, the added energy of this is not great enough
to overcome the barrier to motion and so a force must be applied to allow the contact line to jump across the valley. If water is added to the drop the contact line will be pinned at A (right side of figure) until the liquid-air interface “reaches down” and wets B. A near-180° advancing contact angle is predicted. In order for the drop to recede from B to A (left side of figure) a force must be applied as well. A different energy barrier must be overcome (we draw two lines in the energy diagram - bottom of figure); If water is removed from the drop, the contact angle will decrease until the receding contact angle (of a smooth sample of the same material) is reached before receding. A lower angle may be observed due to pinning (i in the figure), and deformation of the drop (increasing the surface area to volume ratio) is required to overcome this barrier.
Figure 5.16  A pictorial representation of advancing and receding of a water droplet on a surface of model roughness that pins the water drop with corresponding energy diagram.

Figure 5.17 shows a model surface of different roughness. To advance from A to B, the contact line can make several small steps with much lower energy barriers than that described in Figure 5.16 thereby easing the transition. Further facilitating motion, metastable state A is much less stable than that indicated in Figure 5.16. Here the contact line is less continuous, makes less contact with solid and more with air and has to distort from linear to maximize contact with the plateaus. This metastable contact line is higher
in ground state energy than that indicated in Figure 5.16. When the energy barrier to
motion is lowered to less than the noise of the system, the 3-phase contact line is likely
dynamic, shifting constantly (advancing and receding) as the energy required for motion
is already overcome. As long as drop movement on a surface like this is slower than the
many small reversible incremental advancements and recessions the contact line is
already making due to noise, all that needs to be overcome for drop motion is inertia. At
this point the surface is ultrahydrophobic.

Figure 5.17  A pictorial representation of advancing and receding of a water
droplet on an ultrahydrophobic surface of model roughness that does not pin the water
drop with corresponding energy diagram
This model makes two very important predictions about wettability: 1) Wettability is purely a 3-phase contact line problem (1-dimensional). Classically, wettability is a 2-dimensional surface effect concerned with the surface energetics underneath a drop. The model proposes that to elicit changes to wettability, one just needs to modify the interaction of the surface with the 3-phase contact line – the rest of the drop is irrelevant. 2) Topology (shape) as well as topography (size) are important factors of the roughness. Whereas the topography of roughness is important in lowering the energy barrier to motion and in determining the amount of “steps” it takes to go from A to B, both topology and topography are significant in modifying contact line shape. This, in turn, is what determines ground state energy – a critical feature of drop motion. Classically, topology is irrelevant to the wettability outside of error correction factors; it does not matter if the features are squares or circles, only, for example, that the porous surface is 50% air and 50% surface.

Figures 5.16 and 5.17 are meant as models for the polypropylene surfaces treated with argon/PTFE plasma for 60 and 90 min, respectively. Figure 5.18 shows higher magnification SEM micrographs of these surfaces. The features in the 60 min reacted sample are larger, further apart and less contorted than those of the 90-min reacted sample. The 60 min sample exhibits relatively wide (0.5 - 1 μm) ridges with straight or gradually curving sections of ~5 μm that are spaced by several microns. The 90 min sample exhibits thinner, much more contorted ridges that are spaced by a micron or less. Envisioning the features in these micrographs as the “plateaus” of Figure 5.16 and 5.17, the 3-phase contact lines on the 90 min samples will be less continuous, more contorted and less stable and the barriers between metastable states will be lower than those of the
60 min samples. Although we cannot determine which parts of these surfaces will be in contact with water at the 3-phase contact line, it is likely that water penetrates portions of some of the valleys of the 60 min sample. The lower (almost absence of) hysteresis observed in samples treated for 90 min or more is due to both an increase in the ground state energy of the metastable states and a decrease in the energy barriers between metastable states.

Figure 5.18 Higher magnification scanning electron micrographs of polypropylene samples treated with argon/PTFE plasma for a) 60 min and b) 90 min

5.6. Summary

RF plasma sputtering of various polymers was studied under conditions such that no classical sputtering can take place. A mechanism is proposed for sputtering in which polymer degradation to monomer must occur at the target and then this monomer must (plasma) repolymerize on the substrate. The literature suggests that this is the case for PTFE. The present work shows that this process is more general and that PIB, PoMS, and PCTFE behave in this fashion, although not as cleanly as does PTFE. In all cases the
sputtered polymer was similar to the plasma polymer, but different from the conventional polymer based on IR, XPS, and water contact angle analysis. Ablation rates were calculated for all polymers studied as well as others to better understand the process. No relation between etching rate and sputtering was found. In general, chemical structure was the determining factor in ablation rate differences between polymers. Oxygenated polymers etch faster than non-oxygenated, but rates do not correlate with oxygen content.

Etching rates of polymers were as follows: polyethers > polyacrylates > hydrocarbons > halocarbons. Another important factor is the physical state of the polymer. Within specific categories of polymers, glassy polymers have more narrow distributions of ablation rates than do semicrystalline polymers. This work suggests that polymers with low ceiling temperatures and strong bonds (that will depolymerize under sputtering conditions) are candidates for sputtering targets to prepare supported thin films.

The knowledge obtained was used to simultaneously roughen and fluorinate biaxially oriented polypropylene using an inert gas plasma and PTFE as a solid phase reactant. The ablation rate of polypropylene is enhanced by the PTFE, presumably due to reactive ion etching caused by fragmented TFE species. Reaction time can be used to control the nature of the surface roughness; features become smaller, more pronounced, more contorted and closer together with increasing reaction time. After a critical reaction time (between 60 and 90 min), the surfaces become ultrahydrophobic - water droplets roll easily on horizontal surfaces. Contact angles are as high as $\theta_A/\theta_R = 172^\circ/169^\circ$ and hysteresis is very low. We explain this ultrahydrophobicity in terms of the shape and continuity of the 3-phase (liquid/solid/vapor) contact line and develop a model based on
this explanation. Metastable ground states for the droplets are high in energy and the barriers between metastable states are low.
APPENDIX A

PLASMA POLYMERIZATION OF MIXED MONOMER GASES FOR ULTRAHYDROPHOBIC POWDERS

A.1. Plasma Powders

With so much interest in wettability and in plasma methods of late, it is no wonder that alternate methods to those previously described have potential. Recently, materials possessing high contact angles have been synthesized by plasma polymerization of fluorocarbons; the contact angles of the resulting surfaces are dependent on the type of surface morphology generated. Washo reports a contact angle between 165-170° for a plasma polymerized tetrafluoroethylene using a RF inductively coupled flow reactor.\(^6^9\)

The plasma polymer is in powder form and the micrographs show a high surface roughness with crater-like features. For D.C. plasma polymerized vinylidene fluoride\(^7^5\), the contact angles were found to be 162° at the anode versus 119° at the cathode with corresponding roughness of 270 nm and 90 nm, respectively. The highest contact angle reported for plasma polymerized -CF\(_3\) substituted perfluorohexenes was 127° with a corresponding mean roughness of 0.38 nm.\(^7^6\) In these reports, the contact angle hysteresis was not reported and the extent of the hydrophobicity of these surfaces is not known.
A.1.1. Formation

Plasma powder formation is essentially the same process as film formation. The critical parameters controlling deposition rate (power, pressure, and flow rate) also control powder vs. film formation. This fact is easily explained when one considers the polymerization mechanism. As monomer molecules are activated in the reactor they react with their neighbors in the gas-phase forming oligomeric species. At some point the oligomer diffuses to the surface and "sticks". The progressive buildup (and post-adsorption reactions) of oligomers leads to the film of plasma polymer. Now considering that the way to control the speed of deposition becomes dependent upon maximizing gas-phase propagation and oligomer deposition, the proper ratio of initiating activated monomers to monomer neighbors (power/flow rate controlled) and the diffusional path length of the activated monomers and oligomers are key. Unfortunately, it becomes easy to see that if the gas-phase propagation is allowed to become too fast it overwhelms deposition and the oligomers grow into particlals before deposition. This explains the current observations that a relatively high pressure is needed for powder formation. The high pressure increases the gas-phase reaction rate and decreases the diffusional path-length relative to adsorption. The power/flow rate has a much smaller effect upon powder formation, but in general a low flow rate is needed. The last influence is the monomer itself. By the previous analysis, reactive monomers should show a higher propensity to form powders. In fact, generally this is true. Previous reports of monomer powder formation follow the general order: compounds with aromatic or triple bond
functionality > compounds with double bonds or cyclic structures > those without any of the aforementioned groups.

A.1.2. Initial Work

Various fluorocarbon gases were plasma polymerized on PET and analyzed for forming hydrophobic surfaces in Hsieh’s thesis.\textsuperscript{77} Emphasis was given to fluoroacrylates as these are highly reactive fluorocarbons. The most hydrophobic surfaces were generated with monomers that contain either carbonyl groups or double bonds that form powders. It was shown that monomers that have difficulty polymerizing in the gas phase (whether it does not have double bonds as in perfluorohexane or the site of the double bond is structurally hindered as in perfluoromethylpentene) do not form the necessary roughness to show ultrahydrophobicity. For the other monomers examined, a minimum monomer concentration as controlled by the monomer pressure was necessary to form powder structures. When the powder successfully deposited onto the support surface, a hydrophobic surface was formed. The chemical composition was not a major contributor as the F/C ratio of these powders is at most 1.3. For the monomers that have high F/O and C/O ratios, some polymerization occurred through the elimination of the carbonyl group and formed a low adherent powder coating. A minimum length for the fluorinated alkyl chain in the acrylate was necessary for high receding contact angle (and ultrahydrophobicity). The chain length must have been at least 3 carbon lengths or the chain must be branched.
A.2.  Materials and Methods

PET films (DuPont Mylar, 5 mil) were rinsed with distilled water and methanol, extracted in refluxing hexane for 2 h, and then dried (room temperature, 0.05 mm, >24 h). Perfluorohexane (PFH), 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene (NFH), styrene, methyl acrylate, acrylonitrile, and ethyl cyanoacrylate were purchased from Aldrich and used as received. Water was purified using a Millipore Milli-Q® system that involves reverse osmosis followed by ion-exchange and filtration steps. Plasma polymerizations were carried out in a home-built inductively coupled pyrex reactor in which flow rate, power (13.56 MHz - supplied by an Astron RS-35A power supply and a Yaesu FT-840 HF transceiver), and pressure can be controlled. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer - Physical Electronics 5100 spectrometer with Al K$_\alpha$ excitation (15 kV, 400 W) at a take-off angle of 75° (between the plane of the sample surface and the entrance lens of the detector optics). Atomic concentration data were determined using sensitivity factors obtained from samples of known composition: C$_{1s}$, 0.200; O$_{1s}$, 0.501; N$_{1s}$, 0.352; F$_{1s}$, 1.00. Contact angle measurements were made with a Ramé-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Dynamic advancing ($\theta_A$) and receding angles ($\theta_R$) were recorded while the probe fluid (water, purified as described above) was added to and withdrawn from the drop, respectively.

PET film samples were taped onto a glass slide with one sample upstream and another downstream. The glass slide was inserted into the reactor which was then evacuated to ~0.05 mm. Monomer gases were introduced using a needle valve and the
pressure was equilibrated to the desired pressure by adjusting the stopcock to the pump.

After equilibrium pressure was reached and the reactor was exposed to the monomer for at least 10 minutes, radio frequency at 20 W was applied for 15 minutes. The total flow rate was measured to be 1.7 sccm. When mixed systems were used, the monomer flow rates were adjusted to the desired ratios. The total monomer pressure used was 0.5 mm. After the plasma was turned off, monomer gas was allowed to flow through the system for 10 minutes before evacuating the chamber to \(-0.05\) mm for 10 minutes and isolating the PET film samples.

A.3. Results and Discussion

This work is seeking to extend the previous work of Hsieh and McCarthy with fluorinated acrylate plasma powders. That work successfully created powder coatings of the correct size to show ultrahydrophobicity using fluorinated acrylates. Unfortunately these materials are extremely expensive materials. It would be advantageous if this process could be extended to other, cheaper systems. In the previous sections of this thesis it is demonstrated that fluorinated acrylates are not likely to be magic materials. Instead, they are materials that combine high reactivity (for gas-phase formation) with fluorinated functionality. By separating these two critical features we may use more common starting materials in an effort to duplicate the success of the previous system.

In this effort the system will comprise of a powder forming monomer consisting of either methyl acrylate, styrene, or acrylonitrile. Ethyl cyanoacrylate was also attempted, but its high reactivity presented handling difficulties that were never overcome.
with this reactor. A fluorinated monomer is also used in conjunction with the powder monomer to induce a hydrophobic nature (typically in a 1:1 ratio). These monomers were either perfluorohexane (PFH-ane) or perfluorohexene (PFH-ene). For control, reactions with no fluorinated monomer were also done. Reactions were carried out at the conditions most conducive to powder formation in the previous work (flow rate \( \sim 1.7 \) sccm, pressure = 0.5 mm, power = 20 W, time = 15 min.). Samples were taken from two places in the reactor (labeled upstream and downstream) as powder formation can be placement specific. Samples were then immediately taken for XPS and contact angle analysis. Results are presented in Table A.1.

The first powder forming monomer studied was methyl acrylate. This was done to chemically duplicate the previous fluorinated acrylate system. Unfortunately, methyl acrylate does not form powders at the reaction conditions. This is determined by visible detection and is given in the “Powder” column of Table A.1. It is to be expected then that a mixture of methyl acrylate and PFH-ane would also not produce powder (1:1). It is known that PFH-ane does not produce powder on its own. The inability of this system to produce powder results in a small rise advancing and receding contact angles. This also results in a small rise in hysteresis. On the other hand a mixture of methyl acrylate and PFH-ene does produce powder (1:1). Unfortunately, it is not of sufficient size or roughness to enable ultrahydrophobicity. The contact angle hysteresis is raised dramatically due to a sizable increase in advancing angle.

Styrene was then substituted for the methyl acrylate as the powder forming monomer. Styrene does form powder on its own and should help with formation of powders in the mixed system. However, the greater propensity of styrene to form
powders cannot overcome the slow gas-phase reaction of the PFH-ane (1:1). The resultant film has a contact angle behavior similar to the methyl acrylate - PFH-ane system (a typical behavior for fluorinated hydrocarbon systems). Again the mixture with PFH-ene produced powders (1:1). In this case however, the downstream sample had a hysteresis that was remarkably reduced. Water droplets did not seem to like to be in contact with the surface and so the surfaces were considered to be ultrahydrophobic. The upstream sample had a larger hysteresis, but this was still reduced from the methyl acrylate system.

The last system presented has acrylonitrile as the powder forming monomer. Like styrene it forms powder on its own and is more reactive in the gas phase than the previous two monomers studied. When mixed with PFH-ane (1:1) this system, unlike the others, does produce powder. It is not ultrahydrophobic, however. The mixture with PFH-ene (1:1), like that of styrene, has a drastic decrease in contact angle hysteresis. The downstream sample has a hysteresis drop down to 6° – nearly as good as other ultrahydrophobic systems. The upstream sample is similar in behavior to the upstream sample of the styrene system. Another ratio was attempted for this system (3:1) in an effort to produce better powders (smaller and rougher). This was unsuccessful do to the low fluorination of the resultant powder.

When one takes a look at the data as a whole, a few trends may be observed. First, as we add better powder forming monomers, better powders result. This, of course, makes sense. Also, PFH-ane has a tendency to quench powder formation in the system. This is likely due to its slow gas-phase reaction rate stemming from the saturated nature. PFH-ene, however is amenable to powder formation as its unsaturation increases its
reactivity. In general, the upstream samples are not as good as the downstream samples.

As was mentioned before, powder formation is regio-specific in the reactor. Lastly, degree of fluorination of the powder has very little effect upon the resultant contact angles once it has attained a certain value (the 3:1 acrylonitrile: PFH-ene sample did not attain this value).
Table A.1  Data for plasma copolymerization of powder forming monomers (Comonomer A) and fluorinated monomers (Comonomer B)

<table>
<thead>
<tr>
<th>Comonomer A</th>
<th>Comonomer B</th>
<th>Ratio</th>
<th>Powder</th>
<th>Position</th>
<th>F/C</th>
<th>$\theta_A(\degree)$ / $\theta_R(\degree)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl acrylate</td>
<td>none</td>
<td>no</td>
<td>upstream</td>
<td>0</td>
<td>80 / 50</td>
<td></td>
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<tr>
<td></td>
<td>perfluorohexane</td>
<td>50/50</td>
<td>no</td>
<td>upstream</td>
<td>1.7</td>
<td>116 / 70</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>downstream</td>
<td>0</td>
<td>85 / 56</td>
<td></td>
</tr>
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<td></td>
<td>perfluorohexene</td>
<td>50/50</td>
<td>no</td>
<td>upstream</td>
<td>1.2</td>
<td>114 / 72</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>downstream</td>
<td>1.2</td>
<td>161 / 48</td>
<td></td>
</tr>
<tr>
<td>styrene</td>
<td>none</td>
<td>yes</td>
<td>upstream</td>
<td>0</td>
<td>56 / 0</td>
<td></td>
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<tr>
<td></td>
<td>perfluorohexane</td>
<td>50/50</td>
<td>no</td>
<td>upstream</td>
<td>1.5</td>
<td>110 / 74</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>downstream</td>
<td>1.8</td>
<td>113 / 74</td>
<td></td>
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<tr>
<td></td>
<td>perfluorohexene</td>
<td>50/50</td>
<td>yes</td>
<td>upstream</td>
<td>1.3</td>
<td>127 / 65</td>
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<td>downstream</td>
<td>1.5</td>
<td>165 / 147</td>
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<tr>
<td>acrylonitrile</td>
<td>none</td>
<td>yes</td>
<td>upstream</td>
<td>0</td>
<td>51 / 0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>perfluorohexane</td>
<td>50/50</td>
<td>yes</td>
<td>upstream</td>
<td>1.2</td>
<td>131 / 48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>downstream</td>
<td>1.0</td>
<td>134 / 68</td>
<td></td>
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<tr>
<td></td>
<td>perfluorohexene</td>
<td>50/50</td>
<td>yes</td>
<td>upstream</td>
<td>1.2</td>
<td>115 / 44</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>downstream</td>
<td>1.4</td>
<td>172 / 166</td>
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<tr>
<td></td>
<td>perfluorohexene</td>
<td>75/25</td>
<td>yes</td>
<td>upstream</td>
<td>0.3</td>
<td>56 / 0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>downstream</td>
<td>0.3</td>
<td>57 / 0</td>
<td></td>
</tr>
</tbody>
</table>
A.4. Summary

In an effort to reproduce work done on producing ultrahydrophobic plasma powder coatings in a more cost effective manner, mixed monomer systems consisting of a powder forming monomer and a hydrophobizing fluorinated monomer were studied (1:1). The same reactor and conditions as the previous work was used. Although the best results previously were with fluorinated acrylates, mixtures of methyl acrylate and perfluorohexane or perfluorohexene did not produce ultrahydrophobic powders. With these mixed systems, higher reactivity in the powder forming monomers is needed. Both styrene and acrylonitrile produce ultrahydrophobic powders when mixed with perfluorohexene with the acrylonitrile system producing the best results.
APPENDIX B

INVESTIGATION OF POLYMER THIN FILMS ON CAPACITOR DIELECTRICS FOR IMPROVED CLEARING (SELF-HEALING) PERFORMANCE

B.1. Capacitors

Capacitors are electrical energy storage devices and consist of a dielectric material sandwiched between two electrodes with a voltage across them. The industry is very mature and any improvement has to be very cost effective, but may result in significant market share increase. Being that capacitor production is likely to experience growth due to the increased demand that power generation and electric vehicles are likely to put on production, research into this field is compelling.

It is known that the energy density stored in a capacitor is proportional to the product of the dielectric constant of the material and the square of the voltage applied to the capacitor. Therefore, it is much easier to maximize energy density by stressing the dielectric to near breakdown limits. This solution also has inherent problems as materials near their breakdown limit have increased partial discharges leading to energy loss, capacitance loss, and overall degradation of dielectric material resulting in failure of the capacitor. For these reasons, research into maximizing the voltage applied to a dielectric is the current path to maximizing performance.
B.1.1. Metalized Film Capacitors

In metalized film capacitors the electrodes are very thin layers of metal evaporated on the surface of the dielectric. Typically polypropylene, poly(ethylene terephthalate), or cellulose capacitors based on this construction have qualities not found in other capacitors. The most important of these qualities is known as “clearing”, which is a self-healing process following a partial discharge breakdown. This will be further explained in the following section. Other new phenomena appear in capacitor performance due to the metalized film construction including: clearing, corrosion of conductor layers during cyclical charging, and specific sensitivities of these capacitors to the surface treatment of film and to its thermal history. Our discussion will focus around the polypropylene dielectrics and, specifically, its clearing behavior.

B.1.2. Clearing

In metalized film capacitors, defects such as pinholes, foreign particles, or microflaws in the semi-crystalline polypropylene can lead to a localized breakdown of the film as the voltage is increased. Such a breakdown event results in a discharge of stored charge, with a consequent localized high temperature and pressure. This temperature can reach into the thousands of degrees in and around the area of the discharge. At the same time the film is punctured, the high temperatures vaporize the metalization driving the material outwards from the site. This effectively interrupts the arc of the discharge and electrically isolates the defect site preventing further discharge.
and damage. This self-healing event is known as clearing. The capacitor can now be taken to a higher voltage where further clearing events will isolate flaws. A schematic of the process is given in Figure B.1 and a scanning electron micrograph is provided in Figure B.2. Notice the initial puncture site in the polypropylene film at the center of B.2, surrounded by the demetallized region which is only \(\sim 5 \text{ to } 10 \text{ mm}^2\).

**Figure B.1**  A schematic of clearing\textsuperscript{78}
In a metalized film capacitor, clearing is deliberately carried out at a higher voltage than the operating voltage. It is known as pre-clearing and is done to isolate defects in the manufacture and improve performance. In service, clearing of lower energy may occur, reflecting the aging of the capacitor. When clearing occurs it is presumed that no conducting bridges of graphite are formed from decomposition of polymer. In reality, this does occur in some instances and can lead to catastrophic short-circuiting of the capacitor. This effect is highly dependant upon the chemical and physical makeup of the polymer. For instance, cellulose performs well but polystyrene does not. If a short circuit does not occur, then capacitor life is arbitrarily chosen as a 5% reduction in capacitance. As successive clearing events happen the small demetalizations add up to a significant portion of capacitance area.

It can be seen from the previous explanation that any decrease in either short-circuit formation (by eliminating potential graphitization) or in demetalization required to
isolate the defect would lead to lifetime improvements. In addition, maximizing the energy to perform the event would also be helpful for preventing energy loss and thermal damage.

B.2. **Materials and Methods**

Breakdown measurements were carried out with a home-built apparatus using a high-speed dual channel oscilloscope as the detector. A sandwich of metalized polypropylene capacitor grade dielectric was placed between two brass electrodes. The brass electrodes acted as connections to the metalization, which were the actual electrodes. This method was to simulate real capacitor conditions. The stack was placed under pressure and experiments carried out. A power source and function generator were used to apply a voltage ramp to a capacitor across the films. Voltage was measured by the oscilloscope as was current across a resistor between the hot and ground brass electrodes. Cleared area was measured by measuring the size of the area with a ruler and approximating as an ellipse. Biaxially oriented capacitor grade polypropylene (6 μm thick) was obtained from Aerovox, Inc. Polyoxymethylene (POM), poly (α-methylstyrene) (PaMS), cellulose acetate (CA), cellulose nitrate (CN), perfluorohexene (PFH), ethylene (Eth), and oxygen were purchased from Sigma-Aldrich and used as received. Films were applied using either a home-built plasma reactor described in chapter 5 or by a draw down solution casting technique. We used a Techniques TDS340A 100MHz, 500 MS/SEC, 2 CH Digital oscilloscope with HV-P60 high voltage probe (2000:1 att).
B.3. Results and Discussion

In an effort to improve capacitor performance, various thin films were applied to capacitor grade metalized polypropylene (PP). It was hoped that these films would: 1) influence clearing efficiency by reducing the energy to produce a cleared area, 2) increase the breakdown voltage of the dielectric, 3) reduce carbonation from self-healing events, or 4) reduce damage associated with clearing. It is known that celluloid materials perform better in these regards and it is thought that the oxygen content helps to reduce carbonation and eases the combustion events inherent with the discharge. With this in mind, films of ethylene/oxygen mixtures were produced by plasma discharge. Various ethylene/oxygen ratios were used. Table B.1 shows the results of dielectric breakdown experiments on the resultant films. No statistically significant difference in breakdown voltage or efficiency (clearing area/voltage) was seen in any sample (as compared to the control – Neat). Error in the voltage measurement is \( \sim 0.5 \text{ kV} \) and in the efficiency measurements \( \sim 4.0 \text{ mm}^2/\text{kV} \). In addition, no visible differences were detected in the breakdown area (damage or carbonation). Plasma polymers of perfluorohexene (PFH) were studied in hope that the fluorine would help quench any plasma discharge involved in the clearing process. No significant results were attained.

In an effort to increase oxygen content of the thin film, poly(oxymethylene) (POM) was applied to the dielectric via a draw down solution casting technique where a solution of polymer is applied to a substrate and a rod with a wire wrapped around it is drawn over the substrate to remove excess solution. Film thickness is determined by solution concentration and wire diameter. No significant results were attained with POM.
To increase the amount of material in the gas-phase during breakdown, poly(α-methylstyrene) (PaMS) was applied to the dielectric. Again, no promising results were produced. Thinking that the better test of our hypothesis was to use a known material, cellulosic materials were coated on the dielectric and studied. Cellulose acetate (CA) and cellulose nitrate (CN) were used with little success.

In a last attempt with this research, varying the thickness of the thin films was tried. Table B.2 shows that little, if any, effect of POM and CA upon capacitor clearing performance at any thickness can be expected. At this stage, the research was terminated due to lack of confidence in the underlying thesis. It is doubtful that thin films would influence clearing performance, or at the very best, that any effects are too small to be determined as they lie within error.

**Table B.1** Data table of the effect of differing polymer thin films on dielectric breakdown experiments

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Voltage (kV)</th>
<th>Area/Voltage (mm²/kV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat</td>
<td>11.6</td>
<td>11.1</td>
</tr>
<tr>
<td>polyoxymethylene</td>
<td>11.5</td>
<td>9.8</td>
</tr>
<tr>
<td>poly(α-methyl styrene)</td>
<td>12.5</td>
<td>9.0</td>
</tr>
<tr>
<td>cellulose acetate</td>
<td>10.4</td>
<td>9.9</td>
</tr>
<tr>
<td>cellulose nitrate</td>
<td>11.4</td>
<td>10.1</td>
</tr>
<tr>
<td>plasma-perfluorohexene</td>
<td>2.9</td>
<td>3.9</td>
</tr>
<tr>
<td>plasma-ethylene</td>
<td>2.8</td>
<td>2.6</td>
</tr>
<tr>
<td>plasma-ethylene/O₂ (3:1)</td>
<td>2.8</td>
<td>2.6</td>
</tr>
<tr>
<td>plasma-ethylene/O₂ (2:1)</td>
<td>2.8</td>
<td>2.6</td>
</tr>
<tr>
<td>plasma-ethylene/O₂ (1:1)</td>
<td>3.3</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Table B.2  Data table of the effect of differing polymer thin film thickness on dielectric breakdown experiments

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Thickness</th>
<th>Voltage (kV)</th>
<th>Area/Voltage (mm²/kV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>polyoxymethylene</td>
<td>0.1</td>
<td>4.4</td>
<td>30.7</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>4.6</td>
<td>34.0</td>
</tr>
<tr>
<td>cellulose acetate</td>
<td>0.1</td>
<td>4.9</td>
<td>24.8</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>5.0</td>
<td>32.2</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>5.0</td>
<td>28.1</td>
</tr>
</tbody>
</table>

B.4.  Summary

As part of a comprehensive effort to improve capacitor dielectric performance in the area of clearing (self-healing), thin films of various polymers were applied to the surface of capacitor grade polypropylene. Oxygenated, fluorinated, nitrated, and hydrocarbon thin film materials were applied and then characterized by dielectric breakdown voltage, clearing efficiency, and visible carbonation and damage. These films failed to produce any effect and the overall research showed that no effect can be expected of thin film application upon clearing performance.
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