PSEUDOFUORINATION OF POLYMER SURFACES
USING FREON GASES

by

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ABSTRACT

Hydrocarbon polymers were immersed in inductively coupled glow discharges of CF₃H and C₂F₆. The two types of discharges gave fluorinated products similar to each other but different from CF₄ or F₂ reaction products. ESCA C₁s spectra showed distinct CF₃ and CF₂ peaks, with the CF₃ groups present in greater quantity than in polymers treated with CF₄ or F₂. Optical emission spectroscopy failed to detect atomic fluorine lines in the plasma glow.

The ESCA C₁s spectra of widely different polymers were nearly indistinguishable: polyoxymethylene (POM), cellulose acetate butyrate (CAB), polyvinyl fluoride (PVF), polyvinylidene fluoride (PVF₂), and low density polyethylene (LDPE). The two oxygen-containing polymers lost nearly all oxygen atoms after only a few seconds in the plasma, possibly because of free radical attack. Control experiments with polytetrafluoroethylene (PTFE) indicated that true surface reaction took place, rather than polymerization and deposition.

Advancing contact angle measurements with formamide did not show the normal drop or minimum in angle with progressive fluorination. Rather, contact angle increased monotonically in all sets of reactions, reaching the PTFE value of 93° for polymers fluorinated in the glow. LDPE treated with C₂F₆ in a Faraday cage for 60 minutes had a contact angle of 134°; the curve of angle versus time increased monotonically from 78° (untreated) toward an asymptotic value of 135°. This angle is the predicted value for formamide on a zero energy surface.

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# Table of Contents

Abstract .................................................. 2  
Acknowledgements ......................................... 3  
Table of Contents ......................................... 4  
List of Figures ............................................. 5  
List of Tables .............................................. 7  

Chapter 1: INTRODUCTION .................................. 8  

Chapter 2: BACKGROUND .................................. 12  
2.1 PLASMAS ............................................. 12  
2.2 ESCA .................................................. 24  
2.3 CONTACT ANGLE ..................................... 41  
2.4 EMISSION SPECTROSCOPY ............................. 46  

Chapter 3: FLUORINE CHEMISTRY ......................... 48  

Chapter 4: RESEARCH PLAN ............................... 58  

Chapter 5: EXPERIMENTAL APPARATUS AND PROCEDURE 62  

Chapter 6: EXPERIMENTAL RESULTS ..................... 64  
6.1 UNTREATED POLYMERS ................................ 67  
6.2 ARGON ION SPUTTERING ............................... 67  
6.3 HELIUM PLASMA TREATMENT ......................... 67  
6.4 EFFECT OF FORWARD POWER ........................... 73  
6.5 EFFECT OF GAS CONCENTRATION IN HELIUM ........ 73  
6.6 RESULTS WITH PTFE ................................ 76  
6.7 RESULTS WITH PVF .................................. 80  
6.8 RESULTS WITH PVF2 ................................ 82  
6.9 RESULTS WITH CAB .................................. 85  
6.10 RESULTS WITH POM ................................ 89  
6.11 RESULTS WITH LDPE ................................. 94  
6.12 CAGE REACTIONS ................................... 98  
6.13 EMISSION SPECTROSCOPY ............................ 105  
6.14 GENERAL EVOLUTION OF C1S SPECTRA .............. 105  

Chapter 7: DISCUSSION ................................... 115  

Chapter 8: CONCLUSIONS .................................. 126  

References ................................................. 129  

Appendix: Rotameter calibration curves .................. 133
LIST OF FIGURES

1. ESCA survey spectrum of untreated PTFE 32
2. ESCA survey spectrum of untreated POM 33
3. ESCA C1s spectrum of untreated PTFE 36
4. ESCA C1s spectrum of untreated POM 37
5. ESCA C1s spectrum of untreated PVF 38
6. ESCA C1s spectrum of untreated LDPE 68
7. ESCA C1s spectrum of untreated POM, showing contamination 69
8. ESCA C1s spectrum of untreated CAB 70
9. ESCA C1s spectrum of untreated PVF2 71
10. ESCA C1s spectrum of PTFE after argon ion sputtering 72
11. ESCA C1s spectrum of POM after C2F6 at 1 Watt 74
12. ESCA C1s spectrum of POM after C2F6 at 100 Watt 75
13. ESCA C1s spectrum of treated PTFE, with no CF3 peak 77
14. ESCA C1s spectrum of treated PTFE, with large CF3 peak 78
15. Typical ESCA C1s spectrum of treated PTFE 79
16. Typical ESCA C1s spectrum of PVF treated for 60 minutes 81
17. Typical ESCA C1s spectrum of PVF2 treated for 60 minutes 83
18. PVF2 contact angle vs. reaction time 84
19. Typical ESCA C1s spectrum of treated CAB 86
20. CAB %F vs. reaction time in CF3H 87
21. CAB %F vs. reaction time in C2F6 88
22. Typical ESCA C1s spectrum of treated POM 90
23. POM %F vs. reaction time in CF3H 91
24. POM %F vs. reaction time in C2F6 92
25. POM contact angle vs. reaction time 93
26. Typical ESCA C1s spectrum of treated LDPE 95
27. LDPE %F vs. reaction time in CF3H glow
28. LDPE contact angle vs. reaction time in C2F6
29. ESCA C1s spectrum of POM treated in CF3H cage reaction
30. ESCA C1s spectrum of LDPE treated in CF3H cage reaction
31. ESCA C1s spectrum of POM treated in C2F6 cage reaction
32. ESCA C1s spectrum of LDPE treated in C2F6 reaction
33. LDPE contact angle vs. reaction time after C2F6 cage reaction
34. Emission spectrum of He plasma (650-800 nm)
35. Emission spectrum of CF3H plasma (650-800 nm)
36. Emission spectrum of C2F6 plasma (650-800 nm)
37. ESCA C1s spectrum of POM showing peak growth
38. ESCA C1s spectrum of POM showing peak growth
39. ESCA C1s spectrum of POM showing peak growth
40. ESCA C1s spectrum of POM showing peak growth
41. ESCA C1s spectrum of CAB showing peak growth
42. ESCA C1s spectrum of PVF2 showing peak growth
43. Typical ESCA C1s spectrum of treated POM
44. Typical ESCA C1s spectrum of treated CAB
45. Typical ESCA C1s spectrum of treated PVF2
46. POM %O vs. reaction time
47. Rotameter calibration curve for helium
48. Rotameter calibration curve for CF3H
49. Rotameter calibration curve for C2F6
LIST OF TABLES

1. Contact angles of various polymers with formamide ........................................... 45
2. Diatomic bond energies and bond lengths ............................................................. 49
3. Critical surface tensions of various polymers ....................................................... 59
4. Standard heats of formation of some methylenic radicals .................................... 60
5. Effect of forward power on products stoichiometry .............................................. 73
6. Results with PTFE ................................................................................................... 76
7. Results with PVF .................................................................................................... 80
8. Results with PVF2 .................................................................................................. 82
9. Results with CAB .................................................................................................. 85
10. Results with POM ................................................................................................ 89
11. Results with LDPE .............................................................................................. 94
12. Results of cage reactions ...................................................................................... 98
13. Results of LDPE/cage reactions ......................................................................... 103
This thesis is concerned with polymer surface modification, a subject typical of chemical engineering research in that it has a pure and an applied side. From an application oriented viewpoint, fluorination of an inexpensive polymer gives enhanced surface properties normally associated with expensive materials. From a more strictly chemical perspective, free radical reactions in a nonequilibrium environment can lead to interesting effects on polymeric substrates. Also there has historically been much interest and value attached to the chemistry of carbon, especially the creation of carbon-carbon bonds.

Engineering application of polymer science to materials problems has shown polymers to be increasingly useful, with blends, copolymers, and composites having a particularly bright future. The judicious combination of inexpensive components can yield remarkable materials, e.g. graphite-epoxy composites, fiberglass reinforced plastics, and styrene-butadiene elastomers. These three examples pertain to bulk properties such as stiffness, impact resistance, and yield strength, but one need not modify the entire bulk of an article in order to change the surface properties.

Rather, a common means of such alteration is the application of a coating such as paint, lacquer, or wax. What makes chemical modification appealing is that the new surface layer is native, not deposited. Fluorination actually changes the substrate instead of
putting down a coating on it.

Appreciation of pseudofluorination requires a understanding of Teflon and its attractiveness as an engineering material. Its chemical name is polytetrafluoroethylene (PTFE) and it consists of long chains of CF groups:

\[
\begin{align*}
\text{F} & \text{ F} & \text{ F} & \text{ F} & \text{ F} \\
\ldots & \text{C} & \text{ C} & \text{ C} & \text{ C} & \ldots \\
\text{F} & \text{ F} & \text{ F} & \text{ F} \\
\end{align*}
\]

PTFE has extraordinary surface properties, such as low friction coefficient, chemical inertness and solvent resistance, and low water wettability. Polyethylene (PE), on the other hand,

\[
\begin{align*}
\text{H} & \text{ H} & \text{ H} & \text{ H} & \text{ H} \\
\ldots & \text{C} & \text{ C} & \text{ C} & \text{ C} & \ldots \\
\text{H} & \text{ H} & \text{ H} & \text{ H} & \text{ H} \\
\end{align*}
\]

cannot compare with PTFE regarding surface characteristics but is less expensive and easier to process. One can envision the fabrication of a large PE object, followed by the transformation of its surface into a PTFE-like region. This process would incorporate the advantages of both materials—the convenience of working with PE, and the superior surface properties of PTFE.

PTFE owes those excellent characteristics to the CF groups of which it consists. The operating hypothesis of this research is that a CF surface will possess in greater measure those things which make a CF surface attractive. Pseudofluorination is the reaction of CF
radicals with a substrate, where the CF$_3$ radical is regarded as a large "pseudohalogen:"

\[ \text{F F F F} \]
\[ \text{FCF FCF FCF FCF} \]
\[ \ldots \text{C---C---C---C} \ldots \]
\[ \text{FCF FCF FCF FCF} \]
\[ \text{F F F F} \]

It is interesting to note that the reaction of a CF$_3$ group with a carbon chain backbone leads to a fluorocarbon product without the creation of any carbon-fluorine bonds. From a purely chemical point of view, creation of carbon-carbon bonds has traditionally carried much scientific weight. Ironically, minimization of F activity is crucial to the formation of a CF$_3$ surface. Fluorine is known for its high reactivity, but because thermodynamic considerations become essentially inoperative in the nonequilibrium environment of a plasma, many unlikely and unfavorable reactions are achievable in principle.

So-called cold plasmas as used in this work occur at low pressure (1 mm Hg) and room temperature. However, the kinetic distribution of particle speeds is not the Maxwellian bell curve centered about some central value. Rather, there is a nonequilibrium distribution of speeds, with most particles moving as they do at room temperature but a small fraction having extraordinarily high energies. Such an environment is conducive to fast reactions between otherwise unreactive species.

The attractiveness of the particular system used here, involving
Freon gases in an inductively coupled plasma, include the following:

- Freon gases—nontoxic, noncorrosive (cf. F2 gas)
- Room temperature operation
- Fast reactions—on the order of minutes
- Inductive coupling—no internal electrodes, less contamination
- Dry—no liquids to dispose of (cf. HF wet processes).

The pre-experimental part of this research involved selection of CF3-containing freon gases and suitable hydrocarbon polymers for modification. Experimental work consisted of the synthesis and analysis of the resulting surfaces.
2.1 PLASMAS

In order to consider plasma-enhanced modification of polymer surfaces, one should have some understanding of plasmas and their applications. Classical chemical education does not generally include study of plasmas, and a classically trained person seeking to understand the subject would ask the two obvious questions:

(1) What is a plasma?
(2) Why use a plasma?

The following discussion is intended to answer those two questions.

By plasma is meant an ionized gas, with overall neutrality throughout most of its volume, which behaves differently from a non-ionized gas. Of course, no gas in equilibrium can be completely non-ionized since there must always be a balance:

\[ G \leftrightarrow G^+ + e^- \]

where \( G \) represents a neutral gas molecule, \( G^+ \) an ionized gas molecule, and \( e^- \) an electron.

The concentration of electrons and ions are negligible at room temperature. A quick statistical-mechanical calculation of the equilibrium constant leads to the Saha equation, which gives these concentrations as functions of temperature:
\[
\frac{\text{ne}}{\text{nn}} = 15 \quad (3/2) \\
\frac{\text{ni}}{\text{nn}} = (2.4 \times 10^{-19}) T \exp(-V_i/kT)
\]

where \( \text{ne} \) = number density of electrons, cm\(^{-3}\),
\( \text{ni} \) = number density of ions, cm\(^{-3}\),
\( \text{nn} \) = number density of neutral molecules, cm\(^{-3}\),
\( T \) = gas temperature, K,
\( k \) = Boltzmann's constant, 1.38 \times 10^{-16} \text{ erg/K},
\( V_i \) = ionization energy of a gas molecule, erg.

For room temperature and atmospheric pressure, one may calculate the
degree of ionization of N with \( T=300 \text{K} \), \( V_i=(14.5 \text{eV})(1.6 \times 10^{-19} \text{ erg/eV}), \)
\( 19 -3 \) 2 \(-122 \)
and \( \text{nn}=P/kT=3\times 10^{12} \text{ cm}^2 \), finding \( \text{ni/nn}=10^{-2} \). Thus it makes no sense
to speak N as a plasma under standard conditions, even though there
is some ionization. As the temperature increases, the degree of
ionization increases slowly before "taking off" rapidly due to the
exponential dependence, until full ionization is reached in the limit
of infinite temperature. There is no sharp phase transition
temperature corresponding to melting or boiling points, but the
behavioral difference between plasma and gas is arguably as great as
those between gas and liquid, liquid and solid. Accordingly, plasmas
have been called the fourth state of matter.

As well as having an appreciable degree of ionization, a plasma
behaves differently from its non-ionized counterpart. Specifics of
plasma behavior are the subject of another section, but the following
list of natural and man-made plasmas should bring to mind their
distinctive characteristics:
stellar interiors, solar wind, solar corona, interstellar space, Van allen belts, Aurora Borealis, lightning, fire, ionosphere, neon signs, and fluorescent lights.

At least 90\% of the mass of the universe exists in the plasma state.

Specification of the state of a gas involves specification of the temperature and pressure; the same holds for a plasma. Pressure is related to number density by the ideal gas law \( P = n k T \), or \( P_i = n_i k T \) for each species \( i \) of a multicomponent gas. It is the convention to speak of number density in a plasma rather than pressure. Typical electron number densities are \( n_e = 10^{-12} \) cm\(^{-3} \). Number densities of individual species correspond to partial pressures in a gas mixture. Unlike before, each component may have its own temperature.

The idea of temperature differing for each species may at first seem strange, so a brief consideration of thermal equilibrium follows. A gas in thermal equilibrium consists of many particles with different speeds: there is a distribution of thermal velocities. The distribution is simply a bell curve centered around some most probable, or average, speed which corresponds to the temperature \( T \).

For a single particle, \((1/2)mv^2\) is associated with \((3/2)kT\),

\[
\text{where } m = \text{mass of the particle, and} \int \text{v = velocity of the particle.}
\]

For a collection of particles, the average kinetic energy \( (1/2)\text{mv}^2 \) is related to what is called "the" temperature of the av
system. However, each particle moves with a particular speed corresponding to a particular temperature.

In a plasma, then, electrons may have their own average $T$, ions a different one, and neutrals still another. So-called cold plasmas comprise room temperature gases which have been ionized into room temperature ions and neutrals, while electrons move with velocities corresponding to much higher temperatures. Cold plasmas are not formed by high temperatures, and since the system would like to collapse into thermal equilibrium, an external driving force is needed to produce and maintain such a plasma.

Strong electric and magnetic fields will produce a plasma by accelerating free electrons, thus promoting ionizing collisions with neutrals. A spark plug does exactly this, as a strong electric field generates a plasma as long as the field is present. Capacitive coupling between two plates is an extension of the spark plug physics, in which a rapidly alternating potential creates a plasma. The generation method used in this research is inductive coupling, whereby a high frequency AC potential is applied across the ends of a metal coil. Current flow through the coil induces strong enough fields to cause ionization of the gas within the coil.

It is interesting to consider the collisional processes taking place, where a collision is an event in which one particle transfers a significant amount of momentum to another. A gas consisting only of electrons in motion would be dominated by electrostatic forces--coulomb collisions. It makes little sense to think of hard sphere
collisions, or physical contact, when considering electron-electron repulsion. The repulsive force falls off with \( r^2 \), where \( r \) is the separation between two electrons. However, a gas consisting only of neutral atoms, e.g. argon, would be dominated by collisions much more like hard sphere collisions. These so-called Van der Waals forces fall off with \( r^7 \), as also do the forces of the popular Lennard-Jones model. A typical cold plasma has both true coulombic (long distance) and non-coulombic (short distance) collisions.

Collisions may be elastic or inelastic: total energy must be conserved, but not necessarily kinetic energy. Of particular interest is an elastic collision between an electron and a heavy particle such as a neutron. Very little energy can be transferred, given the mass ratio on the order of 10.

Understanding plasma chemistry requires an understanding of the reactants, i.e. the species present in a plasma. Certainly electrons, ions, and neutral molecules are present. Also to be expected are excited state molecules and ions, metastables, and--when the gas contains polyatomic molecules--free radical fragments. In fact, without knowing anything about plasma chemistry, one could reasonably expect that an increased supply of free radicals would lead to productive chemistry. Electronic relaxation processes cause photon emission, often intense, which is the raison d'etre of the neon sign and the fluorescent light.

Photons are emitted as a result of one of three types of electron transition: bound-bound, bound-free, or free-free. A bound-bound
transition is a discrete jump of an electron from a higher energy level to a lower one, giving off a photon whose energy is equal to the difference in energies of the two levels involved. Such line radiation gives a vapor lamp its color, e.g. a sodium vapor lamp emits a bright yellow light.

A bound-free transition, or radiative capture, occurs when a free electron of arbitrary kinetic energy moves into a particular energy level of a molecule with which it collides, liberating a photon isoenergetic with the energy difference. (The inverse process is called photoionization, which absorbs radiation and ejects an electron).

A free-free transition occurs in the collision of any particle with a heavy species, because the changing dipole moment of the heavy results in the emission of radiation. This is called bremsstrahlung, or continuum, radiation. Unlike its two counterparts, this type of transition has no inverse absorbing process. It should be easy to understand why lightning is so bright, why welders wear protective filter glasses, and why cold plasmas used in chemistry are often called glow discharge plasmas (GDP's).

Before discussing plasma applications, which are myriad, it is appropriate to explain how plasmas behave differently from non-ionized gases. The walls of a plasma-containing enclosure become negatively charged with respect to the contents because fast moving electrons are more likely to hit the wall than their massive counterions. Any
electrically isolated surface in contact with a plasma serves as an electron sink to which electrons diffuse until the resulting field compensates for the gradient. Then electron flux toward the wall must be balanced by ion flux, which is slower and therefore rate limiting. These relatively immobile ions occupy a region just adjacent to the wall, a positively charged region which shields the bulk gas from the wall potential.

In fact, free charges will surround any charged object in contact with the plasma. Water molecules orient themselves around free protons, just as they will hydrate any other aqueous ion. Similarly, plasmas exhibit self-organizing, self-shielding behavior, the region of "hydration" being known as the sheath. In this research polymer films are immersed in a plasma, whereupon the polymer film becomes negatively charged and is surrounded by a sheath of positive ions.

This shielding behavior occurs in response to time-varying potentials, too. Incoming electromagnetic waves cause the plasma sheath to oscillate, thus the sheath acts as a mirror and reflects those waves. The ionosphere reflects short-wave radio signals in just this way, as it will do to any waves of frequency sufficiently low that the plasma electrons can move quickly enough. These shielding and mirroring effects are intrinsic characteristics of plasmas and do not occur in neutral gases.

Elementary chemistry textbooks explain the high electrical conductivity of metals by describing a metal as a collection of positive ions floating in a sea of free electrons. That description
fits a plasma well but cannot explain plasma transport phenomena similarly, as the appropriate phenomenological coefficients are generally tensorial. Volumes and volumes have been devoted to transport processes in plasmas, waves in plasmas, and other effects peculiar to ionized gases. A brief introduction thereto is a book by Chen (1974).

All transport is inherently non-equilibrium, but GDP's are so far out of equilibrium that classical thermodynamics and kinetics become essentially inapplicable. For the synthetic chemist the situation may be interesting vis-a-vis products, but for the engineer the situation is terrible with respect to understanding mechanistic details.

Hopefully the preceding discussion of what a plasma is has suggested answers to the second question--why use a plasma?--even before the formal consideration of applications. A general answer is that a plasma enhances momentum and energy transfer at low temperatures. A more specific answer is that a plasma can create free reactive species leading to high reaction rates and otherwise inaccessible products and reactions.

For example, ultraviolet radiation from a GDP can create active sites on a solid substrate and form free radicals in the gas phase. This research deals with production of the CF radical, generated by collisions and by radiation absorption in CF and CFH gas. Free radical sites and unsaturation in the polymer surface can stem also from ion bombardment and photoabsorptive processes.
Homogeneous gas-phase reactions serve as the simplest example of GDP application to synthetic chemistry. For instance one could reasonably expect Xe and Ar to be more reactive in a plasma than under ordinary conditions. The high energy environment activates them, and indeed rare gas halides have been so produced. A less exotic case is the activation of \( N_2 \), a notoriously inert molecule. Nitrogen has been used in the plasma production of silicon nitride on semiconductor wafers.

In fact, the semiconductor industry makes the most extensive use of plasma processing. For as integrated circuit technology is largely surface technology, so too gas-solid reactions occurring in a plasma are intrinsically surface phenomena. Chemical vapor deposition (CVD), or vapor phase epitaxy (VPE), is the growth of a film upon a substrate. Tetrachlorosilane in a hydrogen plasma decomposes, depositing silicon atoms on a solid surface below. A silane/ammonia/nitrogen plasma yields silicon nitride, while a silane/oxygen mixture gives \( SiO_2 \) growth on the substrate. The future holds great promise for fabrication of electrical interconnects on microchips by metal vapor deposition on microchips.

More important to very large scale integration (VLSI) is the potential etching behavior of a GDP. A typical processing sequence involves many masking steps, with the subsequent removal of each mask. By mask is meant any protective layer on a wafer, such as plasma-deposited \( Si_3N_4 \) or \( SiO_2 \). Plasma etching offers a simple means of mask removal, avoiding the handling of wet chemical etchants. Typical wet etches consist of mixtures of HF, HNO\(_3\), HPO\(_3\), HCl, etc., all
unpleasant to use. Risk of contamination increases with handling and introduction of wet chemicals. Other associated problems include capillarity effects, etch isotropy, and waste reagent disposal. Use of an inductively coupled plasma etch circumvents these difficulties.

Standard etchant gases include fluorocarbons, particularly mixtures with oxygen. Surface ablation occurs chiefly by two mechanisms: desorption following surface reaction with free radicals, and physical milling of the surface. Cognizance of the mechanics of etching figures into a better understanding of polymer modification.

Plasma polymerization, recently a popular area of study, allows for deposition of polymeric films on inert substrates. Such films do not show the pinhole defects present in thin films put on by spin casting. Unsaturated gaseous monomers such as tetrafluoroethylene will polymerize in a GDP, forming an amorphous macromolecular solid in the reactor. More surprising is the polymerization of saturated hydrocarbons as a result of the high energy environment. That is, atomic bond cleavage creates reactive species, and carbon-containing radicals link into an amorphous network. Film growth by plasma polymerization gives a product morphologically dissimilar from that of classical vinyl addition polymerization. For this research, however, the more important point is simply that one may grow a polymeric coating in a GDP.

Contrast this type of modification with the etching behavior so vital to the semiconductor industry. Depending on reaction
conditions, a GDP may alter surface properties either by polymerization or etching, two opposite effects. There is a third, intermediate application of GDP's to surface modification, and that use is the subject of this particular investigation.

The two previously mentioned means of surface changes directly affect the lattice or backbone structure of a solid. The plasma may deposit or remove backbone atoms from the substrate, effectively raising or lowering the surface height. But a third way of alteration does not affect the integrity of the lattice. Consider polyethylene (PE), essentially comprising long chains of carbon:

\[ \ldots-C-C-C-C-C-\ldots \]

Since carbon has four bonding electrons, PE's chemical structure is

\[ \begin{array}{cccccc}
    & H & H & H & H & \\
\ldots-C-C-C-C-C-\ldots & & & & & \\
    H & H & H & H & \\
\end{array} \]

The hydrogen atoms are not really part of the lattice but are best thought of as simply saturating the carbon backbone atoms. Etching of PE would mean breaking of carbon-carbon bonds and removal of carbon chain fragments, with the associated hydrogen atoms going "along for the ride." Precisely the reverse would occur in plasma polymerization. An alternative reaction concentrates on the H rather than the C.

The work of Corbin (1983) and Anand (1981) involved replacement
of those pendant hydrogens with fluorine atoms throughout a thin surface region. That is, a PE surface took on the chemical structure of Teflon:

\[ \begin{array}{c}
  \text{F} \\
  \text{F} \\
  \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
  \text{F} \\
  \text{F} \\
\end{array} \]

Teflon (PTFE) is an attractive engineering material largely because of its surface properties: low coefficient of friction, excellent chemical resistance, and hydrophobicity (not wettable by water). It is this sort of chemistry which is the subject of this research.

In conclusion, a few points are worth remembering. First, reactor design and analysis cannot be done easily because the chaotic, non-equilibrium environment cannot be modelled in any useful way. That is, classical thermodynamics, kinetics, and transport theory have yet to be applied to GDPs in a successful and comprehensive fashion. Second, small scale use is far more practical than large scale. Third, and most significant, the non-equilibrium environment allows for investigation of hitherto less accessible chemistry but at low temperatures and fast reaction times.
2.2 ESCA

Chemical analysis and characterization play an indispensable role in materials science and synthesis. Although analysis can stand on its own as a field of scientific study, synthesis alone cannot, for there must be some way to examine what has been made. In that sense all organic and inorganic synthetic chemists must be also analytical chemists. This reasoning extends to much of engineering in general, and in particular to this study of polymer surface modification.

Before examining the intersecting areas of polymer characterization and surface study, it is appropriate to review some fundamental concerns of analytical chemistry:

*Is the technique non-destructive?
*What amount and form of sample are required?
*What are the accuracy and precision?
*What are the detection limits?
*How reproducible is the technique?
*Are there interference and contamination effects?
*What specific information can be learned?

There is nearly always a tradeoff between confidence and convenience: the more certainty is needed in an analysis, the more time, money, and effort must be spent.

Surface analysis differs sufficiently from bulk analysis that most bulk techniques do not apply or at least must be modified somehow. Adamson (1976) classifies surface study techniques into four general areas:
(1) Microscopy

(2) Diffraction and scattering

(3) Spectroscopy

(4) Other, such as conductance, contact angle, coefficient of friction, etc.

The information sought in this research is the degree and nature of fluorination of a hydrocarbon polymer surface; within that context one can select appropriate methods of analysis.

The four best known instrumental techniques of organic structural analysis are nuclear magnetic resonance (NMR), ultraviolet spectroscopy (UV), mass spectrometry (MS), and infrared spectroscopy (IR). NMR is strictly a bulk technique and not easily applied to insoluble solids. UV spectroscopy sees multiple bonds, unsaturated rings, and conjugated electron systems. However, it works best on liquids and certainly could not differentiate C-F bonds from C-H bonds. MS gives a molecular weight distribution spectrum after the sample has been "cracked" into molecular fragments. This method has been applied to inorganic surfaces, but the cracking process would be too severe an assault on most polymers to give useful information. IR gives vibrational characteristics of different functional groups and could easily distinguish between fluorocarbon and hydrocarbon moieties. Internal reflectance IR can be used on polymer surfaces as Corbin did in studying their fluorination.

The primary investigative technique in this study is called Electron Spectroscopy for Chemical Analysis (ESCA), or X-ray
Photoelectron Spectroscopy (XPS). ESCA is a popular method for studying surfaces, particular organic surfaces, which gives information about elemental composition as well as details of molecular structure. This method consists of irradiation of a surface with ionizing x-rays followed by the collection of the ejected electrons. The principles of ESCA can be examined by considering five general topics: the physics (or theory), the radiation source, the system, the sample, and the information gathered.

The fundamental principles of ESCA can be understood within the context of the law of conservation of energy. An x-ray photon of known energy is completely absorbed by an electron having some unknown amount of energy. The electron is then ejected from its atom, traveling with a measurable kinetic energy exactly equal to the difference between the original x-ray energy and the electronic binding energy:

\[
Ex = Eb + Ek
\]

where \(Ex\) = x-ray energy, 
\(Eb\) = electron's original binding energy, 
\(Ek\) = measured kinetic energy of the ejected electron.

The exact binding energy of an electron is characteristic of its environment. The simple Bohr model of the atom postulates discrete electronic energy levels. ESCA simply measures the \(Eb\) of an atomic core electron and that value depends on the atomic number (identity) and valence state of the atom being ionized.
Spectroscopic techniques in general employ a probing field--some sort of interrogating radiation--and then collect the resulting information which may be matter, energy, or something else. ESCA in particular studies the energy distribution of electrons ejected from a solid, under the assumption that the distribution is characteristic of the material. For example, carbon 1s electrons have an $E_b$ of about 285 electron volts (eV), so a distribution which shows a peak near 285 eV implies that the sample contains carbon.

Only atoms near the surface contribute to the distribution because electrons from deeper atoms get scattered and dispersed before they can escape the solid. With no external help from the instrument, the sample itself filters out all electrons except those from surface atoms, even though the incident x-rays penetrate deeply into polymers. This filtering effect makes ESCA a surface-sensitive method.

Other surface techniques heir to the self-filtering effect (called inelastic backscattering) include ultraviolet photoelectron spectroscopy (UPS), and Auger spectroscopy (which uses electrons as the ionizing source). Auger emission occurs when an excited, ionized atom lowers its energy by moving an upper level electron down to fill the gap in the core level, simultaneously ejecting an upper level electron.

ESCA uses x-rays of known energy as its ionizing radiation. Implicit in the operating equation $E_x = E_b + E_k$ is the assumption that $E_x$ has a known, exact value. However, as required by the uncertainty principle, x-radiation lines from bound-bound transitions have finite
linewidth. The task is to filter that linewidth as much as possible while retaining sufficient intensity for the analysis.

Heavier elements emit stronger, broader x-rays while lighter elements show reduced linewidth and reduced signal. ESCA systems use aluminum or magnesium as the source element because their K lines are reasonably simple and narrow. Their K-alpha:1,2 lines are sufficiently close that they form a composite envelope on the order of 0.8 eV wide. A monochromator eliminates the K-alpha:3,4 and K-beta lines which would cause spurious peaks, called satellites, in the distribution spectrum. Such filters also reduce bremsstrahlung and resulting radiation damage to the sample, thus increasing overall signal-to-noise ratio.

The ESCA system functions under vacuum, generally less than 10 torr, in order that interferences be reduced. Primary interference results from adsorbed contaminants on the face of the sample. One rule-of-thumb states that at 10 torr, the rate of adsorption is one monolayer/second, for unit sticking coefficients. Sticking coefficients are usually closer to 0.01 than unity, but since analyses are generally far longer than one second, lower pressure is a necessity. The lower pressure also allows the electron mean free path to be longer than the the distance to the detector, so the vacuum atmosphere does not get appreciably in the way of the electron counter.
A clean sample is attainable in principle, but often elusive in practice. Oil and dirt are removable by water or solvent rinsing and vacuum drying. Atmospheric carbon contamination, however, is almost unavoidable, for air contains CO and CO, as well as all manner of soot and hydrocarbons. Yet even a perfectly clean surface put into the system becomes susceptible to contamination from back-diffusion of vacuum pump oil, an insidious effect.

The form of the sample is relatively insignificant, although it must exist as a solid under vacuum, which is no problem for most polymers. Only a few square millimeters are scanned in the analysis, so any reasonable size can be accommodated. Electron emission is most efficient with a flat, smooth surface, but powders or fibers can be analyzed using longer counting times.

ESCA gives quantitative elemental analysis, e.g. 37% A, 20% B, 43% C. The elements present are identified by the appearance of certain characteristic lines or peaks, stemming from core level ionization. (Helium does not form compounds, and hydrogen has only one electron, but all other elements are detectable). The relative amounts of the elements present are based on the peak areas in the spectrum. Twice the amount of carbon will lead to twice as many ejected electrons and a peak twice as large.

Information about valence state and chemical environment comes from the exact peak position, i.e. the exact value of Eb. A peak between 284 and 294 eV means carbon; a peak at 284.8 eV means CH-type
carbon rather than CF or carbonyl carbon. Although the analysis may require resolution to <0.1 eV, the source radiation linewidth is on the order of 0.8 eV. While exact Eb values are certainly unattainable, it is nevertheless customary to give peak positions (chemical shifts) to the nearest 0.1 eV.

A priori calculation of chemical shifts are not made, although the theoretical framework is understood. To a first approximation, the Eb of a core electron is linearly related to the nuclear atomic charge by a proportionality constant characteristic of the particular core level. The valence-sensitive shifting comes from an added potential term accounting for electron-electron repulsion. So,

\[ Eb = kZ + V \]

where \( Z \) = nuclear charge,
\( k \) = constant for the core level of interest,
\( V \) = electrostatic repulsion potential term.

\( V \) is a Madelung-type potential which contributes oxidation state information. Electronegative elements like O and F withdraw electrons from C atoms, so the remaining C electrons are more tightly bound, i.e. have a higher binding energy.

These two potentials are responsible for the primary information available from ESCA. Secondary effects do contribute to fine structure and peak splitting in a small way. For example, x-ray absorption may perturb the electronic structure enough that true Eb values cannot be measured. Neglect of this effect is called the frozen orbital approximation. Many atomic radiative processes are
subject to line splitting resulting from electron spin effects. For instance, the bright yellow sodium D line is really a doublet, split because sodium's unpaired electron is involved in exchange coupling. Such spin-orbit coupling often leads to noticeable peak splitting, especially in metals. Spin splitting occurs in ESCA when an unpaired electron couples with the photohole left by ejection.

Two secondary spectral features which can actually be helpful are shake-up satellites and the Auger parameter. Shake-up satellites appear when photoionization, which causes a sudden electronic potential change, provokes a second electronic transition. That type of transition, usually involving an outer electron and an unfilled orbital, commonly occurs in first row transition elements and conjugated organic systems. The secondary emission occurs with lower Ek than the primary emission, so the apparent Eb is higher than the main peak value. Thus a shake-up satellite appears as a small peak just to the higher Eb side of the primary peak, even though the true secondary Eb has not been measured. The appearance of such a satellite portends some sort of unfilled orbital and is characteristic of phenyl groups. Satellites appearing at lower Eb values occur when the x-ray monochromator does not remove all of the higher energy K-beta lines, causing peaks which are completely extraneous and not helpful.

The Auger parameter is defined as the energy difference between an Auger line and a photoelectron line. Figures 1 and 2 are the ESCA survey spectra of PTFE and POM. PTFE's fluorine lines at 590 eV and
Figure 1: ESCA survey spectrum of untreated PTFE
Figure 2: ESCA survey spectrum of untreated POM
625 eV are Auger lines, while the POM spectrum does not have such features. Each shows the carbon peak near 290 eV, PTFE has the 690 eV fluorine line, and POM has the 530 eV oxygen line.

NMR spectra are commonly referenced to tetramethylsilane (TMS), a compound added to the sample, because TMS introduces a convenient datum. In that arrangement an internal zero point exists, from which chemical shifts are measured. The Auger parameter serves as an internally consistent measurement, independent of many interference effects. The most attractive feature of the Auger parameter is that it is unaffected by sample charging, an effect so important that it is the subject of the next section.

A solid which is emitting electrons will become positively charged unless those electrons are replaced. Polymers are nonconductors, so when the surface becomes charged, the uncharged bulk cannot supply electrons to refill the holes and neutralize the positive charge. That charge is a retarding potential, making it progressively more difficult for each electron to leave. If the polymer surface has a potential of 10 volts, then an emitted electron must spend 10 eV of its energy in overcoming the potential, and the calculated Eb will be off by 10 eV. It would be a trivial matter to shift the spectrum back by the right amount if the surface potential could be accurately known. Unfortunately, it is very difficult to measure the charging without upsetting the analysis, but some sort of correction must be made. The two most common approaches are the direct resupply of lost electrons and use of a standard.
A common way to supply electrons to nonconductors is to use an electron gun, for example a tungsten filament. The hot tungsten wire floods the sample with low energy electrons, essentially by boiling them off the filament (thermionic emission). A more elegant means of correction is to allow charging while using a standard for later compensation.

Correction using a standard means keeping track of a line whose unshifted position is known, then moving the spectrum back until that line takes its proper place. The operating assumption is that the reference peak moves exactly as much as every other. The standard may be either internal (part of the sample) or external (deliberately added to the sample). One may thus use carbon contamination to one's advantage in presuming that a small hydrocarbon peak can be found and shifted back to 285 eV. This correction is convenient and helps make up for the nuisance of almost unavoidable contamination.

Figures 3 and 4 are the ESCA C spectra of PTFE and POM, respectively. These unshifted spectra exhibit a large peak from the polymer and a small peak from contamination. Figure 5, the spectrum of PVF, has no separate hydrocarbon peak because the signal from contamination coincides with the signal from one of the true peaks. Contamination referencing requires quite a bit of faith, however, because carbon can appear as CO, CO, formaldehyde, and all sorts of other compounds which need not necessarily be associated with 285.0 eV. An increasingly popular alternative is to use a deliberately added external standard.
This technique is based on the evaporative deposition of gold onto part of the analyte surface and location of the Au 4f \( \frac{7}{2} \) line at 83.8 eV. Gold is quite inert and should not react with the sample. Also, gold is a conductor and should maintain electrical equilibrium with the surface. Although biased referencing has been used a relatively short time, it seems to work well.

Of course there are some uncorrectable difficulties resulting from charging, not least of which is the possibility of nonuniform surface charging. It should not be difficult to conceive of that happening on insulating samples, the result of which would be peak broadening.

ESCA's atomic concentration detection limits are about 1% for most elements, with concentration uncertainties about 3%. Sample homogeneity must always be a concern in ESCA. Surface xy-inhomogeneity, i.e. in plane, cannot be detected or dealt with since the distribution spectrum gives an overall, integral analysis. Inhomogeneity in the z-direction raises the question of where the surface ends and the bulk begins. ESCA does sample most strongly from the top 5 nanometers (50 Angstroms), but the decay in sensitivity is exponential. Again, the spectrum is an integral one, this time weighted by a depth factor

\[ [1 - \exp(-zS)] \]

where \( z \) = depth into the sample, and
\( S \) = a constant accounting for inelastic backscattering.
S may not be strictly constant but may be S(z), which would obscure the analysis further.

A real problem regarding sample homogeneity is the common assumption that a surface represents bulk stoichiometry as well, in a sense judging the book by its cover. Another hitherto neglected consideration has to do with capture/emission cross-sections. Some elements are naturally more likely to capture an x-ray and eject a photoelectron, i.e. core shell emissivity varies from element to element and even between levels in a given element. What this means is that peak areas cannot be directly ratioed but must first be normalized. Therefore atomic sensitivity factors are determined from analysis of pure compounds.

A crucial assumption is that atomic sensitivity does not change from compound to compound. For example, the fluorine sensitivity factor programmed into the instrument used in this analysis is based on lithium fluoride salt as a standard. It may be that F emissivity in LiF differs from that of F in fluorocarbon polymers. However, determination of F sensitivity in fluorocarbon polymers assumes that surface stoichiometry is known. One should therefore be careful in the use of absolute sensitivity factors and use the results of quantitative ESCA analyses with the knowledge that there are many sources of possible uncertainty.
2.3 CONTACT ANGLE

One of the most striking features of Teflon is the way water beads up on the surface. Contact angle experiments quantify such solid-liquid interactions by examining droplets on a surface. The familiar example of water on the hood of a car illustrates this phenomenon: water streaks and spreads easily on an unwashed car hood, spreads less on a clean hood, and beads up on a waxed hood. The water can tell the difference between the different solids it touches, as a droplet makes a particular angle of contact with the surface below.

In contact angle phenomena a liquid drop is in mechanical equilibrium with a solid, where the drop forms a given tangent angle with the solid. Water in a glass exhibits a small rise at the solid-liquid interface; mercury in a thermometer tube does the same. Mercury has a high surface tension and does not wet most surfaces. The Hg-Hg interactions are more favorable than the Hg-solid ones, so the drop of mercury tends to ball up and reduce the area of contact, with an angle near $140^\circ$ on many common materials. A hemisphere resting on a flat surface makes an angle of exactly $90^\circ$.

Experiments have shown the necessity of distinguishing between advancing and receding angles. Recalling the thermometer example, advancing angle is the angle when the fluid rises, receding angle when the fluid falls. The two are generally quite different, with many systems showing a strong hysteresis effect. Common causes of hysteresis include contamination and surface roughness. For meaningful data, one must therefore specify whether the angle is
advancing or receding, assuming a clean, smooth surface in equilibrium with the liquid.

Quantitative studies often give the cosine of the angle rather than the angle itself. Zisman (1960) has derived a linear relationship between the cosine of the angle and the surface tension of the liquid. Indeed, for chemically similar liquids, a plot of the cosine of the advancing angle versus liquid surface tension usually gives a straight line. Extrapolation of the curve to unit cosine (to zero angle) gives a surface tension value called CST, the critical surface tension. This quantity is taken as characteristic of the solid, not of the liquids used.

This result is a profound one in that a solid surface can now be described in terms of surface tension, regardless of the liquids used to find CST. PE has a critical surface tension of 30–35 dyn/cm, PVF2 about 25, and PTFE about 18. A logical conclusion is that CST decreases with increasing fluorination. A PTFE surface is presumed to consist entirely of CF groups, and an argument can be made that a polymeric surface of CF groups should have an even lower CST. It is this prospect of modifying polymer wettability which is partially responsible for motivating this research.

CST is not the same as the solid surface tension, although it is similar, and a good understanding of its nature has been difficult to come by. Pittman (High Polymers, ed. Wall) has reviewed the subject of fluorocarbon surface properties and the attempt to elucidate the
important factors affecting CST. Semi-theoretical correlations relate CST to glass transition temperature (Lee), solubility parameter (Gardon), and surface density (Schonhorn and Ryan).

It is known that H replacement by F lowers CST, but precisely why that happens is a matter of some dispute. Probably the best way to think of the physical situation is in terms of geometry/morphology and in terms of electronic/molecular effects.

A monolayer of perfluorinated long chain carboxylic acid will have a very low critical surface tension. CF\(^3\) COOH has CST about 6 dyn/cm, the lowest value yet reported. Its structure is predominantly \(-\text{CF}_2\) yet its CST is much less than PTFE's because the acid "stands up" so that mostly CF\(^3\) groups make up the surface. One researcher claims that the

major differences in the wettability of polyethylene and monolayers of fluorocarbons and hydrocarbons are determined largely by the differences in the packing density of the groups in the surface and not by differences in the "molecular" interactions. (Hoernschmeyer)

This claim is supported by the low energy solid surfaces of polyacrylates with perfluorinated side chains, e.g. poly(1,1-dihydroperfluorooctyl acrylate) has CST = 10.4 dyn/cm despite the polar acrylate linkages. Dimethyl silicone liquids have a CST near 20 dyn/cm, but monolayers show a methyl surface with CST = 24 dyn/cm, again because of orientation effects (Rodriguez).
One final remark regarding contact angle and critical surface tension relates to the extreme values achievable. Intuition suggests that the minimum critical surface tension possible should be exactly zero, i.e. negative surface tension makes no physical sense. Thus in principle a zero energy represents the limiting case, even if it is not practically realizable.

Intuition also suggests that the greatest contact angle achievable should be 180°, which would occur when the liquid beads up perfectly into a sphere, touching the surface only at a tangent point. Experience argues that gravity would prevent such a thing from happening, but it is possible to conceive of solid-liquid interactions so unfavorable that the 180° angle would occur. Thus the liquid would take on perfect sphericity and the solid would be completely unwettable.

These extremes need not occur simultaneously: the solid may reach zero energy before the liquid reaches 180°, or vice versa. There is no a priori reason to assume that 180° and zero energy must correspond. Indeed experiments have shown (Shafrin and Zisman, 1964) that a solid surface will take on its zero energy value long before the liquid angle goes to 180°. So every liquid has a maximum limiting value of contact angle less than 180°. It is predicted by extrapolation that water on a zero energy surface would have an equilibrium angle of 156°, hexadecane 109°, and formamide 135°. The uncertainties in these values are on the order of a few degrees, typical of contact angle uncertainties.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polytetrafluoroethylene</td>
<td>93°</td>
</tr>
<tr>
<td>Polytrifluoroethylene</td>
<td>76°</td>
</tr>
<tr>
<td>Polyvinylidene fluoride</td>
<td>59°</td>
</tr>
<tr>
<td>Polyvinyl fluoride</td>
<td>54°</td>
</tr>
<tr>
<td>Low density polyethylene</td>
<td>78°</td>
</tr>
<tr>
<td>Polyoxymethylene</td>
<td>45°</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>74°</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>66°</td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>61°</td>
</tr>
<tr>
<td>Nylon 66</td>
<td>50°</td>
</tr>
</tbody>
</table>
2.4 EMISSION SPECTROSCOPY

Fire glows so brightly because the high temperature flame contains significant amounts of excited species. Just as every flame may have different colors, so too every glow is uniquely characteristic of the particular glowing species present. Optical emission spectroscopy is the analysis of the radiation given off by excited atoms or molecules.

An optical spectrometer has "an entrance slit, a dispersing device, and one or more exit slits, with measurements are made at selected wavelengths, or by scanning over the range."(Analytical Chem., 1974) The instrumentation consists of five major components:(Bauer, 1978) source, sample, analyzer, detector, and recorder. A simple example is the analysis of air in an inductively coupled plasma system. The rapidly changing field excites the species which make up the sample (Ar, N, O, etc.) and the mixture emits radiation. An analyzer (e.g. prism) disperses the radiation into its constituent wavelengths which are scanned by the detector and recorded. In this case, there would be a spectrum with three major sets of peaks, or bands: Ar bands, N bands, and O bands.

Some atoms emit much more strongly than others; generally speaking, an element has a few strong lines and many weaker ones. Qualitative analysis is based on the uniqueness of each element's spectral "fingerprint," which may be found in standard tables.(Pearse and Gaydon; Zaidel; Weast) Quantitative analysis is done by correlating the intensity of emission with the amount of emitting
substance present—if sample B contains 3.05 times as much sodium as sample A, then the sodium lines from sample B should be 3.05 times as intense as those from sample A.

Individual atoms emit when relaxing from an excited electronic state to one of lower energy. Polyatomics show additional spectral features because they can undergo vibrational and rotational transitions as well as electronic transitions. In all cases, the frequency of emitted radiation is directly proportional to the energy change of the transition.
Chapter 3  FLUORINE CHEMISTRY

Fluorine, element nine, a diatomic gas at room temperature, is the lightest member of the halogen family. This family of elements consists of fluorine, chlorine, bromine, iodine, and astatine, all of which tend to have an oxidation state of -1 in their compounds. The halogens are known for their electronegativities, the magnitudes of which increase as atomic weight decreases, with fluorine's electronegativity the highest of any element. Every halogen has seven electrons in its outer shell, one less than the "magic number" of eight (which the noble gases have). Because of this, the halogens truly behave as a family; the alkali metals (Li, Na, K, etc.) each have one electron more than the noble gas structure and they too behave as a family. However, for reasons to be discussed, fluorine stands somewhat apart from its relatives when it comes to chemistry.

Interestingly, fluorine compounds do not occur frequently in nature, so most of its chemistry is man-made. In fact, none of the halogens occurs naturally in the diatomic state because of their high reactivity. It is almost invariably true that whatever the halogens do in general, fluorine does the most strongly. $F_2$ reacts vigorously for two main reasons: the F-F bond is weak, and the bonds formed upon reaction are stronger than the ones they replaced.

The F-F bond requires about 37 kcal/mol to be broken, low in comparison to other diatomics (Weast; Solomons).
TABLE 2
Approximate bond energies and bond lengths of some diatomics

<table>
<thead>
<tr>
<th>Energies (kcal/mol)</th>
<th>Bond Lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F2</td>
<td>1.417</td>
</tr>
<tr>
<td>O2</td>
<td>1.208</td>
</tr>
<tr>
<td>H2</td>
<td>0.746</td>
</tr>
<tr>
<td>N2</td>
<td>1.098</td>
</tr>
<tr>
<td>Cl2</td>
<td>1.988</td>
</tr>
<tr>
<td>Br2</td>
<td>2.290</td>
</tr>
<tr>
<td>I2</td>
<td>2.662</td>
</tr>
</tbody>
</table>

Nitrogen has such a low reactivity because of the large amount of energy needed to dissociate it. F's anomalously low bond energy related directly to its electronegativity, which prevents good overlap of bonding orbitals. Fluorine and iodine have about equal bond energies, despite a nearly 2 to 1 ratio of bond lengths and a 7 to 1 ratio of masses. F dissociation therefore occurs readily, and the rates of elemental fluorination reactions can be high.

In addition to favorable kinetics, fluorination is usually thermodynamically favorable as well. Again because of fluorine's high electronegativity, it tends to form bonds which are stronger than the ones replaced. For example, F will generally replace H where it is bonded to carbon:

\[\text{C-H + F} \quad \longrightarrow \quad \text{C-F + H}\]

with a significant amount of energy liberated in the process. Such exothermic reactions are often explosive, and this has likely been responsible for the less than enthusiastic response which fluorination has traditionally received.
Nevertheless, the uniqueness of fluorine chemistry has slowly overcome such reluctance and many fascinating discoveries have followed. Neil Bartlett's pioneering work (1971) on synthesizing noble gas compounds qualifies as such a find. Xenon forms XeF,$^2$ XeF,$^4$, XeF,$^6$, and other fluorocompounds.

Noble gas compounds are not the only interesting fluorine compounds. Far more useful are the freons, low molecular weight fluorocarbon gases and liquids. CF$_2$Cl$_2$ and CF$_3$Cl serve as the most commonly used working fluids in home refrigeration, while freons can also be used as aerosol propellants. Fluothane, CF$_3$CClHBr, is probably the best general anaesthetic ever made and enjoys tremendous popularity in medicine. Biological uses of fluorocarbons appear to have a bright future, in light of the amazing work done on such things as artificial blood (Weiss and LeBlanc; Vanleer). Animals have had their entire blood supply replaced by a fluorocarbon substitute, with their bodies slowly manufacturing natural blood and eventually refilling the veins with it. Other applications of such materials include the drug 5-fluoro-uracil, artificial veins and body parts, and membranes for dialysis. Perhaps more interesting is the inductive effect which fluorine exerts through other atoms in a molecule.

The CF$_3$ group behaves as an electronegative group as a consequence of the three fluorine atoms drawing electrons from the carbon. An illustration of the inductive effect, often used in elementary chemistry textbooks, involves acetic acid, CH$_3$COOH. This is a weak acid, having $K_a = 1.8 \times 10^{-5}$, and it may be compared with fluoroacetic acid, CH$_2$FCOOH, whose $K_a = 2.2 \times 10^{-3}$. The F atom pulls electrons away from the carboxyl group.
from the alpha carbon strongly enough to loosen the hold on the acidic
proton at the opposite end of the molecule. CF COOH has a $K$ of $5.9 \times 10^{-1}$
a since the combined action of three F's magnifies the inductive
effect. Lagow (1979) exploited that effect in making Xe(CF$_3$)$_2$, a
compound with Xe-C bonds but no Xe-F ones. The common factor among all
these materials and compounds is the uniqueness of the F atom.

The peculiar success of organic fluorine chemistry derives largely
from fluorine's small size, i.e. its ability to replace H without an
adverse effect on the size and shape of the base molecule. Because
the C-F bond is so strong, such reactions tend to give stable, inert
products. Fluoropolymers in particular constitute a special class of
materials sufficiently interesting that some discussion of their
properties is in order.

The best known fluoropolymer, polytetrafluoroethylene (PTFE), was
discovered by accident (Garrett). PTFE turned out to have superior
thermal, electrical, chemical, and surface properties. A highly
3 crystalline, dense (2.2 g/cm$^3$) polymer, it owes its high melting point
(327 K) and extraordinary thermal stability to the C-F bonds of which
it consists. PTFE cannot really be heated into a melt like typical
plastics because the required temperature for flow is too great for
the C-C bonds in the backbone. Given suitable processing techniques,
however, the ability of PTFE to endure high temperature service makes
it a useful material.

Hydrocarbon polymers generally act as good thermal and electrical
insulators. They are poor conductors of heat and current on account of the tight binding of valence electrons. PTFE has exceptional electrical properties, having a dielectric constant of 2.0 and a high-frequency loss factor among the lowest of any solid (Billmeyer).

PTFE exhibits outstanding chemical resistance, being almost totally insoluble and impervious to solvents, acids, and bases—-even at elevated temperatures. Accordingly the polymer encounters much use in high temperature corrosive applications, making an excellent barrier or containing material for hard-to-handle substances. The importance of this natural inertness of fluorocarbon materials can hardly be overemphasized.

Equally attractive are PTFE's surface characteristics: low coefficient of friction, low wettability, and low adherability. The non-stick frying pan illustrates at once the thermal, chemical, and surface advantages of using PTFE. In fact, there have been some attempts made at modifying such surfaces because they are too inert for some applications. Adhesives, inks, and dyes tend not to bond well to PTFE, so ways of modifying it have developed (Cheshire; Martin).

Not every plastic article could be made of PTFE, and for good reason, as there are serious complications inherent in its use. Many uses need a soluble, or a clear, or perhaps a rubbery material, none of which PTFE is. Probably the two greatest drawbacks are cost and processing characteristics. With a cost over 10 times that of PE, PTFE cannot always be justified as a material of construction. Even
ignoring the cost, PTFE just does not melt flow like other thermoplastics.

Injection molding, blow molding, and solvent casting make up three of the most common fabrication techniques used on polymers. From a fabrication standpoint, PTFE more closely resembles a ceramic or a metal than a plastic, with sintering and powder metallurgy techniques the main methods encountered. These sorts of special processes add to the cost of the final article, and it should be easy to see why polymer surface fluorination has received such attention.

For applications having moderately complex geometry, coupled with demanding surface or barrier requirements, the designer may have to make a compromise. An expensive but easily moldable material like PE satisfies manufacturing needs, while a chemically resistant high performance material like PTFE meets functional needs. One possible solution is the surface fluorination of an already fabricated object. Several existing industrial processes do this on containers. Blow molding in particular admits to such reactions, by the inclusion of fluorine in the otherwise inert blowing gas. The inner surface of the container reacts with the fluorine, forming a PTFE-like skin.

With the preceding discussion in mind, it is appropriate to mention other fluoropolymers before moving on to previous research in the area. Polyvinylidene fluoride (PVF2) is a sort of a hybrid between PE and PTFE, consisting of alternating CH and CF units. $\text{CH}_2 \text{CF}_2$ Predictably, it displays intermediate properties and is used as a
coating and jacketing material because it can be molded into an article with reasonably good thermal and chemical resistance. Polyvinyl fluoride and the chlorofluoroplastics behave similarly, all being processable and having some degree of elevated resistance to their environment. The recently developed perfluoropolyethers and perfluoroalkoxy-based polymers compare to PTFE in chemical and thermal properties, but they show much improved processability and will undoubtedly become more widely used.

The history of polymer fluorination begins with PE as might be expected, the interest generally being in forming a bonded layer of perfluorinated material (Rudge). Corbin briefly reviewed the subject, detailing the chronology of such investigations. Recognition of the peculiarities of organofluorine chemistry was made by Lagow and Margrave (1979), who were able to fluorinate a wide variety of substances. By this time, more rigorous analysis of the fluoropolymer products was being done.

Clark has led the way in ESCA analysis of fluoropolymers, showing the wealth of information obtainable by that method (1976). His research has shown the efficacy of quantitatively identifying and distinguishing the different groups present within a polymeric surface: CH₂, CHF, CF₂, CF₃, etc. This technique serves as the primary analytical tool in this thesis, as it supplies elemental analysis and valence state information. ESCA has shown (and other methods agree) that the product of directly fluorinated PE differs from standard, emulsion polymerized PTFE. Rather, nearly all such surface fluorinated products show more crosslinking and less
crystallinity than their more classically produced counterparts.

Direct fluorination is simple, spontaneous, versatile, and controllable, probably proceeding by free radical chain reaction. The difficulties with the method include the handling of \( \text{F}_2 \) itself and overcoming the kinetics of the reaction. Initially the fluorination tends to proceed extremely quickly, followed by an ever declining reaction rate. Thus reactions often begin with cold, dilute \( \text{F}_2 \) and end with hot, pure \( \text{F}_2 \) under pressure. The nature of the slowdown has been attributed (Pollock and Jones) to the deactivating effect of \( \text{F}_2 \) atoms on the fewer remaining H's, until the last C-H bonds become very resistant to attack. In some cases, UV light has been used to remove the last hydrogens (Adcock).

Plasma enhanced fluorination processes enjoy greatly accelerated kinetics, with reaction times on the order of minutes and seconds instead of days and hours. The plasma environment is presently understood to activate gaseous species, with similar activation of the polymer suspected. Plasma methods are not limited to \( \text{F}_2 \) as the source of F radicals: common treating gases include CF, C F, and SF, each 4 2 6 6 relatively innocuous in comparison with \( \text{F}_2 \). Many patents exist dealing with "quick zap" treatment of fibers and polymeric articles (Manion and Davies; Auerbach; Kock and Smits). One interesting material made by plasma fluorination is graphite fluoride, which is made in a fluorine plasma in a fluidized bed reactor, with graphite the starting material (Lagow et al, 1972).
All of the examples listed involve direct coupling of F radicals to a polymeric surface. In no case has fluorocarbon deposition been meant, but rather a true reaction, with replacement of H atoms by F atoms. Deposition can occur because of polymerization in the plasma, even with completely unsaturated compounds used as the feed. In the high energy scramble of the glow, radicals and unsaturated species can be formed in sufficient number to cause polymerization. The chaotic high energy environment gives plasma reactions their versatility while simultaneously confounding analysis of the reaction mechanisms.

Tetrafluoroethylene, the monomer used in conventional synthesis of PTFE, can be used in a plasma to produce a perfluorinated product, and there are many reviews of the subject of plasma polymerization (Bell, 1976; Bell, 1980; Libby). Interestingly, the product formed in the discharge is quite different from the "normal" PTFE (O'Kane and Rice), showing more crosslinking (Nakajima et al) and less crystallinity. There is a mix of CF, CF₂ and CF₃ groups, with CF₂ making up over 90% of the total surface carbon. Conventional emulsion polymerized PTFE, on the other hand, is essentially linear, with little branching, presumably because branching mechanisms would involve cleavage of C-F bonds. Deposition rate and surface properties have been correlated (Washo) with reaction conditions.

A closed metal "Faraday" cage can be placed in a plasma reactor to act as a filter for ionic effects, under the assumption that charged species will not enter but will stick to the cage. So whatever forms within the cage should come from nonionic mechanisms. Buzzard (1982) has observed that cage PTFE differs from both normal
and plasma PTFE. This finding illustrates one of the major unsolved problems of plasma chemistry, i.e. determination of whether ionic or radical mechanisms dominate. The uncharged \( \text{CF}_2 \) diradical is known to be active in polymerization and fluorination reactions (Olsen and Osteraas), but its exact role remains a mystery.

As might be expected, there is a difference between plasma deposited polymers and chemically bonded, reacted layers. Pavlath and Pittman showed that fluorocarbon deposits on inorganic substrates were easily removed while those on organic ones appeared to be grafted in a truer sense (1979). Their work with \( \text{CF}_2 \) and \( \text{PE} \) suggested direct coupling of \( \text{CF}_2 \) groups to the backbone. They found that unsaturated gases gave a higher F content in the product than did saturated gases. However, after solvent extraction of the surface, the product formed from unsaturated gases had less F than its counterpart. This result indicates a fundamental difference between polymerization/deposition and true surface reaction.

Other types of fluorination processes include electrochemical (see Cotton and Wilkinson) and ion beam methods (Hu et al). Also, a great number of fluorine sources have been studied, although the low molecular weight fluorocarbons are the most common in plasma work. In nearly all cases, the reaction mechanisms are only poorly understood, if at all; but despite the lag in understanding, fluorination research efforts are continuing and will undoubtedly do so in the future.
Chapter 4

RESEARCH PLAN

Among the recent studies of fluorination reactions, the work of Anand and Corbin showed the feasibility of creating a CF type surface on a hydrocarbon polymer in a plasma. They used $F_2$, $CF_4$, and $SF_6$ in an inductively coupled glow discharge plasma, with various polymers under different conditions. Their results indicated the importance of atomic $F$ in the cage and elemental reactions. Glow reactions, on the other hand, defied simple characterization, often exhibiting simultaneous etching, polymerization, and reaction. Photon/polymer processes may also have been significant.

One of the major characteristics of their research was the ability to use F radicals to perfluorinate PE to a PTFE-like surface, having about a 93 advancing contact angle with formamide. $SF_6$ reactions left no S on the substrate, and $CF_4$ reactions as well seemed to be dominated by F activity—whence $CF_4$ derives its popularity as an etchant in the semiconductor industry.

Contact angle and critical surface tension experiments have shown that surface energy decreases with fluorination (Zisman, 1964):
TABLE 3

Critical surface tensions of various polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Critical surface tension</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>31 (dyn/cm)</td>
</tr>
<tr>
<td>PVF</td>
<td>28</td>
</tr>
<tr>
<td>PVF2</td>
<td>25</td>
</tr>
<tr>
<td>Poly(trifluoroethylene)</td>
<td>22</td>
</tr>
<tr>
<td>PTFE</td>
<td>18.5</td>
</tr>
<tr>
<td>Poly(hexafluoropropylene)</td>
<td>16.2</td>
</tr>
</tbody>
</table>

These data suggest that a trifluoromethylated PE would have an even lower critical surface tension, and a preliminary research objective was formulated: creation of a CF surface on a polymer.

Devising a specific research plan required consideration of several aspects of organic fluorine chemistry. Most importantly, fluorination using F radicals would almost certainly give a CF$_2$ surface which is just what must be avoided. Another fluorinating agent is difluorocarbene (CF$_2$), reactive in its linear triplet state (Solomons), and prone to polymerization (Bryant). Based on the known chemistry of the methylene diradical (CH$_2$), difluorocarbene is suspected of similar behavior (Olsen and Osteraas):

\[
\text{R-R'} + \text{CF}_2 \rightarrow \text{R-CF-R'}
\]

Addition of entire CF groups, then, makes the most sense as an experimental approach. Reaction gases therefore must yield CF$_3$ with a minimum of F and CF.$^2$
CF-containing gases such as CF\textsubscript{3}H and CF\textsubscript{3} do supply radicals in a plasma environment (d'Agostino et al.; Truesdale and Smolinsky). The CF\textsubscript{3} radical is relatively favorably formed, having a negative heat of formation (Weast):

\begin{table}
\centering
\begin{tabular}{|c|c|}
\hline
Radical & Hf (298) kcal/mol \\
\hline
CH & 142 \\
CH\textsubscript{2} & 92 \\
CH\textsubscript{3} & 34 \\
CF\textsubscript{2} & -46 \\
CF\textsubscript{3} & -112 \\
\hline
\end{tabular}
\caption{Standard heats of formation of some methylenic radicals}
\end{table}

Its molecular weight puts it between chlorine and bromine,

\begin{align*}
F &< Cl < CF\textsubscript{3} < Br < I \\
19 &< 35.5 < 69 < 80 < 120
\end{align*}

and it has been described as a pseudohalogen, having an electronegativity about comparable to that of chlorine (Cotton and Wilkinson).

**PSEUDOFLUORINATION HYPOTHESIS:**

1. CF\textsubscript{3}H or ----> CF\textsubscript{3} + ... \\
   CF \textsubscript{2} 2 6

2. -CH - + CF ----> -C(CF\textsubscript{3}) - \\
   2 3 3 2
The polymers studied were selected on two bases: their use in previous work (for purposes of comparison), and peculiar structural features potentially conducive to pseudofluorination and its analysis. The series comprising PE and its fluorinated relatives has been studied before and belongs in this research. POM has no C-C bonds, as well as a low formamide contact angle, while CAB is a semi-crystalline polymer having many different types of carbon atoms.

Reaction conditions which were varied included reaction time, power supplied to the plasma, gas composition and flowrate, and use of a Faraday cage. Techniques of analysis were optical emission spectroscopy (for presence of F radicals in the plasma), ESCA (for presence of CF and CF\textsubscript{2} groups on the polymer surface), and advancing contact angle (for change in wettability and surface energy).

Three final notes are in order regarding the proposed reactions. First, pseudofluorination involves the formation of C-C bonds, but not C-F bonds, even though the end result is a fluorinated surface. Second, CF\textsubscript{3}H and CF\textsubscript{2}6 have the same F/C ratio and thus supply the reactor with similar feeds. Third, CF\textsubscript{3}H also furnishes H radicals which may scavenge active F radicals, irreversibly forming HF which can then be swept away.
Chapter 5 EXPERIMENTAL APPARATUS AND PROCEDURE

Experiments were performed by immersing small pieces of polymer sheet or film in a CF$_3$H or CF$_2$H$_6$ glow discharge plasma. The heart of the experimental system was the reactor/generator, an LFE Corporation PDS-301. This self-contained unit, although designed for semiconductor etching applications, was well suited for the present research. The reactor chamber was a quartz barrel, 20 cm long by 20 cm in diameter, having four perforated rods acting as inlet manifolds for uniform introduction of the reaction gases. Copper metal tubing was wound around the outside of the barrel for the inductive coupling, and a 13.56 MHz A.C. potential was applied across the copper coil.

A Sargent-Welch 1402 vacuum pump kept the system pressure below 1 torr, as measured by thermocouple pressure gauge tubes. Two Teledyne Hastings DV-4R stainless steel tubes took pressure reading just upstream and downstream of the reactor and a VL-2 switching attachment allowed use of only one meter for the two readings.

Matheson 3320 regulators on the cylinders of CF$_3$H and CF$_2$H$_6$ (Matheson) kept a 10 psig pressure on the inlets to the Matheson 7472T 3-way mixing rotameter with stainless steel high precision needle valves. Airco helium constituted the third gas fed to the rotameter. All the plumbing was 1/4 inch o.d. copper tubing, using brass Cajon and Swagelok fittings.

Samples were cut into 1/2 x 3/2 cm rectangles from film or sheet, washed with distilled water, wiped dry, and then placed into the
reactor four at a time. A 6 x 6 cm glass plate supported polystyrene clips which held the samples in a vertical position. This assembly either stood alone in the reactor or in a 12 x 12 cm closed, cylindrical, copper mesh cage. An initial helium flush emptied the chamber of residual gases, then the reaction gas mixture was introduced. A typical run involved five minutes of glow reaction at 20 W forward power and less than 0.1 W reflected power, 20 standard cm$^3$/min gas flow, at less than 1 torr. After shutoff of the glow, helium cleared the chamber of reaction gases for a few minutes, then air was let in and the samples were removed.

The samples were next analyzed by ESCA and contact angle. Optical emission spectroscopy and contact angle procedures were identical to those described by Corbin.

ESCA was done on a Physical Electronics 548 ESCA/Auger spectrometer at less than 5 x 10$^{-8}$ torr. Spectral acquisition consisted of a two minute survey scan from 0 to 1000 eV, followed by a thirty minute scan of those regions showing peaks from C, F, and O electrons. All spectra were smoothed and had satellites removed, and the relative amounts of C, F, and O were found by integration of their normalized peak areas. A thermionically emitting tungsten filament supplied low energy electrons to the samples during analysis, and a bias was applied which led to about a 10 eV shift in most spectra.
Chapter 6  

EXPERIMENTAL RESULTS 

The results presented here are given in the context of the experimental goal of creating a predominantly CF$_3$-type surface on a polymer. Reaction products can be characterized qualitatively (shape of the C spectrum) and qualitatively (contact angle; atomic 1s concentrations of F, C and O on the surface). The reaction gases used were CF$_3$H and CF$_2$H, both pure and diluted with helium. The polymer substrates used included the following materials: polyoxymethylene (POM), cellulose acetate butyrate (CAB), low density polyethylene (LDPE), polyvinyl fluoride (PVF), polyvinylidene fluoride (PVF2), and polytetrafluoroethylene (PTFE).

Reaction times varied from one second to one hour. Forward power varied from one watt to 100 watts, with reflected power always near zero. Gas flow rates ranged from 20 to 80 standard cm$^3$ per minute (sccm), with the rotameter calibrated for each gas using soap bubbles in a buret.

Advancing contact angle measurements employed formamide as the liquid on protractor-and-stage device, giving precision of about 3°. A syringe was used to place droplets of formamide on the sample surface, and liquid was added until a constant angle resulted. Values measured here are compared with those reported in the literature.

ESCA spectra and atomic concentrations as determined by peak areas are presented. The ESCA spectra have not been shifted to their correct values because of some experimental difficulties discussed
below (Swift). Consequently, peak positions appear about 10 eV too low, but this shift in no way affects the interpretation or integration of the spectra.

The basis of evaluation of the success and quantification of the results of the pseudofluorination experiments were contact angle and atomic concentration measurements. Atomic concentration measurements and F/C ratios are interchangeable and have the same information content for a surface containing only F and C. Since the surface studied nearly always had some oxygen, F/C ratio does not tell the whole story.

Fluorine concentrations may often be suspiciously low because of atmospheric carbon contamination (CO, CO₂, hydrocarbons, etc.) and apparent F/C ratios will drop accordingly. Regarding F/C ratio, pseudofluorination might seem at first to tend toward a value of 3.0; upon further reflection, however, it should become evident that the 2.0 F/C ratio of a CF₂ surface also applies to a CF₃ surface as well.

\[
\begin{array}{cccccc}
F & F & F & F & F \\
-C--C--C--C- \\
F & F & F & F \\
\end{array}
\quad\begin{array}{cccccc}
F & F & F & F \\
CF & CF & CF & CF & CF \\
-C--C--C--C- \\
CF & CF & CF & CF \\
F & F & F & F \\
\end{array}
\]

Both of the above structures have an F/C ratio of 2.0, both fully saturated by fluorine.

ESCA gives integrated atomic concentrations for the region of analysis but cannot give a profile of stoichiometry with depth, i.e.
vertical inhomogeneity is not detectable. So a fully fluorinated top monolayer on a fluorine-free base will give an apparent stoichiometry which is deceptive. Consider the following sets of chains:

\[
\begin{array}{cccccc}
F & F & F & F & F & F \\
FCF & FCF & FCF & FCF & FCF & FCF \\
F & F & F & F & F & F \\
\end{array}
\]

Each set of chains has an overall F/C ratio of 1.5, yet the sets are different from each other and vertically inhomogeneous. Attainment of the maximum value of 2.0 requires the entire ESCA sampling depth to have the 2.0 value and requires the surface to be free of carbon contamination. For these reasons, a perfectly pseudofluorinated surface would have an F/C ratio no greater than 2.0, and very possibly less.

Most of the reactions run gave products with 45%-65% fluorine, although hydrocarbon contamination generally lowered the apparent value. For this reason, when a particular reaction was done more than once, the highest %F value is given in the tables. The concentration values are given to the nearest tenth of a percent, in spite of
uncertainties on the order of 3%, because oxygen signals were often present at less than 1% and rounding might imply the absence of oxygen.

6.1 UNTREATED POLYMERS

Untreated polymers were analyzed by ESCA for surface stoichiometry and the characteristic C electron spectra. Some adventitious carbon contamination was present in nearly all cases, but the spectra were otherwise as expected. Figures 6 through 9 are the electron spectra of some of the untreated polymers.

6.2 ARGON ION SPUTTERING

The ESCA spectrometer was used to bombard the polymer surfaces of POM and PTFE with argon ions. This bombardment had a disruptive effect, increasing unsaturation in the polymer, but surprisingly the contamination was still present. Figure 10 shows the effect of the bombardment on the C1s spectrum of PTFE.

6.3 HELIUM PLASMA TREATMENT

Polymers treated in a helium plasma showed virtually no signs of change. This particular experiment was performed to assess the effect of high energy electrons in the glow discharge on hydrocarbon polymers. With no significant observable effects, changes on fluorocarbon plasma treatments may be tenably attributed to chemistry and chemical reactions rather than to physics and electron bombardment.
Figure 6: ESCA C$_{1s}$ spectrum of untreated LDPE
Figure 7: ESCA C\textsubscript{1s} spectrum of untreated POM, showing contamination
Figure 8: ESCA C$_{1s}$ spectrum of untreated CAB
Figure 9: ESCA C₁s spectrum of untreated PVF2
Figure 10: ESCA $C_{1s}$ spectrum of PTFE after argon ion sputtering
6.4 EFFECT OF FORWARD POWER

Increasing the power coupled to the plasma increases the intensity of the glow, since energetic recombination events occur more often. Power affected the kinetics of the reaction as anticipated. Cleavage of a CF group from its original molecule calls for 2 to 3 times the energy needed for F dissociation. The %F on the surface of POM varied strongly with power for the CF treatments, but not for the CF3H reactions. The reaction time was 5 minutes at 20 sccm. Figures 11 and 12 show that POM gives the same product at 1 W as at 100 W.

| TABLE 5 |
| Effect of forward power on product stoichiometry |
| gas | %F | Power(W) |
| C2F6 | 31.4 | 1 |
| C2F6 | 53.4 | 20 |
| C2F6 | 63.6 | 100 |
| CF3H | 54.5 | 1 |
| CF3H | 60.7 | 20 |
| CF3H | 58.1 | 100 |

6.5 EFFECT OF GAS CONCENTRATION IN HELIUM

Most of the reactions were done in pure, undiluted fluorocarbon gas. However, a few runs were made at 16% and 25% concentration in helium. Since dilution had no effect at these levels, hereafter the fluorocarbon concentration is not regarded as important.
Figure 11: ESCA C_1s spectrum of POM after C_2F_6 at 1 Watt
6.6 RESULTS WITH PTFE

PTFE was chosen as a base substrate because it should react very little in the plasma. The only likely effect would come from chain scission, since breaking C-F bonds requires more energy than breaking C-C bonds. Atomic concentrations on the surface were generally indicative of contamination by atmospheric carbon since the F/C ratios were artificially low. The C\textsuperscript{1s} spectra did show the presence of CF\textsubscript{3} groups in nearly all cases, although the CF\textsubscript{2} peak was invariably larger.

<table>
<thead>
<tr>
<th>gas</th>
<th>time (min)</th>
<th>%F</th>
<th>%C</th>
<th>%O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF\textsubscript{3}H</td>
<td>5</td>
<td>46.8</td>
<td>49.2</td>
<td>3.9</td>
</tr>
<tr>
<td>CF\textsubscript{3}H</td>
<td>15</td>
<td>56.3</td>
<td>41.8</td>
<td>2.0</td>
</tr>
<tr>
<td>C\textsubscript{2}F\textsubscript{6}</td>
<td>5</td>
<td>61.9</td>
<td>37.3</td>
<td>0.8</td>
</tr>
<tr>
<td>C\textsubscript{2}F\textsubscript{6}</td>
<td>15</td>
<td>60.0</td>
<td>37.5</td>
<td>2.5</td>
</tr>
<tr>
<td>He</td>
<td>15</td>
<td>60.3</td>
<td>35.5</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Also present in each of the C\textsuperscript{1s} spectra were hydrocarbon peaks with corrected positions near 285 eV. Figures 13 and 14 represent the extremes, the former showing no CF\textsubscript{3} peak, the latter showing a large CF\textsubscript{3} peak. Figure 15 typifies the results with PTFE, showing a small CF\textsubscript{3} shoulder on the CF\textsubscript{2} peak.

Advancing contact angle experiments with formamide on these samples indicated no change in surface energy, as measured values were always about 95°.
Figure 13: ESCA C<sub>1s</sub> spectrum of treated PTFE, with no CF<sub>3</sub> peak.
Figure 14: ESCA $C_1s$ spectrum of treated PTFE, with large CF$_3$ peak
Figure 15: Typical ESCA C$_1s$ spectrum of treated PIFE
6.7 RESULTS WITH PVF

PVF belongs to the series of fluorinated polyolefins, having one F and three H's in each repeating unit. The two interesting aspects of working with PVF are the deactivating effect of the one F on the reactivity of the three H's and also the surprisingly low contact angle. PVF's contact angle of $54^\circ$ is lower than LDPE's $78^\circ$ or PTFE's $93^\circ$, even though PVF is intermediate in chemical structure. This low value probably results from dipole moments on the surface of the polymer. Figure 16 shows that hydrogens remained even after an hour of treatment.

<table>
<thead>
<tr>
<th>gas</th>
<th>time (min)</th>
<th>%F</th>
<th>%C</th>
<th>%O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF3H</td>
<td>5</td>
<td>61.8</td>
<td>37.4</td>
<td>0.8</td>
</tr>
<tr>
<td>CF3H</td>
<td>60</td>
<td>61.7</td>
<td>37.5</td>
<td>0.8</td>
</tr>
<tr>
<td>C2F6</td>
<td>5</td>
<td>58.4</td>
<td>38.6</td>
<td>1.8</td>
</tr>
<tr>
<td>C2F6</td>
<td>60</td>
<td>59.7</td>
<td>38.8</td>
<td>1.1</td>
</tr>
</tbody>
</table>

In each case, the treated PVF had a contact angle of about $90^\circ$. 

80
Figure 16: Typical ESCA C1s spectrum of PVF treated for 60 minutes
6.8 RESULTS WITH PVF2

The next fluorinated polyolefin is PVF2, with two F's and two H's in each repeat unit. This polymer is, in a sense, midway structurally between PTFE and LDPE. Its contact angle, however, has a lower value than either one, being 59°, some 20° below LDPE and 45° less than PTFE. Here, as in PVF, the deactivating effect of fluorine atoms should have an adverse effect on further reaction. However, there was essentially no difference between the PVF2 product and its PVF and PTFE predecessors. The C spectra did differ from PTFE's, though, with treated PVF and PVF2 identical, each showing hydrogens remaining after 60 minutes of reaction (compare figure 15 with figures 16 and 17).

**TABLE 8**

Results with PVF2

<table>
<thead>
<tr>
<th>gas</th>
<th>time (min)</th>
<th>%F</th>
<th>%C</th>
<th>%O</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF3H</td>
<td>1 sec</td>
<td>38.1</td>
<td>57.7</td>
<td>4.2</td>
<td>78°</td>
</tr>
<tr>
<td>CF3H</td>
<td>5 sec</td>
<td>63.1</td>
<td>36.3</td>
<td>0.6</td>
<td>90°</td>
</tr>
<tr>
<td>CF3H</td>
<td>15 sec</td>
<td>54.2</td>
<td>43.5</td>
<td>2.4</td>
<td>90°</td>
</tr>
<tr>
<td>CF3H</td>
<td>30 sec</td>
<td>55.4</td>
<td>42.2</td>
<td>2.4</td>
<td>94°</td>
</tr>
<tr>
<td>CF3H</td>
<td>60 sec</td>
<td>55.0</td>
<td>42.4</td>
<td>2.6</td>
<td>91°</td>
</tr>
<tr>
<td>C2F6</td>
<td>1 sec</td>
<td>34.6</td>
<td>59.9</td>
<td>5.4</td>
<td>75°</td>
</tr>
<tr>
<td>C2F6</td>
<td>15 sec</td>
<td>52.5</td>
<td>42.3</td>
<td>5.2</td>
<td>93°</td>
</tr>
<tr>
<td>C2F6</td>
<td>30 sec</td>
<td>53.1</td>
<td>43.9</td>
<td>3.0</td>
<td>95°</td>
</tr>
<tr>
<td>C2F6</td>
<td>45 sec</td>
<td>52.0</td>
<td>45.0</td>
<td>3.1</td>
<td>93°</td>
</tr>
<tr>
<td>C2F6</td>
<td>1 min</td>
<td>47.7</td>
<td>48.8</td>
<td>3.4</td>
<td>93°</td>
</tr>
<tr>
<td>C2F6</td>
<td>5 min</td>
<td>47.3</td>
<td>50.0</td>
<td>2.7</td>
<td>90°</td>
</tr>
<tr>
<td>C2F6</td>
<td>15 min</td>
<td>58.2</td>
<td>40.6</td>
<td>1.2</td>
<td>92°</td>
</tr>
<tr>
<td>C2F6</td>
<td>30 min</td>
<td>58.7</td>
<td>39.3</td>
<td>2.1</td>
<td>95°</td>
</tr>
<tr>
<td>C2F6</td>
<td>60 sec</td>
<td>64.6</td>
<td>35.0</td>
<td>0.5</td>
<td>93°</td>
</tr>
<tr>
<td>He</td>
<td>15 min</td>
<td>35.1</td>
<td>59.8</td>
<td>5.1</td>
<td>60°</td>
</tr>
</tbody>
</table>

Figure 18 presents the contact angle data for PVF2.
Figure 17: Typical ESCA C₁s spectrum of PVF₂ treated for 60 minutes.
6.9 RESULTS WITH CAB

Cellulose acetate butyrate has the most complex structure of any of the polymers studied here. The repeat unit consists of a pyranose ring (five carbons and one oxygen); successive rings are linked by oxygen atoms. CAB differs from cellulose by the presence of pendant acetyl and butyryl groups, and the sites for prospective fluorination are many.

**TABLE 9**

Results with CAB

<table>
<thead>
<tr>
<th>gas</th>
<th>time (min)</th>
<th>%F</th>
<th>%C</th>
<th>%O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF3H</td>
<td>1</td>
<td>25.1</td>
<td>60.3</td>
<td>14.5</td>
</tr>
<tr>
<td>CF3H</td>
<td>5</td>
<td>60.3</td>
<td>38.3</td>
<td>1.3</td>
</tr>
<tr>
<td>CF3H</td>
<td>15</td>
<td>61.2</td>
<td>37.3</td>
<td>1.5</td>
</tr>
<tr>
<td>C2F6</td>
<td>1 sec</td>
<td>8.2</td>
<td>70.5</td>
<td>21.3</td>
</tr>
<tr>
<td>C2F6</td>
<td>15 sec</td>
<td>35.6</td>
<td>48.9</td>
<td>15.6</td>
</tr>
<tr>
<td>C2F6</td>
<td>30 sec</td>
<td>33.4</td>
<td>53.7</td>
<td>12.9</td>
</tr>
<tr>
<td>C2F6</td>
<td>45 sec</td>
<td>57.0</td>
<td>38.7</td>
<td>4.3</td>
</tr>
<tr>
<td>C2F6</td>
<td>1</td>
<td>48.0</td>
<td>43.2</td>
<td>8.8</td>
</tr>
<tr>
<td>C2F6</td>
<td>3</td>
<td>53.0</td>
<td>40.4</td>
<td>6.6</td>
</tr>
<tr>
<td>C2F6</td>
<td>5</td>
<td>35.9</td>
<td>46.9</td>
<td>17.2</td>
</tr>
<tr>
<td>C2F6</td>
<td>15</td>
<td>48.1</td>
<td>43.9</td>
<td>8.1</td>
</tr>
<tr>
<td>He</td>
<td>15</td>
<td>0.0</td>
<td>59.7</td>
<td>40.3</td>
</tr>
</tbody>
</table>

Figure 19 is a typical C spectrum for CAB, and figures 20 and 21 present fluorine concentration data.
Figure 19: Typical ESCA $C_{1s}$ spectrum of treated CAB
Figure 20.
Figure 21.
6.10 RESULTS WITH POM

POM has no C-C bonds, as its backbone is made up of alternating carbon and oxygen atoms. This tough, semicrystalline polymer has a formamide contact angle of about 45°, lower than most carbon chain polymers, because of the dipole between the more positive CH units and the more negative oxygen atoms. The hydrogens are the only proper site for attack by fluorine, but chain scission would certainly supply places for free radical reaction.

TABLE 10

<table>
<thead>
<tr>
<th>gas</th>
<th>time (min)</th>
<th>%F</th>
<th>%C</th>
<th>%O</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF3H</td>
<td>1 sec</td>
<td>65.9</td>
<td>16.1</td>
<td>17.9</td>
<td>90°</td>
</tr>
<tr>
<td>CF3H</td>
<td>5</td>
<td>60.7</td>
<td>37.0</td>
<td>2.3</td>
<td>92°</td>
</tr>
<tr>
<td>CF3H</td>
<td>15</td>
<td>55.0</td>
<td>42.2</td>
<td>2.8</td>
<td>90°</td>
</tr>
<tr>
<td>C2F6</td>
<td>1 sec</td>
<td>10.3</td>
<td>63.4</td>
<td>26.2</td>
<td>59°</td>
</tr>
<tr>
<td>C2F6</td>
<td>15 sec</td>
<td>45.5</td>
<td>44.6</td>
<td>9.9</td>
<td>92°</td>
</tr>
<tr>
<td>C2F6</td>
<td>30 sec</td>
<td>47.5</td>
<td>43.8</td>
<td>8.7</td>
<td>92°</td>
</tr>
<tr>
<td>C2F6</td>
<td>45 sec</td>
<td>54.4</td>
<td>39.8</td>
<td>5.8</td>
<td>98°</td>
</tr>
<tr>
<td>C2F6</td>
<td>1</td>
<td>53.5</td>
<td>39.1</td>
<td>7.4</td>
<td>99°</td>
</tr>
<tr>
<td>C2F6</td>
<td>3</td>
<td>55.8</td>
<td>40.0</td>
<td>4.2</td>
<td>94°</td>
</tr>
<tr>
<td>C2F6</td>
<td>5</td>
<td>53.4</td>
<td>39.2</td>
<td>7.4</td>
<td>97°</td>
</tr>
<tr>
<td>C2F6</td>
<td>15</td>
<td>42.7</td>
<td>46.6</td>
<td>10.7</td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>15</td>
<td>0.0</td>
<td>51.0</td>
<td>49.0</td>
<td>45°</td>
</tr>
</tbody>
</table>

Figure 22 presents the C 1s electron spectrum of POM treated for 5 minutes, while figures 23 through 25 give %F and contact angle information.
Figure 22: Typical ESCA $C_{1s}$ spectrum of treated POM
Figure 23.
6.11 RESULTS WITH LDPE

LDPE was added in the course of this research, based on the results of the CAB and POM runs. LDPE has been the most extensively studied polymer in fluorination experiments and thus provides some basis for comparison.

<table>
<thead>
<tr>
<th>gas</th>
<th>time (min)</th>
<th>%F</th>
<th>%C</th>
<th>%O</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF3H</td>
<td>1 sec</td>
<td>9.2</td>
<td>88.8</td>
<td>2.0</td>
<td>78°</td>
</tr>
<tr>
<td>CF3H (25%)</td>
<td>5</td>
<td>64.0</td>
<td>35.6</td>
<td>0.4</td>
<td>86°</td>
</tr>
<tr>
<td>CF3H</td>
<td>60</td>
<td>63.6</td>
<td>35.8</td>
<td>0.6</td>
<td>91°</td>
</tr>
<tr>
<td>C2F6</td>
<td>1 sec</td>
<td>28.1</td>
<td>69.5</td>
<td>2.5</td>
<td>79°</td>
</tr>
<tr>
<td>C2F6</td>
<td>1</td>
<td>52.8</td>
<td>44.4</td>
<td>2.7</td>
<td>90°</td>
</tr>
<tr>
<td>C2F6</td>
<td>5</td>
<td>60.1</td>
<td>37.6</td>
<td>2.3</td>
<td>94°</td>
</tr>
<tr>
<td>C2F6</td>
<td>60</td>
<td>60.1</td>
<td>38.8</td>
<td>1.1</td>
<td>93°</td>
</tr>
<tr>
<td>He</td>
<td>15</td>
<td>0.2</td>
<td>77.2</td>
<td>22.6</td>
<td>78°</td>
</tr>
</tbody>
</table>

See figures 26 through 28.
Figure 26: Typical ESCA $C_{1s}$ spectrum of treated LDPE
LDPE/GLOW/C2F6

Figure 28.
6.12 CAGE REACTIONS

All of the previously cited experimental results came from glow reactions, i.e. the polymer was in full contact with the plasma. An alternative condition calls for the sample to be enclosed inside a Faraday cage of metal screen or mesh. Such a screen prevents charged species from reaching the polymer.

<table>
<thead>
<tr>
<th>gas</th>
<th>polymer</th>
<th>time (min)</th>
<th>%F</th>
<th>%C</th>
<th>%D</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF3H</td>
<td>POM</td>
<td>60</td>
<td>63.0</td>
<td>35.0</td>
<td>2.0</td>
<td>93°</td>
</tr>
<tr>
<td>CF3H</td>
<td>LDPE</td>
<td>60</td>
<td>62.6</td>
<td>36.6</td>
<td>0.8</td>
<td>93°</td>
</tr>
<tr>
<td>CF3H</td>
<td>CAB</td>
<td>60</td>
<td>61.9</td>
<td>36.5</td>
<td>1.6</td>
<td>--</td>
</tr>
<tr>
<td>CF3H</td>
<td>PVF2</td>
<td>60</td>
<td>64.5</td>
<td>34.2</td>
<td>1.3</td>
<td>93°</td>
</tr>
<tr>
<td>C2F6</td>
<td>POM</td>
<td>60</td>
<td>62.9</td>
<td>35.6</td>
<td>1.5</td>
<td>104°</td>
</tr>
<tr>
<td>C2F6</td>
<td>LDPE</td>
<td>60</td>
<td>66.5</td>
<td>32.9</td>
<td>0.6</td>
<td>134°</td>
</tr>
<tr>
<td>C2F6</td>
<td>CAB</td>
<td>60</td>
<td>60.9</td>
<td>37.8</td>
<td>1.3</td>
<td>--</td>
</tr>
<tr>
<td>C2F6</td>
<td>PVF2</td>
<td>60</td>
<td>63.8</td>
<td>34.1</td>
<td>2.1</td>
<td>103°</td>
</tr>
</tbody>
</table>

Figures 29 and 30 are typical of the CF3H reactions, figures 30 and 31 typical of the C2F6 reactions.

Following the lead of the LDPE/C F experiment and the high contact angle, that run was repeated in a series of such experiments.
TABLE 13

Results of LDPE/cage reactions

<table>
<thead>
<tr>
<th>gas</th>
<th>polymer</th>
<th>time (min)</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2F6</td>
<td>LDPE</td>
<td>1 sec</td>
<td>85°</td>
</tr>
<tr>
<td>C2F6</td>
<td>LDPE</td>
<td>15 sec</td>
<td>90°</td>
</tr>
<tr>
<td>C2F6</td>
<td>LDPE</td>
<td>1</td>
<td>92°</td>
</tr>
<tr>
<td>C2F6</td>
<td>LDPE</td>
<td>5</td>
<td>125°</td>
</tr>
<tr>
<td>C2F6</td>
<td>LDPE</td>
<td>20</td>
<td>130°</td>
</tr>
<tr>
<td>C2F6</td>
<td>LDPE</td>
<td>60</td>
<td>134°</td>
</tr>
</tbody>
</table>

A plot of contact angle versus reaction time shows an asymptotic approach to about 135° (see figure 33).

The contact angle measurements on the first three samples have a 5 degree uncertainty because of surface heterogeneity; that is, the angle varied somewhat over the different areas of the polymer. The same uncertainty applies to the last three measurements for a different reason. It is simply more difficult to make a good measurement at such high values. Reflected and refracted light give an illusion of sphericity of the small drop, making large angles harder to measure than small ones. The angles did not change over time after the samples were left in air for several days.

The LDPE/C F cage reactions were highly reproducible, more so than the glow reactions. Some improvement in reproducibility might have come from better experimental technique but the cage reactions with LDPE gave consistently tighter results than the others.
Figure 33.
6.13 EMISSION SPECTROSCOPY

Optical emission spectroscopy was performed on the plasma emission between 650 and 800 nanometers, with the intent of looking for atomic fluorine lines (figures 34 through 36). The helium plasma showed a very small F peak at about 706 nm, consistent with the 0.2% F in helium treated LDPE in the glow. Also present were some N bands, suggesting an air leak into the vacuum system upstream of the chamber. The CF$_2$ and C$_2$F$_3$ spectra showed only the hydrogenic line at about 656 nm which comes from H or He atoms, with no evidence of F radicals.

6.14 GENERAL EVOLUTION OF C1S SPECTRA

A general growth pattern emerged from the reactions done at short times. Figures 37 through 40 show the full evolution of the spectra of POM, although CAB (fig. 41), PVF, PVF2 (fig. 42), and LDPE followed the same form. A small CF$_2$ signal appears first, then CF$_3$. These two peaks then grow until they equal or exceed the size of the native peaks, with a composite four or five part spectrum resulting. For long reactions, the native CH$_2$ peak diminishes with the replacement of hydrogens.
Figure 34: Emission spectrum of He plasma (650-800 nm)
Figure 35: Emission spectrum of CF$_3$H plasma (650-800 nm)
Figure 37: ESCA C1s spectrum of POM showing peak growth
Figure 38: ESCA C_{1s} spectrum of POM showing peak growth
Figure 39: ESCA $C_{1s}$ spectrum of POM showing peak growth
Figure 40: ESCA $C_1s$ spectrum of POM showing peak growth
Figure 42: ESCA $C_{1s}$ spectrum of PVF2 showing peak growth
Chapter 7

DISCUSSION

Interpretation of the results requires reliance on the ESCA $^{1s}$ C spectra in order to assess the relative importance of the CF content of the surface. The atomic concentrations as found by ESCA have uncertainties of several percent, but the general appearance and shape of the spectra can provide valuable additional information.

The lack of reproducibility of atomic concentration measurements stems from several sources. First among them is contamination, a somewhat random effect. Also, the plasma is not an equilibrium environment, so there is no fundamental reason to expect perfect reproducibility of reactions. Past experience with PE has proven reproducible to within a few percent. The runs with PE in this work were also well behaved; however, the runs with other polymers were not nearly so reproducible.

Knowledge of the contents of the reactor would help greatly in understanding the pseudofluorination reactions. Almost every sample contained oxygen after reaction, the source of which may have been the chamber walls ($\text{SiO}_2$) or an air leak upstream. Almost every sample showed some carbon in the 285 eV region, indicating contamination which would cause F/C ratios to be too low. There were some samples without significant hydrocarbon contamination, and these tended to have fluorine concentrations above 60% as would be expected.

The emission spectrum between 650 and 800 nm showed no evidence of atomic fluorine, although the argument from silence is not
definitive in ruling out the presence of some F radicals.

Reaction conditions did not have strong effects on the products. In particular, flowrates, concentrations, and forward power had very little effect. Glow reactions gave essentially the same products with CFH as with CF. As CFH is not known for its tendency to polymerize, the implication is that CF did not polymerize either.

The reactions using PTFE led to a product with mostly CF carbon and a lesser amount of CF carbon. The CF groups could have come from chain scission's creation of reactive sites. If polymerization were depositing material on the surface, then the polymer underneath might eventually become covered up and invisible as far as ESCA is concerned. Such did not appear to happen, as the CF peak was not changed much with reaction. Still, deposition cannot yet be entirely ruled out.

PVF and PVF2, after a few minutes reaction, gave contact angles the same as PTFE, suggesting a perfluorinated, CF₄-type top layer. The ESCA C₁s spectra showed the presence of CF as well.

Similar results came from CAB and POM. POM's contact angle increased to the 93 value of PTFE, and the spectra of both polymers indicated CF and CF on the surface. The unexpected result of the POM and CAB reactions was the rapid loss of almost all oxygen from the substrate. In a CFH glow for only one second, POM showed a drop in oxygen content from about 50% to less than 20%. The glow went out
after one second, although active species may have persisted for a few seconds before the helium flush swept them away.

If polymerization were an active process in the glow reactions, then it seems unlikely that a one second glow could produce enough deposition to cover over most of the POM oxygen below the coating. An alternative explanation is that the weak C-O bonds are disrupted violently in a near vaporization of the polymer surface region. In CAB the pendant chains could be cleaved, but whether the rings could be so thoroughly broken is another question.

Corbin's similar results with poly(dimethyl silicone) also defied explanation, but the Si-O silicone backbone is known for its flexibility, while POM and CAB are tough and rigid. This loss of oxygen atoms from the polymer backbones cannot be adequately understood based on the data of this research.

Another feature peculiar to these reactions is the monotonic increase in contact angle for the PE series. Substitution of one fluorine atom for a hydrogen in the ethylenic repeat unit causes a drop in advancing contact angle from 78° to 54°, while a second substitution of F for H raises it only slightly to 59°. The third replacement gives a value of 76°, still less than LDPE's 78°. Corbin and Anand observed the initial decrease in contact angle for partially fluorinated LDPE, using \( F^2 \), \( CF^4 \), and \( SF^6 \).

For the samples fluorinated with CF \( H \) and CF \( F \) in the glow, \( 3 \) \( 2 \) \( 6 \).
contact angle increased without any drop at all, until the 93° value was reached. The LDPE/C F cage reactions also showed a monotonic increase in angle, asymptotically approaching an angle of about 135°.

The 135° limiting value of the LDPE/C F cage reactions has more significance than just an experimental asymptote. As shown by Shafrin and Zisman (1964), each liquid possesses a maximum value of equilibrium contact angle. For water the limit is 156°, for n-hexadecane 109°, and for formamide 135°. There is considerable uncertainty (5°) in this limit, since it is based on the extrapolation of a best fit line from practically attainable surface energies to a zero energy surface.

This limiting value applies to the equilibrium angle. Surface roughness could cause a value greater than the equilibrium one and the limit could be exceeded. However, the LDPE used here gave a 78° untreated contact angle, with 77°-79° commonly accepted. The fully fluorinated (glow) LDPE gave 93° angles and not higher. Additionally, the general behavior of LDPE contact angles was reproducible and well behaved; the smooth curve of angle versus reaction time strongly suggests that increases in angle because of roughness were not present.

Advancing contact angle is not strictly the same as equilibrium contact angle but advancing angle is understood to be characteristic of the low energy portion of a heterogeneous surface, and receding angle characteristic of the high energy part. In any case, the proximity of the measured angle to the theoretical maximum, coupled
with the great increase over the PTFE value, are indicative of a very low energy surface.

Another interesting result of this research relates to the indistinguishability of the shapes a C\textsuperscript{1s} spectra of widely different 1s reactions. That is, it is impossible to tell any difference between POM, CAB, and PVF2 after a few minutes in the glow discharge (compare figures 43, 44, and 45). This similarity suggests that deposition is occurring. Yet the C\textsuperscript{1s} spectra of PTFE (for example, fig. 15) under the same conditions are different—if deposition were happening, then the inert PTFE should provide a substrate just as acceptable as POM, CAB, or PVF2.

On the basis of the preceding results, one possible scenario is presented. Having ruled out deposition as an important process, it is still necessary to explain the odd disappearance of oxygen from the backbone of POM and CAB (see fig. 46). Even in the cage reactions, these polymers lost nearly all of their oxygen, so the filtering effect of the Faraday screen did not stop the loss. A pure helium plasma did not change the structure of POM, so radiation and electrons alone do not suffice to disrupt the polymers. Chemical attack by free radicals remains the most likely factor in breaking up the chains.

PE and its fluorinated relatives are known to crosslink in a glow discharge. One way to think about such crosslinking is to view the polymer solid as a crystal lattice. The lattice consists of carbon atoms at the lattice sites, with bonds linking each site to two of its neighbors. Immersion of the lattice in the glow causes a loss of
Figure 43: Typical ESCA $C_{1s}$ spectrum of treated POM
Figure 44: Typical ESCA C$_{1s}$ spectrum of treated CAB
Figure 45: Typical ESCA C$_{1s}$ spectrum of treated PVF2
structural integrity of the lattice near the surface, with bonds now breakable and reformable (hence crosslinking) when the glow is extinguished and the lattice takes on a fixed configuration.

This sort of lattice loosening in an oxygen containing solid polymer would leave the oxygen atoms most vulnerable to chemical attack for the following reasons:

(1) The C-O bond is weaker than C-C, C-H, or C-F
(2) Oxygen atoms are reactive and tend to form volatile products
(3) Oxygen compounds cannot catenate or crosslink like carbon chains.

In such a case, oxygen products would be desorbed and swept away, while carbon/hydrogen/fluorine compounds would remain as part of the lattice. Such a model could also account for Corbin's loss of all the silicon and oxygen atoms from the backbone of PDMS, leaving only fluorinated hydrocarbon residue. This model is also consistent with the observed weight loss of PDMS after reaction, while a photoactivation/deposition mechanism would cause an increase in sample mass.

The small size of the CF shoulder on the CF peak in the C $^3$ spectrum of the LDPE with the 134° contact angle can best be explained in the context of a CF top layer on a CF region below. The difficulty with this explanation is that the samples with a greater CF content should have at least an equal contact angle. However, the
typical evolution of $C_1$ spectra involved appearance of the $CF$ signal $C_2$ before $CF$. It may be that surface and subsurface fluorination occurs $C_3$ in significant quantity to a $CF$ product, while $CF$ groups couple with $C_2$ the polymer only in the top few layers.

In conclusion, two effects characterize the bulk of this work. One is the loss of oxygen from the backbone of the polymer substrates, perhaps owing to a lattice loosening followed by radical attack and desorption of volatile products. Second is the difference between the products of $CFH/CF$ reactions and the $F/CF/CS$ reactions. The $C_3$ differences in ESCA spectra and contact angle suggest a prominent $CF$ role in the former and domination of $F$ radicals in the latter.
Chapter 8

CONCLUSIONS

The data obtained in these experiments raise as many questions as they answer, in that a better understanding of the reactions requires considerable further investigation. Based on the following conclusions gathered from the project, some suggestions for continued study are made.

*CFS3H and C2F6 plasma fluorinated a variety of hydrocarbon and oxygen containing polymers, generally giving a CF3 containing product

*CFS3H and C2F6 glow discharges gave essentially identical products which differed from products of a CF4 glow discharge

*Based on emission spectroscopy and ESCA spectra, the CF3 radical plays a more important role than the F radical in CF3H and C2F6 plasmas

*Based on experiments with PTFE, deposition and polymerization do not seem to occur in the plasma—true surface reaction happens instead

*Progressive reaction as far as perfluorination can be done with a monotonic increase in formamide contact angle—there is no minimum corresponding to the partially fluorinated polyethylenes

*The C1s spectra of widely different polymers were indistinguishable, showing distinct CF2 and CF3 peaks

*Nearly all oxygen disappears from oxygen-containing polymers, even from the backbone, possibly because of lattice loosening, radical attack, and desorption of volatile products

*LDPE treated in a Faraday cage in C2F6 for 60 minutes had a contact angle of 134°; the curve of angle versus time approached an asymptotic value of about 135°, the maximum for formamide

Multiple internal reflectance infrared spectroscopy and angle-resolved ESCA could play major roles in establishing the structure of
these modified surfaces, particularly regarding the presence of CF groups. Emission spectroscopy scanning from 800 nm down to less than 500 nm may show the continuum emission centered at 614 nm which has been attributed to CF radicals (Flamm). Scanning from 200 nm to 400 nm could detect the CF continuum centered at 290 nm (Truesdale and Smolinsky). A set of experiments monitoring sample mass should also be done.

Especially in the case of the LDPE/C F cage reactions, knowing the critical surface tension is desirable. The experimental work requires making advancing contact angle measurements with a series of chemically similar liquids such as the normal alkanes. Those liquids are particularly attractive because they do not exhibit hydrogen bonding, and their contact angles are low and easy to measure. Also, the n-hexadecane maximum angle is known and knowledge of the n-hexadecane angle would contribute to the characterization in two ways at the same time. Measurement of advancing contact angle with another liquid whose maximum is known (e.g. CH I ) should also be done.

Finally, further parametric studies of the effects of reaction conditions, gas composition, and solid structure would aid understanding of the pseudofluorination process. Promising avenues of experiment include changing reaction conditions such as surface velocity and residence time of the gases. The effect of mixtures of CF-containing gases, or sequential treatment by different gases, would be interesting. For example, one such reaction would be a glow discharge of CF Cl + CF H, followed by cage treatment in CF .
Different types of heterochain polymers also should be examined, in pursuit of elucidating the heteroatomic loss effects: polyesters, polythioethers, and N-containing chains.
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HELIUM TUBE A AT 20 PSIG AT ROOM TEMP

FLOWRATE (CC/MIN)

READING

Figure 47.

134
Figure 48.
FREON-23 TUBE C AT 20 PSIG AT ROOM TEMP

FLOWRATE (CC/MIN)

READING
FREON-116 TUBE B AT 20 PSIG AT ROOM TEMP

Figure 49.