1-1-1987

Modification of synthetic polymers :: surface modification of poly(vinylidene fluoride) and poly(chlorotrifluoroethylene), and preparation of semiconducting polymers by bulk modification of poly(vinylidene fluoride), polybutadiene and poly(trifluoroethylene)/

Anthony Jay Dias
University of Massachusetts Amherst

Recommended Citation

Dias, Anthony Jay, "Modification of synthetic polymers :: surface modification of poly(vinylidene fluoride) and poly(chlorotrifluoroethylene), and preparation of semiconducting polymers by bulk modification of poly(vinylidene fluoride), polybutadiene and poly(trifluoroethylene)/" (1987). *Doctoral Dissertations 1896 - February 2014*. 714.
https://scholarworks.umass.edu/dissertations_1/714

MODIFICATION OF SYNTHETIC POLYMERS: SURFACE MODIFICATION OF POLY(VINYLIDENE FLUORIDE) AND POLY(CHLOROTRIFLUOROETHYLENE), AND PREPARATION OF SEMICONDUCTING POLYMERS BY BULK MODIFICATION OF POLY(VINYLIDENE FLUORIDE), POLYBUTADIENE AND POLY(TRIFLUOROETHYLENE)

A Dissertation Presented

By

Anthony Jay Dias

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

DOCTOR OF PHILOSOPHY

February 1987

Polymer Science and Engineering

MODIFICATION OF SYNTHETIC POLYMERS: SURFACE MODIFICATION OF POLY(VINYLIDENE FLUORIDE) AND POLY(CHLOROTRIFLUOROETHYLENE), AND PREPARATION OF SEMICONDUCTING POLYMERS BY BULK MODIFICATION OF POLY(VINYLIDENE FLUORIDE), POLYBUTADIENE AND POLY(TRIFLUOROETHYLENE)

A Dissertation Presented

By

Anthony Jay Dias

Approved as to style and content by:

Thomas J. McCarthy, Chairperson of Committee

David A. Tirrell, Member

C Pete Lillya

Peter C. Lillya, Member

Edwin L Thomas

Edwin L. Thomas, Department Head
Polymer Science and Engineering

October, 1986

ACKNOWLEDGEMENTS

There are several people whose help during the course of my graduate career I wish to acknowledge. Many thanks to my advisor, Dr. Thomas McCarthy, whose advice, enthusiam and encouragement helped to make this research much easier than it might have been, and whose ideas and insight provided an impetus to the initial phases of this investigation. Thanks are also due to the other members of my committee, Professors Tirrell and Lillya.

My fellow students did much to make going to school fun. I would like to thank them as a whole and in particularly, the members of 142G: Jan, Chris, Rick, Cady, Jim and Joan for their help, friendship and tolerance over the past several years.

Thanks are also due to the talented guys in the glass-blowing shop (Tim, Larry and Gordon); they could quickly prepare complicated glassware from even my lousy sketches.

Much love and thanks are given to Pat, whose constant encouragement, patience, understanding, love and friendship helped make this work possible.

ABSTRACT

Modification of Synthetic Polymers: Surface Modification of Poly(vinylidene fluoride) and Poly(chlorotrifluoroethylene), and Preparation of Semiconducting Polymers by Bulk Modification of Poly(vinylidene fluoride), Polybutadiene and Poly(trifluoroethylene)

Anthony Jay Dias, B.A. Kean College of New Jersey
Ph.D. University of Massacusetts
Directed by: Dr. Thomas J. McCarthy

February 1987

Part 1 of this dissertation is directed at the preparation of "model" polymer surfaces through the application of surface selective organic chemistry.

Room temperature phase-transfer catalyzed dehydrofluorination of the surface of poly(vinylidene fluoride) using aqueous sodium hydroxide and tetrabutylammonium bromide results in the formation of conjugated double bonds in a layer which is 10Å to 20Å thick. That the reaction was surface selective was indicated by UV-Vis: in autoinhibition becomes apparent after one minute and the absorbance reaches its maximium value after 10 minutes. Other analytical data (XPS, contact angle, gravimetric) are also consistent with a surface selective modification.

Reaction of poly(chlorotrifluoroethylene) with methyllithium and phenyllithium at low temperatures. These results clarified both the reaction mechanism and the structure of the products. This modification was extended to introduce hydroxyl, carboxylic acid and aldehyde groups by using organometallic reagents containing protected functional groups. It was found that the thickness of the modified layer is very dependant on reaction temperature (low temperatures enhanced surface selectivity) and on reaction solvent (surface selectivity was enhanced by using a nonswelling, noncoordinating solvent like heptane). Through the proper choice of reaction conditions the thickness of the modified layer could be kept to within the XPS sampling depth.

The reactivity of the surface confined carboxylic acid groups was examined using esterification reactions. The carboxylic acid group site density was established through liquid scintillation radioassay of PCTFE film which was reacted with $[^{14}C]$2-lithio-2,4,4-trimethyl-2-oxazoline. The site density ($(5.6\underline{+}1.7)\text{x}10^{-1}$ moles/cm^2) was then used to obtain percent conversions for the esterification reactions. The percentage of surface carboxylic acid groups which were esterified ranged from 10.4% (H_2SO_4) to 23.2% (thionyl chloride/DMF).

Methods for the bulk modification of poly(1,3-butadiene), poly(vinylidene fluoride), and poly(trifluoroethylene), with the purpose of synthesizing soluble conjugated polyenes, are presented in Part II. The potassium _t_-butoxide catalyzed positional isomerization

of poly(1,3-butadiene) to form poly(acetylene-co-ethylene) was found to proceed readily in THF/DMSO solution. The dehydrofluorination of poly(vinylidene fluoride) in DMF solution was accomplished using potassium _t_-butoxide in DMF as a base. Poly(trifluoroethylene) was eliminated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in THF solution and also heterogeneously by reacting poly(trifluoroethylene) film with a solution of DBU in heptane.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

LIST OF TABLES

Page

Part I.

Chapter III.

LIST OF TABLES (continued)

Part II.

Chapter III.

LIST OF FIGURES

LIST OF FIGURES (continued)

Part II.

Chapter II.

LIST OF FIGURES (continued)

Page

Chapter III.

LIST OF EQUATIONS AND SCHEMES

Page

Part I.

Chapter III.

Part II.

Chapter III.

Part I: SURFACE MODIFICATION OF CHEMICALLY RESISTANT POLYMERS: PREPARATION OF TWO-DIMENSIONAL ARRAYS OF POLAR FUNCTIONAL GROUPS

CHAPTER I: INTRODUCTION

Current applications of organic polymers have reached a level of sophistication which often requires complete knowledge of structure-property relationships. In order to obtain information concerning these correlations, it is necessary to deal in diverse fields of science including morphology, rheology, organic chemistry, physical chemistry and mechanics. Many of these fields deal with overall macroscopically observed properties and relate these to molecular models using a variety of theories. Often it is necessary to create systems with limited variables, to idealize applications and to create models based upon simple precepts in order to make an intractable problem approachable. Simultaneous use of the processes of experimentation and modelling can serve to advance the understanding of a complex system. Information that is gained about polymer structure can often, through the application of suitable theory, give information concerning observable properties and vice versa. With correlatable data, polymer structures can be engineered to maximize a desired property and reduce or eliminate an undesirable one. This type of approach has not been pursued to an appreciable extent in the field of organic polymer surface chemistry.

Organic polymer surface chemistry is a well established area of study which impacts a wide range of scientific and commercial applications. Often it is in these applications that problems arise which are related to the interfacial chemistry of polymers. Wetting, wear, adhesion, friction, and biocompatibiltiy all involve processes which occur primarily at the surface of polymers[1]. Information concerning these phenomena has been obtained largely empirically. In spite of the recent availability of sophisticated methods for characterizing the surface of polymers, there has been little movement away from the empirical method of study.

Unlike information obtained about most other structure-property relationships, there have been few attempts[2] to relate microscopic surface characteristics to macroscopic behavior like wetting or adhesion. In addition, data concerning structure-reactivity relationships is noticeably missing from the literature pertaining to organic polymer surfaces. These relationships may be important[3,4] and the extent to which the science of organic chemistry can be applied to organic functional groups confined to two dimensions has not been tested. The chemical environment of functional groups is affected by the state of the material. Molecules in solution tend to have spheres of solvation which influence reaction rates and product distributions. Functional groups confined to a surface have these solvation forces attenuated. In addition, the polymer surface presents large geometrical constraints on the system. Reactions, such as an Sn2 displacement which requires nucleophic attack at 180° from the leaving group, will be severely hindered. Surface physics will also affect reactivity: the tendency of a surface to minimize its surface energy is especially pronounced in polymers where surface mobility is high, therefore reactions which have polar transition states may exhibit unusually high activation barriers.

A primary factor for this absence of progress is the lack of substrates suitable for studies at the molecular level. New methods have to be developed for functionalizing and modifying polymer surfaces which produce materials whose structures are understood at the molecular level. This development would make possible detailed explorations of surface structure-reactivity correlations for these new materials. When these materials have been exhaustively characterized, the knowledge gained about surface chemistry, reactivity and structure could be used to microscopically alter the structure of the material and observe the changes which occur in the macroscopic surface properties. It is this fundamental information that is needed in order to completely understand observed interfacial phenomena.

Interfacial phenomena play an important role whenever and wherever materials are used. Thus understanding these phenomena is crucial to the advance of materials science. There have been many sophisticated studies of solid-gas interfaces, using metal substrates, during the last 20 years. Most of these studies have been conducted with high vacuum analytical techniques and these studies have provided much information about the role of surfaces in catalysis, adsorption, corrosion and adhesion. These studies have also served to illustrate the need for clean, well defined substrates: often these substrates are single crystal samples which are cleaned by ion etching directly in a high vacuum chamber. Most of these surfaces adsorb oxygen and form an oxide immediately upon exposure to the atmosphere, hence they are handled only in high vacuum systems. The work that has been done on solid-solution interfaces has not been as successful or as sophisticated. The metal is seldom inert to solvents: solvents adsorb on the metal surface, complex with the reactants or products and can mobilize species which would otherwise remain attached to the metal-gas or metal-solution interface. This reactivity has hampered the use of metal surfaces in these types of studies.

Solid organic polymer surfaces offer several advantages as substrates to study surface structure-reactivity-property relationships: 1) Generally, as a class of materials, polymers exhibit low surface energies in comparison to the high surface energies of most metals, hence the surface can be freed of contaminants by extraction with a suitable solvent. The surfaces are also clean in the sense that, unlike most metals, polymers do not undergo spontaneous oxidation. This means that polymers can readily be used to study interfacial phenomena under normal laboratory conditions, thus facilitating the study of solid-solution interfaces. 2) Polymers exhibit surface structures which are largely dependant upon both temperature and environment. The mobility of the outermost chains is affected by temperature changes which are easily achieved in the laboratory and are typically within 100°C of room temperature. Most solid metals undergo interfacial changes only at elevated temperatures, typically 300 - 1000°C[5]. In addition, specific interactions between the solvent and the polymer can cause changes in the mobility of the interface. Solvents may swell or wet the surface to different degrees thereby resulting in the formation of a different interface. This is not true of other materials, thus polymers provide a unique opportunity to alter the interface by changing the solvent and temperature. 3) Since most polymers are soluble, the reactivity of surface confined functional groups can be compared to their reactivity in solution. Even when insoluble polymers are used as the substrate, it is possible to model the reaction using low molecular weight analogs of the substrate which are soluble. Thus with polymers it is possible to examine both surface reactions and reactions in solution with the same model substrate.

The importance of polymer interfaces have prompted a considerable amount of research into the chemical modification of polymer surfaces[6]. The methods used commercially involve: Plasma treatment[7], corona discharge treatments[8], copolymerization[9], chemical reduction[10], and chemical oxidation[11]. Many of these procedures were discovered empirically and have been applied to a wide variety of substrates including: polyethylene, polystyrene, polypropylene, and poly(tetrafluoroethylene) to name a few. In fact these methods have been commercially applied to most, if not all, existing commercial polymers. This widespread indiscriminate application of these methods to polymers which differ widely in their properties correlates well with the empirical nature of many of these investigations. Most of these modifications involve reaction conditions and highly reactive reagents which tend to restrict selectivity in product formation and structural integrity of the polymer surface. Typically under the conditions used for modification, the products (modified polymer) are more reactive than the starting material (unmodified polymer). This leads to secondary reactions which occur preferentially at more reactive modified sites. The resulting autocatalysis leaves a surface which is not amenable to model studies; the chemical heterogeneity and the changes in the surface microtopography represent intractable complications for characterizing the surface at a molecular level.

The ideal substrate for molecular level characterization studies is one in which the surface of the polymer contains polar functional groups in a very thin (on the order of a few atomic dimensions), well defined layer on the surface. The remaining polymer should be unchanged and be chemically and structurally resistant to a wide variety of solvents and reagents. The preparation and characterization of 2-dimensional arrays of polar functional groups on the surface of poly(vinylidene fluoride) and poly(chlorotrifluoroethylene) are the primary foci of this dissertation. This dissertation discribes detailed studies of several new procedures which have been developed to modify the surfaces of PVF_2 and PCTFE. These procedures make use of an array of analytical methods to characterize the surfaces at a molecular level. The preparation of these substrates through chemical modification addresses important questions concerning the structure of and reactivity at the polymer-solution interface: the roles of solvent, temperature and transport in reactions at polymer surfaces. In addition this thesis illustrates, using the esterification of surface carboxylic acid groups, how these substrates can be used to explore the reactivity of surface-confined functional groups.

The remaining sections of this introduction present a brief critical overview of some of the current methods which are used for polymer modifications. The majority of this review concerns the wet chemical modifications, oxidizing acid and organic reducing solutions, since these methods are pertinent to the work at hand. In addition the surface analytical methods which are used in this thesis are introduced in sufficient detail to enable the unfamiliar reader to understand their applications toward the characterization of the surfaces described in this thesis. Together these analytical methods have permitted the detailed characterizations of the surfaces at a level necessary for the use of these surfaces as models. The chapter concludes with sections which describe PCTFE and PVF_2 with regard to their physical description, preparation, applications and current methods of modification.

Blends, copolymers, and homopolymers which contain a variety of functional groups are widely used as substrates for surface studies. Poly(vinyl alcohol) is a homopolymer that has been widely studied. It is prepared by the hydrolysis of poly(vinyl acetate). The resulting polymer gives a surface which is highly polar, hydrophilic and most certainly contains hydroxyl functionality. The problem with this substrate and most homopolymers is that the usual methods of surface characterization cannot be unambiguously employed to study the surface. The presence of large quantities of functionality in the bulk as well as the surface seriously complicates the interpretation of the data. Blends and copolymers suffer from similar experimental difficulties[12]. These techniques involve using various amounts of functional monomers and polymers within an unreactive matrix polymer such as polyethylene. These materials have been used successfully in the study of polymer functional group mobility[13,14]. In these studies the polymer is placed in a variety of polar and nonpolar environments and monitored by a combination of analytical methods including contact angles, XPS, and ATR-IR (these methods are described below). The studies show that polar functional groups diffuse away from the surface when in contact with a nonpolar environment and reorient with the groups toward the interface when in a polar environment[14]. The use of these substrates for the study of reactions at surfaces was not generally successful[12].

Chemical Oxidations: The oxidation of the surface of a polymer as a means for increasing the surface energy represents the largest class of surface modifications. This field includes: photooxidation, corona discharge treatment, flame treatment, plasma treatments, (photo, gamma-ray, and thermally induced free radical) grafting reactions as well as wet chemical oxidation methods. For the most part, each of these methods was discovered empirically and many are successfully deployed by industry to modify a large number of polymer systems.

Photooxidation[15,16], in regard to photostability, has been a concern for polymer scientists for quite some time. This is especially true for systems possessing chromophores (like polystyrene) and many studies have been conducted which examine the effect of UV light on polymers[17]. Recently high intensity UV lasers have been used to modify polymers through excitation of their surfaces, both in the presence of air and in vacuum[18]. In the second case if the laser photons are applied in a continuous fashion then the polymer undergoes considerable ablation. If however the polymer is irradiated in air, then the radicals which are produced during irradiation react with oxygen and functionalize the surface. Upon extended exposure these undergo further photolysis and the polymer again becomes etched. The surface has been shown to contain a variety of oxygen species which included hydroperoxides; these hydroperoxides have been quantitated by reacting them with potassium iodide. The kinetics of the reaction on the surfaces indicate that the maximum number of functional groups is introduced after 25 minutes of irradiation. These surfaces have also been characterized by XPS and ATR-IR. These results indicate that the modification extends to a considerable depth. This is not surprising

surprising since radicals can be produced throughout the penetration depth of the light source, approximately 3000 Å[19]. Additionally the surface has undergone ablation which results in a roughened surface making detailed molecular level characterization difficult.

Corona discharge treated polymers tend to show lower contact angles indicating higher surface energies[20,21]. These methods are widely practiced for the modification of polyolefins. The technique is simple; a film of polymer is passed through a gap having a high electrical potential. Air in the gap is ionized and the corona which forms reacts with the film. The early studies suggested that the surface chemical changes were not important in promoting autoadhesion (the sticking of two polymer surfaces together - autoadhesion is usually measured in terms of peel strengths which is the force required to pull the films apart). These conclusions were based largely upon reflectance IR and since changes were not observed, the differences in adhesion were attributed to the formation of surface electrets[22]. Later studies involving XPS showed the importance of oxidation in improving adhesion[23]. This research also illustrates the complex nature of the surface that results from the discharge. A variety of oxidized carbon species were found on the surface which include carboxylic acid, hydroperoxide, hydroxyl and ketone functionalities. In addition the nature of the oxidation indicates that the surface is crosslinked.

Although these surfaces contain a wide variety of functional groups, autoadhesion was attributed to hydrogen bonding between carbonyl and enol functions on opposite discharge treated surfaces[24]. This conclusion was based upon XPS derivatization studies: pentafluorophenyl hydrazine reacted with the carbonyls causing a drop in the adhesive strength (peel test) and the reaction of surface hydroxyl groups with di-isoproxytitanium bisacetylacetonate resulted in an increase in the peel strength. These observations do not provide enough data to draw conclusions about molecular level surface structure-property relationships. This method does not allow for the introduction of controllable amounts of a single functional group, instead the prepared surface remains chemically heterogeneous.

Flame treatments increase the surface energy of the polymer but often at the expense of polymer integrity[25]. This method uses high temperature flames to oxidize the surface of the polymer. This technique is used mainly to treat large thick objects like bottles and the increased surface energy is evident in the ease in which the surfaces are printed. The XPS studies on the oxidized surface indicate that a variety of oxidized carbon species are introduced as well as nitrogen functionality. These result from the complex mixture of excited species which are generated from the combustion of hydrocarbons. It is also likely that ionization events lead to the production of chain radicals which react with oxygen as well as adjacent chains. The depth of these modifications was estimated from XPS to be less than 100Å. Although the surface results in a thin modified layer the large variety of functional groups introduced tend to make this substrate unattractive for use as a model surface.

The grafting of a high surface energy material onto a low energy polymer represents a simple and attractive method for modifying the surface[26,27]. These methods all employ more or less the same methodology: the polymer to be modified is exposed to a solution containing a source of radicals and the reagent which is to be grafted. The radicals are then generated by the application of heat or light. Gamma-rays may be used to generate radicals directly from the polymer chains and in these cases an external source of radicals is not necessary. The surfaces which result from these treatments can vary from extensively grafted to lightly grafted, which is controlled mainly by the time of exposure. These methods, however, generally give surfaces which contain functional groups over a wide distribution of environment. This is the result one expects from a statisical incorporation of the grafting reagent as well as from generation of radicals far from the polymer surface. In order to incorporate a molecule, a radical must be generated on the chain in the presence of a second radical or unsaturated molecule so that reaction can occur. This event does not always occur; radicals which are generated on the chain can also result in chain cleavage and crosslinking from reactions with other polymer bound radicals. Though these modifications are interesting and commercially useful, they are not a good means of preparing substrates for model studies.

Plasma treatments represent another class of reactions which are widely used to modify surfaces[28-30]. These methods involve the generation of a plasma of a gas (element, molecule or monomer) in the presence of the surface which is to be modified. The exposure of the polymer to these plasma conditions often result in considerable crosslinking and oxidation of the polymer. The extent of these changes is a function of the gas used, the length of time of exposure and the power of the discharge. The chemical functionality introduced is largely dependent upon the experimental system: both high purity gases and clean equipment are essential. Even with care the surfaces which are produced with even low energy plasmas contain a considerable amount of chemical heterogeneity. Studies show that a thin layer (100 Å) of the polymer surface can be modified by this method[31], however the surface is chemically heterogeneous. These conclusions were reached based upon XPS, contact angle data and quantitative radiolabeling. The quantitative use of radiolabelling techniques requires that a reagent react specifically and completely with a functional group. The obtained values actually represent the number of molecules on the surface which have reacted. This is equal to the total number present only if complete selective reaction was achieved. This is a problem with all surface labelling methods: How complete and how specific is the labelling reaction? These problems can only be addressed once suitable model substrates are available.

Wet chemical oxidations of polyolefins involve the use of highly reactive oxidizing solutions such as: potassium cholorate in sulfuric acid[32], aqueous chromic acid[33] and potassium permanganate[34]. The most widely studied surface is a polyethylene surface which has been oxidized with aqueous chromic acid[35]. The surface produced using chromic acid was analyzed by most of the appropriate analytical techniques: XPS, radiolabelling, contact angles, fluoresence labelling, ATR-IR and SEM. The surface was shown to be chemically heterogeneous. The oxidized sites were labeled and it was found that the primary products were carboxylic acids and ketones. The site density for carboxylic acids was obtained and this was found to be constant over a wide range of reaction times. The surface produced using this method also appeared to be reasonably mobile. The polymer bound functional groups could readily diffuse into the bulk of the polymer. Thus the surface layer which resulted was a heterogeneous collection of oxidized carbon. The surface microtopography is rough and the functional groups are distributed over a large thickness of the surface. The results obtained are not surprising. As expected from the chemistry of the oxidation, chains ends should all terminate in carboxylic acid groups. The interior portions of the chain, which are only partially oxidized are the sites of the ketone functionality. It also is consistent that the level of carboxylic acid functionalization should reach a plateau since the acids can only result from the cleavage of chains. Eventually the molecular weight of the surface will be low enough that many of the smaller portions of the chain will be removed. Given enough time the entire polymer could be oxidized to carbon dioxide. Another drawback to using this substrate is that the oxidation reaction results in a crosslinked surface which also perturbs the surface structure-property relationships.

Chemical Reductions. The surfaces of fluorocarbon polymers generally have very low surface energies, hence they do not adhere to many substrates. This fact tends to limit their direct application. A method for increasing the surface energy of poly(tetrafluoroethylene) (Teflon) involves the chemical reduction of the fluorocarbon surface to an unsaturated surface devoid of fluorine, and subsequent partial oxidation of the unsaturated surface. The early investigators[36] applied a variety of analytical techniques including XPS toward the characterization of these materials. Much was learned about XPS on polymers using these polymers as substrates. The surfaces which resulted were black and contained large amounts of carbonaceous material which was not prone to air oxidation. This product could readily be removed by a variety of strong oxidizing agents and the resulting Teflon had a decreased contact angle though the XPS indicated that the surface was substantially Teflon. This surface was not stable and could be removed simply by rough handling. In addition the surface was no longer smooth, the reduction had resulted in extensive changes in the surface microtopography. These results indicate that a corrosive, non-surface-selective, reaction occured. The layer which formed was extremely heterogeneous both chemically and physically. The reaction was rapid and not controllable. It was also not possible to exclude oxygen incorporation during the reaction. These materials are also produced electrochemically and are being used by a number of investigators[37]. The electrochemically produced surfaces are produced by a method which is more controllable but which still produces largely heterogeneous materials. These surfaces have been functionalized by reacting the surface with a variety of reagents including ammonia, bromine and sulfur.

Substrates are also being prepared by the chemical modification of the surface produced using bezoin dianion as a reducing agent[38]. This surface, unlike the other reduced Teflon surfaces, is prone to air oxidation and the color changes from gold to colorless upon exposure to the atmosphere. This method was capable of producing surfaces which were essentially free of oxygen and represents an improvement over other reductive methods. The surface was also reacted with reagents that are known to react with double bonds. Thus upon reacting the surface with borane in tetrahydrofuran and then exposing the surface to hydrogen peroxide and sodium hydroxide a surface that was shown to contain hydroxyl functionality was produced. The first step of the modification is also not surface selective in nature and the resulting surface is heterogeneous. If the reaction is run to low conversion then significant quantities of unreacted Teflon remain. This makes the characterization of these surfaces and the study of reactivity-property relationships using these substrates difficult.

The purpose of this review is to introduce the reader to some of the current methods for modifying the surface of polymers. In general, these surfaces are chemically heterogeneous, have their functionality distributed over thick surface layers, typically have crosslinked surfaces and usually are altered in their microtopography. These materials are not suitable for studies in surface structure-property and structure-reactivity relationships. The ideal surfaces for these studies would contain two-dimensional arrays of polar functional groups on chemically resistant polymers such as poly(vinylidene fluoride)(PVF_2) and poly(chlorotrifluoroethylene)(PCTFE).

Poly(vinylidene fluoride) is the polymer formed from the free radically initiated, emulsion or suspension polymerization of 1,1-difluoroethylene. It is a semicrystalline (35 - 65 % crystalline) polymer which exhibits unusual dielectric properties[39]. The density of the polymer is 1.75 and the index of refraction is 1.42. The polymer has a glass transition temperature (T_g) that is reported to be -40°[39] and 13°[40]. The polymer melts at 151-184°C and can be readily pressed into films. The use of the polymer is widespread. It has high mechanical and impact strength, abrasion resistance, resistance to UV and nuclear radiation and a resistance to most chemicals and solvents. The polymer crystallizes in a number of crystal habits, some of which exhibit large piezoelectric activity. It is these piezoelectric forms which have made PVF_2 so attractive. The applications of PVF_2 include: latex finishes and paints, wire jackets, liners for pipes and tank linings as well as transducers. The surface energy of the polymer is not extraordinarily low; water contact angles are: $90\pm2^{\circ}$ advancing and $60\pm2^{\circ}$ receding.

There have been few reported modifications of PVF_2[41-44]. These involve the reaction of the PVF_2 film with a base. It was reported that ammonia or ammonia and alkali metal amides modify PVF_2. The film gives, upon uniaxial extension, light polarizers[41]. Adhesion of the polymer was improved by treating the film with aqueous solutions of

PVF_2 were realized using NaOH and phase transfer catalysis[43]. The work presented in this thesis uses phase transfer catalysis under mild conditions[44] to modify the surface of PVF_2.

Poly(chlorotrifluoroethylene) is a crystallizable polymer with a calculated density for the amorphous and crystalline polymers of 2.075 and 2.185 respectively[45]. The actual density of the polymer reflects the crystallinity ranging from 45% (d=2.1) to 65% (d=2.13). The polymer has a melting transition of 211 - 216°C and a Tg of 71-99°C[45]. The polymer exhibits good mechanical properties from -240 to 205°C and its refractive index is 1.435[46]. PCTFE is inert to most chemicals and oxidizing agents; however, PCTFE is swollen by ethers, halogenated materials and aromatic solvents[46]. It has the lowest water vapor transmission rate of any polymer and it is highly impermeable to gaseous vapors[47].

The polymer is formed from bulk, solution, suspension and emulsion polymerization of chlorotrifluoroethylene. PCTFE has been found to react quite well with a variety of organometallic reagents[48]. The methods employed in these modifications were such that the polymer was extensively modified. It was the reports that PCTFE underwent a clean reaction with alkyllithium reagents which initially prompted this study into organometallic methods of modifying PCTFE. The proposed mechanism of the reaction was not consistent with the products which were observed for the reaction of PCTFE film and low molecular weight oil with methyllithium and this prompted our research into this mechanism[49]. Once this reaction was examined in detail, it was discovered that it could be controlled through choices of temperature and solvent. This thesis presents this work as well as the extension of this reaction to the incorporation of polar functional groups.

Surface Characterization. An important objective of this research (as stated above) was to develop analytical techniques capable of monitoring surface reactions. Thus a large portion of the work presented in this thesis involves analytical chemistry. Sensitivity is a major obstacle in surface analysis. If the functional groups are indeed present in two-dimensional arrays on the surface of the polymer, then the functional group density can be estimated, using values obtained for close-packed monolayers[50], to be 10^{-9} moles/cm^2. This type of substrate is amenable to several analytical techniques (contact angle, XPS and SEM) but does not contain functional groups in concentrations high enough for detection by standard NMR and IR. In order to fully characterize the surfaces it was necessary to combine chemistry (reaction kinetics and derivatization reactions) and analytical observational tools to form chemistry-spectroscopy hybrid techniques which permit the characterization of the surface at the molecular level. The analytical methods include techniques which directly monitor the surface such as: contact angle, XPS, SEM and ATR-IR. Each of these techniques is sensitive to different surface regions and the thickness of the sampled surface varies (as discussed below) from several angstroms, in the case of contact angles, to a micrometer or more, in the case of ATR-IR. In addition, indirect methods of monitoring surface reactions include: gravimetric analysis and UV-Vis spectroscopy, as well as methods which employ the derivatization of the surface functional groups with analytically sensitive probes (spin, fluorescence, and radioisotopic labelling). The combination of the indirect and direct analytical methods when coupled with chemistry provide a means for characterizing the surfaces at a level necessary for detailed structure-reactivity relationships. The surface analytical methods which were successfully applied in the thesis are presented in the following paragraphs.

Contact Angle Measurements were measured on flat films by use of a Ramé-Hart optical bench contact angle goniometer. The only probe fluid used in obtaining the measurements was water which was distilled twice: once from a regular still, the second time from a Gilmont still. The water was stored in polypropylene bottles prior to use.

The contact angle method itself has several variations and a vast body of literature exists on each[51]. This literature will only be reviewed here where warranted. The method which was applied in this thesis involves dynamic contact angles: the advancing angle is that angle which is made between a drop of water and the solid surface, measured while water is added; conversely, the receding angle is that angle that is measured as water was removed from the drop. This technique was reproducible to within 1^{o} for all of the polymers used in this study.

In general, much information about the outer few angstroms of a surface is obtained from contact angle measurements. This includes information about the nature of the groups exposed at the surface, the distribution of the functional groups, surface roughness and surface chemical reactions.

The surfaces of polymers generally have low surface energies which mean that they will have high water contact angles (the water in the droplet interacts with itself rather than the polymer chains). When a reaction is carried out on these polymers the modified polymer does not usually have the same surface energy as the original polymer and these differences are observed as changes in the contact angles. When polyethylene is exposed to chromic acid the surface is oxidized. The presence of polar functionality is indicated by the decrease in the water contact angle. Contact angles thus provide a rapid, qualitative indication that a reaction has occurred. The quantitative and qualitative identification of specific functional groups is not attainable, but information about their distribution is attainable from contact angle data.

Information about functional group homogeneity was obtained both from the scatter in the contact angles which was measured in a variety of positions on the same sample and from the contact angle hysteresis. The scatter in the contact angles was quite easily obtained. The scatter was large if the surface contained unreacted material. Once the surface had become homogeneous with respect to contact angle measurement, the amount of scatter was reduced to 1-2°, the usual scatter for homogeneous polymer surfaces. The contact angle hysteresis also provides information about functional group heterogeneity. Johnson and Dettre[52] have examined theoretically the effect of small amounts of polar functionality on a nonpolar surface as well as the reverse case. They predict that in the case of small amounts of polar functionality, the advancing angle will decrease only slightly and the receding angle will decrease dramatically. In the case of nonpolar functionality on a polar surface the advancing angle will increase dramatically and the receding angle will change only slightly. These predictions are helpful when interpreting the experimentally measured contact angles.

Contact angle measurements are very useful when used in conjunction with other analytical techniques. When reaction kinetics at polymer surfaces are followed using several analytical methods including contact angles, information about the nature of the chemical reaction is sometimes obtained. Water contact angles are sensitive to the thinnest surface, the outer few angstroms. Generally then, if a reaction is proceding surface-selectively then the contact angles will attain a plateau value early in the reaction. If however, the reaction is corrosive then the contact angles change even after the reaction has progressed far into the bulk of the polymer. The contact angle method is not useful if the modified polymer is succeptible to secondary reactions which also cause changes in the observed contact angles and which were not the result of the original modification. An example where this is the case is the reduction of Teflon to form unsaturated material[53]. This unsaturated material is prone to oxidation and it is therefore not possible to determine whether the observed contact angle changes are the result of the reduction or of the subsequent oxidation of the reduced material.

Contact angle data also gives information about the surface roughness. Both theoretical[54,55] and experimental[56] verifications of the effect of roughness on contact angles are found in the literature. The effect of random surface roughness, with amplitude and wavelength below the micrometer range has experimentally been shown to: increase the advancing angle if the contact angle on the smooth surface is greater than 86°, decrease the contact angle on the smooth surface if the contact angle is less than 60°, and remain the same if the contact angle is between 60° and 86°. This corresponds to the prediction of the Wenzel relation:

$$\mathrm{Cos}\ \theta = r\mathrm{Cos}\ \theta_m$$

where θ is the observed contact angle, θ_m is the microscopic local contact angle and r is a roughness factor.

Contact angle measurements have been recently demonstrated to be sensitive to the pH of the probe fluid when the surface contains ionizable functionality[2]. This study used oxidized polyethylene for a substrate which was known to contain carboxylic acid groups. When the contact angle was measured with acidic water, no dependance on pH was observed. The contact angle decreased and the contact angle/pH plots resembled titration curves as the pH of the water was increased. It thus appears that this method can be used to detect the presence or absence of easily ionizable functional groups.

X-Ray Excited Photoelectron Spectroscopy. Surface analysis by x-ray excited photoelectron specroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), represents a direct method for monitoring surface reactions. The instruments used for obtaining XP spectra were the Kratos XSAM 800 and the Perkin Elmer 5100. XPS is a widely used surface spectroscopy and is in many respects, the best instrument for the study of polymer surface modifications[57]. The polymer film was mounted under nitrogen on a sample holder and loaded into a nitrogen purged antechamber. This sample was then isolated from the nitrogen and the antechamber was opened to the turbopump for 5 minutes (pressure $< 10^{-4}$T). The antechamber was then isolated from the turbopump and the valve to the ultrahigh vacuum chamber was opened. The sample was then loaded into the variable angle specimen holder and the chamber was once again isolated. The base pressure of the ultrahigh vacuum chamber containing the polymer was typically 5×10^{-9} Torr.

The technique involves irradiation of the sample with nearly monoenergetic soft x-rays and energy analysis of the emitted electrons. The obtained spectrum is a plot of the number of emitted electrons per energy interval verses their kinetic energy. Each element has a unique spectrum which results from the photoionization of core electrons. These characteristic electron energies allow elemental analysis as well as chemical state identification. The mean free path of electrons is very small in solids (5 to 60 Å depending upon the kinetic energy[58]), therefore the electrons that are emitted originate from a depth which is less than 100 Å. Quantitative data can be obtained from the peak heights or areas and knowledge of x-ray cross-sections.

When a sample is irradiated with monochromatic photons of frequency v, the photons may be absorbed resulting in the emission of electrons given by the Einstein relation[59]:

$$hv = E_{BE} + E_K$$

E_{BE} is the ionization or binding energy of the $k^{\underline{th}}$ species of electron in the material, and E_K is the kinetic energy of the ejected electron. The relation must be corrected for artifacts introduced by the experiment thus corrections for the spectrometer work function (SP) and sample charging (SA) are needed:

$$hv = E_{BE} + E_K + SP + SA$$

The anodes used for the experiments presented in this thesis include both Mg Kα x-rays (1253.6 eV) or Al Kα x-rays (1486.6 eV). Most analysis was done using the Mg Kα source and the kinetic energies of the electrons was thus limited to below 1.25 KeV.

In addition to obtaining information about the chemical compostion of the surface, XPS was used to probe the vertical distribution of functional groups in the polymer surface. This was accomplished nondestructively by making use of the angular dependency of the depth of the emitted photoelectrons. The angle between the source and the analyzer is fixed at 45^o, but the angle of the sample holder with respect to the analyzer is variable. When the sample is tilted toward the analyzer so that the surface of the film is perpendicular to the analyzer (90^o), then the maximum sampling depth is achieved. As the sample is rotated away from the analyzer, the electrons from within the bulk are forced to travel further and as a result, fewer will emerge from out of the sample. When electrons emerge at an angle of 15° from the surface, near grazing, they have originated mostly from near the surface. Detected electrons emerging at 90° originate from a depth greater than 4 times those emerging at 15°. The exact sampling depth is a quantitiy which is generally not known. There have been several attempts at obtaining these values. Experiments using Langmuir-Blodgett fatty acid films gave results which suggested that escape depths were in the region of 50 Å for 1000 eV electrons[60]. These early values are dependent upon absolute intensities and are crude estimates[61]. In addition no angular dependent studies using Langmuir-Blodgett films have been conducted. These studies are necessary when studying ordered films in order to rule out the possibility of electron channeling phenomena. More recent investigations involving the deposition of thin films of polyparaxylylene produced by insitu polymerization of paraxylylenes onto a given substrate. Then the relative intensities of a given core level as a function of angle were measured. These studies indicate that the mean free path is 14 Å for C_{1s} electrons excited by Mg Kα irradiation of kinetic energy 969 eV[61]. The sampling depth can be estimated from this escape depth. For a smooth specimen, 90% attenuation occurs at a depth of 8.3 Å for an angle of emergence of 15° and 37 Å for a 75° angle of emergence. These values arise from substitution of the appropriate values into the equation representing the intensity of a signal from a given core level arising from a surface layer of thickness d,

$$I = I_{inf} \left(1 - e^{-d/d_e \sin\theta} \right)$$

where I_{inf} is the intensity observed for an infinitely thick layer, Θ is the takeoff angle and d_e is the mean electron free path[62,63]. Thus for the angles used (15° and 75°) in the experiments contained in this thesis, the XPS represents a reasonably surface sensitive analytical method.

The usefulness of the XPS data was extended through the use of polymer surface derivatizations. That peaks with a particular BE in the XP spectra of polymers could correspond to more than one type of functional group was realized in the early days of polymer surface modification studies. The initial investigators used the bromination of double bonds as a means of deconvoluting the C_{1s} spectrum that resulted from treating Teflon with sodium solutions[64]. The intensity of the Br which appeared in the spectrum was used for quantitation of the original number of unsaturated groups. This method uses reagents which react selectively with a particular functional group of interest, and introduces into the surface a tag or label atom which is easily recognized in the XPS and is sometimes capable of quantitation. This derivatization method is necessary because basic XPS information is inadequate for the study of most of the currently used modifications, which result in complex polymer surface structures. There is a large body of literature dealing with derivatization methods and the problems inherent with their application[64,65]. Ideally the derivatization reaction should proceed to completion within the total XPS sampling depth, quickly and under mild conditions. These reactions which proceed rapidly at room temperature when conducted in solution are often slowed when conducted on surfaces. This alteration in the reactivity of surface confined functional groups is one motivation for this thesis work. It is hoped that with suitable two-dimensional substrates unambiguous information will be attained about the reactivities of these functional groups. A method to overcome the barriers presented by the surface is to make use of solvents which can swell the polymer. This introduces additional problems in that these solvents can induce a variety of changes in the polymer surface. Surface reorganization can be induced by certain solvents, and the functional groups can migrate to and from the surface. These effects have been studied by Everhart and Reilly[66]. Again these studies dealing with polymer functional group mobility can be facilitated by using substrates whose preparation is contained within this thesis. These solvents can also cause problems in that low molecular weight material produced during the modification, can be brought to the surface. In addition it also is generally more difficult to remove unreacted reagent from the polymer and Soxhlet type extractions are usually necessary. These solvent aided reactions are generally a compromise between achieving complete derivatization and avoiding solvent induced artifacts.

Scanning Electron Microscopy. Examination of the surfaces of polymers before and after surface treatments provides information about the changes in surface morphology which occur upon reaction. This method has been widely used for studying the changes in microtopography which result upon surface modification. These changes are very apparent when the modification is corrosive in nature. In these cases the surfaces are etched and pitted.

The principle of the SEM as used in this study, the emissive mode, is quite basic[67]. Electrons are excited from a tungsten filament, accelerated by a voltage (1 - 30 KeV) and directed down the center of an electron optical column consisting of magnetic lens. These lenses cause a fine electron beam to be focused onto the specimen suface. Scanning coils placed before the final lense cause the electron spot to be scanned across the specimen surface in the form of a square raster. The currents passing through the coils are made to pass through the corresponding deflection coils of a cathode ray tube which produces a similar raster on the screen in a synchronous fashion.

The electron beam excites the emission of secondary electrons from the specimen surface. These emitted electrons strike the collector and the resulting current is amplified and used to modulate the CRT. Hence there is a direct correspondence between the number of secondary electrons collected from any point and the brightness of the point on the CRT screen.

The secondary electrons are emitted from a shallow region of the surface and hence are very sensitive to changes in the surface microtopography. Thus secondary electron images are good indicators of the corrosive nature of a reaction. The scanning electron images were obtained for this thesis using a JEOL 100 STEM operating in the SEI mode or on a JEOL 35 SEM again imaging with secondary electrons.

Attenuated Total Reflection Infrared Specroscopy (ATR-IR). All spectra were obtained either on an IBM 38 FTIR at 4 cm^{-1} resolution or a Perkin Elmer 283 dispersive spectrophotometer. ATR spectra were obtained with a variable angle micro-ATR accessory. The internal reflection elements (IRE) used with the attachment were KRS-5 and Germanium, 10x5x1 mm with an entrance angle of 45^o. Single beam spectra were recorded on both spectrometers. The spectra recorded on the FTIR were ratioed against a stored background spectrum which permitted the calculation of absorbance and transmittance spectra. In the ATR experiments, the background spectra were of the IRE without a covering polymer recorded at 45^o both before and after the mounting of the polymer films. Contamination of the IRE was monitored in this manner. The contaminated IRE was cleaned by carefully rubbing the IRE with a lens tissue wetted with THF.

The attenuated total reflection spectroscopic method has been applied to a wide variety of "surface" problems since its introduction and development by Harrick[68] and others[69]. With this method IR spectroscopy can be applied to films whose thicknesses range from 0.1 to 3.0 micrometers. The experimental difficulties in using ATR-IR to study these substrates are often great. The ATR-IR experiment requires placing the absorbing substrate in contact with an optically more dense IRE. Reproducing the contact between the film and the IRE is often very difficult. In addition the films must be relatively smooth if quantitative results are desired. These problems were highlighted in a study by Mirabella[70]. In this study there were large variances in the intensitities of the absorbance bands which resulted from a lack of reproducibility of contact between the sample and the IRE.

The theoretical basis for ATR-IR is well understood and has been developed in its present form by Harrick and du Pré[71,72]. The strength of interaction of infrared radiation with the lower-refractive-index medium, when using a higher-refractive-index IRE, can be expressed as an effective thickness (d_e)[71]. The d_e is defined as the thickness of a film of the sample material that would give the same absorbance for transmission as that obtained in the ATR experiment. The d_e for bulk films assuming the low-absorption approximation, is[72]:

$$d_e = n_{21}\, E_o^2\, d_p \,/\, (\, 2 \cos \theta \,)$$

where $n_{21} = n_2 / n_1$ (n_2 is the refractive index of the rarer medium and n_1 is that of the denser medium), E_o is the electric field amplitude at the interface between the rarer and denser media, θ is the angle of incidence and d_p is the depth of penetration. The $1/\cos \theta$ term accounts for the sampling area variation as θ is changed. The electric field at the interface penetrates the sample as a evanescent field the amplitude of which decays exponentially with distance into the rarer medium[71]. The depth of penetration is arbitrarily defined as the distance into the rarer medium at which the electric field amplitude of the evanescent wave has fallen to a value of E_oe^{-1}. This occurs when

$$d_p = L_1 \,/\, 2\ \mathrm{Pi}\ (\, \sin^2\theta - (n_{21})^2\,)^{1/2}$$

where L_1 is the wavelength in the denser medium.

Substitution of this into the equation for d_e yields equations for the effective thickness of the incident electric field. However it is more useful to know the depth into the surface which is being sampled. This depth is controlled by the decay of the evanescent wave which, for the low absorption case[73], is given by

$$E = E_o e^{-gz}$$

$$g = (2 \, Pi \, (\sin^2\theta - (n_{21})^2)^{1/2}) / L_1$$

where E is the electric field amplitude at depth z normal to the surface and g is the electric field amplitude decay constant. It can be seen from the previous equations that $g = 1 / d_p$ and that at $z = d_p$, E is roughly 1 / e (37 %) of E_o. Thus one can see that the usual estimated sampling depth which involves d_p is an underestimation. A closer estimation is that $z = 2 \, d_p$ which accounts for 90% of E_o. Under these conditions the d_p for Ge with PCTFE film (n = 1.43) and PVF_2 film (n = 1.42) at 3000 cm^{-1} and 1600 cm^{-1} are 0.22 and 0.41 micrometers respectively. With the KRS-5 crystal the d_p are: for PCTFE at 3000 cm^{-1} and 1600 cm^{-1}, 0.63 and 1.2 micrometers respectively; for PVF_2 at 3000 cm^{-1} and 1600 cm^{-1}, 0.62 and 1.15 micrometers respectively.

These calculations indicate that ATR-IR will be useful only when the modified surface is reasonably thick. It is not an extremely surface sensitive method like XPS or contact angle. This fact is often overlooked when surfaces and modification reactions are analyzed by ATR.

Gravimetric Analysis Gravimetric analysis of polymer surface reactions is a new anaytical technique which was developed in our laboratory[74]. It can be a precise quantitative method for monitoring surface reactions. The mass change which occurs upon reaction was measured with a Cahn 29 electrobalance. The ultimate sensitivity of the balance is 1 X 10^{-7} g. The procedure for obtaining precise quantitative data, though simple, is very time consuming. The polymer films must first be extracted with a suitable solvent to remove contamination and low molecular weight material. Then the film must be freed of solvent by heating under vacuum until a constant mass is achieved.

PCTFE required a 30 minute reflux with methylene chloride to obtain clean film. The film required drying for 72 h (90°C, 0.05mm) to reach constant mass (mass was judged to be constant when the same mass was obtained over a 72 h period). Film treated in this manner did not lose further mass when exposed to the conditions used for the surface modifications.

PVF_2 was likewise extracted for 30 minutes with methylene chloride. These films were dried at 0.05mm and 35°C for 3 days or until constant mass was reached. The film was again consistently free of contaminants and once again the control films did not lose mass under the conditions of the modification reactions.

In weighing and reacting the film it was important not to scratch them and stirbars could not be used. Instead the film was agitated during reaction and washing by shaking the film with a Fisher Vortex Genie. It was also important to be patient and make sure that a constant mass was reached after each stage of the modification.

Another consideration when dealing with these fluoropolymers is that they can build up a considerable static charge which can attract dust. It was thus necessary to reduce the levels of charge present when weighing the film. This was accomplished both by placing a radioactive polonium source inside the weighing chamber near the weighing pan; and by treating the film with a Zerostat, a piezoelectric device which serves to discharge the polymer film. The film was then sprayed with dustoff holding the can at least 20 cm from the film surface. The film, now free of dust and static, was then weighed. This procedure was repeated 4 times and the values were averaged.

When these steps are carefully followed then gravimetric analysis of polymer surface reactions, though time consuming, is a precise useful analytical method which is convenient, easily used, and inexpensive (relative to other surface spectroscopic methods).

Ultraviolet-Visible Light Spectrometry. UV-Vis spectra were recorded using a Perkin Elmer Lambda 3A spectrophotometer. The UV-Vis spectra were either obtained on polymer solutions or directly from polymer films. The absorbance of the films were obtained on 25 and 125 micrometer thick films of PCTFE or PVF_2 by placing them directly in the beam using a film holding attachment. The unmodified films were free of significant absorbance down to 230 nm. In addition spectra were recorded as a difference by placing an unmodified film in the reference beam and a modified film in the sample beam. The samples were matched prior to reaction to ensure a flat baseline. Upon reaction the films were monitored for chromophore formation by following changes introduced in the previously flat baseline.

Radioisotopic Labeling. Radioisotopic labeling has been widely used in the study of polymer surface chemistry. The theory behind this method is quite simple: attach a radioactive isotope of an element to a functional group on the surface and, through liquid scintillation counting or another radioassay method, determine the sample disintegration rate. The radioactive decay process involves simple first order kinetics:

$$N_t = N_o e^{-dT}$$

Where N_t and N_o are the disintegration rates at time = t and at time = 0 respectively. A plot of the logarithm of the disintegration rate vs. time gives a straight line with a slope equal to a characteristic decay constant (d). This constant is normally represented as the half-life which is characteristic for each isotope. The radioassay method used monitors a quantity which can by though of as events observed per unit time. These observed events are proportional to the actual radioactive disintegration rate, thus

$$DPM = E\ (CPM)$$

where DPM is the actual disintegrations per minute, CPM is counts per minute and E is the experimentally determined detection efficiency or the proportionality constant for the radioassay method. This efficiency can be divided into an energy dependent term which is an intrinsic property of the detection medium and a geometric factor which depends upon the angle between the source and the detector.

Radiolabelling experiments have been widely used to determine the number of functional groups present in a sample. In these experiments, the modified surface is treated with a compound containing a radioactive isotope, under conditions which effect reaction. Then the increase in the radioactivity of the sample is determined and attributed to the reaction of the functional groups.

This thesis uses radiolabelling experiments to determine the number of functional groups and examines the esterification of the PCTFE-COOH surface using tritiated alcohol.

References

1. Clark, D.T.; Feast, W.J. Polymer Surfaces, Wiley Interscience: New York, 1978 and references therein.

2. Holmes-Farley, S.R.; Reamey, R.H.; McCarthy, T.J.; Deutch, J.; Whitesides, G.M. **Langmuir** 1985, 1, 725

3. For a discussion of chemistry in fractal dimensions, see: Pfeifer, P.; Avnir, D. **J. Chem. Phys.** 1983, 79, 3558

4. For a discussion of the theory of chemistry in reduced dimensions see: Astumian, R.D.; Schelly, Z.A. **J. Am. Chem. Soc.** 1984, 106, 304

5. Somorjai, G.A. Principles of Surface Chemistry, Prentice Hall: Englewood Cliffs, New Jersey, 1972

6. Reference 1, pages 213 - 234 and references therein

7. Nuzzo, R.G.; Smolinsky, G. **Macromolecules** 1984, 17, 1012

8. Bell, A.T.; Hollahan, J.R., Eds., Techniques and Applications of Plasma Chemistry, Wiley Interscience:New York, 1974

9. Clark, D.T.; Peeling, J.; O'Malley, J.M. **J. Polym. Sci.: Polym. Chem. Ed.** 1976, 14, 543

10. Dwight, D.W.; Riggs, W.M. **J. Colloid Interface Sci.** 1974, 47, 650

11. a) Rasmussen, J.R.; Stedronsky, E.R.; Whitesides, G.M. **J. Am. Chem. Soc.** 1977, 99, 4736 b) Rasmussen, J.R.; Berbreiter, D.E.; Whitesides, G.M. ibid, 1977, 99, 4746

12. Bonafini, J.A.; McCarthy, T.J. Master of Science Degree Dissertation, University of Massachusetts: Amherst, Massachusetts, 1984

13. Rukenstein, E.; Gourisanhar, S. **J. Colloid Interface Science** 1985, 107, 488

14. Gagnon, D.R.; McCarthy, T.J. **J. Appl. Polym. Sci.** 1984, 29, 4335

15. Blais, P.; Day, M,; Wiles, D.M. **J. Appl. Polym. Sci.** 1973, 17, 875

16. Peeling, J.; Clark, D.T. **Polym. Degradation Stab.** 1981, 3, 92

17. Owen, E. Degradation and Stabilization of PVC, Appl. Sci. Pub.: London, 1984

18. Lazare, S.; Hoh, P.D.; Baker, J.M.; Srinivasian, R. **J. Am. Chem. Soc.** 1984, 106, 4288

19. Srinivasian, R.; Leigh, W.J. **J. Am. Chem. Soc.** 1982, 104, 6784

20. Rossman, K. **J. Polym. Sci.** 1956, 19, 141

21. Amouroux, J.; Goldman, M.; Revoil, M.F. **J. Polym. Sci.: Polym. Chem. Ed.** 1982, 20, 1373

22. Briggs, D. in Brewis, D.M. ed., Surface Analysis and Pretreatment of Plastics and Metals, Applied Science: London, 1982

23. Blythe, A.R.; Briggs, D.; Kendall, C.K.; Rance, D.G.; Zichy, V.J.I. **Polymer** 1979, 19, 1273

24. Briggs, D.; Kendall, C.K. **Polymer** 1979, 20, 1053

25. Briggs, D.; Brewis, D.M.; Konieczko, M.B. **J. Mat. Sci.** 1979, 14, 1344

26. Oster, G.; Shibata, O. **J. Polym. Sci.** 1957, 26, 233

27. a) Yamamoto, F; Yamakawa, S. **J. Polym. Sci.: Polym. Phys. Ed.** 1979, 17, 1581 b) Charlesby, A. Atomic Radiation and Polymers, Pergaman Press: New York, 1960, (Chapter 22)

28. Clark, D.T.; Wilson, R. **J. Polym. Sci.** 1983, 21, 837

29. Collins, G.C.S.; Lowe, A.C.; Nicholas, D. **Eur. Polym. J.** 1973, 9, 1173

30. Hudas, M. in reference 8, 122

31. Clark, D.T.; Dilks, A. **J. Polym. Sci.: Polym. Chem. Ed.** 1977, 15, 2321

32. Baszkin, A.; Ter-Minassian-Saraga, L. **J. Polym. Sci., Part C** 1971, 243

33. Briggs, D.; Zichy, V.J.I.; Brewis, D.M.; Comyn, J.; Dalm, R.H.; Green, M.A.; Konieczko, M.B. **Surface Interface Anal.** 1980, 2, 107

34. Borisova, T.K.; Kiselev, A.V.; Korolev, A.Y.; Lygin, V.I.; Solomonova, I.N. **Kolloidn Zh.** 1966, 28, 792

35. See reference 1, reference 11, and reference 33 and also references contained therein.

36. Dwight, D.W.; Riggs, W.M. **J. Colloid Interface Sci.** 1974, 47, 650

37. a) Barker, D.J.; Brewis, D.M.; Dahm, R.H. **J. Materials Sci.** 1979, 14, 749 b) Kavan, L.; Dousek, F.P.

Carbon 1986, 1, 61

38. A preliminary account of this appeared in Costello, C.A.; McCarthy, T.J. **Macromolecules** 1984, 17, 2529

39. Dohany, J.E.; Robb, L.E. in Kirk-Othmer Encyclopedia of Chemical Technology, Wiley Intersciene: New York, 1980, 11, 64

40. Aldrich Catalog/Handbook of Fine Chemicals, 1986

41. Murayama, N.; Kodo, T. **Chemical Abstracts** 92:77679k (1980)

42. Seki, S.; Sato, K.; Sasakawa, A. **Chemical Abstracts** 76:p73362y (1972)

43. Kise, H.; Ogata, H. **J. Polym. Sci.: Polym. Chem. Ed.** 1983, 21, 3443

44. Dias, A.J.; McCarthy, T.J. **Macromolecules** 1984, 17, 2529

45. West, A.C. in reference 39, 11, 49

46. Kel-F 81 Engineering Manual, 3M Company, St. Paul, Minnesota

47. Hoffman, J.D.; Weeks, J.J. **J. Chem. Phys.** 1962, 37, 1723

48. a) Huth, J.A.; Danielson, N.D. **Anal. Chem.** 1982, 54, 930
    b) Danielson, N.D.; Taylor, R.T.; Huth, J.A.; Siergiej, R.W.; Galloway, J.G.; Paperman, J.B. **Ind. Eng. Chem. Prod. Res. Dev.** 1983, 22, 303

49. Dias, A.J.; McCarthy, T.J. **Macromolecules** 1985, 18, 1826

50. Alexander, A.E.; Hibberd, G.E. in Weissberger, A.; Rossiter, B.W. eds., Techniques of Chemistry, Wiley Interscience: New York, 1972, 1, 575

51. Adamson, A. Physical Chemistry of Surfaces, 4th ed. Wiley: New York, 1982 p. 328

52. a) Johnson, R.E.; Dettre, R.H. **J. Phys. Chem.** 1964, 68, 1744
    b) Neumann, A.W.; Good, R.J. **J. Colloid Interface Sci.** 1972, 38, 341

53. Kaelble, D.H.; Cirlin, E.H. **J. Polym. Sci. Part A** 1971, 29, 363

54. Wenzel, R.N. **Ind. Eng. Chem.** 1936, 28, 988

55. Huh, C.; Mason, S.G. **J. Colloid Interface Sci.** 1977, 60, 11

56. Busscher, H.J.; Van Pelt, A.W.J.; DeBoer, P.; DeJong, H.P.;

Arends, J. **Colloids and Surfaces** 1984, 9, 319

57. a) Holm, R.; Storp, S. **Surface Interface Anal.** 1980, 2, 96
b) Clark, D.T. in reference 1 Chapter 16

58. Clark, D.T.; Powell, C.J. **Surface Science** 1974, 44, 29

59. Einstein, A. **Ann. Phys.** 1905, 17, 132

60. Henke, B.L. **Adv. X-ray Anal.** 1969, 13, 1

61. Clark, D.T.; Thomas, H.R. **J. Polym. Sci.: Polym. Chem. Ed.** 1977, 15, 2843

62. Clark, D.T. in Briggs, D. ed. Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy, Heyden and Sons: London, 1977 p. 211

63. Clark, D.T. in Ivin, K.J. ed Sructural Studies of Macromolecules by Spectroscopic Methods, Wiley Interscience: London, 1979

64. Riggs, W.; Dwight, D.J. **J. Electron Spectr.** 1974, 5, 447

65. Batich, C.D.; Wendt, R.W. **Abstr. Amer. Chem. Soc., Div. Polymer Chem., Houston** 1980, 179

66. Everhart, D.S.; Reilley, C.N. **Surface Interface Anal.** 1981, 3, 126

67. Joy, D.C.; Hren, J.J.; Golstein, J.I. eds. Introduction to Analytical Electron Microscopy, Plenum Press: New York, 1979

68. Harrick, N.J. Internal Reflection Spectroscopy, Wiley Interscience: New York, 1967

69. a) Flournoy, P.A.; Shaffers, W.J. **Spectrochim. Acta.** 1966, 22, 5
b) Hansen, W.N. **Anal. Chem.** 1963, 35, 765 c) Hannah, R.W. **Appl. Spectrosc.** 1963, 17, 23

70. Mirabella, F.M. **J. Polym. Sci.: Polym. Phys. Ed.** 1982, 20, 2309

71. Harrick, N.J. **J. Opt. Soc. Am.** 1965, 55, 851

72. Harrick, N.J.; duPrè, F.K. **Appl. Opt.** 1966, 5, 1739

73. The low absorption case approximation is met even for intense bands in polymers; see reference 69a and reference 72 for an explanation of the approximation.

74. Bonafini, J.A.; Dias, A.J.; Guzdar, Z.A.; McCarthy, T.J. **J. Polym. Sci.: Polym. Lett. Ed.** 1985, 23, 33

Chapter II: Experimental Section

A. Materials

acetic acid (A)
[1-^{14}C]acetic acid (P)
[^{3}H]acetic acid, sodium salt (NE)
acetic anhydride (A)
acetone (A)
2-amino-2-methyl-1-propanol (A)
barium oxide (F)
benzophenone (A)
benzyl chloride (A)
borane-tetrahydrofuran (A)
boron trifluoride etherate (A)
bromine (A)
2-(2-bromoethyl)-1,3-dioxolane (A)
3-bromo-1-propanol (A)
butyllithium (A)
tert-butyllithium (A)
calcium hydride (A)
carbon tetrachloride (A)
1,1'-carbonyldiimidazole (A)
m-chloroperoxybenzoic acid (A)
decane (A)
1,8-diazabicyclo[5.4.0]undec-7-ene (A)
1,3-diaminopropane (A)
dichloroacetic acid (A)
dichloromethane (F)
dichlorophenylhydrazine (A)
dichlorotriphenylphosphorane (Alfa)
dihydropyran (A)
diisopropylamine (Alfa)
dimethylformamide (A)
3,5-dinitrobenzoyl chloride (A)
2,4-dinitrophenylhydrazine (A)
diphenylacetic acid (A)
1,3-dithiane (A)
dodecane (A)
drierite (F)
ethanol (F)
ethylene glycol (A)
ethyl ether (F)
ethyl vinyl ether (A)
FAD ionic buffer (F)
ferric ammonium sulfate (F)
heptafluorobutyryl chloride (A)
heptane (A)
hexafluoro-2-propanol (F)
hexane (A)
hydrochloric acid (F)
4-hydroxy-TEMPO (A)
lead (IV) oxide (A)

Materials (continued)

lithium metal (Alfa)

lithium aluminum hydride/THF (A)

magnesium metal (F)

magnesium sulfate (F)

mercuric acetate (A)

mercuric chloride (A)

mercuric trifluoroacetate (A)

methanol (F)

methyl chloride (M)

methyl iodide (F)

methyllithium (A)

molecular sieves - 3A (F)

naphthalene (A)

nitric acid (F)

nitrogen (M)

OCS scintillation fluid (Am)

octadecanol (A)

octanol (F)

osmium tetroxide (A)

oxalyl chloride (A)

palladium chloride (A)

phenyllithium (A)

phosphorous pentoxide (F)

poly(chlorotrifluoroethylene) (Al, 3M, Afton, PSS)

polyethylene (SPP)

polytetrafluoroethylene (BG)

poly(ethylene-co-tetrafluoroethylene) (Du)

poly(vinylidene fluoride) (WP)

potassium chlorate (A)

potassium cyanide (A)

potassium fluoride (F)

potassium permanganate (F)

potassium thiocyanate (F)

pyridine (A)

reforming gas(10% H_2, 90% N_2) (M)

R3-11 catalyst (C)

silver nitrate (A)

sodium metal (A)

sodium borohydride (A)

sodium chloride (F)

sodium hydroxide (A)

sulfuric acid (F)

tetrabutylammonium bromide (A)

tetrahydrofuran (F)

tetramethylammonium hydroxide (A)

thionyl chloride (A)

Materials (continued)

toluene (F)

p-toluenesulfonic acid (A)

tribromoethanol (A)

3,4,5-tribromophenylisocyanate (Alfa)

trichloroacetylisocyanate (A)

trichloroethanol (A)

2,3,5-trichlorophenylhydrazine (Alfa)

triethylphosphite (A)

trifluoroacetic acid (A)

2,4,4-trimethyl-2-oxazoline (A)

Sources: A = Aldrich; Afton = Afton Plastics Molding Co. (Lakeland, Minnesota); Al = Allied Corporation; Alfa = Alfa; Am = Amersham ; BG = Bergoff; C = Chemalog (S. Plainfield, N. J.); Du = Dupont; F = Fisher; M = Matheson; NE = New England Nuclear; P = Pathfinder Laboratories; PSS = Polysciences; WP = Westlake Plastics (Lenni, Penn.); SPP = Scientific Polymer Products; 3M = Minnesota Mining & Manufacturing Plainfield, N. J.)

B. Material Handling

Many of the materials used and the products whose preparation are described in this thesis are sensitive to air and water. Thus it was necessary to prepare and analyze these materials in carefully controlled anaerobic environments. The methods for obtaining suitable environments are well established in the literature and widely practiced, therefore these techniques will be discussed only briefly here^1.

The inert gas lines used were constructed out of 1/4" O.D. copper tubing and brass Swagelock fittings. The inert gas was either prepurified nitrogen or prepurified nitrogen passed through a column of R3-11 catalyst, to remove oxygen, and through a column of drierite, to remove water. Connections were made to the gas line using 1/4" I.D. Tygon tubing and the syringe needles were attached to male Luer lock to 1/4" I.D. tubing.

The vacuum lines were constructed at the University of Massachusetts glass shop. The line (figure 1-2-1) was connected to a Precision vacuum pump through a liquid nitrogen cooled trap. The other end of the line was connected to a balast (1 liter). The vacuum was monitored using a Teledyne-Hastings vacuum meter and gauge. Typical operating pressure for the vacuum line was 0.05 mm Hg.

Schlenk glassware was prepared at the University of Massachusetts glass shop. The distinguishing feature of Schlenk glassware is that it typically has two openings: one is a sidearm containing a 4 mm straightbore Teflon stopcock and terminated in a 14/20 ₮ female

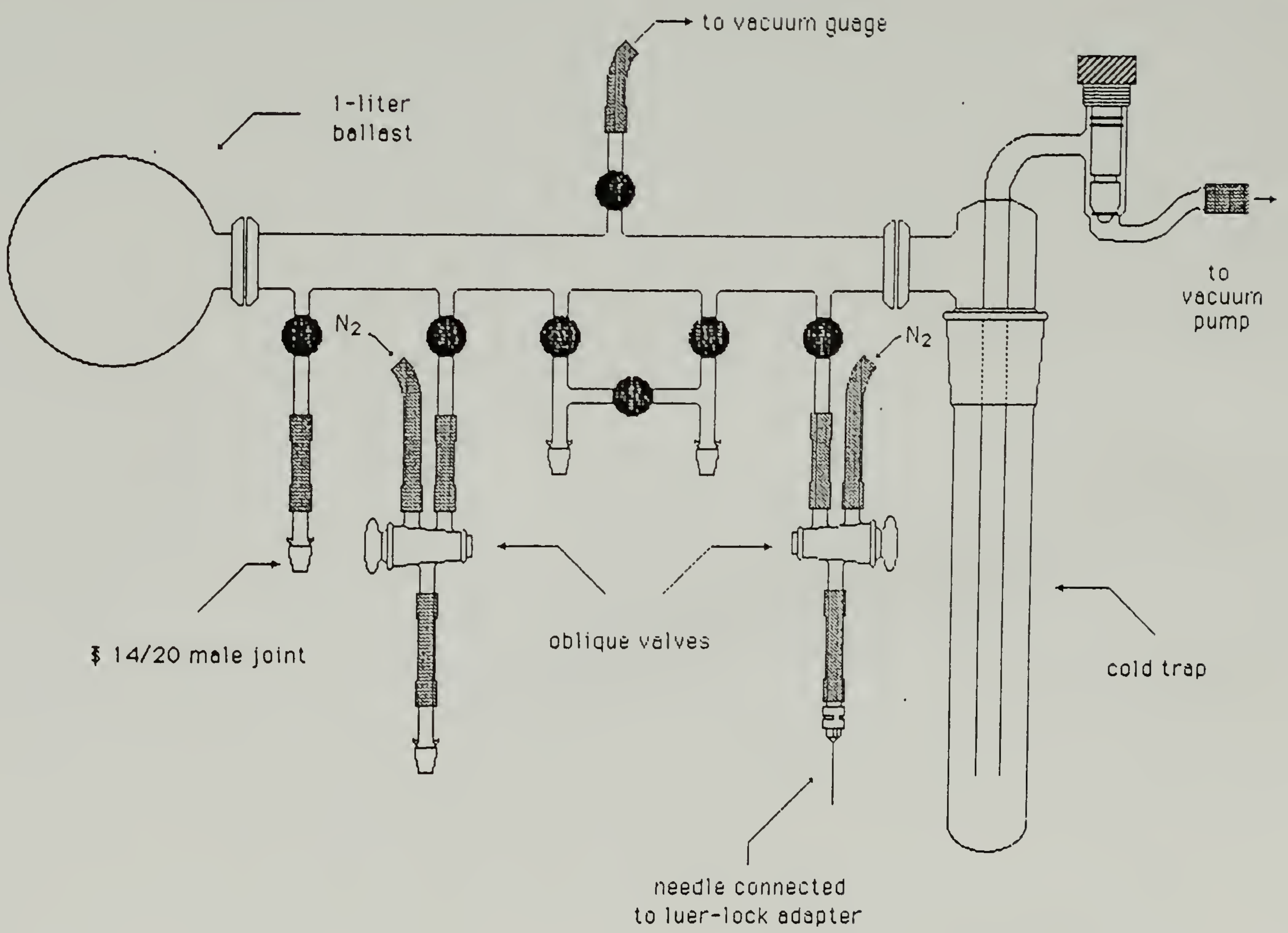


Figure 1-2-1. Vacuum Manifold

connection; the other opening is a 24/40 $ male joint or a #25 O-ring connection (figure 1-2-2). Using this glassware it was possible to flow nitrogen through the sidearm while adding or removing solids from the tube. Additionally, fluids were transported into and out of the tubes using cannula and a positive pressure of nitrogen.

Certain operations require the removal of the samples from the reaction vessels. When the operation involved only short time periods (1 - 2 minutes), they were carried out in polyethylene glovebags (I^2R) under a nitrogen atmosphere. Longer procedures were run in a Vacuum Atmosphere Company dry box.

C. Purification of Solvents and Reagents.

Distillations were done through a 10 cm Vigreux column. Continuous distillations were run under nitrogen using a distillation head equipped with a overflow return tube at the bottom of the reservoir. Vacuum distillations were run using a 10 cm Vigreux column; the pressure was monitored with a mercury manometer and regulated with a Manowatch (I^2R Company). Trap-to-trap distillations were run using the apparatus depicted in figure 1-2-3 or using two vessels attached directly to the vacuum manifold. In this method the solvent is thoroughly degassed: freeze the solution with liquid nitrogen (-195°C), open the frozen solution to the vacuum until the minimum pressure is observed, close the stopcock to the vessel and allow it to warm to room temperature. This freeze-pump-thaw cycle is repeated three times which removes the dissoved gases. The degassed solvent is again frozen and the vessel is evacuated until the minimum pressure is reached. If the distillation is run on the vacuum

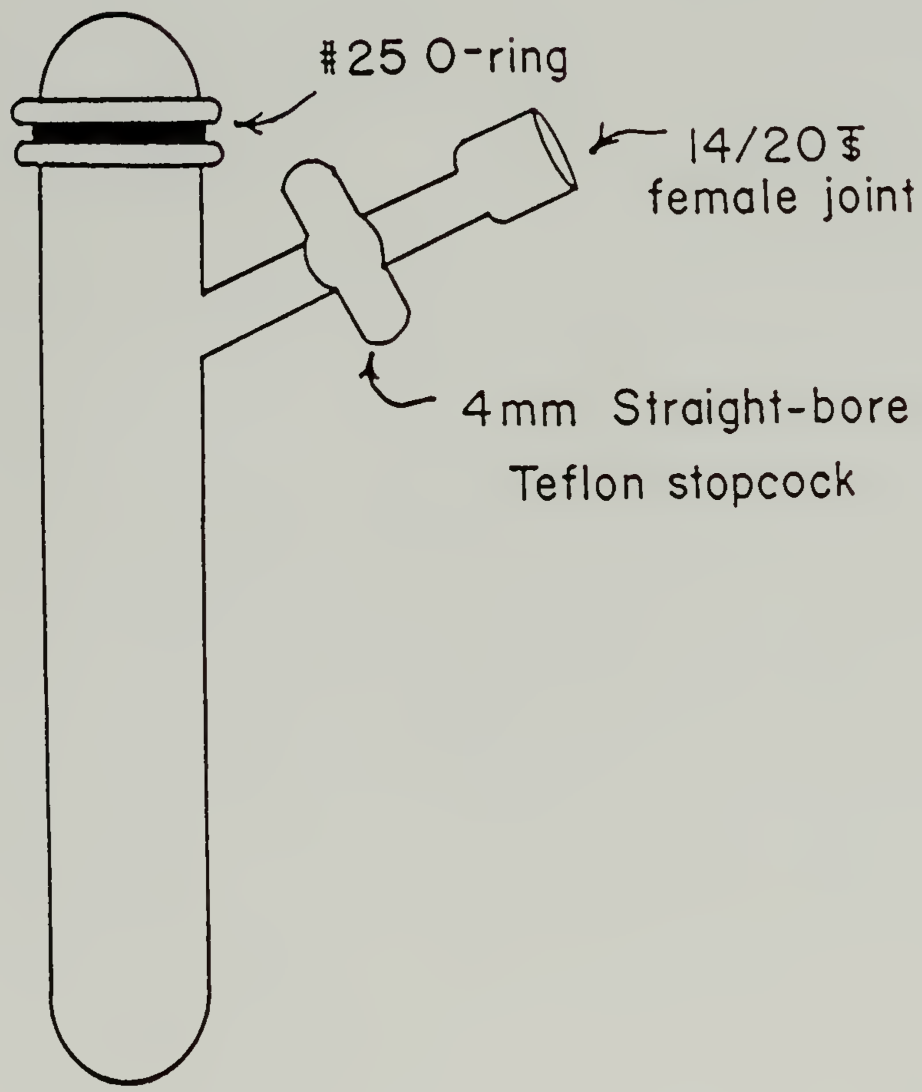


Figure 1-2-2. Schlenk Tube

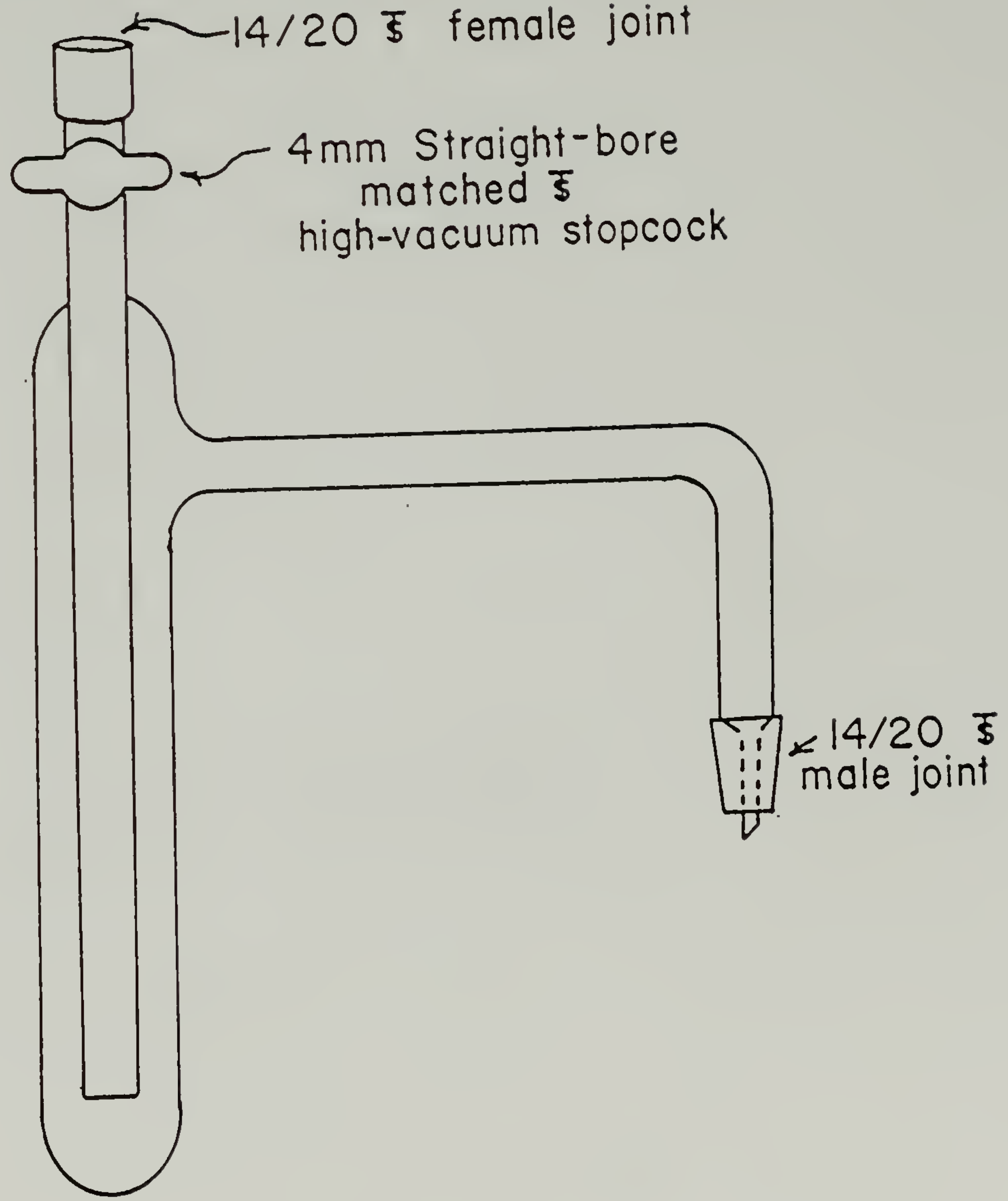


Figure 1-2-3. Trap-to-trap Apparatus

manifold then the stopcock to the vacuum is closed and the liquid nitrogen dewar is removed from the frozen solvent and placed on the receiver. The stopcock to the receiver is then opened. When the distillation is complete then the stopcock to the reciever is closed and the receiver is removed and placed under nitrogen. When the trap-to-trap apparatus is used, the dewar is removed from the solvent and placed on the apparatus trap, without closing off the vacuum source. Upon completing the distillation, the stopcock is closed and the solvent is removed and stored under nitrogen.

Distillations from sodium benzophenone dianion necessitated special steps in order to achieve the deep purple color of the dianion rapidly: A new bottle of HPLC grade solvent (uninhibited) was opened under a stream of nitrogen and quickly stoppered with a rubber septum; using a cannula and a positive pressure of nitrogen the solvent was transferred into a nitrogen purged, septum stoppered schlenk flask containing a magnetic stirring bar; the solvent was sparged 1 hour with prepurified nitrogen; benzophenone (2 g/ liter) and freshly cut sodium (1 g/ liter) were added to the flask under a stream of nitrogen. The mixture was stirred until the purple dianion color was achieved (3 - 6 h). The solvent was then ready for distillation.

<u>Acetic acid</u> was fractionally distilled from phosphorous pentoxide (bp 118°C) and stored under nitrogen.

<u>2-Amino-2-methyl-1-propanol</u> was distilled from calcium hydride (bp 165°C) and used promptly.

<u>Benzyl chloride</u> was distilled trap-to-trap and stored under nitrogen.

Boron trifluoride etherate was distilled trap-to-trap and stored under nitrogen at 0°C.

2-(2-Bromoethyl)-1,3-dioxolane (BED) was distilled trap-to-trap from calcium hydride and stored under nitrogen.

3-Bromo-1-propanol was dissolved in an equal volume of dichloromethane. This solution was placed in a separatory funnel and washed with H_2O (20 ml), saturated sodium bicarbonate (2 X 20 ml), and saturated sodium chloride (20 ml). The solution was dried with magnesium sulfate, filtered, and concentrated using a rotary evaporator. The bromopropanol was vacuum distilled from potassium carbonate (bp 60 - 64°C, 5 mm). The distillate was stored under nitrogen over potassium carbonate in the freezer.

Carbon tetrachloride was distilled from phosphorous pentoxide (bp 77°C) and stored under nitrogen.

Decane was distilled from calcium hydride (bp 174°C) and stored under nitrogen.

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was vacuum distilled from calcium hydride (bp 80°C , 0.6 mm) and stored under nitrogen.

Dichloromethane ($MeCl_2$) (2 L) was stirred over sulfuric acid (2 X 50 ml). The $MeCl_2$ was then washed with water (2 X 100 ml), dried with magnesium sulfate, filtered and distilled from phosphorous pentoxide (bp 40°C).

Dimethylformamide (DMF) was vacuum distilled from barium oxide (bp 77°C , 40 mm) and stored under nitrogen.

Dihydropyran was distilled trap-to-trap from calcium hydride and stored under nitrogen.

1,3-Dithiane (DT) was purified by sublimation (0.05 mm , 20°C).

Dodecane was distilled from calcium hydride (bp 216°C) and stored under nitrogen.

Ethanol (2 L) was refluxed (24 h) with magnesium turnings (2 g) under nitrogen, then distilled (bp 76°C) and stored under nitrogen.

Ethyl ether was continuously distilled from sodium benzophenone dianion and stored under nitrogen.

Ethyl vinyl ether was fractionally distilled (bp 33°C) under nitrogen and promptly used.

Heptane was continuously distilled from sodium benzophenone dianion.

Hexafluoro-2-propanol (F_6iP) was distilled from 3A molecular sieves (bp 59°C) and stored under nitrogen.

Hexane was distilled from calcium hydride (bp 69°C) and stored under nitrogen.

4-Hydroxy-TEMPO was dried by azeotropic distillation using heptane (mp 70°C) and stored in the glove box.

Methanol (2 L) was refluxed (24 h) with magnesium turnings (2 g) under nitrogen, then distilled (bp 65°C) and stored under nitrogen.

Molecular sieves (3A) were activated by heating them to 300°C in a stream of nitrogen. After 2 h they were cooled to room temperature and stored under nitrogen.

Octadecanol ($C_{18}OH$) (1 g) was placed into a 50 ml flask and heptane (30 ml) was added. The heptane was distilled until 5 ml remained, this was removed under vacuum (0.05 mm). The powder was stored in a desicator.

Octanol (C_8OH) (500 ml) was refluxed (24 h) with magnesium turnings (0.5 g) under nitrogen, then distilled (bp 196°C) and stored under nitrogen.

Oxalyl chloride was vacuum distilled (bp 60°C , 750 mm) and stored under nitrogen.

Poly(chlorotrifluoroethylene) film (Kel-F, Aclar, PCTFE) was extracted (30 min) in refluxing $MeCl_2$ then dried (0.05 mm, 90°C) until a constant mass was achieved.

Poly(chlorotrifluoroethylene) oil was fractionally distilled and the middle fraction (bp 60 - 80°C , 0.05 mm) was stored under nitrogen and used.

Polyethylene was extracted (30 min) in refluxing $MeCl_2$ and dried (24 h , 0.05 mm).

Poly(ethylene-co-tetrafluoroethylene) (Tefzel) was extracted (30 min) in refluxing $MeCl_2$ then dried (24 h , 0.05 mm , 40°C).

Polytetrafluoroethylene (Teflon) was extracted (30 min) in refluxing $MeCl_2$ then dried (24 h , 0.05 mm , 40°C).

Poly(vinylidene fluoride) (PVF_2) was extracted (30 min) in refluxing $MeCl_2$ then dried (0.05 mm , 40°C) until a constant mass was achieved.

Pyridine was distilled from calcium hydride (bp 115°C) and stored under nitrogen.

R3-11 catalyst was activated by heating it to 160°C overnight in a stream of forming gas.

Tetrahydrofuran was continuously distilled from sodium benzophenone dianion and stored under nitrogen.

Thionyl chloride (50 g) was placed in a 100 ml flask and triethylphosphite (5 g) was added dropwise to the stirred thionyl chloride. The thionyl chloride was fractionally distilled (bp 79°C) and stored under nitrogen.

Toluene was continuously distilled from sodium benzophenone dianion and stored under nitrogen.

Tribromoethanol (Br_3EtOH) was sublimed (0.05 mm , 30°C) and stored in a foil covered dessicator at -4°C.

Trichloroethanol was vacuum distilled from 3A molecular sieves (bp 90°C , 100 mm) and stored under nitrogen.

2,4,4-Trimethyl-2-oxazoline (TMO) was vacuum distilled from calcium hydride (bp 70°C , 160 mm) and stored under nitrogen.

[1-^{14}C]acetic acid, [^{3}H]acetic acid (sodium salt), acetic anhydride, borane-tetrahydrofuran complex (1M BH_3 in THF), bromine, butyllithium (1.6M in hexanes), *tert*-butyllithium (1.7M in pentane), calcium hydride, 1,1'-carbonyl diimidazole (CDI), *m*-chloroperoxybenzoic acid (MCPBA), 1,3-diaminopropane (Gold Label), dichloroacetic acid, dichlorophenylhydrazine, dichlorotriphenylphosphorane, diisopropylamine, 3,5-dinitrobenzoyl chloride (DNB), 2,4-dinitrophenylhydrazine (DNPH), drierite, ethylene glycol, FAD buffer, ferric ammonium sulfate, hydrochloric acid, lead(IV) oxide, lithium (dispersion in mineral oil, 1% sodium), lithium aluminum hydride (1<u>M</u> $LiAlH_4$ in THF), magnesium turnings, magnesium sulfate (anhydrous), mercuric acetate, mercuric chloride, mercuric trifluoroacetate, methyl chloride, methyl iodide, methyllithium (1.4<u>M</u> MeLi in ethyl ether), naphthalene, nitric acid, OCS scintillation fluid, osmium tetroxide, palladium chloride, phenyllithium (2<u>M</u> in cyclohexane), phosphorous pentoxide, potassium chlorate, potassium cyanide, potassium fluoride, potassium permanganate, potassium thiocyanate, silver nitrate, sodium, sodium borohydride, sodium chloride, sodium hydroxide, sulfuric acid, tetrabutylammonium bromide, tetramethylammonium hydroxide (2<u>M</u> in methanol), <u>p</u>-toluenesulfonic acid, tribromophenylisocyanate, trichloroacetylisocyanate, triethylphosphite, and trifluoroacetic acid were used as obtained without further purification.

D. Measurements

Many of the instruments used for this dissertation were explained briefly in the introduction. Only those methods which were used but which were not mentioned in the introduction are contained here.

Infrared spectra of thin films cast on NaCl plates were recorded on a Perkin Elmer 283 spectrometer. Infrared spectra of gaseous samples were obtained using a 10 cm pathlength gas cell and the same spectrometer. Proton and ^{19}F NMR were obtained on polymer solutions using a varian XL300. Gas chromatographic analyses were performed with a Hewlett-Packard 5790A gas chromatograph. Capillary GC analyses were obtained with a Hewlett-Packard 5890 gas chromatograph equipped with an electron capture detector and a crosslinked Carboxwax bonded phase silica capillary column. Electron spin resonance measurements were obtained on a Varian E-9 spectrometer. Fluoride analyses were performed with a Corning fluoride-sensitive electrode and a Fisher Accumet pH meter. Chloride analyses were performed by Volhard titration[2].

E. Reduction of Teflon, Tefzel and PVF_2 (1:1-6, 1:12)

A stock solution of sodium naphthalide in THF (250 ml.) was prepared by reacting naphthalene (2 g.) with excess sodium metal in THF for 8 hours. This solution was canulated into a second storage flask and stored under nitrogen.

The film was placed into a purged Schlenk tube and then covered with the sodium naphthalide solution. The solution was removed using a cannula after the desired reaction time and the film was then washed successively with hexane (2x30 ml.), ethanol (3x50 ml.), ethyl ether (2x50 ml.), H_2O (3x100 ml.) and ethanol (1x20 ml.). The film was then dried (0.05mm, 3 h.) before contact angle data and ATR-IR spectra were obtained.

F. Oxidation of Polyethylene, Tefzel and PVF_2. (1:7-10)

The oxidizing solution was prepared immediately before use by adding sulfuric acid (25 ml.) to a crystallization dish containing a magnetic stirring bar and potassium chlorate (3 g.). The mixture was stirred until the potassium chlorate dissolved and the resulting red solution was stirred 15 minutes before using it for the oxidations.

The density of this solution was such that the films floated, therefore it was necessary to notch the film in order to keep track of the oxidized face. The film was floated on the solution for the desired reaction time. The film was removed using Teflon coated forceps and placed in H_2O (500 ml). The film was washed, gently agitating it with the forceps, successively with H_2O (500 ml), ethanol (2x200 ml) and ethyl ether (200 ml). The film was dried (0.05 mm, 3 h) before contact angle data and ATR-IR spectra were obtained.

G. Surface Modification of Poly(vinylidene fluoride).

Elimination of Poly(vinylidene fluoride) Film. (1:13-18, 20, 32, 37, 39) (PVF_2E) A solution containing tetrabutylammonium bromide (0.1 g) in 8N sodium hydroxide (150 ml) was prepared and stirred at stirred at room temperature for 15 minutes before it was used further. A PVF_2 film sample (of size appropriate for the analytical method) was submersed in the base solution for the selected time, removed with forceps, and washed repeatedly in H_2O (5x100 ml) by stirring the water with the forcep-held film and then likewise in ethanol (3x100 ml) before drying at 0.05 mm for 24 hours. The control film was treated identically except the tetrabutylammonium bromide was excluded. The film was examined by XPS, UV-Vis spectroscopy, ATR-IR spectroscopy, contact angle analysis and scanning electron microscopy. The film was further dried (0.05mm, 30°C) to a constant mass for gravimetric analysis.

Temperature Dependence of the Elimination Reaction. (2:14,15) A solution containing tetrabutylammonium bromide (0.1 g) in 8N sodium hydroxide (150 ml) was prepared and stirred at room temperature for 15 minutes before being separated into 3 stoppered Schlenk tubes. The tubes were then equilibriated (15 min) at 0°C, 23°C and 40°C separately. Films were then placed in the solutions for 30, 60 and 300 seconds. The films were then removed and washed repeatedly in H_2O (5x 100 ml) by stirring the water with the forcep held film and then likewise in ethanol (3x100 ml) before drying at 0.05 mm for 24 hours. The films were analyzed by UV-Vis spectroscopy.

Elimination of Poly(vinylidene fluoride) in Solution for the Beer's Law Justification. (1:40, 42, 43; 2:18,19) Poly(vinylidene fluoride) powder (0.200 g) was weighed into a clean, dry, degassed and tared Schlenk tube containing a Teflon-coated stirring bar. The flask was capped, evacuated and purged with nitrogen (5 min) before DMF (30 ml) was introduced via Hamilton Gas-Tight syringe. The mixture was stirred to dissolve the polymer. The predetermined quantity of base was added dropwise via syringe over 15 minutes. The base concentration was determined by titration with 0.1*N* HCl to pH 6. The progress of the reaction was monitored by titrating aliquots of the solution; all reactions were complete (total base comsumption) in less than 24 hours. The resulting brown solution was centrifuged to remove precipitated polymer and insoluble salts. The solution was diluted in serial fashion under nitrogen with DMF to obtain concentrations which were suitable for UV-Vis analysis. The resulting concentrations were determined by evaporating known volumes and weighing the remaining polymer. Residual ash was established by combustion and subtracted from the polymer mass.

Bromination of PVF_2-E Film. (PVF_2-EBr) (1:31, 36-38; 2:1, 2, 4-6, 11) Eliminated film samples (two 1.5 cm x 1.5 cm) were placed in a screw-capped vial which contained 10 ml of 0.2*N* bromine/carbon tetrachloride solution. The films were reacted (15 min) in the dark at 0°C. The films were removed from the bromine solution, washed with carbon tetrachloride (3x10 ml) and then likewise with dichloromethane (3x30 ml). The films were dried (24 h, 0.05 mm) then contact angle and XPS data were obtained. The film was further dried (0.05 mm, 30°C) to constant mass for gravimetric analysis. Control films (from the elimination reaction procedure) were treated identically.

Reaction of PVF_2-E With Chlorine. (2:48) One film each of PVF_2 and PVF_2-E was placed into a O-ring sealed Schlenk tube. The tube was evacuated to 0.05 mm, covered with aluminum foil, and equilibriated (15 min) at 0°C. The tube was then filled with chlorine gas (20 psi) and reacted at 0°C for 15 minutes. The tube was then purged (15 min) with nitrogen. The films were removed, washed with $MeCl_2$ (3x30 ml), then dried (0.05 mm, 30°C) to constant mass. The films were analyzed by gravimetric analysis.

Reaction of PVF_2-E With MCPBA. (1:29, 30; 2:2, 3) One film each of PVF_2 and PVF_2-E was reacted (12 h) with a solution of MCPBA (0.5 g) in EtOH (100 ml). After the reaction time, the film was removed and washed with EtOH (5x30 ml) and ether (1x30 ml) then dried (24 h, 0.05 mm) before contact angle and ATR-IR data were obtained.

The MCPBA treated film was further reacted by placing it in a tube containing 10% aqueous NaOH. The tubes were placed in an oil bath at 60°C for 1 hour. The film was removed, washed with EtOH (5x30 ml) and ether (1x30 ml) then dried (24 h, 0.05 mm) before contact angle and ATR-IR data were obtained.

Reaction of PVF_2-E With Osmium Tetroxide. (2:6) One film each of

PVF_2 and PVF_2-E was placed in an osmium tetroxide reactor for 24 hours. This reactor has solid osmium tetroxide in equilibrium with its vapor and it is the vapor which reacts with the film. After 24 hour the film was removed, washed in succession with H_2O (5x30 ml), EtOH (3x30 ml) and ether (1x30 ml) and dried (24 h, 0.05 mm) before contact angle data were obtained. The film was dried further (0.05 mm, 30°C) to constant mass for gravimetric analysis. The film was then reacted with a solution containing sodium sulfite (1 g) and NaOH (1 g) in EtOH (30 ml) overnight. The film was removed, washed in succession with H_2O (5x30 ml), EtOH (3x30 ml) and ether (1x30 ml) before it was dried to constant mass for gravimetric analysis.

Reaction of PVF_2-E With Palladium Chloride. (2:41) One film each of PVF_2 and PVF_2-E was reacted (16 h) with a solution containing palladium chloride (0.03 g) and cupric chloride (0.03 g) in H_2O (20 ml). The film was removed, washed with H_2O (5x50 ml) and EtOH (3x30 ml), then dried (24 h, 0.05 mm) before contact angle and UV-Vis data were obtained. The film was further dried (0.05 mm, 30°C) to constant mass for gravimetric analysis.

Reaction of PVF_2-E With Potassium Permanganate. (1:20; 2:42) One film each of PVF_2 and PVF_2-E was placed in a crystallization dish which contained aqueous 0.5<u>N</u> potassium permanganate solution (100 ml) at 23°C. The film was reacted for 30 min and also 24 h, then removed, washed with H_2O (5x500 ml) and EtOH (3x30 ml) then dried (24h, 0.05 mm) before XPS and contact angle data were obtained. The film was further dried to constant mass for gravimetric analysis.

Reaction of PVF_2-E With Potassium Chlorate/Sulfuric Acid. (1:81, 2:48) One film each of PVF_2 and PVF_2-E was placed onto a solution containing $KClO_3$ (3 g) in H_2SO_4 (50 ml) for the desired time. The film was removed, washed with H_2O (5x50 ml) and EtOH (3x30 ml), then dried (24 h, 0.05 mm) before XPS and contact angle data were obtained. The film was further dried (0.05 mm, 30°C) to constant mass for gravimetric analysis.

Reaction of PVF_2-E With Mercuric Trifluoroacetate. (2:5) One film each of PVF_2 and PVF_2-E was placed into tubes containing a solution of either $Hg(O_2CCF_3)_2$ (0.5 g), THF (50 ml) and H_2O (2 ml) or $Hg(O_2CCF_3)_2$ (0.5 g), THF (50 ml) and ethylene glycol (2 ml). The film was reacted for 1 hour, removed and washed with H_2O (5x50 ml) and EtOH (3x30 ml), then dried (24 h , 0.05 mm) before contact angle data were obtained. The film was further dried (0.05 mm, 30°C) to constant mass for gravimetric analysis.

Reaction of PVF_2 With 2-Lithio-2,4,4-trimethyl-2-oxazoline.

Preparation of 2-Lithio-2,4,4-trimethyl-2-oxazoline (LiTMO) (2:38B, 40) TMO (0.3 g) was placed via cannula into a nitrogen purged Schlenk tube containing a magnetic Teflon-coated stirring-bar. Ether (10 ml) was added via cannula and the tube was equilibriated (15 min) at -78°C. A solution containing n-BuLi (1.6m, 1.5 ml) in ether (5 ml) was prepared in a second Schlenk tube at -78°C and added dropwise over 15 minutes to the tube containing the TMO solution. The mixture was stirred at -78°C for 60 minutes before it was used in further reactions.

Reaction of LiTMO With PVF_2, PVF_2-E, and PVF_2-EBr. One film each of PVF_2, PVF_2-E and PVF_2-EBr was placed into a nitrogen-purged Schlenk tube and the tube was then placed in a bath at -78°C and equilibriated for 15 minutes. The LiTMO solution (20 ml) was added via cannula to the tube containing the film. The film was reacted (15 min) at -78°C and then the tube was allowed to warm up to room temperature, at which temperature it was maintained for an additional 15 minutes. The reaction was quenched with H_2O (5 ml) and the film was removed and washed in succession with 1<u>N</u> HCl (30 ml), H_2O (5x30 ml) and MeOH (5x30 ml). The film was dried (24 h, 0.05 mm) before contact angle data were obtained.

Hydrolysis of the LiTMO Reacted Film. One film each of the above listed LiTMO reacted film was placed into a 100 ml flask which contained a boiling chip as well as 5N HCl (50 ml). The flask was equipped with a reflux condenser and was heated to reflux. After reflux (30 min) the film was washed with H_2O (3x30 ml) and MeOH (3x30 ml), then dried (24 h, 0.05 mm) before contact angle data were obtained. The contact angle data were also obtained for the film after it was treated (30 min) with 0.1N NaOH (30 ml) at 70°C, then washed with 0.1N HCl (30 ml), H_2O (3x30 ml) and MeOH (3x30 ml). The film was then dried (24 h, 0.05 mm) before contact angle data were obtained.

Hydrolysis of PVF_2-E Film. (1:18, 21, 22, 25, 28) One sample each of PVF_2 and PVF_2-E was floated on concentrated sulfuric acid at 25°C for various times. The film was then removed and placed in H_2O for 5 minutes. The film was washed in succession with H_2O (5x30 ml), EtOH (3x30 ml) and THF (1x30 ml). The film was dried (24 h, 0.05 mm) before XPS, UV-Vis, ATR-IR and contact angle data were obtained. The film was further dried (0.05 mm, 30°C) to constant mass for gravimetric analysis. PVF_2-O refers to a PVF_2-E sample which has been reacted in sulfuric acid (2 min) and then treated as in the above procedure.

Reaction of PVF_2-O With 3,5-Dinitrobenzoyl chloride. (PVF_2-ODN) (1:25, 26, 28, 33, 38) One film each of PVF_2, PVF_2-E, and PVF_2-O was placed into nitrogen purged Schlenk tubes. The films were treated with a solution of 3,5-dinitrobenzoyl chloride (0.6 g) in pyridine (50 ml) for 10 minutes. The film was removed and washed in succession with 0.1N NaOH (3x30 ml), H_2O (3x30 ml) and EtOH (5x30 ml). The film was extracted (8 h) using $MeCl_2$ solvent in a Soxhlet extraction apparatus. The film was dried (24 h, 0.05 mm) before UV-Vis spectra were obtained.

Reaction of PVF_2-O With Trichloroacetyl isocyanate. (PVF_2-OTC) (1:38) One film each of PVF_2, PVF_2-E and PVF_2-O was placed into nitrogen purged Schlenk tubes. A solution containing trichloroacetyl isocyanate (0.2 g) in heptane (10 ml) was added via cannula to each tube. The solution was removed via cannula after 30 minutes and the film was washed under nitrogen with heptane (2x50 ml). The film was removed and further washed with toluene (2x250 ml), then extracted with $MeCl_2$ in a Soxhlet extraction apparatus. The film was dried (24 h, 0.05 mm) before XPS and contact angle data were obtained.

Reaction of PVF_2-O With 2,4-dinitrophenylhydrazine or 2,5-dichlorophenylhydrazine. (PVF_2-ODNP or PVF_2-ODClP) (1:33, 38) One film each of PVF_2, PVF_2-E and PVF_2-O was placed into nitrogen purged Schlenk tubes. A solution containing the desired hydrazine (1 g), H_2O (5 ml), HCl (5 ml) and EtOH (90 ml) was added via cannula to each of the tubes. The film was reacted (4 h), removed and washed with

EtOH (3x30 ml). The film was then extracted (3 h) with EtOH in a Soxhlet extraction apparatus. The film was then dried (24 h, 0.05 mm) before XPS, UV-Vis spectra and contact angle data were obtained.

Reaction of PVF_2-O With 1,1'-Carbonyldiimidazole and Trichloroethanol. (PVF_2-OTCE) (1:38) One film each of PVF_2, PVF_2-E and PVF_2-O was placed into nitrogen purged Schlenk tubes. A solution containing CDI (0.25 g) in toluene (50 ml) was prepared and this solution (15 ml) was added to each tube. The film was reacted 1 hour before trichloroethanol (0.2 ml) was added to each via syringe. The tubes were then heated to 70°C and reacted for 3 hours. The film was removed, washed with toluene (2x250 ml), and extracted (3 h) with pentane in a Soxhlet extraction apparatus. The film was dried (24 h, 0.05 mm) before XPS and contact angle data were obtained.

Reaction of PVF_2-O With Sodium Borohydride. (PVF_2-OHB) (2:7, 9; 4:64) One film each of PVF_2, PVF_2-E and PVF_2-O was placed into nitrogen purged Schlenk tubes. A solution containing sodium borohydride (0.3 g) in EtOH (20 ml) was prepared and added to each of the tubes. The film was reacted for the desired time, removed and washed in succession with aqueous saturated ammonium chloride (1x30 ml), H_2O (5x30 ml) and EtOH (2x30 ml). The film was dried (0.05 mm, 24 h) before XPS and contact angle data were obtained. The film was further dried (0.05 mm, 30°C) to constant mass for gravimetric analysis.

Reaction of PVF_2-OHB With Heptafluorobutyryl Chloride. (2:7, 9) One film each of PVF_2, PVF_2-O and PVF_2-OHB was placed into Schlenk tubes and the tubes were evacuated to 0.05 mm. A second Schlenk tube containing heptafluorobutyryl chloride (0.2 g) was attached to each of the tubes containing the film. The stopcock connecting the tubes was opened and the film was reacted (5 min) with the vapor. The heptafluorobutyryl chloride was then removed by placing the tube, not containing the film, in a liquid nitrogen dewar. After 5 minutes the tube containing the film was disconnected and the film was washed with THF (5x30 ml). The film was then dried (24 h, 0.05 mm) and contact angle data were obtained. The film was further dried (0.05 mm, 30°C) to constant mass before gravimetric data were obtained.

Reaction of PVF_2-OHB With Trichloroacetylisocyanate (4:64) One film each of PVF_2, PVF_2-E, PVF_2-O and PVF_2-OHB was placed into a Schlenk tube and the tube was evacuated to 0.05 mm, then purged (15 min) with nitrogen. A solution containing trichloroacetylisocyanate (0.5 g) in $MeCl_2$ (20 ml) was added to the tube via cannula and the films were reacted overnight. The solution was removed via cannula and the films were washed in succession with $MeCl_2$ (3x30 ml), THF (3x30 ml) and $MeCl_2$ (3x30 ml). The films were then dried (24 h, 0.05 mm) before XPS and contact angle data were obtained.

Reaction of PVF_2-O With Lithium Aluminium Hydride. (PVF_2-OHL) (4:64) One film each of PVF_2, PVF_2-E and PVF_2-O was placed into a Schlenk tube. The Schlenk tube was evacuated to 0.05 mm and then purged (15 min) with nitrogen. The films were then covered with 1M $LiAlH_4$/THF (20 ml) solution. The films were reacted (16 h), the solution was removed via cannula, and the films were washed under nitrogen successively with THF (3x30 ml), aqueous saturated ammonium chloride (1x30 ml), H_2O (3x30 ml), MeOH (3x30 ml) and $MeCl_2$ (3x30 ml).

The films were then dried (24 h, 0.05 mm) before XPS and contact angle data were obtained.

Reaction of PVF_2-OHL With Trichloroacetylisocyanate (4: 64) One film each of PVF_2, PVF_2-E and PVF_2-O which were treated with $LiAlH_4$ using the previous procedure, was placed into a Schlenk tube and purged (15 min) with nitrogen. The films were then covered with a solution containing trichloroacetylisocyanate (0.5 g) in $MeCl_2$ (20 ml) and reacted 16 hours. The solution was removed via cannula and the film was washed under nitrogen with THF (3x30 ml) and $MeCl_2$ (5x30 ml). The films were dried (24 h, 0.05 mm) before XPS and contact angle data were obtained.

H. Surface Modification of Poly(chlorotrifluoroethylene). (PCTFE)

Phase Transfer Catalyzed Modification of PCTFE Using Hydroxide Anions (1:34) PCTFE film was reacted (48 h) in a septum-stoppered tube with a solution containing tetrabutylammonium bromide (0.1 g) in 8N NaOH (150 ml). The film was removed and washed with H_2O (3x50 ml) and EtOH (5x200 ml) before it was extracted (3 h) with EtOH in a Soxhlet extraction apparatus. The film was dried (24 h, 0.05 mm) before contact angle data were obtained.

Phase Transfer Catalyzed Surface Modification Using Cyanide Anions. (1:34, 38) PCTFE film was reacted (48 h) in a septum-stoppered tube at 25 and 80°C with a solution containing potassium cyanide (5 g), tetrabutylammonium bromide (0.1 g) and H_2O (20 ml). The film was removed, washed with H_2O (3x50 ml) and EtOH (5x200 ml), then extracted (3 h) with EtOH in a Soxhlet extraction apparatus. The film was dried (24 h, 0.05 mm) before ATR-IR, XPS and contact angle data were obtained.

The film was further reacted under conditions favorable to hydrolysis of the cyano groups. The film was refluxed (8 h) with 10% aqueous NaOH. The film was then washed with H_2O (3x50 ml) and EtOH (5x200 ml), then dried (24 h, 0.05 mm) before ATR-IR, XPS and contact angle data were obtained.

Phase Transfer Catalyzed Modification of Low Molecular Weight PCTFE Oil Using Cyanide Anions. (2:21) PCTFE oil (2 g) was weighed into a Schlenk tube and the tube was evacuated to 0.05 mm and then purged (15 min) with nitrogen. DMF (50 ml) was added and the tube was agitated to dissolve the polymer. The solution was transferred into a 250 ml nitrogen purged flask which was equipped with a septum-stoppered condenser and a Teflon coated magnetic stirring bar. The apparatus was connected to a glass-T which was connected to a nitrogen line and an oil filled bubbler; this kept the apparatus under a nitrogen atmosphere during heating. A solution containing KCN (2.3 g) and tetrabutylammonium bromide (0.2 g) in H_2O (5 ml) was prepared and diluted to 10 ml with DMF. The cyanide solution was added via cannula to the stirred polymer solution. The solution immediately assumed and deep red color, the flask was placed in a bath at 110°C and reacted 24 hours. The mixture was filtered and the polymer was isolated by vacuum distillation. The resulting fractions were analyzed by IR spectroscopy.

Surface Modification of PCTFE Using Organometallic Reagents.

Standardization of Methyllithium, Phenyllithium, Butyllithium and tert-Butyllithium. Diphenylacetic acid (0.1 g) was placed in a nitrogen-purged Schlenk tube containing a Teflon-coated stirbar, and THF (10 ml) was added via cannula. The lithium reagent was diluted at -78°C with THF (1:5) in a calibrated Schlenk tube and this was added dropwise via cannula to the stirred diphenylacetic acid solution. The endpoint was taken as the first appearance of yellow.

Reaction of PCTFE Film With Methyllithium (2:29, 53; 3:33) A 2.0 x 1.5 cm sample of PCTFE film was placed in a nitrogen-purged Schlenk tube and ether (10 ml) was added via cannula. The tube was placed in a bath at -78°C for 15 minutes and methyllithium (0.5M in ether, 10 ml) was added via syringe. The reaction was allowed to proceed at -78°C for the desired time, and then methanol (5 ml) was added. The film was removed and washed in succession with 1N HCL (100 ml), H_2O (3x100 ml) and MeOH (3x100 ml). The film was then dried (24 h, 0.05 mm) before XPS and contact angle data were obtained. The films were further dried to constant mass (0.05 mm, 60°C) before UV-Vis and gravimetric measurements were made.

Reaction of PCTFE Oil With Methyllithium. (2:26, 29, 44, 45, 50; 3:2, 4, 30, 33, 34) PCTFE oil (1 g) was dissolved in ether (10 ml) in a nitrogen-purged Schlenk tube and placed in a bath at -78°C for 15 minutes before the methyllithium solution was added. The methyllithium solution was prepared in a graduated Schlenk tube under nitrogen by diluting the desired amount to 15 ml with ether. This solution was also cooled to -78°C for 15 minutes prior to its dropwise addition (over 15 minutes) to the stirred polymer solution. After the addition was complete, the reaction was stirred at -78°C for an additional 15 minutes, allowed to warm up to room temperature, at which temperature it was maintained for 15 minutes, and then quenched with MeOH (5 ml) or H_2O (5 ml). Pentane (0.5 ml) was added as a GC internal standard and the mixture was analyzed by GC analysis at 25°C with a 10'x1/8" ss 15% AW600 on ChromP column. The reaction mixture was then extracted with 0.1N HNO_3 (3x30 ml). The organic layer was concentrated to an oil by rotary evaporation and was further dried (24 h, 50°C, 0.05 mm) before NMR, IR and UV-Vis data were obtained. The aqueous layers were combined and analyzed for chloride and fluoride. The gaseous products from this reaction were isolated with a series of traps at temperatures of 0, -78 and -200° C.

Qualitative Analysis of Gaseous Products. (2:27; 3:2) The reaction was executed using PCTFE oil (0.58 g, 5mmol) and 5 mmol of MeLi at -78°C using the method describe in the previous procedure. This time the Schlenk tube was connected to a series of nitrogen-purged traps at the previously described temperatures. The Schlenk tube was then allowed to warm up to room temperature while the connection to the traps was open. It was kept at room tempature for 30 minutes after which time the traps were closed off. The traps were then analyzed by GC and IR. The traps were sampled for IR spectroscopy by evacuating a 10 cm gas IR cell to 0.05mm and then refilling the cell with the content of the trap. After obtaining the IR spectrum of the trap contents, the purity of the contents of the cell was checked by GC. The cell was stoppered and sampled with a 1 ml Gas-Tight Hamilton syringe. A 0.5 ml sample of the gas was injected onto the GC column.

The observed spectra and retention times were compared to those obtained for ether, methyl chloride, methyl fluoride and methane.

Methyl Fluoride was prepared for this study by reacting methyl iodide (1 g) with a solution of tetrabutylammonium bromide (0.1 g) and potassium fluoride (2 g) in H_2O (5 ml). The methyl fluoride gas was dried by passing it through a drierite filled tube and it was collected with a liquid nitrogen trap.

Methane was prepared for this study by reacting under nitrogen methyllithium (0.5M in ether, 10 ml) with 2-propanol (2 ml). The methane was dried by passing it through a drierite column, and then it was collected with a liquid nitrogen trap.

The Trapping Efficiency was examined by preparing a saturated ether solution at -100°C of methyl chloride, methyl fluoride and methane. The tube containing this solution was connected to the same series of traps and the tube containing the ether solution was allowed to warm to room temperature at which temperature it was maintained for 30 minutes. The traps were closed and the contents were analyzed by GC.

Quantitative Analysis of the Gaseous Products (2:28; 3:30, 33) The response factor for methyl chloride verses the pentane internal standard was obtained by GC; a known quantity of pentane was added to a methyl chloride standard containing 0.25 mg of methyl chloride in 1 ml of methanol. The procedure for reacting PCTFE oil with MeLi was followed until the stage where the tube was warmed up to room temperature. At this point, pentane (0.5 g) was added to the tube to act as the GC internal standard. The stopcock on the tube was closed and the tube was allowed to warm to room temperature, at which temperature it was maintained for 15 minutes before it was replaced in the -78°C bath for another 30 minutes. The tube was filled with ether and allowed to warm to room temperature. The solution was sampled for GC using a 1 microliter syringe.

Quantitative Analysis of the Salt Solution.

Fluoride was determined using a fluoride-sensitive electrode and a Fisher Accumet pH meter operated in the ion concentration mode. The meter was calibrated with fluoride standards (1.9, 19, 190 and 1900 ppm) prepared from known amounts of potassium fluoride in 0.05M HNO_3. These solutions were adjusted to the same ionic strength using an equal volume of FAD buffer. The salt solution was divided into two 45 ml portions and diluted with an equal volume of the ionic buffer. The fluoride content was obtained directly off the meter in ppm.

Chloride was determined using the Volhard titration[2] method. The sample was divided into two 45 ml portions and placed into 150 ml Erlenmeyer flasks containing a magnetic stirring bar. Then silver nitrate (0.5 ml, 0.1 F) was added via burette. Ferric ammonium sulfate (5 ml, 10g/100ml 6 F HNO_3) was added to the flask and the solution was titrated with potassium thiocyanate solution (9.8×10^{-2}F) to a brick-red endpoint. A blank was obtained which contained just the reagents. It was also necessary to determine the chloride concentration which was present in the lithium reagent. This was accomplished by titrating 5 ml of the 2-propanol quenched lithium reagent.

Reaction of PCTFE Oil With Methyllithium and Benzyl Chloride (3:4) This reaction was executed using the procedure for the reaction between methyllithium and PCTFE oil except that prior to warming, the solution was purged with purified nitrogen for 10 min, benzyl chloride (1.5 ml) was added via syringe, and the reaction was stirred an additional 15 min at -78° before continuing with the warm-up.

Reaction of PCTFE Oil With Phenyllithium. (3:28, 31, 32, 35) The reaction was executed as above for methyllithium except THF was used as the solvent in place of ether and decane (0.5 ml) was added via syringe as the GC internal standard.

Reaction of PCTFE Powder With Phenyllithium. (3:35) PCTFE powder (0.1 g) was placed in a nitrogen-purged Schlenk tube and THF (10 ml) was added via syringe. The tube was placed in a bath at -78°C for 15 minutes before phenyllithium (0.5 ml) was added via syringe. The reaction was allowed to proceed at -78°C for 10 minutes and then 0.5 ml of MeOH was added; decane (0.5 g) was added and the mixture was analyzed for chlorobenzene by GC. The resulting suspension was extracted with HNO_3 (0.1M, 3x30 ml). The aqueous layers were combined and analyzed for fluoride and chloride. The polymer was isolated by filtration.

Introduction of Hydroxyl Groups Onto the Surface of PCTFE: Synthesis of PCTFE-OH.

Reaction of PCTFE With the Grignard Reagent Prepared From 3-Bromopropyltetrahydropyranyl Ether. (BrMgPTHPE) (3:7, 9, 13, 14)

Preparation of 3-Bromopropyltetrahydropyranyl Ether. (BrPTHPE)

3-Bromo-1-propanol (24.9 g, 0.179 m) was added via cannula to a nitrogen-purged, tared and stoppered flask which contained a magnetic stirring bar. The contents of the flask were stirred while dihydropyran (15.2 g, 0.181 m) was added via cannula along with dichloroacetic acid (1 g). The mixture was stirred 3 hours, and then neutralized with potassium carbonate. The solution was diluted with $MeCl_2$ (100 ml), dried with magnesium sulfate, filtered and the filtrate was concentrated using a rotary evaporator. The concentrate was vacuum distilled from magnesium sulfate through a 6" packed column (bp 105°C, 15 mm). The distillate was analyzed by NMR and IR spectroscopy and was stored over potassium carbonate at 0°C.

Preparation of the Grignard Reagent From the BrPTHPE. Magnesium turnings (0.2 g) were weighed into a 100 ml flask which was equipped with a reflux condenser and which contained a Teflon-coated magnetic stirring bar. The condenser was stoppered and the system was purged (15 min) with nitrogen while simultaneously heating it with a heat gun. The system was cooled down (15 min) under a stream of nitrogen. An excess (0.1 mmol) of BrPTHPE was added via cannula to a nitrogen-purged and rubber septum-stoppered flask. THF (10 ml) was added via cannula to both the magnesium and to the BrPTHPE flasks. The BrPTHPE THF solution was added via cannula to the stirred magnesium. This mixture was stirred (2 h) under nitrogen after which time most of the magnesium had dissolved (the remaining magnesium appears to be coated with carbon and did not react even when halide was added and the reaction time was extended).

Reaction of BrMgPTHPE With PCTFE Oil. (3:7) PCTFE oil (1.5 g) was placed into a Schlenk tube containing a Teflon-coated stirring bar and the tube was purged (15 min) with nitrogen. THF (10 ml) was added to the polymer and the tube was agitated to dissolve the polymer. The BrMgPTHPE solution was added via cannula to the stirred polymer solution. The reaction was run for 2 hours at room temperature, and then MeOH (5 ml) was added. The solution was dissolved in $MeCl_2$ (150 ml) and extracted with saturated aqueous ammonium chloride (3x30 ml), and then with H_2O (3x30 ml). The $MeCl_2$ was dried with $MgSO_4$, filtered and concentrated to an oil with a rotary evaporator. The oil was dried further (0.05 mm, 50°C, 24 h) before NMR and IR spectra were obtained.

Hydrolysis of the BrMgPTHPE-Modified PCTFE Oil. (3:7) The polymer was refluxed 30 minutes and 60 minutes with 2N HCl (100 ml) and isolated by extraction with $MeCl_2$ (3x50 ml). The $MeCl_2$ was dried with magnesium sulfate, filtered and concentrated to an oil using a rotary evaporator. The oil was further dried (24 h, 0.05 mm, 50°C) before IR and NMR analyses.

Reaction of BrMgPTHPE With PCTFE Film. (3:9, 13, 14) PCTFE film was placed into a Schlenk tube and the tube was purged (15 min) with nitrogen. The BrMgPTHPE solution (10 ml) was added via cannula to the tube, and the film was reacted (30 min) before MeOH (5 ml) was added via syringe. The film was removed and washed in succession with 2N HCl (2x30 ml), saturated aqueous ammonium chloride solution (1x30 ml), H_2O (3x100 ml) and MeOH (3x100 ml). The film was dried (24 h, 0.05 mm) before XPS and contact angle data were obtained.

Hydrolysis of the BrMgPTHPE Reacted PCTFE Film. (3:9, 13, 14) The above modified film was placed into a 100 ml flask which was equipped with a reflux condenser and boiling stone. The film was covered with 2N HCL (50 ml) and the flask was heated to reflux. After 1 hour the film was removed and washed with H_2O (3x100 ml) then MeOH (3x100 ml). The film was dried (24 h, 0.05 mm) before XPS and contact angle data were obtained.

Reaction of PCTFE With Organometallic Reagents Prepared From: Bromopropylethyl Acetaldehyde Acetal.

Preparation of Bromopropylethyl Acetaldehyde Acetal. (BrPAA) (3:22, 36, 37, 39, 50) 3-Bromo-1-propanol (26 g, 0.187 m) was placed into a flask containing a magnetic stirring bar and equipped with a septum-stoppered reflux condenser. The system was purged (15 min) with nitrogen and ethyl vinyl ether (22.6 g, 0.314 m) was added slowly (30 min) via cannula. Dichloroacetic acid (0.3 ml) was added via syringe to the stirred mixture. The temperature rose and a reflux began. An additional 0.1 ml of dichloroacetic acid was added in 1 hour. This was repeated in 4 hours and the mixture was stirred overnight. The mixture was neutralized by stirring (2 h) over potassium carbonate, and then filtered and the excess ethyl vinyl ether was removed via vacuum. The remaining BrPAA was dried with $MgSO_4$ and then vacuum distilled (bp 49 - 51° C, 1 mm) from potassium carbonate. The distillate (31.6 g, 80% yield, 95% pure by GC) was stored over potassium carbonate and was analyzed by NMR and IR spectroscopies prior to its use.

Preparation of the Grignard Reagent From BrPAA. (BrMgPAA) (3:23) Magnesium metal (0.6 g, turnings) was placed into a 100 ml flask which contained a Teflon-coated magnetic stirring bar and which was equipped with a septum-stoppered reflux condenser. The system was dried (15 min), with a heat gun, and cooled (15 min) while the system was purged with nitrogen. THF (40 ml) was added via cannula, and a solution of BrPAA (5.7 g) in THF (15 ml), prepared under nitrogen, was added dropwise (10 min) via cannula to the stirred magnesium. After 30 minutes at room temperature the flask was placed in a 0°C bath and reacted (3 h) until the magnesium dissolved. The yellowish Grignard, BrMgPAA was stored at -20°C in a desicator in the freezer.

Reaction of BrMgPAA With PCTFE Oil. (PCTFE-PAA oil) (3:24) PCTFE oil (1.5 g) was placed into a Schlenk tube which contained a Teflon-coated magnetic stirring bar, and the tube was purged (15 min) with nitrogen before THF (10 ml) was added via cannula. The BrMgPAA solution (40 ml) was added via cannula to the stirred polymer solution and reacted (60 min) at room temperature before MeOH (5 ml) was added via syringe. The reaction mixture was dissolved in $MeCl_2$ (150 ml) and extracted with aqueous saturated ammonium chloride (2x30 ml) and H_2O (2x50 ml). The $MeCl_2$ was dried with $MgSO_4$, filtered and concentrated to an oil using a rotary evaporator. The oil was further dried (24 h, 0.05 mm, 50°C) before NMR and IR spectra were obtained.

Hydrolysis of PCTFE-PAA Oil. (3:24) The PCTFE-PAA oil was placed into a 100 ml flask that contained a magnetic stirring bar and was equipped with a reflux condenser. A solution containing HCl (5 ml), H_2O (20 ml) and MeOH (10 ml) was added and the flask was heated to reflux (1 h). The solution was poured into $MeCl_2$ (100 ml) and the mixture was extracted with H_2O (3x50 ml). The $MeCl_2$ was dried with $MgSO_4$, filtered, and concentrated to an oil using a rotary evaporator. The oil was further dried (0.05 mm, 50°C, 24 h) before NMR and IR spectra were obtained.

Reaction of BrMgPAA With PCTFE Film. (PCTFE-PAA Film) (3:24) PCTFE film was placed into a Schlenk tube and the tube was purged (15 min) with nitrogen before THF (5 ml) was added via cannula. The BrMgPAA solution (5 ml) was added via cannula and the tube was agitated to mix the solutions. The film was reacted (15 min), rinsed under nitrogen with THF (2x30 ml) and MeOH (2x10 ml), and then removed and washed in succession with saturated aqueous ammonium chloride (1x30 ml), H_2O (3x30 ml) and methanol (3x30 ml). The film was dried (24 h, 0.05 mm) before contact angle data were obtained.

Hydrolysis of PCTFE-PAA Film. (PCTFE-OH) (3:24) The PCTFE-PAA film was placed into a 100 ml flask that contained a boiling stone and was equipped with a reflux condenser. A solution containing HCl (5 ml), MeOH (10 ml) and H_2O (20 ml) was added and the flask was heated to reflux (1 h). The film was removed, washed with H_2O (3x30 ml) and MeOH (3x30 ml), and then dried (24 h, 0.05 mm) before contact angle data were obtained.

Preparation of Lithiopropylethyl Acetaldehyde Acetal. (LiPAA) (3:36, 42, 50, 52, 54, 63, 71; 4:2, 6, 12, 65) The LiPAA was prepared either using Eaton's procedure[3], reacting lithium metal (wire and dispersion containing 1% sodium) under nitrogen with a THF solution of BrPAA, or alternatively by metal-halogen exchange. The second method involving metal-halogen exchange was more convenient and was the primary method used in this thesis. BrPAA (0.64 g) was placed in a Schlenk tube which contained a Teflon-coated magnetic stirring bar and which was previously purged (15 min) with nitrogen. The tube was then placed in a -78°C bath for 15 minutes before a solution containing t-BuLi (1.7M, 1.7 ml) in heptane (15 ml) was added. The suspension was stirred (15 min) at -78°C before it was allowed to warm up to -20°C. The solution was kept at -20°C for 15 minutes before it was diluted with THF (15 ml), the solution was then stirred at -20°C for at least 30 minutes before it was used for further reactions.

Reaction of LiPAA With PCTFE Film. (PCTFE-PAA) (3:50, 52, 54, 63, 71, 74; 4:2, 6, 65) PCTFE film was placed, along with a Teflon-coated magnetic stirring bar, in a Schlenk tube and the tube was then purged (15 min) with nitrogen. The tube was placed in a bath at the desired temperature and equilibriated (15 min) before the LiPAA solution, also at the same temperature, was added via cannula. The film was reacted for the desired length of time and the solution was removed via cannula while keeping the tube at the same temperature. The tube was not removed from the temperature bath until after the first MeOH wash. The film was washed, under nitrogen, in succession with MeOH (5x30 ml), H_2O (5x30 ml), MeOH (1x30 ml) and $MeCl_2$ (5x30 ml), and then dried (24 h, 0.05 mm) before XPS, UV-Vis, ATR-IR and contact angle data were obtained. The film was further dried (0.05 mm, 90°C) to constant mass for gravimetric analysis.

Hydrolysis of PCTFE-PAA Film. (PCTFE-OH)

Reaction With HCl. (3:50, 52, 54, 71, 74) The PCTFE-PAA film was refluxed (24 h) in a solution containing HCl (5 ml) and 100 ml of either 50:50 H_2O/MeOH or 50:50 H_2O/Acetone. The film was removed, washed with MeOH (5x30 ml) and $MeCl_2$ (5x30 ml), and then dried (0.05 mm, 24 h) before XPS and contact angle data were obtained. The film was further dried (0.05 mm, 90°C) to constant mass for gravimetric analysis.

Reaction With Trifluoroacetic Acid. (4:2, 6, 65) The PCTFE-PAA film was refluxed (24 h) in a solution containing trifluoroacetic acid (5 ml) and 50:50 H_2O/Acetone (100 ml). The film was removed, washed with MeOH (5x30 ml) and $MeCl_2$ (5x30 ml), and then dried (0.05 mm, 24 h) before XPS, ATR-IR and contact angle data were obtained. The film was further dried (0.05 mm, 90°C) to constant mass for gravimetric analysis.

Esterification of PCTFE-PAA With Heptafluorobutyral Chloride. (3:74; 4:65) One film each of PCTFE and PCTFE-PAA was placed in a Schlenk tube and the tube was purged (15 min) with nitrogen before a solution containing heptafluorobutyryl chloride (0.5 g) in THF (10 ml) was added via cannula. The films were reacted (3 h), the solution was removed via cannula, and the film was washed under nitrogen in succession with THF (3x30 ml), MeOH (3x30 ml) and $MeCl_2$ (5x30 ml). The film was dried (24 h, 0.05 mm) before XPS, ATR-IR and contact angle data were obtained.

Reaction of PCTFE With Organometallic Reagents Containing Masked Aldehylic Functionality. (PCTFE-CHO)

Preparation of the Grignard Reagent From 2-(2-Bromoethyl)-1,3-dioxolane. (BrMgEDO) (2:56; 3:1, 10; 4:24) Magnesium metal (turnings, 0.21 g) was placed into a 100 ml flask along with a Teflon coated magnetic stirring bar and the flask was then equipped with a septum-stoppered reflux condenser. The apparatus was dried by heating it, with a heat gun, and cooling it under a stream of nitrogen. THF (50 ml) was added via cannula and a solution of BED (1.2 g) in THF (5 ml), prepared under nitrogen in a second flask, was added dropwise to the stirred magnesium. The flask was kept in a 25°C bath and after 1 hour the magnesium was dissolved. This solution was then promptly reacted with either PCTFE oil or PCTFE film.

Reaction of PCTFE Oil With BrMgEDO. (PCTFE-EDO oil) (2:56; 3:1) PCTFE oil (1.5 g) was weighed into a nitrogen-purged Schlenk tube which contained a Teflon-coated magnetic stirring bar. THF (10 ml) was added and the mixture was stirred to dissolve the polymer. The BrMgEDO solution was added via cannula to the stirred polymer solution. The solution was stirred (30 min) at room temperature, and then MeOH (5 ml) was added via syringe. The polymer solution was diluted with $MeCl_2$ (150 ml), extracted with saturated aqueous NH_4Cl (3x30 ml) and H_2O (3x30 ml), dried with $MgSO_4$, filtered and concentrated to an oil using a rotary evaporator. The oil was dried (24 h, 0.05mm, 50°C) before NMR and IR spectra were obtained.

Hydrolysis of PCTFE-EDO Oil. (PCTFE-CHO) (2:56; 3:1) PCTFE-EDO oil was placed in a 100 ml flask along with a magnetic stirring bar and the flask was then equipped with a reflux condenser. The polymer was then reluxed (2 h) with 1 of the following three solutions: 6N HCl (60 ml); 6N HCl prepared from 12N HCl (30 ml) and THF (30 ml); or EtOH (55 ml) and HCl (5 ml). After reflux the mixture was extracted with $MeCl_2$ (3x50 ml). The combined $MeCl_2$ was extracted with saturated aqueous sodium carbonate (1x30 ml) and H_2O (3x30 ml), dried with $MgSO_4$, filtered and concentrated to an oil using a rotary evaporator. The oil was dried (24 h, 0.05 mm, 50°C) before NMR and IR data were obtained.

Reaction of PCTFE Film With BrMgEDO. (PCTFE-EDO film) (3:1, 10; 4:24) PCTFE film was placed into a Sclenk tube and the tube was purged (15 min) with nitrogen before THF (10 ml) was added via cannula. The BrMgEDO solution (10 ml) was added via cannula to the Schlenk tube and the film was reacted for 60 minutes before the solution was removed via cannula. The film was washed in succession with MeOH (1x30 ml), saturated aqueous NH_4Cl (2x30 ml), H_2O (2x30 ml), MeOH (3x30 ml) and $MeCl_2$ (3x30 ml). The film was dried (24 h, 0.05 mm) before XPS and contact angle data were obtained.

Hydrolysis of PCTFE-EDO Film. (PCTFE-CHO film) (3:1, 10) PCTFE-EDO film was placed in a 100 ml flask along with a boiling stone and the flask was then equipped with a reflux condenser. The film was refluxed (2 h) in a solution containing 6N HCl which was prepared by mixing equal volumes of ethanol with 12N HCl. The film was then removed and washed in succession with H_2O (3x30 ml), MeOH (3x30 ml) and $MeCl_2$ (5x30 ml). The film was dried (24 h, 0.05 mm) before contact angle data were obtained.

Preparation of 2-Lithio-1,3-dithiane. (LiDT) (3:6, 8, 43, 48, 57, 58, 62, 66, 67, 69, 72; 4:3, 4, 8, 11, 15, 48, 49) 1,3-Dithiane (1 g) was placed into a Schlenk tube along with a Teflon-coated magnetic stirring bar and the tube was purged (15 min) with nitrogen before heptane (10 ml) was added via cannula and the mixture was stirred until the 1,3-dithiane was dissolved. A solution containing *t*-BuLi (1.7*M*, 4.5 ml) or *n*-BuLi (1.5*M*, 5.0 ml) diluted to 10 ml with heptane was prepared and added to the stirred 1,3-dithiane solution. The suspension was placed in a -20°C bath and stirred (30 min) before THF (20 ml) was added via cannula. The colorless solution was stirred (30 min) at -20°C before it was used in further reactions. The resulting solution was approximately 0.15*M* in lithium reagent and it was possible to store the reagent in a desicator in the freezer (<-10°C) for at least a week without observing changes in the reactivity of the solution.

The LiDT was also prepared in THF[4]. 1,3-Dithiane (1 g) was placed in a Schlenk tube along with a Teflon-coated magnetic stirring bar and the tube was purged (15 min) with nitrogen. THF (25 ml) was added via cannula and the mixture was stirred until the 1,3-dithiane dissolved. The solution was placed in a -20°C bath and a solution containing *n*-BuLi (1.5*M*, 5.0 ml) in THF (10 ml) was added. The solution was stirred 2 hours at -20°C before it was used in further reactions. It was also possible to store this reagent in the freezer (<-10^{o}C) for at least a week.

Reaction of LiDT With PCTFE Oil. (PCTFE-DT oil) (3:6, 46; 4:8, 11) PCTFE oil (1 g) was placed into a nitrogen purged Schlenk tube that contained a Teflon-coated magnetic stirring bar. The tube was purged (15 min) with nitrogen before THF (10 ml) was added and the mixture was stirred to dissolve the polymer. The polymer solution was placed in a -78^{o}C bath for 15 minutes before LiDT solution (80 ml), also at -78^{o}C, was added dropwise (30 min) via cannula. The solution was kept at -78^{o}C for 60 minutes, and then allowed to warm up to room temperature, at which temperature it was maintained (15 min) before MeOH (5 ml) was added via syringe. Isolation of pure PCTFE-DT was not satisfactorily accomplished; the resulting modified polymer had limited solubility in most water insoluble solvents. The reaction products were isolated by removing the reaction solvent under vacuum. The remaining solid was placed into H_2O (100 ml) and neutralized with 1N HCl. The solution was extracted with $MeCl_2$ (3x50 ml) and the collected $MeCl_2$ was dried with $MgSO_4$, filtered and concentrated with a rotary evaporator. The resulting mixture was dried (0.05 mm, 50^{o}C, 72 h) before NMR and IR spectra were obtained.

Deprotection of Aldehydes in PCTFE-DT. (PCTFE-CHO oil)

Reaction With Mercuric Chloride, Acetone and Water. (3:46) PCTFE-DT (1.5 g) was placed in a 200 ml flask along with a magnetic stirring bar. Acetone (30 ml) was added and the mixture was stirred until the polymer dissolved. A solution containing HCl (1 ml), $HgCl_2$

(4.5 g), acetone (20 ml) and H_2O (50 ml) was prepared and added to the stirred polymer solution. A condenser was attached to the flask and the mixture was reacted (3 h, 60°C) before it was filtered. The filtrate was extracted with $MeCl_2$ (3x50 ml) and the combined $MeCl_2$ extracts were extracted with H_2O (3x30 ml), dried with $MgSO_4$, filtered, and concentrated to an oil using a rotary evaporator. The oil was dried (24 h, 0.05 mm, 50°C) before NMR and IR spectra were obtained.

Reaction With Cupric Oxide, Cupric Chloride, Acetone and Water. (3:6) PCTFE-DT (1.5 g) was placed in a 200 ml flask which contained a magnetic stirring bar and then acetone (30 ml) was added. The mixture was stirred to dissolve the polymer and a solution containing copper(II) oxide (3 g), copper(II) chloride (3 g), acetone (20 ml) and H_2O (50 ml) was prepared and added to the stirred polymer solution. The flask was equipped with a condenser and then heated. The mixture was refluxed (1 h), filtered and the filtrate was extracted with $MeCl_2$ (3x50 ml). The combined extracts were then extracted with 50 ml H_2O, dried with $MgSO_4$, filtered, and the filtrate was concentrated to an oil using a rotary evaporator. The oil was dried (24 h, 0.05 mm, 50°C) before NMR and IR spectra were obtained.

Reaction With Methyliodide, Acetone and Water. (4:8, 11) PCTFE-DT (1.5 g) was placed, along with a magnetic stirring bar, into a 100 ml flask and acetone (10 ml) was added. The mixture was stirred to dissolve the polymer and a solution containing H_2O (1 ml), acetone (10 ml) and methyliodide (20 ml) was prepared and added to the stirred polymer solution. The flask was wrapped in foil, a condenser was attached, and the flask was heated to reflux. After reflux (48 h) the solution was filtered, and the solvent was removed using a rotary evaporator. The oil was dissolved in $MeCl_2$ (100 ml) and the solution was extracted with H_2O (2x50 ml), dried with $MgSO_4$, filtered and concentrated to an oil using a rotary evaporator. The oil was dried (24 h, 0.05 mm) before NMR and IR spectra were obtained.

Reaction With Trifluoroacetic Acid, Acetone, Water and Mercuric Trifluoroacetate. (4:8, 11) PCTFE-DT (1.5 g) was placed, along with a magnetic stirring bar, into a 100 ml flask and then acetone (20 ml) was added and the mixture was stirred until the polymer dissolved. A solution containing mercuric trifluoroacetate (5 g), trifluoroacetic acid (1 g), acetone (30 ml) and H_2O (50 ml) was prepared and added to the stirred polymer solution. The flask was equipped with a condenser and then mixture was then refluxed (48 h), filtered and extracted with $MeCl_2$ (3x50 ml). The combined $MeCl_2$ extracts was dried with $MgSO_4$, filtered and concentrated using a rotary evaporator. The oil was dried (24 h, 0.05 mm) before NMR and IR spectra were obtained.

Reaction of LiDT With PCTFE Film. (PCTFE-DT film) (3:8, 43, 57, 58, 62, 66, 67, 69, 72; 4:3, 4, 15, 48, 49) PCTFE film was placed into a Schlenk tube and the tube was purged (15 min) with nitrogen before THF or Heptane was added (the LiDT concentration used for the film reactions was typically 0.05M and it was easy to achieve this concentration in solvent systems that ranged from 90% THF down to 10% THF, this made it possible to examine the solvent dependance of the reaction). The Schlenk tube was equilibriated (15 min) in a bath at the desired temperature (-78°C, -20°C or 0°C) before the LiDT solution (20 ml, at the same temperature of the film) was added. The film was reacted the desired time, then the reaction solution was removed via cannula while keeping the tube at the same temperature (the tube was not removed from the bath until after the first MeOH wash was completed). The film was washed, under nitrogen, in succession with MeOH (30 ml), 0.1N HCl (30 ml), H_2O (3x30 ml), MeOH (3x30 ml) and $MeCl_2$ (5x30 ml). The film was dried (0.05 mm, 24 h) before XPS, UV-VIS, ATR-IR and contact angle data were obtained. The film was further dried (0.05 mm, 90°C) for gavimetric analysis.

Deprotection of Aldehydes on the PCTFE-DT Film Surface

Reaction With Mercuric Chloride, Acetone and Water. (3:48, 57, 58, 62, 66, 67) PCTFE-DT film was placed, along with a glass boiling chip, into a 100 ml flask and a solution containing $HgCl_2$ (1 g), in 60 ml (30 ml H_2O , 30 ml acetone) solvent was added. A condenser was attached and the mixture was heated to reflux. After reflux (24 - 48 hours), the film was removed and washed in succession with 0.1N HCl (3x30 ml), H_2O (3x30 ml), MeOH (3x30 ml) and $MeCl_2$ (5x30 ml). The film was dried (24 h, 0.05 mm) before XPS and contact angle data were obtained. The film was further dried (0.05 mm, 90°C) to constant mass for gravimetric analysis.

Reaction With Cupric Oxide, Cupric Chloride, Acetone and Water. (3:8) PCTFE-DT film was placed, along with a glass boiling chip, in a 100 ml flask and a solution containing $CuCl_2$ (1 g), CuO (1 g), acetone (30 ml) and H_2O (30 ml) was added. A condenser was attached to the flask and the mixture was heated to reflux. After reflux (48 h), the film was removed and washed in succession with 0.1<u>N</u> HCl (3x30 ml), H_2O (3x30 ml), MeOH (3x30 ml) and $MeCl_2$ (5x30 ml). The film was dried (24 h, 0.05 mm) before XPS and contact angle data were obtained. The film was further dried (0.05 mm, 90°C) for gravimetric analysis.

Reaction With Methyliodide, Acetone and Water. (3:66) PCTFE-DT film was placed, along with a glass boiling chip, in a 100 ml flask and a solution containing H_2O (1 g), MeI (30 ml) and acetone (30 ml) was prepared and added to the flask. A condenser was attached to the flask and the flask was wrapped in foil before the mixture was heated to reflux. After reflux (48 h), the film was removed and washed in succession with THF (2x30 ml), H_2O (3x30 ml), MeOH (3x30 ml) and $MeCl_2$ (5x30 ml). The film was dried (24 h, 0.05 mm) before XPS and contact angle data were obtained.

Reaction With Mercuric Trifluoroacetate, Trifluoroacetic Acid, Acetone and Water. (3:69, 72; 4:48, 49) PCTFE-DT film was placed, along with a glass boiling chip, in a 100 ml flask and a solution containing mercuric trifluoroacetate (0.5 g), trifluoroacetic acid (1 ml), acetone (10 ml) and H_2O (40 ml) was prepared and added to the flask containing the film. A condenser was attached to the flask and the mixture was heated to reflux. After reflux (48 h), the film was removed, washed with MeOH (3x30 ml) and $MeCl_2$ (3x30 ml), and then extracted (24 h) with $MeCl_2$ using a Soxhlet extraction apparatus. The film was dried (24 h, 0.05 mm) before XPS and contact angle data were obtained. The film was further dried (90°C, 0.05 mm) to constant mass for gravimetric analysis.

Introduction of Carboxylic Acid Groups. (PCTFE-COOH)

Preparation of 2-Lithio-2,4,4-trimethyl-2-oxazoline. (LiTMO) (2:30-38, 43; 3:5, 12, 18, 29, 38, 40, 44, 45, 47, 49, 51, 53, 55, 56, 59-61, 64, 65, 68, 70; 4:1, 5, 9, 14, 16, 18, 21, 23, 25, 27, 41-45, 50-54, 56, 57) Several methods were examined for preparing LiTMO. These methods all involve the reaction of TMO with a lithium reagent; differing only in the selection of the lithium reagent and the solvent.

Method Involving MeLi and Ethyl Ether. (2:30) A Teflon-coated magnetic stirring bar was placed into a Schlenk tube and the tube was capped and purged (15 min) with nitrogen before TMO (1.0 g) was added via cannula. Ether (5 ml) was added via cannula and the mixture was stirred to dissolve the TMO. The tube was placed in a -78°C bath and equilbriated (15 min) before a solution, also at -78°C, containing MeLi (1.1M, 7.3 ml) diluted to 10 ml with ether was added to the stirred solution. The solution was stirred (60 min) at -78°C before using it in further reactions.

Method Involving s-BuLi and Ethyl Ether. (2:31-38, 40, 43; 3:5, 12, 18) The previous method was repeated this time replacing MeLi with s-BuLi (1.3M, 6.3 ml).

Method Involving s-BuLi and Tetrahydrofuran. (3:38) A Teflon-coated magnetic stirring bar was added to a Schlenk tube and the tube was capped, then purged (15 min) with nitrogen before TMO (1 g) was added via cannula. THF (15 ml) was added via cannula and the tube was agitated to dissolve the TMO. The tube containing the solution was stirred (15 min) at -78°C before s-BuLi (1.3M, 6.5 ml) was added via syringe. The solution was stirred (60 min) at -78°C before using the solution in further reactions.

Method Involving t-BuLi and Heptane. (3:40, 41, 44, 45, 47, 49, 51, 53, 56, 59, 60, 61, 65) A Teflon-coated magnetic stirring bar was placed in a Schlenk tube, the tube was capped and purged (15 min) with nitrogen before TMO (1 g) was added via cannula. Heptane (10 ml) was added via cannula to the tube and the tube was agitated to dissolve the TMO. The tube was placed in a -78°C bath and equilibriated (15 min) before a solution containing t-BuLi (1.7M, 5 ml) in 5 ml heptane was added. The suspension was stirred (1 h) before the mixture was used in further reactions. The heptane suspension was diluted with heptane and heptane/THF mixtures to give a LiTMO concentration of 0.05M.

Method Involving n-BuLi and THF. (3:65, 68; 4:1, 5, 9, 21, 23) A Teflon-coated magnetic stirring bar was placed in a Schlenk tube, the tube was capped and purged (15 min) with nitrogen before TMO (1 g) was added via cannula. THF (10 ml) was then added via cannula to the tube and the tube was agitated to dissolve the TMO before it was placed in a bath at -78°C for minutes. A solution containing n-BuLi (1.6M, 5.2 ml) was next added via cannula. The colorless solution was stirred at -78°C for 15 minutes and then placed in a bath at -20°C for an additional 30 minutes. The yellow solution was diluted with the desired solvent (heptane, THF, or heptane/THF) to 0.05M before using it in further reactions.

Method Involving n-BuLi and Heptane. (4:25, 30, 31, 35-47, 50 -61) The procedure was identical to the previous procedure except that heptane was the initially used solvent. The THF was added only after 30 minutes at -20°C. The solution was stirred an additional 15 minutes at -20°C, after the THF addition. The tube was then placed in the bath at the desired reaction temperature before further dilution with THF or THF/heptane to 0.05M.

Reaction of LiTMO With PCTFE Oil. (PCTFE-TMO) (2:30-32, 34-38; 3:29) A Schlenk tube containing a Teflon-coated stirring bar was capped and purged (15 min) with nitrogen before PCTFE oil (1 g) and THF (10 ml) were added via cannula. The mixture was agitated to dissolve the polymer and then the tube was placed in a -78° bath for 15 minutes before the LiTMO solution (0.2M, 50 ml) was added dropwise. The mixture was stirred at -78°C for 1 hour then allowed to warm to room temperature, at which temperature it was maintained for 15 minutes before quenching the reaction with D_2O (5 ml, 2:35) or MeOH (5 ml). The mixture was centrifuged to remove the precipitated salts and the supernatant was decanted and added to H_2O (100 ml). The mixture was acidified with 1N HCl and extracted with $MeCl_2$ (3x50 ml). The combined $MeCl_2$ extracts were dried with $MgSO_4$, filtered and concentrated to an oil using a rotary evaporator. The oil was dried (0.05 mm, 50°C, 24 h) before NMR and IR spectra were obtained.

Hydrolysis of PCTFE-TMO Oil. (PCTFE-COOH oil) (2:30, 31, 34) PCTFE-TMO oil (1 g) was dissolved in THF (5 ml) in a 100 ml flask containing a magnetic stirring bar. 5N HCl (50 ml) was added and a condenser was attached to the flask and the flask was then heated to reflux. After reflux (3 h), the solution was poured into 50 ml cold H_2O and then mixture was extracted with $MeCl_2$ (3x50 ml). The combine extracts were dried with $MgSO_4$, filtered and concentrated to an oil using a rotary evaporator. The oil was dried (24 h, 50°C, 0.05 mm) before NMR and IR data were obtained.

Alcoholysis of PCTFE-TMO Oil. (PCTFE-COOR) (2:32) PCTFE-TMO oil (1 g) was dissolved in MeOH (20 ml) in a 100 ml flask which contained a magnetic stirring bar. Sulfuric acid (0.5 ml) was added and the flask was equipped with a reflux condenser before the mixture was heated to reflux. After reflux (16 h), the mixture was poured into ether (100 ml). The ether was washed with saturated aqueous NaCl (3x30 ml), dried with $MgSO_4$, filtered and concentrated to an oil using a rotary evaporator. The oil was dried (24 h, 50°C, 0.05 mm) before NMR and IR spectra were obtained.

Reaction of LiTMO With PCTFE Film. (PCTFE-COOH film) (2:30, 31, 33, 43; 3:5, 12, 18, 38, 40, 44, 45, 47, 49, 53, 55, 56, 59-61, 65, 68, 70; 4:1, 5, 9, 13, 14, 16-18, 21, 23, 25, 27, 30-32, 35-47, 51-61, 65-68, 70, 71) PCTFE film was placed into a Schlenk tube and the tube was capped and purged (15 min) with nitrogen. The tube was then placed in a bath at the desired temperature and equilibriated (15 min) before the film was covered with the LiTMO solution (0.05M, 20 ml), also at the same temperature. The LiTMO solution was prepared using the previously described methods and the reaction solvents used were: ether (2:30, 31, 33, 43; 3:5, 18); THF (3:38, 65, 68; 4:1, 5, 9);

heptane (3:40, 47, 55, 60); and THF/heptane mixtures (3:21, 23, 41, 44, 45, 49, 51, 53, 56, 59, 61, 65; 4:25, 30, 31, 35-47, 50-61).

Hydrolysis of PCTFE-TMO Film. (PCTFE-COOH film)

Using Aqueous HCl. (2:30, 31, 33; 3:18)

PCTFE-TMO film was placed, along with a glass boiling chip, in a 100 ml flask and then 50 ml of 5N HCl was added. A condenser was attached and the solution was heated to reflux. After reflux (2 h), the film was removed and washed in succession with H_2O (3x30 ml), EtOH (3x30 ml) and $MeCl_2$ (3x30 ml). The film was dried (24 h, 0.05 mm) before contact angle data were obtained.

Using Aqueous HCl and Ethanol. (3:12, 38, 40, 49, 53, 55, 56, 65, 68) PCTFE-TMO film was placed, along with a glass boiling chip, into a 200 ml flask and a solution containing 5N HCl (75 ml) and EtOH (10 -30 ml) was added. A condenser was attached to the flask and the solution was heated to reflux. After reflux (3 h), the film was removed and washed in succession with H_2O (3x30 ml), MeOH (3x30 ml) and $MeCl_2$ (3x30 ml). The film was then dried (24 h, 0.05 mm) before XPS, UV-Vis and contact angle data were obtained. The film was further dried (90°C, 0.05 mm) to constant mass for gravimetric determinations.

Using p-Toluenesulfonic Acid, Water and THF or Diglyme. (4:9, 13, 16, 17, 23) PCTFE-TMO film was placed, along with a glass boiling chip, in a 100 ml flask and a solution containing p-toluenesulfonic acid (1 g), H_2O (10 ml) and THF (30 ml) or Diglyme (30 ml) was added. A condenser was attached to the flask and the mixture was heated to reflux. After reflux (48 h), the film was removed and washed in succession with THF (30 ml), H_2O (3x30 ml), MeOH (3x30 ml) and $MeCl_2$ (5x30 ml). The film was dried (24 h, 0.05 mm) before XPS and contact angle data were obtained.

Using Trifluoroacetic Acid, THF and Water. (4:1, 5, 23) PCTFE-TMO film was placed, along with a glass boiling chip, in a 100 ml flask and a solution containing trifluoroacetic acid (2 ml), H_2O (10 to 100 ml) and THF (10 to 50 ml) was added. A condenser was attached to the flask and the mixture was heated to reflux. After reflux (48 h) the film was removed and washed in succession with MeOH (5x30 ml), H_2O (5x30 ml), MeOH (30 ml) and $MeCl_2$ (5x30 ml). The film was dried before XPS and contact angle data were obtained.

Using Trifluoroacetic Acid, Acetone and Water. (4:21, 25, 27, 30-32, 35-41, 46, 47, 50, 55, 57, 59-61, 66-68, 70) PCTFE-TMO film was placed, along with a glass boiling chip, in a Schlenk tube that was modified by attaching a 5 cm water jacket just below the #25 O-ring seal. The tube was capped and purged (15 min) with nitrogen before a solution containing trifluoroacetic acid (1 ml), acetone (5 to 20 ml) and H_2O (5 to 20 ml) was added. The tube was placed in an oil bath and the solution was heated to reflux under a nitrogen blanket, then the system was closed. After reflux (48 h), the film was removed and washed in succession with MeOH (3x30 ml), H_2O (3x30 ml), MeOH (30 ml) and $MeCl_2$ (5x30 ml). The film was dried (24 h, 0.05 mm) before XPS, UV-Vis, SEM and contact angle analyses were obtained. The film was further dried (90°C, 0.05 mm) to constant mass for gravimetric determinations.

Alkylation With Methyliodide and Basic Hydrolysis. (3:65; 4:9, 21) PCTFE-TMO film was placed into Schlenk tube and the tube was capped and purged (15 min) with nitrogen. A solution containing $MeCl_2$ (5 ml) and MeI (5 ml) was added and then the tube was wrapped in foil and reacted (48 h) at room temperature. The film was removed and washed with $MeCl_2$ (5x30 ml). The film was dried (24 h, 0.05 mm) before XPS and contact angle data were obtained. The film was then placed, along with a glass boiling chip, in a 100 ml flask and 50 ml of 1N NaOH solution was added. A condenser was attached and the mixture was heated to reflux. After reflux (8 h) the film was removed and washed in succession with H_2O (3x30 ml), MeOH (3x30 ml) and $MeCl_2$ (5x30 ml). The film was dried (24 h, 0.05 mm) before XPS and contact angle data were obtained.

Use of Radioactive Isotopes.

Synthesis of PCTFE-[^{14}C]COOH. (4:22, 26, 28, 29, 34, 47, 55, 59, 60)

Preparation of 2,4,4-Trimethyl-2-oxazoline. (4:22, 26, 28, 29) This preparation follows Meyer's procedure[5] except a modification was necessary to increase the yield because of the small-scale used. Acetic acid (0.3 - 0.6 g) was added, along with dodecane (15 ml), via syringe to a 30 ml flask containing 2-amino-2-methyl-1-propanol (0.4 - 0.9 g). The mixture was distilled through a 10 cm Vigreux column into a receiver containing dodecane (10 ml) until the temperature of the distillation reached 140°C; the GC of later fractions indicated that they were free of significant quantities of TMO. The contents of the receiver was dried, first with $MgSO_4$ and then with CaH_2, and then redistilled under nitrogen through a 10 cm packed column. The collected distillate was 75% pure (GC, DC200 Hiplates, 120°C for 3.5 min then 30°/min to 170°C for 1.5 min) and the yield was 60-70%.

Preparation of 2-[^{14}C]-2,4,4-Trimethyl-2-oxazoline. (4:34) 2-Amino-2-methyl-1-propanol (0.525 g) was weighed into a 35 ml flask into which a Teflon-coated magnetic stirring bar was added. Acetic acid (0.347 g) was weighed into a tared V-bottom 5 ml flask. The vial containing the [^{14}C]acetic acid (1mCi, 4.5 microliters) was cooled in an ice bath 0°C for 15 minutes. The vial was opened and the nonlabeled acetic acid was added. The resulting solution was tranferred by pipette to the flask containing the 2-amino-2-methyl-1-propanol. Dodecane (20 ml) was added to the flask (the dodecane was used to wash the remaining acetic acid into the flask) and the flask was equipped with a 10 cm Vigreux column, a short path distillation head, and a receiver that contained dodecane (10 ml). The mixture was distilled until the temperature at the head of the column rose to 140°C. The receiver was dried initially with $MgSO_4$, and then with CaH_2. The mixture was redistilled under nitrogen through a 10 cm packed column.

Reaction of [^{14}C]LiTMO With PCTFE Film. (PCTFE-[^{14}C]COOH) (4:47, 55, 59, 60) The amount of [^{14}C]-TMO obtained was calculated to be 0.45 g (based upon GC determined yields and UV-Vis analysis). This was dissolved in heptane (15 ml) and stored in a Schlenk tube. The first experiment used 5 ml of this solution containing (0.15 g)

[^{14}C]TMO. This was removed via cannula and placed in a nitrogen purged Schlenk tube. The tube was then placed in a bath at -78°C for 15 minutes before a solution containing <u>n</u>BuLi (1.6<u>M</u>, 0.9 ml) in heptane (4 ml) was added. After stirring (15 min) at -78°C, the tube was placed in a bath at -20°C for an additional 15 minutes. THF (10 ml) was added and the tube was stirred at -20°C for an additional 15 minutes, and then it was replaced in the -78°C bath once again.

PCTFE film was placed into tubes and the tubes were stoppered with rubber septa and then the tubes were purged (15 min) with nitrogen. The tubes were placed in a bath at -20°C for 15 minutes before the [^{14}C]LiTMO solution was added via cannula to each. The film was reacted (5, 30 and 60 minutes), after which the solution was removed via cannula and then the film was washed with MeOH (5x30 ml). The film was removed and hydrolyzed by refluxing (48 h) in a solution containing H_2O (50 ml), acetone (12.5 ml) and trifluoroacetic acid (5 ml). After reflux the film was washed with $MeCl_2$ (3x30 ml) and extracted with $MeCl_2$ in a Soxhlet extraction apparatus (the $MeCl_2$ was replaced at 12 hour intervals). The film was removed and dried (48 h, 90°C, 0.05 mm) before liquid scintillation data were obtained.

The efficiency factor for the liquid scintillation analysis was established by diluting a known quantity of [^{14}C]-TMO with THF to give a solution with an actual activity of 2.24 microcuries/ml. Then 1 ml of this solution was diluted with the OSC fluid (4 ml) and the radioactivity was measured. The measured counts per minute were compared to the known activity of the sample and the efficiency of the method was established at 87%. The method was also checked to see if the presence of the film significant quenches the fluoresence by counting the same sample twice; once without a film and then again with a film added.

The observed counting rate for the modified film was high enough to permit further dilution of the [^{14}C]TMO, so a solution containing unlabeled TMO (0.386 g) in heptane (10 ml) was added. The total volume was 20 ml and 5 ml was taken for each of the remaining experiments. These experiments consisted of reacting: 1 film each at -20°C (5, 30 and 60 min); 6 films at -20°C for 60 minutes; and 3 films at -78°C for 60 minutes. A set of control films was measured for each set of films and the control consisted of exposing the film for 60 minutes at the reaction temperature to a solution containing [^{14}C]TMO, heptane and THF, followed by reacting them under the same hydrolysis and workup conditions as the [^{14}C]LiTMO reactions.

Preparation of [^{3}H]Ethanol. (4:62, 63, 64A)

Reaction of Sodium Acetate in Acetic Acid and Ethanol With BH_3/THF (4:62, 63) A solution containing acetic acid (1.8 g), ethanol (0.1 g) and sodium acetate (0.05 g) in THF (10 ml) was prepared under nitrogen in a Schlenk tube and pentane (0.2 g) was added as a GC internal standard. A Teflon-coated stirring bar was added to a 100 ml graduated cylinder, the cylinder was stoppered with a rubber septum and then purged (15 min) with nitrogen. BH_3/THF solution (1M, 40 ml) was placed in the cylinder via cannula and then the cylinder was placed in a bath at 0°C for 15 minutes. The acetic acid solution was added via cannula to the stirred BH_3/THF and the mixture was stirred 15 minutes at 0°C before it was allowed to warm up to room temperature, at which temperature it was maintained for 60 minutes and then it was again replaced in the 0°C bath. The tube was attached, using a glass T joint, to a nitrogen line and a oil filled bubble-trap and kept under a nitrogen blanket. A slight excess of H_2O (2.3 ml) was added dropwise via syringe and after the addition, the tube was removed from the bath and stirred at room temperature for 1 hour. The solution was dried initially with $MgSO_4$ and then CaH_2 (0.2 g) was added. The mixture was stirred 16 hours before it was distilled. The yield by GC (AN600 column, 50°) was 90% and there was no acetic acid present by GC.

Reaction of [^{3}H]Sodium Acetate in Ethanol and Acetic Acid With BH_3/THF. (4:64A) The previous reaction was repeated this time, but the sodium acetate was replaced with [^{3}H]sodium acetate (5mCi) and the quantity of acetic acid (1.132 g) and ethanol (0.445 g) was different. The distillation was also modified: when the volume of the pot reached approximately 10 ml, an additional 25 ml of THF was added and the distillation was continued until near dryness. The distillate volume was brought up to 75 ml with THF and it was stored in a Schlenk tube in a dessicator.

Analysis of the Resulting EtOH/THF for Alcohol Content. (4:64b) The THF/[^{3}H]EtOH (1 ml) was diluted in serial fashion with pyridine to give a concentration of approximately 50 ppm (1/10 x 1/10 x 3/10 ml). A solution of EtOH in THF was prepared and used to calibrate the method, this was diluted in serial fashion with pyridine to give concentrations from 34 to 82 ppm. Portions (2 ml) of these solutions and a blank (2 ml pyridine) were placed in 125 ml flasks and the flasks were stoppered with rubber septa. 3,5-Dinitrobenzoyl chloride (1 g) was dissolved in pyridine (10 ml) at 40°C and 1 ml was added via syringe to each of the flasks. The flasks were stirred for 30 minutes after which H_2O (20 ml) was added to each. The solutions were extracted with pentane (3x5 ml) and the pentane was combined, filtered and the volume was brought up to 20 ml with pentane. 1 ml portions of the pentane extracts were placed in tubes which contained 5 ml DMF. 1,3-Diaminopropane (1 ml) was added via syringe to each tube and these were shaken. The UV-Vis spectrum was recorded for each; the maximum absorbance was at 530 nm and this value was obtained for each. The absorbance of the blank was significant and was subtracted from the absorbance obtained for each of the samples.

Acid Catalyzed Alcoholysis of PCTFE-TMO Film. (2:43; 3:5) PCTFE-TMO film was placed, along with a glass boiling chip, in a 100 ml flask and a solution containing sulfuric acid (5 ml) and an alcohol was added. The alcohols examined were: MeOH (50 ml), EtOH (50 ml) and hexafluoroisopropanol (5 ml) in THF (45 ml). The flask was equipped with a condenser and the mixture was heated to reflux. After refluxing (3 h) the film was removed and washed in succession with EtOH (30 ml), H_2O (5x50 ml), MeOH (3x50 ml) and $MeCl_2$ (3x50 ml). The film was dried (24 h, 0.05 mm) before contact angle data were obtained.

Using p-Toluenesulfonic Acid. (4:16, 17) PCTFE-TMO film was placed, along with a glass boiling chip, in a 50 ml flask and a solution containing tribromoethanol (1 g), *p*-toluenesulfonic acid (1 g) and diglyme (20 ml) was added to the flask. A condenser was attached to the flask and the mixture was heated to reflux. After reflux (8 h), the film was removed and washed with $MeCl_2$ (30 ml), and then extracted (8 h) with $MeCl_2$ using a Soxhlet extraction apparatus. The film was dried (16 h, 0.05 mm) before XPS and contact angle data were obtained.

Using Boron Trifluoride Etherate. (4:18) PCTFE-TMO film was placed, along with a glass boiling chip, in a 50 ml flask and a solution containing BF_3-etherate (5 ml) and either tribromoethanol (1 g) or MeOH (1 ml) in ether (20 ml) was added. A condenser was attached to the flask and the mixture was heated to reflux. After reflux (48 h), the film was removed and washed with $MeCl_2$ (30 ml) and then extracted with $MeCl_2$ using a Soxhlet extraction apparatus. The film was dried (24 h, 0.05 mm) before XPS data were obtained.

Using Trifluoroacetic Acid. (4:14) PCTFE-TMO film was placed, along with a glass boiling chip, in a 100 ml flask and a solution containing tribromoethanol (1 g), trifluoroacetic acid (1 ml) and THF (50 ml) was added. A condenser was attached to the flask and the mixture was heated to reflux. After reflux (48 h) the film was removed and washed with $MeCl_2$ (30 ml) and then extracted with $MeCl_2$ using a Soxhlet extraction apparatus. The film was dried (24 h, 0.05 mm) before XPS data were obtained.

Esterification Reactions of PCTFE-COOH. (PCTFE-COOR)

Acid Catalyzed Esterification. (4:68, 70) PCTFE-COOH film was placed, along with a glass boiling chip, in a 100 ml flask and a solution containing the acid (1 ml of BF_3-etherate or 1 ml of H_2SO_4) and the alcohol (10 ml of octanol, 1 g octadecanol in 10 ml THF, 5 ml of [^3H]ethanol/THF, or 1 g tribromoethanol in 10 ml THF) was added to the flask. A condenser was attached to the flask and the mixture was heated to reflux. After reflux (48 h), the film was removed and washed with $MeCl_2$ (5x 30 ml). In the case of [^3H]EtOH, the film was extracted (48 h) under nitrogen with $MeCl_2$ in a Soxhlet extraction apparatus; the $MeCl_2$ was changed at 12 hour intervals. The film was dried (24 h, 0.05 mm) before XPS data were obtained. The film was further dried (48 h, 0.05 mm) before liquid scintillation data were obtained.

Acid Chloride Formation.

Reaction of PCTFE-COOH With Oxalyl Chloride. (3:49; 4:23) PCTFE-COOH film was placed, along with a glass boiling chip, in a 50 ml flask which was then stoppered and purged (15 min) with nitrogen. A solution containing either 1 ml oxalyl chloride in THF (10 ml) or 1 ml oxalyl chloride and 1 ml pyridine in toluene (10 ml) was prepared under nitrogen and was added to the flask containing the film. The film was reacted (48 h) at room temperature, the solvent was removed via cannula, and the film was washed under nitrogen with THF (3x30 ml). A solution containing tribromoethanol (0.1 g) in THF (10 ml) was next added. The film was reacted 24 hours then the film was removed and washed with THF (3x30 ml) and $MeCl_2$ (3x30 ml). The film was dried (24 h, 0.05 mm) before XPS and contact angle data were obtained. The film was further dried (90°C, 0.05 mm) to constant mass for gravimetric determinations.

Reaction of PCTFE-COOH With: Thionyl Chloride, Thionyl Chloride/ Pryidine, or Thionyl Chloride/Dimethylformamide. (4:13, 17, 25, 36, 40, 70) PCTFE-COOH film was placed, along with a glass boiling chip, in a 50 ml flask and a rubber septum stoppered condenser was then attached. The system was purged (15 min) with nitrogen and attached, using a glass-T connector, to an oil-filled bubble trap and a nitrogen line; in this, the system was heated under a nitrogen atmosphere. A solution containing the desired reagent was added via Teflon cannula to the flask. The mixture was reacted (48 h) at both room temperature and at 60°C and then the solution was removed via cannula. The film was washed, under nitrogen, with THF (3x 30 ml) and then a solution of the alcohol was added via cannula and reacted (48 h) before the film was removed. The film was washed with $MeCl_2$ (5x30 ml) and then extracted (8 h) with $MeCl_2$ using a Soxhlet extraction apparatus.

The reaction solutions and the corresponding alcohol solutions used in the above procedure were: 1) Thionyl chloride (5 ml) in diglyme (10 ml) reacted at 60°C; tribromoethanol (1 g) in diglyme diglyme (10 ml). 2) Thionyl chloride (5 ml) in pyridine (10 ml); tribromoethanol (1 g) in $MeCl_2$ (10 ml). 3) Thionyl chloride (5 ml), DMF (0.5 ml) in $MeCl_2$ (5 ml); the alcohol solution consisted of an alcohol (either octanol (5 ml), tribromoethanol (1 g), hexafluoropropanol (1 g), trichloroethanol (5 ml) or [^3H] EtOH/THF (5 ml)) in either $MeCl_2$ (10 ml) or THF (10 ml). When [^3H]EtOH was the chosen alcohol the modified films were extracted (48 h) with $MeCl_2$, replacing the $MeCl_2$ at 12 hour intervals, in a Soxhlet extraction apparatus before the film was dried (48 h, 0.05 mm) for liquid scintillation analysis. All other reacted films were dried (0.05 mm, 24 h) before XPS and contact angle data were obtained.

Reaction of PCTFE-COOH With Triphenylphosphorane Dichloride. (40) PCTFE-COOH film was placed in a Schlenk tube, modified with a 5 ml cooling jacket located just below the #25 O-ring seal, and the tube was capped and purged (15 min) with nitrogen. A solution containing triphenylphosphorane dichloride (0.5 g) in $MeCl_2$ (10 ml) was prepared under nitrogen and added to the tube via cannula. The mixture was heated to reflux under nitrogen before the system was closed. After reflux (48 h), the solution was removed via cannula and the film was washed in the tube under nitrogen with $MeCl_2$ (5x30 ml). One film was removed in the drybox, placed in a second Schlenk tube and dried (24 h, 0.05mm) before XPS was obtained. Additional film was removed in the drybox and placed in Schlenk tubes. This film was reacted (24 h) with a solution containing either octanol (5 g) or octadecanol (5 g) in $MeCl_2$ (10 ml). The film was then removed, washed with $MeCl_2$ (5x50 ml) and dried (24 h, 0.05 mm) before XPS data were obtained.

Reaction of PCTFE-COOH With 1,1'-Carbonyldiimidazole. (4:27, 32, 35, 37, 39, 41, 46, 70) PCTFE-COOH was placed in a Schlenk tube, the tube was capped and purged (15 min) with nitrogen before a solution containing CDI (0.5 g) in either $MeCl_2$ (15 ml) or THF (15 ml) was added. The film was reacted (48 h), and then the solution was removed via cannula. The film was washed in the tube under nitrogen with $MeCl_2$ (5x30 ml), and then dried (24 h, 0.05 mm) before XPS was obtained. The film was then reacted (24 h) with a solution of an alcohol (either 4-hydroxy-TEMPO (0.2 g), octanol (1 g), octadecanol (1 g), tribromoethanol (1 g), hexafluoroisopropanol (1 g) or [^{3}H]EtOH/THF (5 ml)) in either $MeCl_2$ (15 ml) or THF (15 ml). The solution was removed via cannula and the film was washed in the tube under nitrogen with $MeCl_2$ (5x30 ml) then extracted (8 h) using $MeCl_2$ in a Soxhlet extraction apparatus. When [^{3}H]EtOH was the chosen alcohol the film was extracted (48 h) and the $MeCl_2$ was changed at 12 hour intervals. The film was dried (24 h, 0.05mm) before XPS and contact angle data were obtained. The film was further dried (90°C, 0.05 mm) to constant mass for gravimetric determinations. The radiolabelled film was dried (48 h, 0.05 mm) for liquid scintillation analysis.

Reduction of PCTFE-COOR[^{3}H] with Tributyltin Hydride. (4:71) Liquid scintillation analysis was first obtained for the PCTFE-COOH film which was esterified with [^{3}H]EtOH using three methods: acid catalysis, $SOCl_2$/DMF and CDI. After radioassay each film was separately placed in labeled tubes and the tubes were stoppered with rubber septa then purged (15 min) with nitrogen. A solution (4 ml) which contained AIBN (0.1 g), Bu_3SnH (1 ml) and THF (3 ml) was added via cannula to each tube containing the film from the radiolabelling experiments as well as to a tube containing a unreacted piece of PCTFE.

The tubes were placed in a bath at 65^{o}C and reacted (24 h). At the end of this time period the tubes all contained homogeneous solutions of poly(trifluoroethylene). The volume of solvent in each tube was checked and in each case it was found to be 4 ml. A portion (2 ml) of this solution was added separately to labeled scintillation vials. The efficiency was established by adding a known amount of radioactivity to the vial containing the unreacted polymer solution. The vials were all filled with OCS scintillation fluid (3 ml) and the solutions were analyzed.

Reaction of PCTFE-COOH Film With Base. (4:50, 67) PCTFE-COOH film was placed in a Schlenk tube, the tube was capped and purged (15 min) with nitrogen before a solution of base was added. The base solutions, prepared under nitrogen, examined contained: either (DBU (1 g), tetramethylammonium hydroxide (1 g) or isopropylamine (1 g)) in THF (10 ml) or (NaOH (1 g) or $Ca(OH)_2$ (saturated, 1 g)) in H_2O (20 ml). The film was reacted (24 h) with the solution, the film was removed and washed with $MeCl_2$ (5x50 ml). The film was dried (24 h, 0.05 mm) before XPS and contact angle data were obtained.

Reduction of PCTFE-TMO With Borane/Tetrahydrofuran and Acetic Acid (PCTFE(H)TMO) (4:38, 57, 66) PCTFE-TMO film was placed in a Schlenk tube, the tube was capped and purged (15 min) with nitrogen before a solution of 0.1$\underline{M}$ BH_3/THF solution (20 ml) was added via cannula. The film was reacted (24 h) and then the solution was removed via cannula. The film was washed in the tube under nitrogen with THF (3x30 ml) before a solution which contained acetic acid (2 g) in THF

(20 ml) was added via cannula. This solution was reacted (24 h), the film was removed, washed with MeOH (3x30 ml) and $MeCl_2$ (3x30 ml), and then extracted (8 h) with $MeCl_2$ using a Soxhlet extraction apparatus. The film was dried (24 h, 0.05 mm) before XPS and contact angle data were obtained.

Hydrolysis of PCTFE(H)TMO. (PCTFE(H)COOH) (4:57, 66) The hydrolysis procedure was described above and involved refluxing (48 h) the film in a water-jacketed Schlenk tube with a solution containing trifluoroacetic acid (1 ml), acetone (2.5 ml) and H_2O (10 ml).

Reduction of PCTFE-COOH and PCTFE(H)COOH With Borane/Tetrahydrofuran and Acetic Acid. ($PCTFECH_2OH$ and $PCTFE(H)CH_2OH$) (4:57, 66) One film each of PCTFE-COOH and PCTFE(H)COOH was reacted in a Schlenk tube using the procedure presented for the reduction of PCTFE-TMO film.

XPS Label Study of the Borane Reductions: Tribromophenylisocyanate Reaction With PCTFE, PCTFE-TMO, PCTFE(H)-TMO, PCTFE-COOH, PCTFE(H)COOH, $PCTFECH_2OH$, and $PCTFE(H)CH_2OH$. (4:38, 57, 66) One film each from the above list was placed in nitrogen purged Schlenk tubes and a solution containing tribromophenylisocyanate (1 g), $MeCl_2$ (10 ml) and THF (10 ml) was added to each. The film was reacted (24 h) with the solution and then the solution was removed via cannula. The film was washed in the tube under nitrogen in succession with THF (3x30 ml) and $MeCl_2$ (5x30 ml). The film was extracted (8 h) with $MeCl_2$ using a Soxhlet extraction apparatus before the film was dried (24 h, 0.05 mm) for XPS and contact angle measurements.

References.

1. Shriver, D.F. Manipulations of Air Sensitive Compounds, McGraw-Hill: New York, 1969

2. Vogel, A.I. in A Textbook of Quantitative Inorganic Analysis, Longmans Green & Co.: London, 1961, p. 267

3. Eaton, P.E.; Cooper, G.F.; Johnson, R.C.; Mueller, R.H. **J. Org. Chem.** 1972, 37, 1947

4. Corey, E.J.; Seebach, D. **Angew. Chem. Internat. Ed.** 1965, 4, 1075

5. Meyer, A.I.; Temple, D.L.; Nolen, R.L.; Mihelich, E.D. **J. Org. Chem.** 1974, 39, 2778

CHAPTER III: RESULTS AND DISCUSSION

Oxidation and Reduction of Chemically Resistant Polymers.

The oxidation of polyethylene and the reduction of polytetrafluoroethylene (Teflon) using wet chemical methods have been widely studied in both academic and industrial laboratories. The exposure of polyethylene to oxidizing acid solutions results in a chemically complex surface. The surface energy of the polymer increases and this manifests itself in lower water contact angles. In addition the modification is extensive enough to observe carbonyl bands in the ATR-IR spectra. The reduction of Teflon with alkali metal solutions is also an area in which an extensive amount of research has been conducted. These methods defluorinate the surface of Teflon and the resulting graphitic carbon gets partially oxidized; together these changes result in a black, oxidized Teflon layer which is readily wet by water.

The experiments conducted on poly(vinylidene fluoride) (PVF_2) and poly(ethylene-co-tetrafluoroethylene) (Tefzel) represent initial attempts at developing methods which would permit the controlled introduction of functional groups. Thus PVF_2 and Tefzel were viewed as substrates which might be expected to exhibit chemistry similar to Teflon and polyethylene. The presence of fluorine might perturb the chemistry enough to allow controllable oxidation and likewise the presence of methylene units might alter the reduction chemistry and prevent the extensive corrosive reduction exhibited by Teflon.

Results and Discussion.

When Teflon, Tefzel and PVF_2 film were exposed under nitrogen to a solution of sodium naphthalide in THF, rinsed and dried, contact angles, ATR-IR and visual observation indicated that only Teflon was reduced. Teflon turned black immediately upon exposure to the solution. Neither Tefzel nor PVF_2 exhibited any visual color changes even after extended reaction times. That Teflon was reduced and the other polymers were not was evident from the changes in the ATR-IR. Only Teflon exhibited any changes in the ATR-IR spectrum (Ge, 45°): a broad absorbance located from 1500 cm^{-1} to 1700 cm^{-1} which is consistent with the formation of carbonyl and unsaturated C=C functionalities, as well as a decrease in the C-F intensity at 1200 cm^{-1}. The surface of Teflon exhibited a dramatic drop in contact angle upon even the shortest (4 sec) exposure to the solution. PVF_2 did not undergo significant contact angle changes and the contact angles for Tefzel did change upon longer exposures to the solution. This data is summarized in Table 1-3-1.

Table 1-3-1: Advancing/Receding Water Contact Angle Data for Sodium Naphthalide Reduction (degrees)

	Reaction Time			
Material	0	4 seconds	5 minutes	60 minutes
Teflon	121±1 92±1	77±1 9±1	55±2 9±.5	33±4 0
Tefzel	97±1 82±1	92±1 70±1	90±5 59±4	79±1.5 36±1
PVF_2	91±1 61±1	88±1 61±1	87±.5 48±2	87±2 42±2.5

The contact angle data suggest that the surface of Tefzel was modified, but exactly what reaction caused these changes was not obvious. These contact angle changes become large only after extended reaction times and, unlike Teflon, the film does not change color. These results suggest that the film is not undergoing reduction and that it will probably not be possible to functionalize Tefzel in this manner with the degree of certainty that is required for use as a model substrate.

When polyethylene was exposed to an oxidizing solution composed of potassium chlorate/sulfuric acid for short times, rinsed, and dried at reduced pressure, contact angles and ATR-IR indicate that an extensive oxidation has occurred. When this same solution was used to treat Tefzel and PVF_2, little resemblance to the same extensive modification was observed. The contact angle data is summarized in Table 1-3-2. Tefzel underwent only a slight change in contact angle even after 60 minutes. The contact angle did decrease when PVF_2 was exposed to the solution for 60 minutes but this drop was not as much as that shown by polyethylene oxidized for 1 minute. Again the ATR-IR (Ge, 45^{o}) was unable to detect changes in the polymer films. These surfaces were not examined by XPS which could possibly identify the source of the contact angle decrease. However, again this modification did not appear suitable for preparing surfaces for the study of surface structure-reactivity relationships.

Table 1-3-2: Advancing/Receding Water Contact Angles for Oxidation (degrees)

Material	Reaction Time		
	0	1 minute	60 minutes
Polyethylene	91±1 50±4	59±1 10±2	56±2 0
PVF_2	91±1 61±1	88±2 61±3	78±2 49±3
Tefzel	97±1 82±1	95±2 65±4	93±2 52±2

Surface Modification of Poly(vinylidene fluoride).

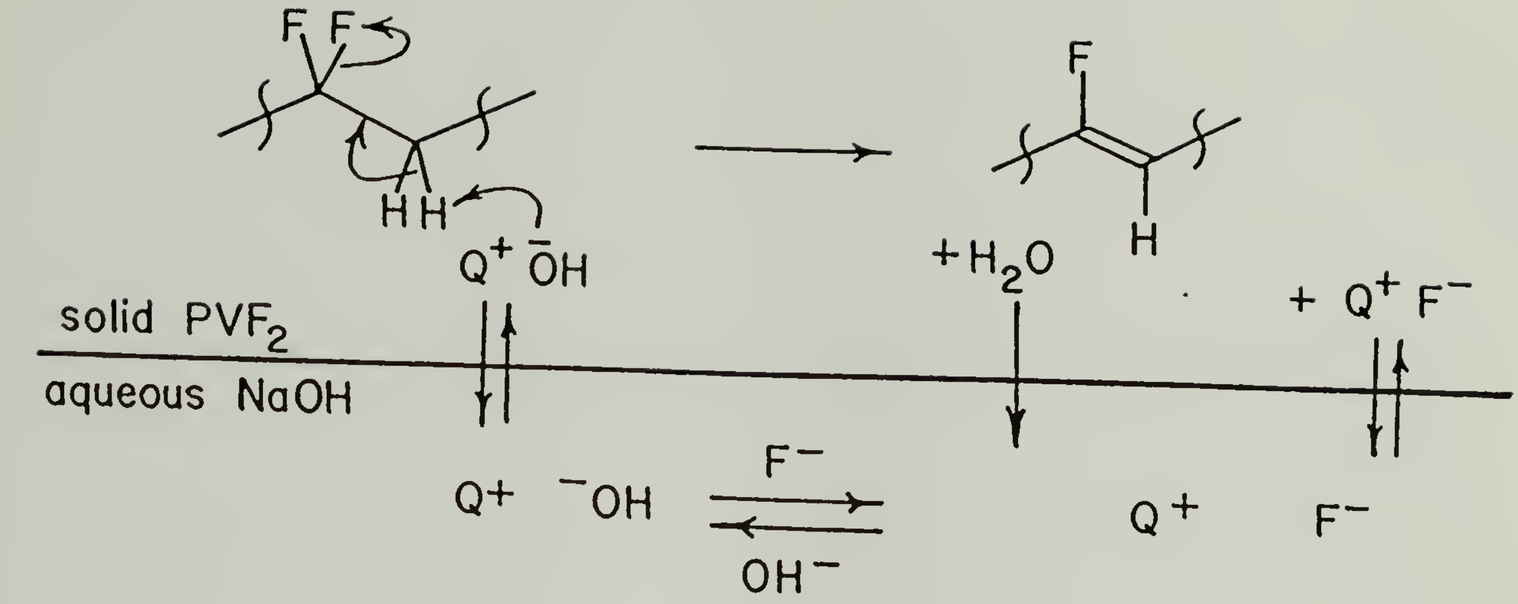
Introduction: The requisite substrate for the study of surface structure-reactivity-property relationships can not be prepared by any established methods of surface modification; therefore, new techniques had to be developed. The ideal model for these studies has functional groups only in a thin layer of the surface (within the 50 Å XPS sampling depth). The method for producing this type of layer should therefore be surface-specific; the boundary between the modified and unmodified phases should be parallel to the surface. A necessary requirement for surface-specific reactions is that the reaction rate of a reagent with a surface be fast in comparison to the rate of diffusion of the reagent into the surface. This condition is not sufficient; however, not all diffusion controlled reactions are surface-specific (for example, the sodium naphthalide reduction of Teflon). In addition a surface-specific reaction requires that the reacted surface decelerate rather than accelerate the reaction rate: as is the case for metals, like aluminum, which form a thin oxide layer; the aluminum oxide layer prevents the diffusion of oxygen to the aluminum surface and further oxidation is prevented. The first requirement, diffusion controlled reaction rates, can usually be inferred from knowledge about organic reactions in solutions; the second requirement, autoinhibition, cannot be a priori be determined.

Another requirement that should be met if surface-specific reactions are to occur on polymers is that of generating a sharp interface between the polymer and the reagent. Polymers are unique materials in that their interfaces are altered by changes in solvent and temperature. This is a result of the greater mobility of the polymer molecules at the surface compared to other materials like metals and ceramics. The more the mobility of the polymer chains is reduced the more surface selective the reaction will be: less polymer is exposed to the reagents and the diffusion constants for the reagents will be lowered.

Extensive modifications of PVF_2 were reported in the literature. These methods involved the reaction of PVF_2 with a base under a variety of conditions including phase transfer catalysis[1]. Dehydrohalogenation is an attractive method for modifying PVF_2; it is a facile reaction and the resulting conjugated material can be further derivatized to introduce functional groups. Thus if the dehydrofluorination can be controlled and limited to the surface, then further reaction with the double bonds would also be limited to this region. Using this two-step method, functional groups could be introduced onto the surface in a layer whose thickness is dependant upon the thickness of the elimination.

Results and Discussion.

When PVF_2 film is submersed in 8 N sodium hydroxide solution containing a catalytic amount of tetrabutylammonium bromide for 60 s at room temperature, rinsed with water and then ethanol, and dried at reduced pressure, contact angle data, XPS, gravimetry, and UV-Vis and ATR-IR spectroscopies indicate that a surface-selective dehydrofluorination is effected (eq 1-3-1). In the absence of tetrabutylammonium bromide, the reaction proceeds at a rate at least 2 orders of magnitude slower. The basis for the surface selectivity of this reaction is the autoinhibitive nature of the phase transport step of this phase-transfer-catalyzed reaction. Applying phase-transfer catalysis[2,3] to surface modification of PVF_2, the outer few angstroms of the solid organic polymer is regarded as the organic phase; hydroxide ion is transported from an aqueous phase in contact with the polymer to this "organic phase" where dehydrofluorination is effected. The nonmolecular terminology "wetting" may be appropriate here: water and PVF_2 in contact with one another define a sharp interface; that is, water neither dissolves nor swells the polymer. Hydroxide ion (in the absence of phase-transfer catalysts) does not induce dehydrofluorination because the basic solution does not "wet" the film. Tetrabutylammonium ion transports hydroxide ion across this interface (serves as a "wetting agent") where it can react to form poly(fluoroacetylene). The eliminated surface is impenetrable under these reaction conditions, hence elimination is confined to the surface. Figure 1-3-1 shows a plot of absorbance (at 410 nm) vs time



Equation 1-3-1. Phase Transfer Catalyzed Dehydrofluorination of Poly(vinylidene fluoride)

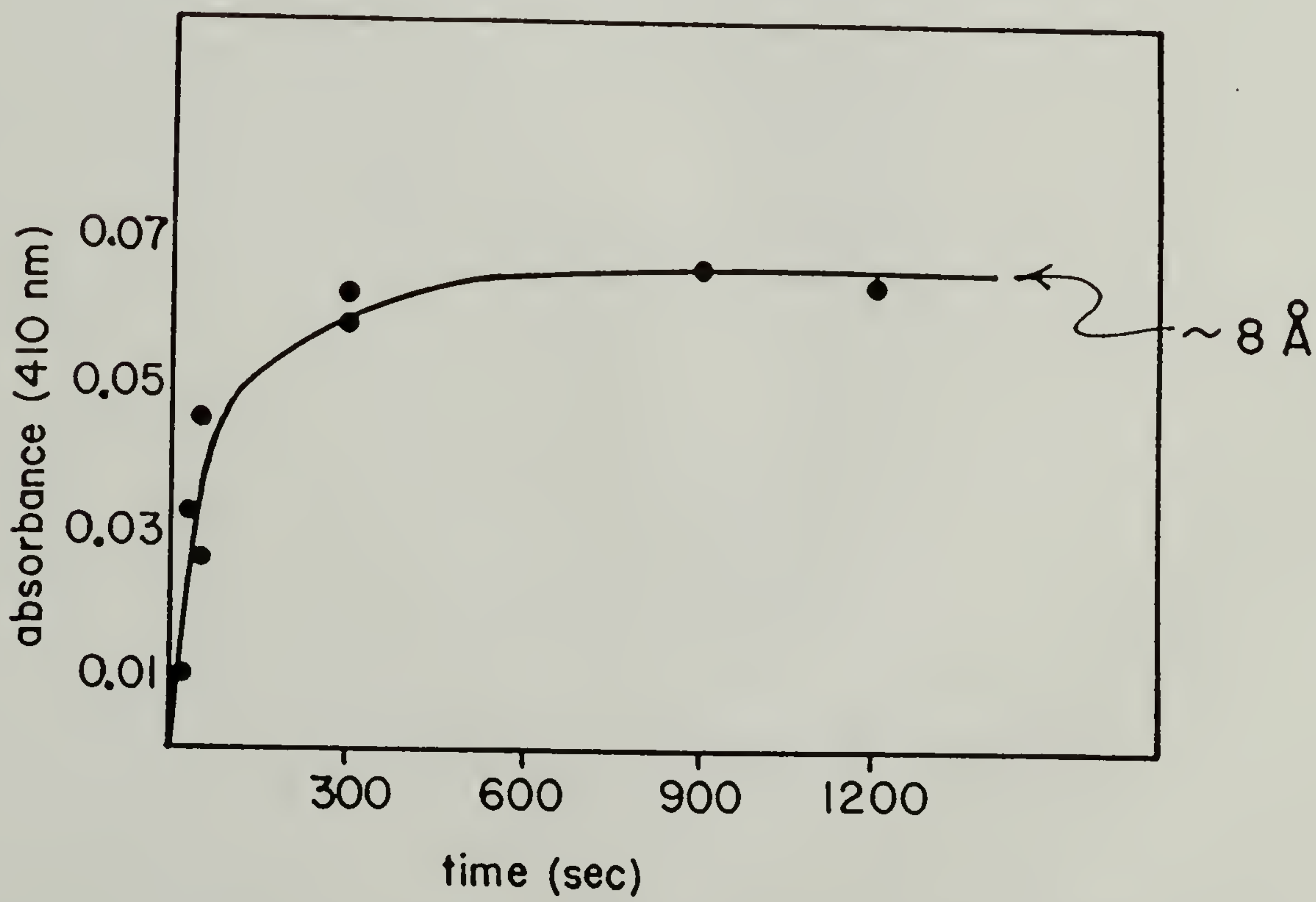


Figure 1-3-1. Absorbance vs. time plot of dehydrofluorination of poly(vinylidene fluoride).

for this reaction; autoinhibition is apparent. More extensive modification reactions of PVF_2[4] and poly(vinyl chloride)[5] based on phase-transfer catalysis have been reported.

Advancing and receding water contact angles (Table 1-3-3) indicate that elimination (60 s) followed by hydration (treatment with concentrated H_2SO_4 and then water) introduces polar functionality. The decrease in contact angles upon elimination is probably due to partial oxidation of the conjugated surface. The data indicate that the uncatalyzed reaction proceeds to a negligible extent under these conditions. Contact angle data for short reaction times suggest that elimination produces a homogeneously modified surface at the level of this analysis:[6] Scatter in contact angles is greater than 2° for reaction times less than 30 s. For longer reaction times, the scatter is less than 0.5°. This indicates that the surface is heterogeneous at reaction times less than 30 s but becomes homogeneous thereafter.

Attenuated total reflectance infrared spectra indicate that the depth of elimination is shallow with respect to the sampling depth of this technique: these is no discernable difference between spectra. The sampling depth at 1580 cm^{-1} using the conditions of this experiments is about 1 micrometer. Secondary electron images of the samples before and after elimination exhibit no change in microtopography at a resolution of 60 Å.

Three independent estimates of the depth of the elimination reaction were made. Figure 1-3-2 exhibits XP spectra for the elimination and bromination reactions. The increase in oxygen upon

	Θ_A, deg	Θ_R, deg
PVF_2	88.0 ± 1.0	66.0 ± 1.0
$PVF_2 \xrightarrow[TBAB]{NaOH}$	83.5 ± 0.5	40.5 ± 0.5
$PVF_2 \xrightarrow{NaOH}$	88.0 ± 1.0	62.0 ± 1.0
$PVF_2 \xrightarrow[TBAB]{NaOH} \xrightarrow[(2)\ H_2O]{(1)\ H_2SO_4}$	71.5 ± 0.5	18.5 ± 0.5
$PVF_2 \xrightarrow{NaOH} \xrightarrow[(2)\ H_2O]{(1)\ H_2SO_4}$	85 ± 2	59 ± 2

Table 1-3-3. Advancing and Receding Water Contact Angle Data

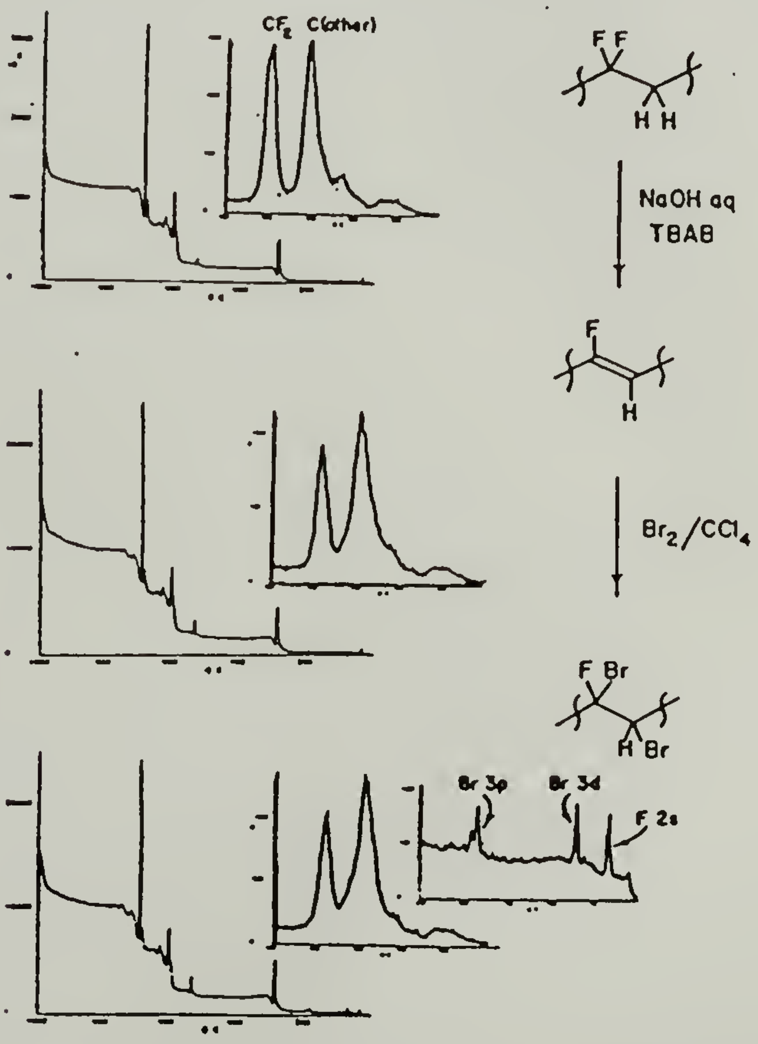


Figure 1-3-2. XP spectra of eliminated and eliminated/brominated poly(vinylidene fluoride).

elimination is likely due to oxidation of regions of extended conjugation. By cutting and weighing the appropriate peaks and factoring photoelectron cross-sections, three estimates of reaction depth were obtained. The XPS sampling depth used for calculations was 100 Å and no correction was made for the variation of this value with kinetic energy. Comparison of the ratio of the CF_2 peak area to the other carbon peak area, before and after elimination yields an estimate of 12 Å. Comparisons of bromine $3d_{3/2}$ & $3d_{5/2}$ and the bromine $3p_{1/2}$ & $3p_{3/2}$ peaks with the fluorine 2s signal give values of 2.6 and 2.2 Å respectively. This technique cannot be considered quantitative; the three values depict its poor precision. There are many sources of error: the estimated sampling depth, the assumption that the material has a homogeneous composition throughout (which we know to be false) and the error associated with taking ratios of numbers with small differences. The data do suggest that a small portion of the XPS sampling depth has been modified and is consistent with more precise estimates: The UV-Vis absorbance of a film eliminated for 60 s corresponds to a depth of 8.5 Å. Dissolution of the film in DMF followed by solution analysis yields an estimate of 8.1 Å. These estimates assume that the elimination performed in solution gives rise to the same products as the surface elimination. Gravimetric analysis has proved to be the most precise method for determining the average reaction depth. Films with surface areas of 9 cm^2 gain 6.2 ± 0.3 micrograms upon elimination (60 s) and bromination, which corresponds to a reaction depth of 18.1 ± 0.7 Å (95% confidence based upon ten measurements).

The reaction was highly sensitive to temperature variations. Figure 1-3-3 shows a plot of absorbance (at 410 nm) vs. time for this reaction at three temperatures (0°C, 23°C, and 40°C); the sensitivity of this reaction to temperature is readily apparent. The quantity of material eliminated at 40°C was more than twice that obtained at 20°C, and in addition the reaction at 40°C does not exhibit the same extent of autoinhibition that is observed at the lower temperature. The data also suggest that very little elimination occurred when the temperature was lowered to 0°C. This may mean that the surface selectivity can be enhanced further by reacting the film below room temperature.

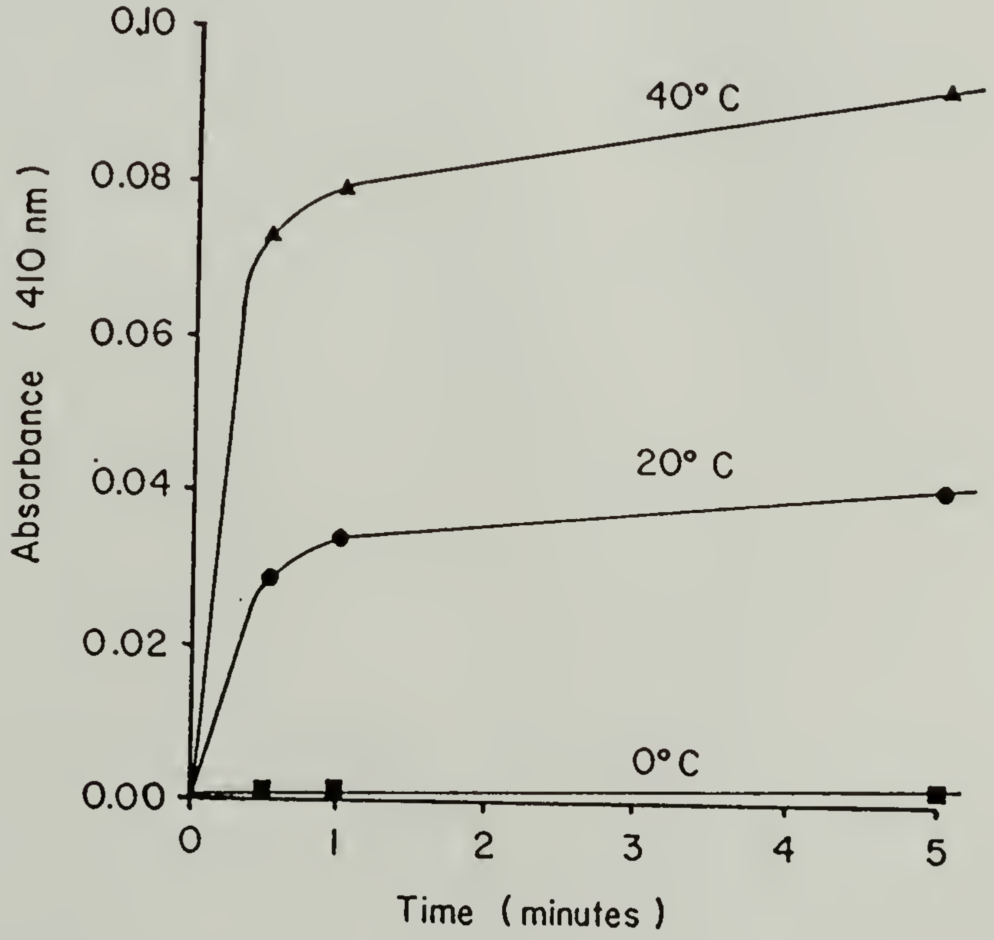


Figure 1-3-3. Absorbance vs. time plot of dehydrofluorination of poly(vinylidene fluoride) at 0°, 20°, and 40°C.

The unsaturation was further reacted with a variety of reagents which are known to react with double bonds in solution. In addition to reacting the films under bromination and hydrolysis conditions, the modified surface was reacted with: Chlorine; MCPBA; osmium tetroxide; palladium chloride; potassium permanganate; potassium chlorate/sulfuric acid; mercuric trifluoroacetate and 2-lithio-2,4,4-trimethyl-2-oxazoline. These derivatizations were initially analyzed by contact angle and gravimetric analyses, the results are summarized in Table 1-3-4. Where warranted the surfaces were additionally analyzed by XPS. The surface produced upon H_2SO_4/H_2O hydrolysis was the most reproducible and hence was used as a substrate for further XPS studies.

The bromination of PVF_2-E (1 min PTC elimination) resulted in a large decrease in the color of the film, however the film remained slightly tinted. This indicates that some residual unsaturation remained, what effect this has on the gravimetric results is unknown. Chlorination, at 0^oC in the dark, of PVF_2-E resulted in the complete removal of color. When this reaction was monitored with gravimetry, it was discovered that the control PVF_2 also reacted with chlorine as evidenced by the mass increase. Thus chlorination, though more complete, was not selective enough to react with just the unsaturation and this reaction was not persued further.

Reaction of PVF_2-E with MCPBA also resulted in the complete removal of color from the modified film. The contact angles decreased (Table 1-3-4) upon exposure to MCPBA and the surface became even more hydrophilic when the MCPBA treated surface was exposed to sodium

Table 1-3-4. Gravimetric and Contact Angle Data for the Reactions of Eliminated Poly(vinylidene fluoride).

Reaction	Contact Angles (degrees) Advancing	Receding	Mass Change (mg)
PVF_2+Br_2	88±1	66±1	0.000±0.001
PVF_2E+Br_2	83±1	41±1	0.006±0.001
PVF_2+Cl_2	85±1	50±1	0.020±0.003
PVF_2E+Cl_2	84±1	46±1	0.024±0.002
PVF_2+MCPBA	84±1	51±2	0.087±0.011
PVF_2E+MCPBA	78±1	23±3	0.120±0.010
PVF_2+OsO_4	73±2	26±1	0.123±0.005
PVF_2E+OsO_4	71±2	20±1	0.115±0.003
PVF_2+$KMnO_4$	86±1	62±1	0.000±0.001
PVF_2E+$KMnO_4$	63±2	15±2	0.002±0.001
PVF_2+$KClO_3/H_2SO_4$	87±1	58±1	-0.002±0.001
PVF_2E+$KClO_3/H_2SO_4$	71±1	32±2	0.003±0.001
PVF_2+$PdCl_2$	87±2	62±3	0.002±0.001
PVF_2E+$PdCl_2$	104±1	48±1	0.002±0.001
PVF_2+$Hg(O_2CCF_3)_2$/ H_2O	86±2	53±2	0.086±0.011
PVF_2E+$Hg(O_2CCF_3)_2$/ H_2O	79±1	22±1	0.079±0.012
PVF_2+$Hg(O_2CCF_3)_2$/ ethylene glycol	84±3	51±2	0.092±0.006
PVF_2E+$Hg(O_2CCF_3)_2$/ ethylene glycol	77±2	21±1	0.109±0.010
PVF_2+ 1)H_2SO_4 2) H_2O	85±2	59±2	0.000±0.001
PVF_2E+ 1)H_2SO_4 2) H_2O	72±1	18±1	0.001±0.001
PVF_2+ 1)H_2SO_4 (2 h) 2) H_2O	83±2	54±2	0.000±0.001
PVF_2E+ 1)H_2SO_4 (2 h) 2) H_2O	54±3	0	0.002±0.001

hydroxide. Gravimetric analysis indicated that a weight gain occurred which was much larger than would be expected (0.120 mg instead of 0.002 mg) for the epoxidation reaction. Thus either a secondary reaction was occurring or the reagent was soluble in the polymer and as a result gravimetric determinations were not useful for analyzing this reaction. In order to obtain more information about this reaction, PVF_2 was eliminated more extensively and the epoxidation reaction was monitored using ATR-IR spectroscopy. These studies indicate that though the absorbance due to the C=C vibrations (1500 - 1600 cm^{-1}) disappeared, no epoxide absorbance was observed. Thus the expected reaction was not occurring. The ATR-IR and gravimetric data indicated that this system was not ideally suited for the preparation of well characterized model surfaces.

Osmium tetroxide is widely used for staining unsaturation of solid samples for use in electron microscopy. The reagent selectively oxidizes the olefin leaving the rest of the material unreacted. When PVF_2 and PVF_2-E were exposed to OsO_4 vapor, both samples were visually darkened. The dark color was not removed even after the film was exposed to sodium sulfite solution. The contact angle data for both films fell indicating that both surfaces were polar. The samples had large mass gains (0.115 mg). This data indicates that OsO_4 forms a layer on both films whose presence is not dependant on the amount of unsaturation. Therefore the reaction was not examined further.

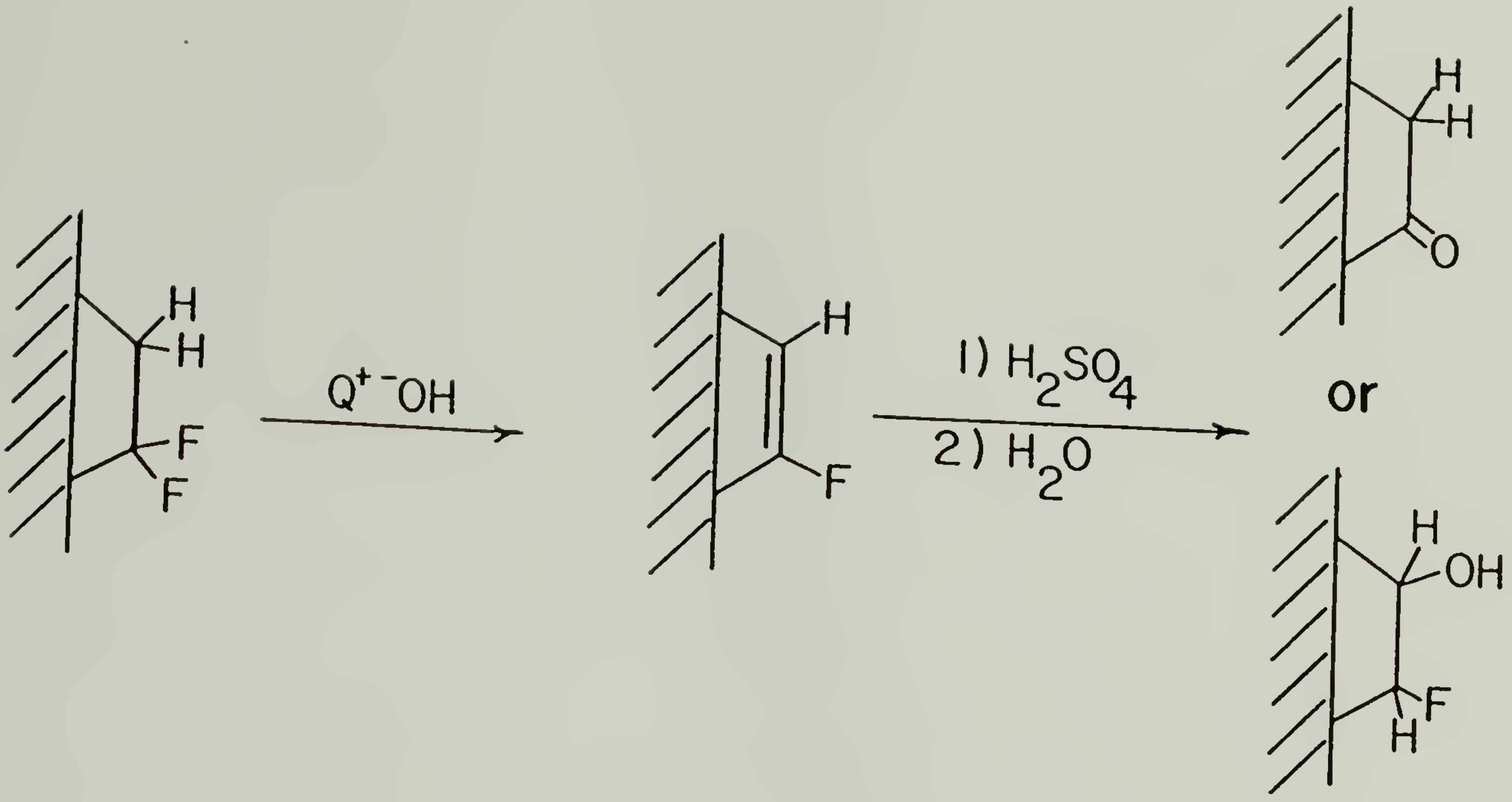
The reaction of PVF_2-E with palladium chloride resulted in an increase in the observed contact angles (104±1, 48±1) which was unexpected since the reaction conditions were such that the olefin should have been oxidized to ketones. The explanation for this increase lies with the heterogeneous nature of the reaction; in general, the surface modification reactions which required the use of suspensions gave roughened surfaces and this sometimes increased the observed contact angles. However the control film (PVF_2) did not show the same increase, so something else may have occurred (adsorption of a contaminant preferentially to the eliminated surface could explain the observed data). The UV-Vis spectrum also did not show an increase in absorbance which was expected (200 - 300 nm) for the carbonyls. Gravimetric analysis indicated both the control and the PVF_2-E film gained 2 micrograms. An attempt was made to label the carbonyl groups with 2,4-dinitrophenylhydrazine[7]. There was no increase in absorbance at 365 nm which would be evidence for the label. Thus the surface produced could not be characterized at the level needed for model surface studies and no further work was done with this surface.

Potassium chlorate in sulfuric acid and alkaline aqueous potassium permanganate both successfully oxidized the conjugated surface. The XPS for both surfaces were consistent with oxidation of the olefin, oxygen intensity increased and the C_{1s} carbon region exhibited increased complexity. The identity of this oxygen functionality could not be unambiguously defined from XPS. However the decrease in the observed contact angle data did correlate with the increased oxygen intensity. These surfaces contained chemically heterogeneous functional groups and no attempt was made to characterize or use these surfaces in further studies.

An attempt was made to react the olefin surface using oxymercuration. Again the surface was initially studied by gravimetric analysis and contact angles. The large mass gain (0.110 mg) indicated once again that a large quantity of reagent was being retained by the polymer. However the contact angles did indicate that an increase in the surface energy was achieved when either H_2O or ethylene glycol was used (Table 1-3-4). Again it was decided, based upon these results, to look for a more suitable reaction and no further work was done with this method.

The hydrolysis of the PVF_2-E surface was mentioned previously and it too gave an increase in the surface energy. The contact angle data presented (Table 1-3-4) represent a surface that was exposed to H_2SO_4 for 2 minutes and then treated with H_2O. This method and time of reaction gave the most reproducible surface. XPS of this surface indicated a large increase in oxygen and little sulfur incorporation. Longer exposures to H_2SO_4 increased the amount of oxygen and introduced various amounts of sulfur into the surface which could not be removed with water. Thus although very low contact angles were generated (adv= 50^o, receding=0^o; 2 hour sulfuric acid treatment) this was the result of considerable sulfonation.

These conditions result in hydrolysis of the unsaturated surface and two products are possible: Ketones (structure A in eq 1-3-2) from anti-Markovnikov addition, and alcohols (structure B in eq 1-3-2) from Markovnikov addition.



Equation 1-3-2. Hydrolysis of eliminated poly(vinylidene fluoride)

Several attempts were made at labelling both ketones and alcohols. The reaction between 3,5-dinitrobenzoyl chloride and alcohols using pyridine as a solvent is used for quantitative analysis of alcohols solutions. This method was not successful when applied to the PVF_2-O surface. The increased absorbance that was observed in the UV was the same for both the control PVF_2 and the PVF_2-O film. A second label which was used for reacting hydroxyl groups was trichloroacetylisocyanate. This label was used for XPS studies and the results indicate that a small quantity of hydroxyl groups (1 atomic percent chlorine in the XPS) was present on the PVF_2-O surface and not on the PVF_2-E.

Carbonyl groups were labeled by hydrazone formation using substituted hydrazines: 2,4-Dinitrophenylhydrazine for UV studies and

3,5-dichlorophenylhydrazine for XPS studies. This time neither UV nor XPS indicated the incorporation of the label. This does not necessarily mean that carbonyl groups are not present. Although there are many studies in which these methods were used for XPS and UV labelling, no model surfaces were ever tested with this method to examine the actual extent of hydrazone formation. Thus if only a 1% conversion is achieved and only a small number of carbonyl functional groups are present, then this technique may fail to identify them.

Carboxylic acid groups were labeled using 1,1'-carbonyldiimidazole and trichloroethanol. Again similar results were obtained, no chlorine was observed in the XPS, and again the same uncertainty is evident: carboxylic acid groups may be present, but the labelling technique has low efficiency and is not sensitive enough to identify them.

The reaction of surface-confined alcohol groups appears to be facile with a number of reagents: including acid chlorides and isocyanates. This apparent ease of reaction as compared to carbonyl or carboxylic acid groups makes the conversion of these functionalities into alcohol groups an attractive method for determining their presence. Two reagents used to accomplish this conversion were: Lithium aluminum hydride in THF and sodium borohydride in ethanol.

That lithium aluminum hydride in THF reacted with PVF_2, PVF_2-O and PVF_2-E was demonstrated by reacting the $LiAlH_4$ treated film with trichloroacetylisocyanate and observing the XPS for increased levels of chlorine. The XPS data in Table 1-3-5 summarizes these observations. In addition to increased chlorine levels the XPS C_{1s} level underwent large changes in the CF_2/CH_2 ratio (fell from 1 to 0.8). These results indicate that $LiAlH_4$ should not be used to reduce functional groups on PVF_2 surfaces, too many side reactions occur which complicate the analysis.

A much more consistent set of data was obtained by using sodium borohydride in ethanol as the reducing agent. In this case there was no observable increase in the XPS chlorine atomic composition when PVF_2 film which was reacted with the reducing agent and exposed to the trichloroacetylisocyanate label. In addition the C_{1s} region did not show any changes. There was an increase for both the PVF_2-E and PVF_2-O film (Table 1-3-5) which confirms that there are indeed carbonyl groups present on the surface which can be reduced by sodium borohydride. It is also apparent from this data that most of the functional groups, prior to reduction, that react with the trichloroacetylisocyanate are introduced during the elimination step. Two possibilities exist: the conjugated backbone has undergone oxidation to give hydroperoxides which eventually decompose to give hydroxyl groups or hydroxide reacts with the substrate during the elimination to form a surface which contains unsaturated ketones. These carbonyl groups undergo keto-enol tautomerization and the isocyanate reacts with the group when it is in the enol form. If this is the only source of oxygen then the number of alcohol groups which are labeled after reduction should be roughly the same as that observed prior to reduction. This is not observed by XPS; instead, twice the amount of chlorine was observed after reduction.

Table 1-3-5. XPS Atomic Composition Data for the Reaction of Trichloroacetyl isocyanate with Modified Poly(vinylidene fluoride) Films.

Material Treated with Trichloroacetyl Isocyanate	Take-off Angle (degrees)	Percent XPS Atomic Composition F	O	N	C	Si	Cl	S
PVF$_2$	75	50.2	3.01	0.26	45.7	0.50	0.17	0.22
	15	45.4	4.76	0.26	41.9	1.12	0.57	0.00
PVF$_2$-E	75	42.5	7.07	0.96	47.7	0.28	0.63	0.80
	15	37.0	9.91	1.32	49.0	0.00	1.44	1.35
PVF$_2$-O	75	35.8	11.9	1.98	47.6	0.38	0.86	1.47
	15	27.7	16.0	2.50	48.5	0.96	1.77	2.63
PVF$_2$-LiAlH$_4$	75	44.6	4.67	0.23	49.5	0.00	0.80	0.28
	15	42.4	5.72	0.47	48.4	1.11	1.51	0.33
PVF$_2$-E-LiAlH$_4$	75	38.9	9.11	1.83	52.7	0.19	2.85	0.45
	15	23.8	13.6	2.78	52.7	0.92	5.17	1.15
PVF$_2$-O-LiAlH$_4$	75	34.9	8.28	1.59	52.0	0.52	2.73	0.00
	15	25.5	12.9	3.12	53.0	0.00	4.42	1.02
PVF$_2$-NaBH$_4$	75	45.5	2.28	0.51	51.9	0.00	0.34	-
	15	48.5	3.41	0.55	47.2	0.23	0.65	-
PVF$_2$-E-NaBH$_4$	75	43.9	4.61	0.91	49.6	0.00	1.01	-
	15	41.5	6.74	1.23	47.9	1.22	2.20	-
PVF$_2$-O-NaBH$_4$	75	40.0	8.19	1.50	49.2	0.12	1.78	-
	15	36.1	11.0	2.49	48.9	0.00	3.42	-

Table 1-3-6. Contact Angle Data for the Reduction of Modified Poly(vinylidene fluoride) Films.

Sample	Water Contact Angles (degrees) Advancing	Receding
PVF$_2$	85±1	48±1
PVF$_2$E	81±1	49±1
PVF$_2$O	69±2	37±1
PVF$_2$-LiAlH$_4$	84±1	52±1
PVF$_2$E-LiAlH$_4$	76±1	42±1
PVF$_2$O-LiAlH$_4$	74±1	40±1
PVF$_2$-NaBH$_4$	85±1	49±1
PVF$_2$E-NaBH$_4$	79±1	45±1
PVF$_2$O-NaBH$_4$	70±2	36±1

This indicates that at least two different oxygen species are present: enolizable ketones or alcohols and nonenolizable ketones. This reaction was also monitored by contact angle and gravimetric determinations; only heptafluorobutyryl chloride was used as the label for the gravimetric determinations. The contact angle data suggests that reduction results in a decrease in surface energy which decreases more upon exposure to the label (Table 1-3-6). Only the reduction step (- 1 microgram) and the PFBCl reaction with the reduced PVF_2-O surface (+2 microgram) exhibited measurable mass changes. This mass gain corresponds to (2 microgram/ 213 g/mole) 9.4×10^{-9} moles of PFBCl which indicates that the surface contains 1 nanomole/cm^2 of hydroxyl groups. This is approximately the site density for a closest packed fatty acid monolayer.

These results indicate that this surface presents a substrate that is suitable for certain types of model studies. It is not, however, the ideal surface. It relies on two steps, which is not in itself bad, for the incorporation of functional groups. These steps must be capable of being monitored at the molecular level. The first step, dehydrofluorination, was demonstrated to be controllable, through reaction kinetics, and was characterized through a combination of analytical techniques at the molecular level. The second step, which involves reaction of the double bonds, presented uncertainties when characterization was attempted: Which oxygen containing functional groups are introduced and how many functional groups are present repesent questions which are not easily answered. The data presented here suggests that at least two types of oxidized carbon are introduced during the elimination and their numbers increase slightly upon reduction.

An alternative method of introducing functional groups which can be better characterized is to incorporate protected functional groups which can be monitored by XPS via the incorporation of a new element. This technique was attempted on PVF_2 using 2-lithio-2,4,4-trimethyl-2-oxazoline (LiTMO). This reagent if incorporated will introduce nitrogen into the XPS and upon deprotection, nitrogen is removed and carboxylic acid groups are introduced. Thus the disappearance of nitrogen can be used to indicate the presence of carboxylic acid groups. The preliminary studies involved the use of contact angles, this data (Table 1-3-7) indicates that a reaction has occurred.

Table 1-3-7. Water Contact Angle Data for the Reaction of 2-Lithio-2,4,4-trimethyloxazoline with Modified Poly(vinylidene fluoride) Films.

Sample	Contact Angles (degrees) Advancing	Receding
PVF_2	88±1	60±1
PVF_2E	84±1	45±1
PVF_2E-Br_2	83±1	41±1
PVF_2+LiTMO	87±1	51±1
PVF_2E+LiTMO	84±1	40±2
PVF_2E-Br_2+LiTMO	85±1	38±1
PVF_2-LiTMO+H_2O	87±1	52±2
PVF_2E-LiTMO+H_2O	80±2	32±2
PVF_2E-Br_2LiTMO+H_2O	79±1	35±3

The data suggest that PVF_2 does not react with the reagent but PVF_2-EBr does. This means that with this method it is possible to introduce carboxylic acid groups into a surface layer whose thickness is controlled by the thickness of the brominated layer. The XPS of the LiTMO treated film was not obtained; therefore, detailed confirmation of whether or not this method worked is not available. The main reason for not pursuing this surface was the lack of large changes in contact angle and mass; at that time these were the only two analytical methods directly at hand. Thus attention was placed at applying this reaction to poly(chlorotrifluoroethylene) which showed large contact angle changes upon exposure to this reagent.

Phase Transfer Catalyzed Modification of Poly(chlorotrifluoroethylene).

Introduction.

The sucessful results achieved using phase transfer catalysis to modify poly(vinylidene fluoride) indicated that this might be a good method to modify other polymers. PCTFE would be a very good candidate for surfaces studies if the surface could be suitably modified. PCTFE was reacted with both hydroxide and cyanide anions in an attempt at preparing a new surface.

Results and Discussion.

When PCTFE film was reacted with 8 N NaOH or KCN (5 g) in a solution containing H_2O (20 ml) and tetrabutylammonium bromide, the film visually appeared to have reacted. The only methods of monitoring the reaction were contact angle and XPS. It was hoped that for the cyanide reaction that the presence of the cyano groups would be indicated by nitrogen in the XPS. Instead XPS only showed an increase in oxygen and no nitrogen; this was unexpected. The hydroxide treated film also had a slight increase in the oxygen intensity. Whereas the hydroxide-treated film had a large drop in contact angle, the cyanide-treated film exhibited an increase (Table 1-3-8) which may mean that the film was roughened. Upon exposure to NaOH the contact angle of the cyanide-treated film fell. This represents only a slight increase in the surface energy. These results were unexpected and the reaction was run on low molecular weight PCTFE oil to obtained more information about this reaction. The reaction mixture containing DMF, KCN, H_2O and tertrabutylammonium bromide was colorless; upon the addition of the polymer the solution turns red. After reaction (24 h) the polymer was isolated as several fractions. Analysis by IR spectroscopy indicated that no fraction contained cyano groups and a large carbonyl (1690 - 1695 cm^{-1}) was observed in both the distilled polymer fraction

Table 1-3-8. Water Contact Angle Data for the Reaction of Cyanide with Poly(chlorotrifluoroethylene).

	Contact Angle Data (degrees)	
Sample	Advancing	Receding
PCTFE	104±1	80±1
PCTFE-CN	113±2	52±2
PCTFE-CN, NaOH	91±1	28±2

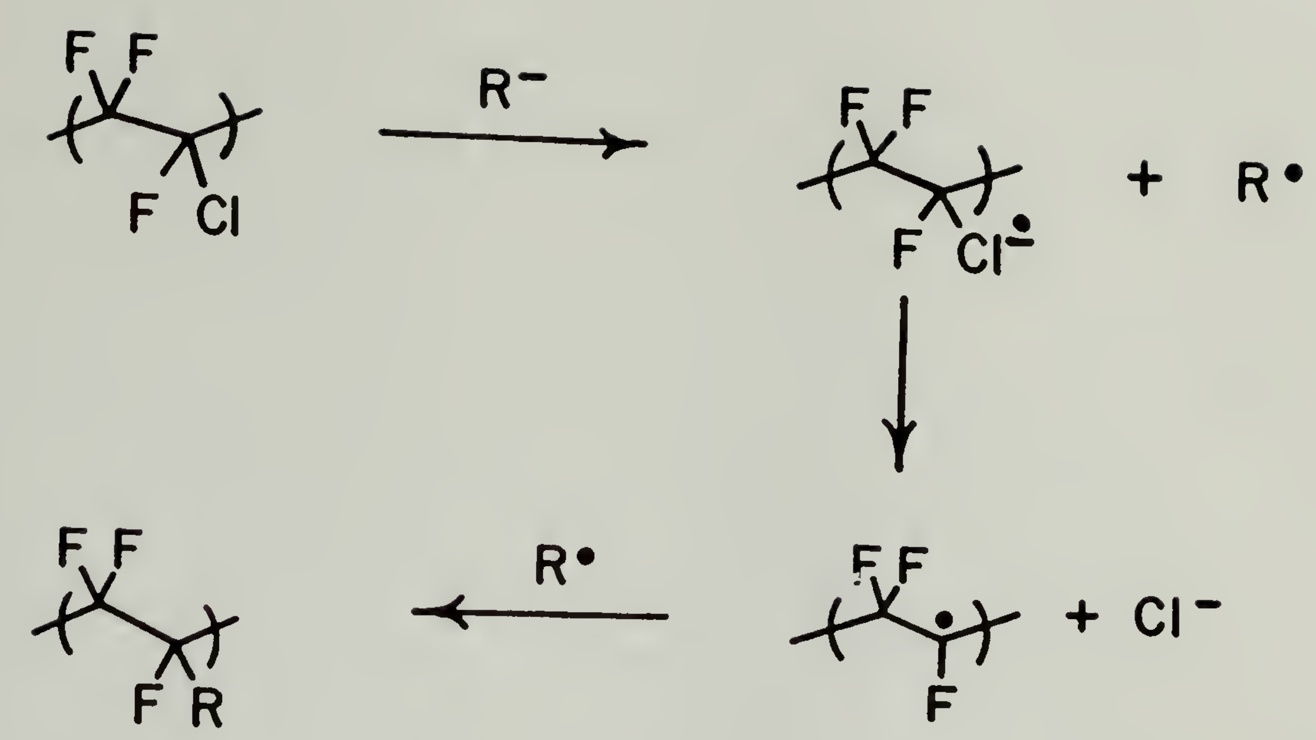
as well as in the remaining residual precipitate. The presence of carbonyl groups in the polymer was not an expected result but it did explain why the XPS showed increased oxygen intensity after treatment with the KCN solution. The reaction is interesting but it did not give results which were easily interpretable on the basis of the reaction chemistry. This reaction was not studied further as a surface modification.

Modification of PCTFE Using Organometallic Reagents.

Introduction. The phase transfer catalyzed dehydrofluorination of poly(vinylidene fluoride) was successful in preparing a two-dimensional surface of conjugated carbon-carbon double bonds. These double bonds were then exposed to a variety of oxidizing conditions in order to introduce polar functionality onto the surface. The polar groups were then introduced into a layer whose thickness was determined by the thickness of the unsaturated layer. The identity of the polar oxygen containing functionality could not be determined unambiguously; oxygen was introduced during the elimination as well as during the oxidation. The difficulty which was encountered during the labeling of the functional groups prompted the search for surfaces which could be prepared using methods which would allow for the unambiguous assignment of the surface functionality.

Poly(chlorotrifluoroethylene) was examined with the intent of using it as a substrate for surface studies. PCTFE has certain advantages over PVF_2: the surface energy of PCTFE is very low which means that the water contact angles of untreated PCTFE are very high (advancing=104°, receding=80°); any changes in the surface can readily be followed by contact angle. PCTFE is not soluble in any solvent at room tempature and it is soluble in a few solvents (mesitylene) at temperatures above 160°C. PCTFE film does not decompose when heated to temperatures below 100°C and can therefore be dried at elevated temperatures which increases the rate at which solvent can be removed from the film. Higher temperatures will also be important for future studies of polymer functional group mobility. The XPS spectrum of PCTFE film indicated that the surface was clean: no oxygen in the XPS survey and a single C_{1s} peak at 295eV (corrected for sample charging) corresponding to the highly oxidized CF_2 and CFCl subunits. The major disadvantage was that few methods for modifying PCTFE exist. The work presented earlier using phase-transfer catalysis was an attempt at using substitution as a method for modifying PCTFE; replacing chlorine with cyanide or hydroxyl groups. These results were ambiguous and the expected reaction did not occur.

A second method for modifying PCTFE involves the use of organometallic reagents. Danielson[8] has studied the reactions of lithium reagents and Grignard reagents with PCTFE powder and proposed the mechanism detailed in Scheme 1-3-1 to explain the incorporation of alkyl and aryl groups. The conditions used in these studies were such that extensive reaction occurred with no apparent surface selectivity.



Scheme 1-3-1. Proposed[8] Mechanism for Alkylation and Arylation of Poly(chlorotrifluoroethylene)

These reports prompted our investigation into these reactions, under less severe conditions, with regard to their products, mechanisms and potential as surface-selective modifications[9].

The surface of the modified polymers was characterized using the methods of surface analysis that were presented in the introduction. These analytical methods can only determine qualitatively whether or not a reaction has occurred. In most cases they do not provide enough information to identify which functional group was introduced. In order to use standard spectroscopic methods (NMR and IR) which have the potential for positively identifying the functionality present, it was necessary to use PCTFE powder and low molecular weight PCTFE oil as substrates. PCTFE oil was used as a model substrate because it was soluble in ether; hence, it could be extensively modified and the products could be quantitated using a variety of analytical methods.

The inference here is that the reaction which occurs in solution is the same as that on the surface. This may not be true and it is expected that certain model reactions will not proceed on polymer surfaces. PCTFE powder was used to check for similarities and differences between solution and surface reactions.

When PCTFE film is allowed to react with excess methyllithium in diethyl ether followed by hydrolytic work up, contact angle data, XPS, UV-Vis, and gravimetric analyses indicate that a reaction has taken place: Table 1-3-9 and Figure 1-3-4 summarize these results. The contact angles fall as the reaction proceeds. This decrease is likely a result of polar groups introduced in the workup (see below) and the reaction of the lithiated polymer with oxygen or carbon dioxide: the increase in oxygen (532 eV) is apparent in the XP spectra. The XP spectra also indicate the complete loss of CF_2 (295 ev) and Cl (277 eV). The UV-Vis spectra indicate a gradual increase in absorbance at 270 nm which can be attributed to conjugated double bonds. Gravimetric analysis indicates a steady decrease in mass. Secondary electron images show that there is no change in microtopograpy at a resolution of 60 Å and ATR-IR spectra exhibit no changes. The sampling depth at these ATR-IR conditions (Ge, 45^{o}) is 0.5 micrometers at 1500 cm^{-1}. These results by themselves indicated only that a somewhat surface-selective reaction has taken place and suggested very little concerning the structure of the product. Except for the appearance of

Table 1-3-9. Contact Angle, UV-Vis, and Gravimetric Changes in PCTFE Film upon Reaction with Methyllithium

Reaction Time (minutes)	Contact Angles $\theta_{adv}/\theta_{rec}$ (H_2O)	Absorbance (270 nm)	Δ M (-μg)
0	104±1/80±1	0	-
2	90±1/54±1	0.02	3±1
10	84±1.5/50±1	0.06	9±1
20	80±1/49±2	0.10	19±1

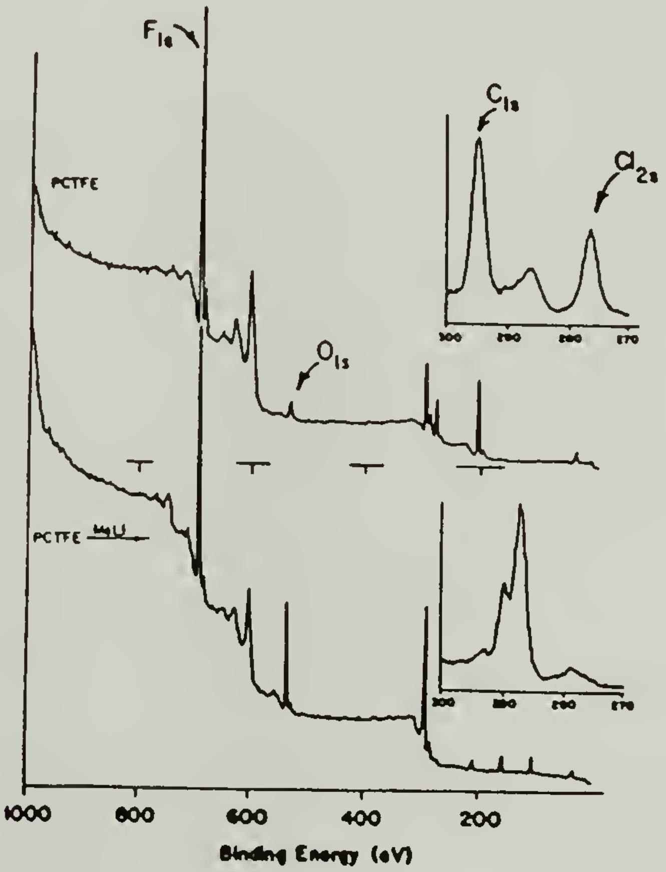


Figure 1-3-4. XP spectra of PCTFE film and PCTFE film after reaction with Methyllithium.

unsaturation, the results are consistent with the reported mechanism (Scheme 1-3-1)[8].

It was possible to gain further insight into the structure of this material as well as the mechanism of the reaction by performing similar experiments on low molecular weight oil in diethyl ether solution. When PCTFE oil is treated with 0.5-1.2 equiv (based on monomer units) of methyllithium in diethyl ether at -78°C a series of reactions occur. Analysis of the gaseous products by GC and IR indicates that methyl chloride and no methyl fluoride is produced. Analysis of the salt produced show that it is composed of lithium fluoride and lithium chloride in a molar ratio of 6.0:1. Quantitative data for these reactions are compiled in Table 1-3-10. UV-Vis spectra of the polymeric product indicate the formation of conjugated double bonds (see below). The infrared spectrum of the polymeric product (Figure 1-3-5) exhibits absorbances consistent with the presence of methyl groups (2980, 2885, 1450, and 1380 cm^{-1}), carbonyls with adjacent fluorine (1790 cm^{-1}) and conjugated carbon-carbon double bonds (1750-1600 cm^{-1}).

Table 1-3-10. Quantitative Analysis of Products of PCTFE Oil-Methyllithium Reactions

equiv. of MeLi/ equiv of PCTFE	F equiv	Cl equiv	MeCl equiv
0.50	0.38±0.04	0.12±0.01	0.53±0.15
0.68	0.55±0.06	0.13±0.01	0.44±0.12
1.2	1.14±0.10	0.19±0.02	0.93±0.09

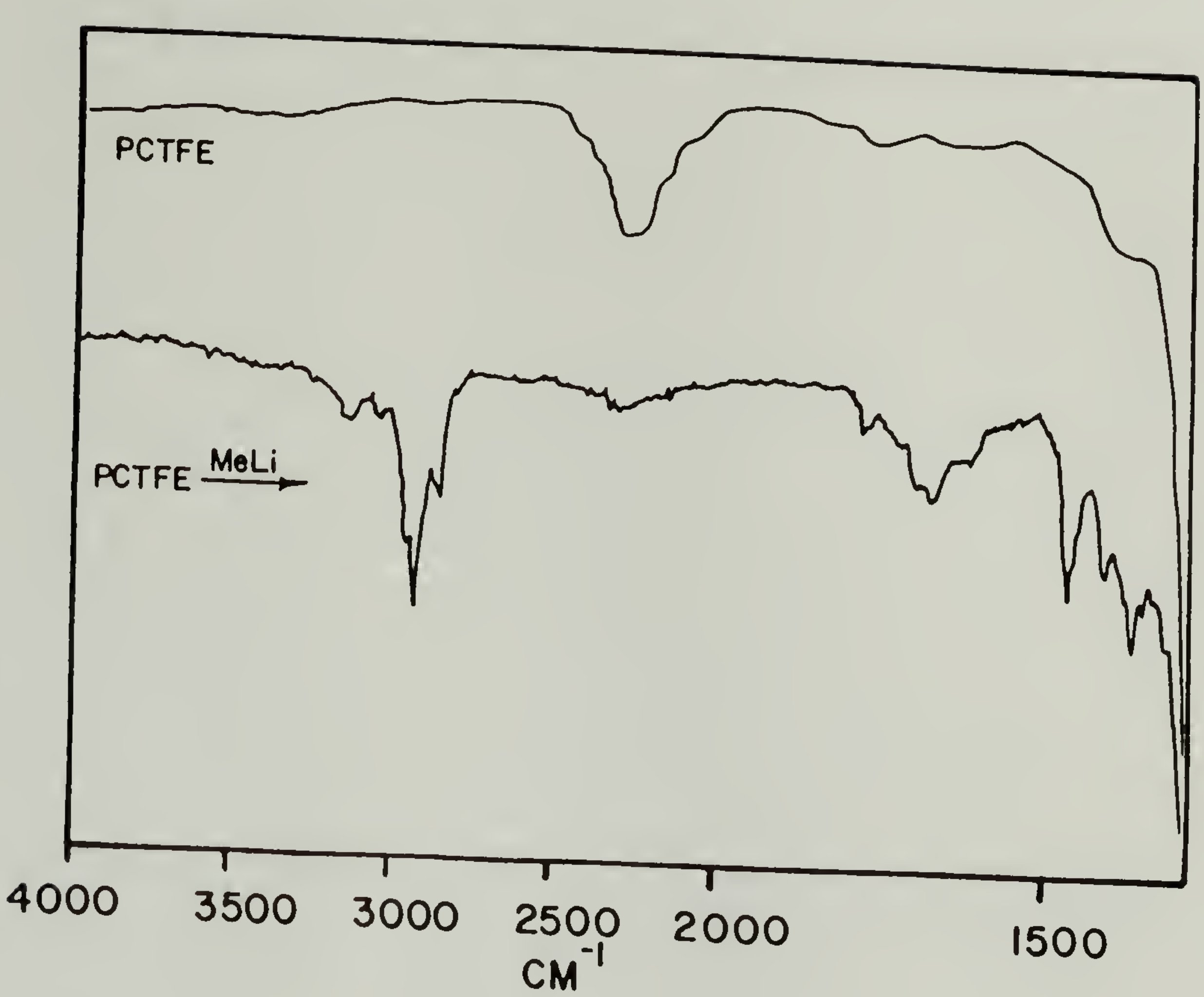


Figure 1-3-5. Infrared spectra of PCTFE oil before and after reaction with 0.5 equiv. of methyllithium

The presence of weak bands above 3000 cm^{-1} may indicate vinyl protons, but these were not observed by NMR and must be present in only small amounts. The proton NMR spectrum (Figure 1-3-6) exhibits two resonances: the one centered at 1.45 ppm is due to the methyl groups and the one at 2.98 ppm is due to the methoxy groups introduced in the work up (see below). Obtaining accurate quantitative data for methyl chloride production was difficult due to its volatility. Analogous experiments using phenyllithium were performed as chlorobenzene analysis is straightfoward. These data are compiled in Figure 1-3-7.

The reported mechanism[8] (Scheme 1-3-1) is not consistent with these data. It does not explain the introduction of unsaturation or the production of methyl chloride, chlorobenzene, and fluoride and the

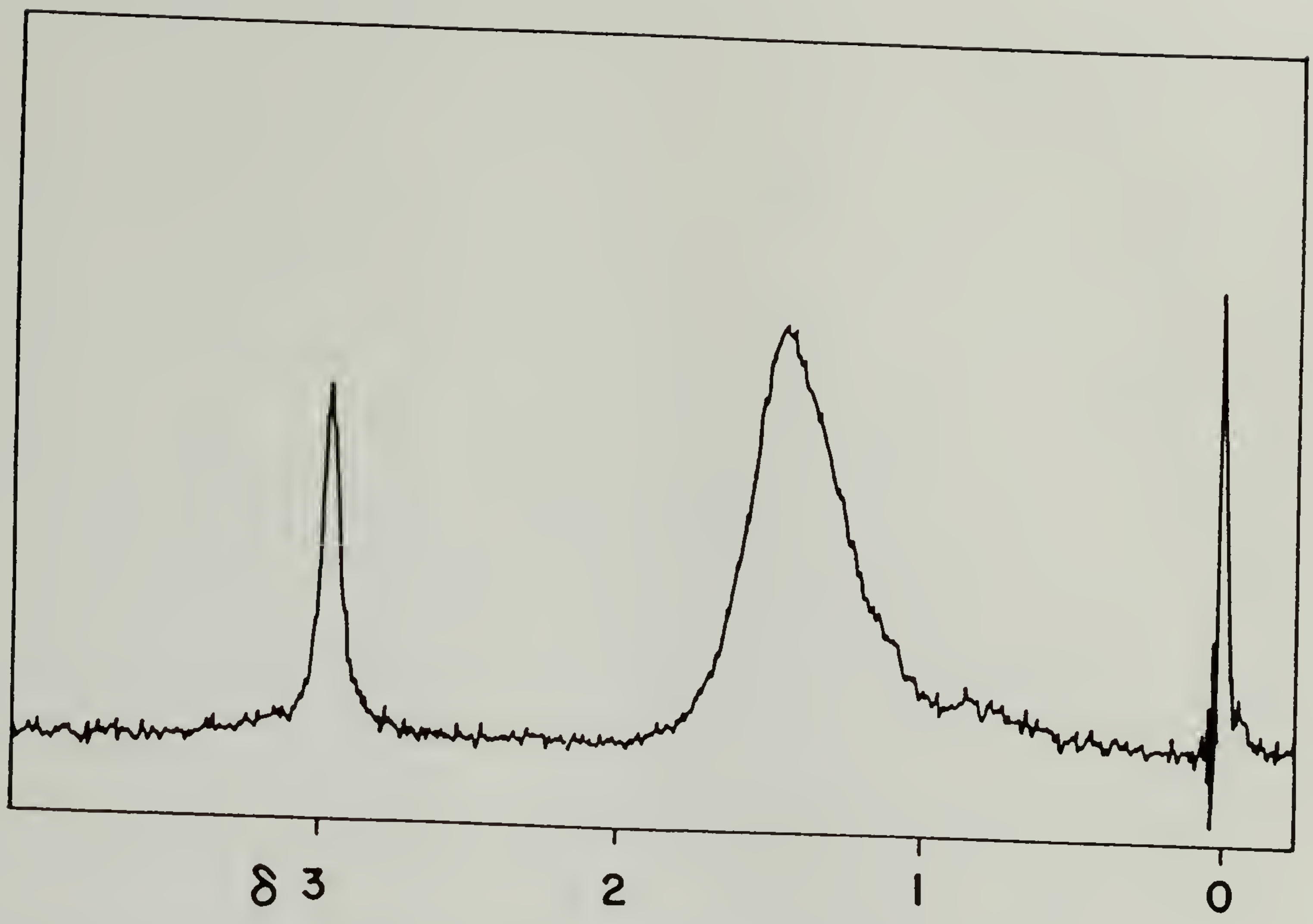


Figure 1-3-6. ^1H NMR spectrum (90 MHz) of PCTFE oil after reaction with 0.5 equiv. of methyllithium and methanol workup.

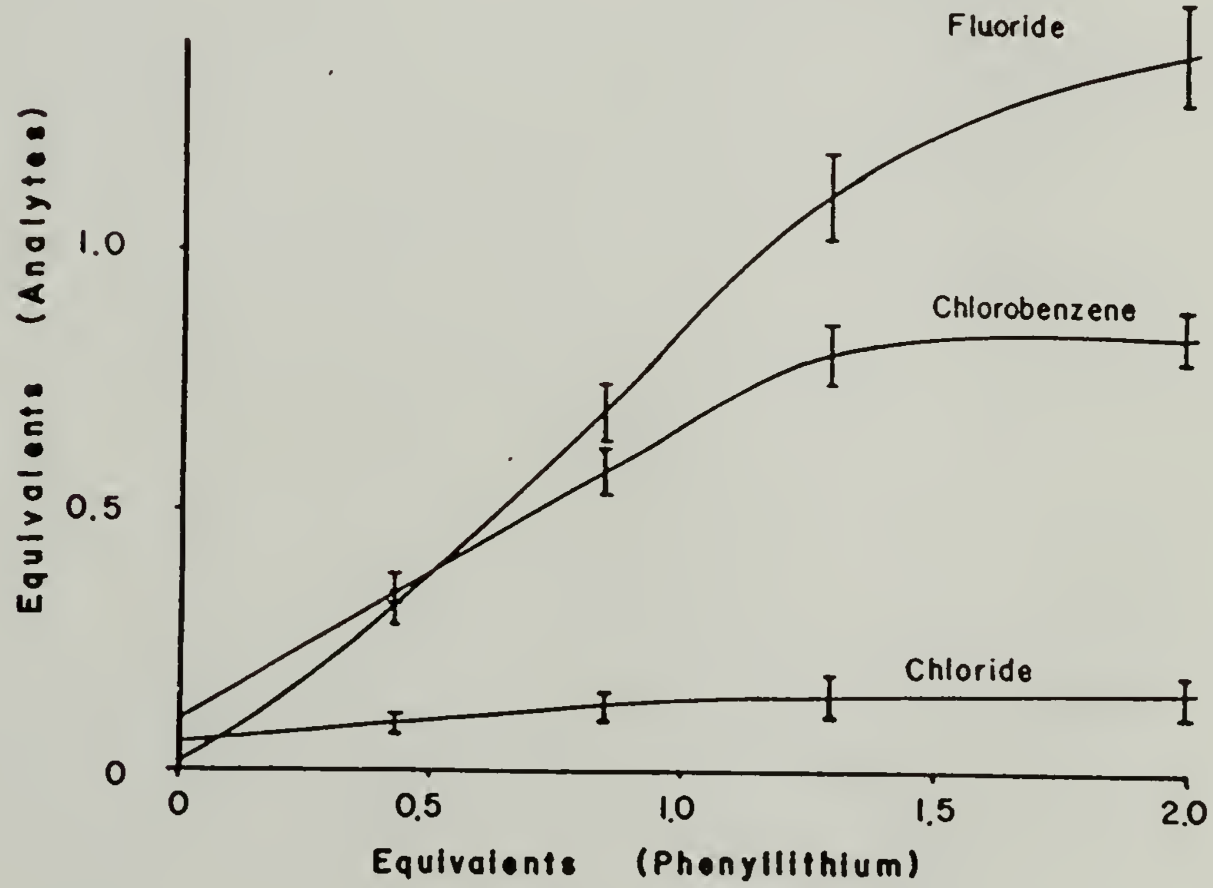
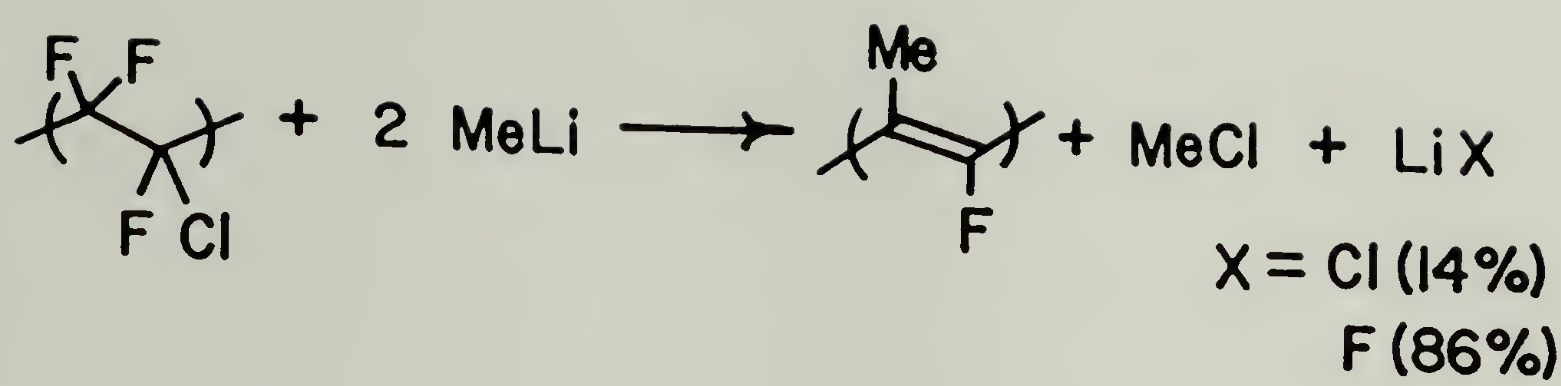
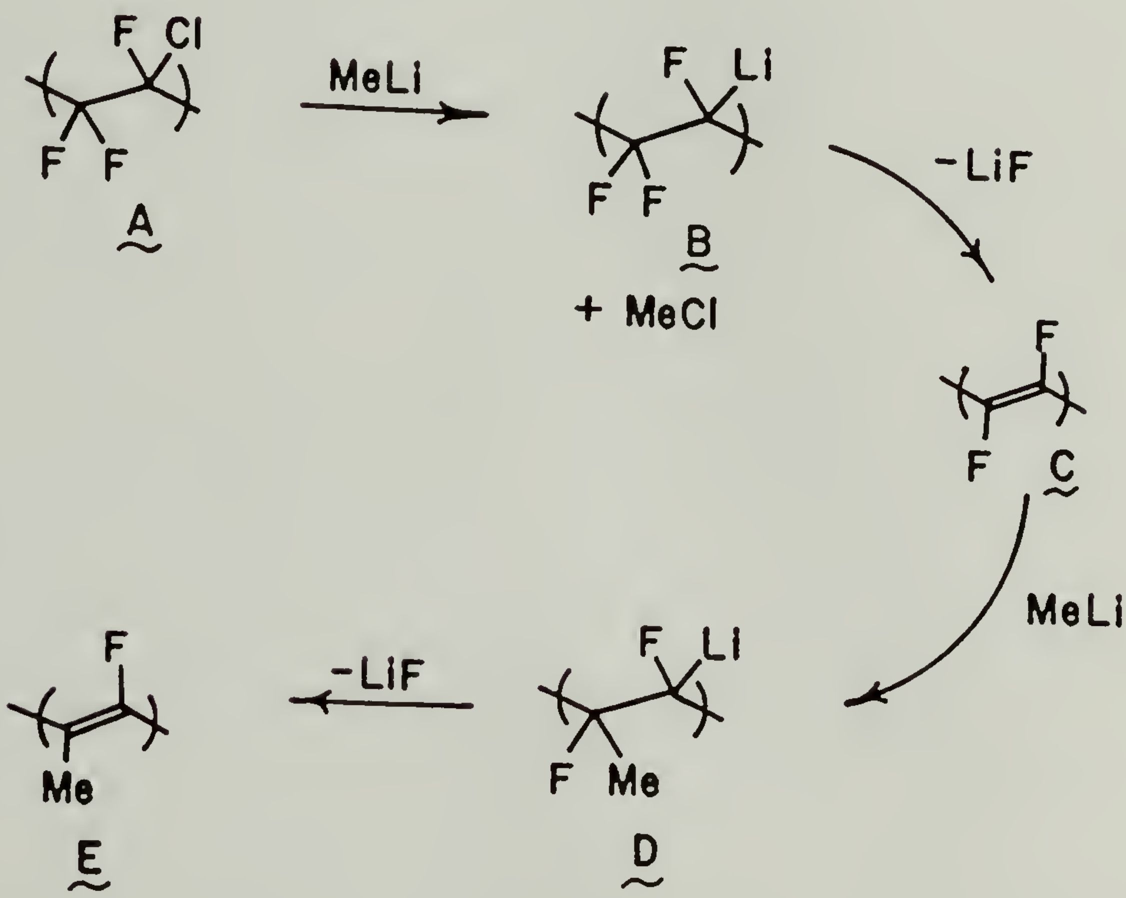


Figure 1-3-7. Plot of Quantitative Analysis of Products Vs. Quantity of Phenyllithium Employed.

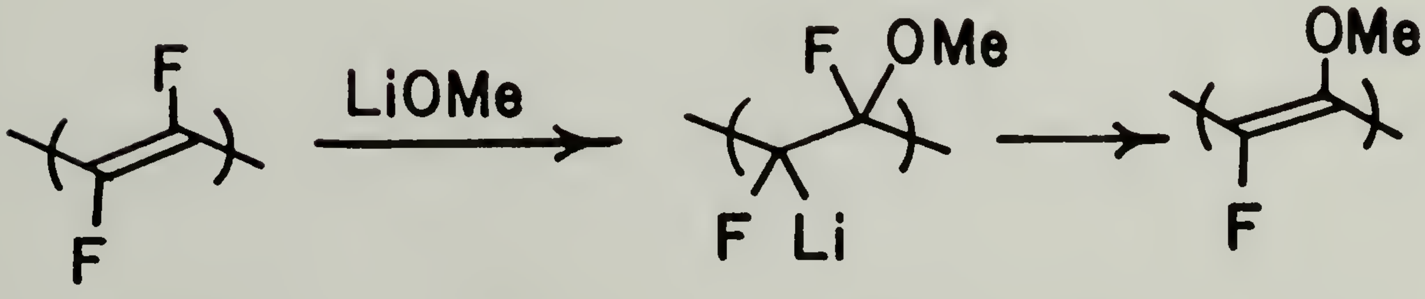
data in Table 1-3-10 and Figure 1-3-7 indicate that the reactions that lead to these products are the principle pathways. That the surface and solution reactions do not proceed by different mechanisms was verified by treating PCTFE powder with phenyllithium and observing chlorobenzene (0.3 mmol) and fluoride (could not quantitate). A more consistent mechanism is that the modification takes place by the series of reactions depicted in Scheme 1-3-2; the modified product consists primarily of a combination of the structures indicated as C and E. The first step is a metal-halogen exchange reaction forming B and methyl chloride. B is not stable[10] and eliminates fluoride to form C and lithium fluoride. Lithium chloride is also produced in lesser amounts: this can be attributed to the 2% head-to-head[11] linkages and to the formation of rings. The lithium fluoride:lithium chloride ratio (6.0:1) suggests ring formation is important. B (or D) could react with oxygen or carbon dioxide to generate the observed carbonyl groups, but this reaction is not general for electrophiles: Benzyl chloride does not react and we infer that neither does methyl chloride and that methyl groups are not introduced via this reaction sequence. A second molecule of methyllithium adds to C, which subsequently decomposes to form E and more salt. Equation 1-3-3 summarizes the reaction stoichiometry. The methanolic workup is responsible for the incorporation of methoxy groups (Figure 1-3-6). Addition of alkoxides to fluorinated olefins is facile[12] and could occur as depicted in equation 1-3-4. E (Scheme 1-3-2) could undergo the same chemistry.



Equation 1-3-3. Stoichiometry for the Reaction of PCTFE Oil with Methyllithium.



Scheme 1-3-2. Proposed Series of Reactions by Which Methyllithium Reacts with Poly(chlorotrifluoroethylene) Oil.



Equation 1-3-4. Reaction of Fluoroolefin with Alkoxide.

Generalization of these solution reactions to the surface modification is (as discussed above) dangerous. The data presented in Table 1-3-9 and Figure 1-3-4 are consistent with the solution reactions, and the reactions of PCTFE powder suggest similarities. A

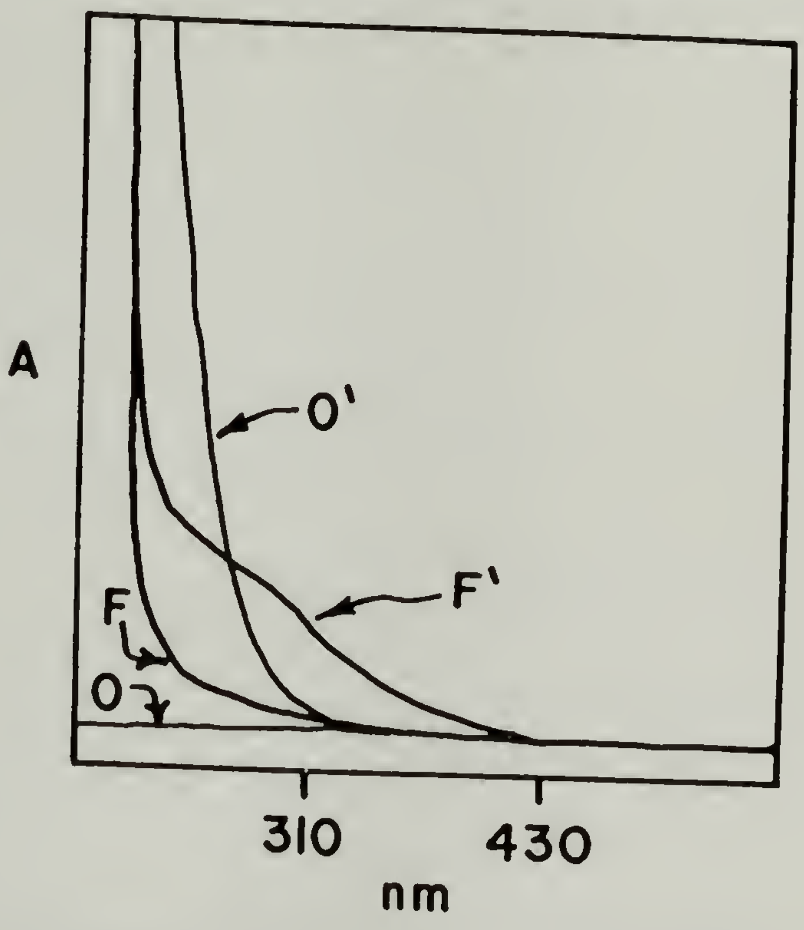


Figure 1-3-8. UV-Vis spectra of PCTFE oil (O), PCTFE oil after reaction (0.5 equiv.) with methyllithium (O'), PCTFE film (F), and PCTFE film after reaction (5 min) with methyllithium (F').

difference exists with regard to the UV-Vis spectra (Figure 1-3-8). The film shows relatively more absorbance at higher wavelengths (dienes and trienes). This could be due to different reactions or to different extents of reaction: that the film surface reaction involves a large excess of lithium reagent suggests the latter.

The surface modification reaction appears to be less surface selective than the two-phase dehydrofluorination of poly(vinylidene fluoride): it does not, however, exhibit autocatalysis and pitting.

If the stoichiometry in equation 1-3-3 is assumed, the mass losses at 2-, 10-, and 20-min reaction times correlate with average reaction depths of 45, 136, and 285 Å, respectively. The contact angle data further suggest that the reaction is not surface selective: changes within the sampling depth (several angstroms) of this technique are occurring after an average of many tens of angstroms of material have reacted.

Organometallic Modification of PCTFE: Introduction of Polar Groups.

Introduction. The modification of PCTFE with methyllithium and phenyllithium was not intended as a means of introducing methyl and phenyl functionalities onto the PCTFE surface. Instead these reactions were examined with the objective of gaining information about the mechanism and products of this reaction. This information was important for understanding the chemistry involved. Three important conclusions were reached: 1) The reaction is not autocatalytic. 2) Incorporation of functional groups involves two steps: lithium-halogen exchange, which results in unsaturation upon decomposition of the unstable lithiated polymer; and reaction of the unsaturated fluoroolefin with a second molecule of lithium reagent. This means that the relative change in UV-Vis absorbance can be used to follow the modification reaction and this change is related to the thickness of the modified layer. Whether or not the two steps are occuring at competitive rates cannot be determined from UV-Vis data alone since the absorbance is actually monitoring the first step, formation of the fluoroolefin, which involves electron transfer. The competitiveness of the two steps can involves electron transfer. The relative rates of the two steps can be determined only if a direct means of monitoring functional groups is available. XPS has the sensitivity to monitor surface reactions, however, it was not useful for this purpose, in this case, since methyl or phenyl groups cannot be readily observed in the XPS.

The utility of this organometallic reaction would be slight were it not for the fact that lithium reagents and Grignard reagents can be prepared from molecules containing protected functional groups. This makes the procedure flexible and a wide variety of functional groups can be introduced in two steps: reaction of the reagent with PCTFE and then treatment of the modified PCTFE with conditions which are known to effect deprotection. Grignard reagents can be prepared from a wide variety of ethers and acetals; these were used to introduce hydroxyl and aldehyde functional groups.[13] Lithium reagents can be prepared from a wide variety of protected functional groups[13] such as: carboxylic acid (oxazoline), aldehyde (dithiane) and hydroxyl (ether) functionalities. Using these lithium reagents it was possible to introduce specific functional groups onto the PCTFE surface.

Results and Discussion.

Reaction of PCTFE With Grignard Reagents. Introduction of Hydroxyl Groups.

Hydroxyl groups were introduced using the Grignard reagents prepared from either bromopropyltetrahydropyranyl ether (BrMgPTHPE) or bromopropyethyl acetaldehyde acetal (BrMgPAA). BrPTHPE was prepared from 3-bromo-1-propanol and dihydropyran. BrPAA was prepared from 3-

bromo-1-propanol and ethyl vinyl ether. The Grignards were prepared as THF solutions by reacting the halide with magnesium metal and the Grignards were used promptly after preparation.

When PCTFE film was reacted in THF with either reagent at room temperature, no visible change in film color was observed. The contact angle data was not reproducible and the contact angle data observed for different experiments covered a broad range (Table 1-3-11). These results indicate that a reaction has occurred on the surface and that the new surface is higher in energy. That hydroxyl groups were introduced was inferred from the analogous reaction using PCTFE oil in ether solution. The absorbances in the IR at 2930, 2870, 1370, and 1260 cm^{-1} for the BrMgTHPE modified oil and 2960, 2870 and 1375 cm^{-1} for the BrMgPAA modified oil correspond to the alkyl vibrations of the protected hydroxyl functionality and upon deprotection an absorbance at 3300 cm^{-1} corresponding to the hydroxyl group was observed.

Table 1-3-11. Contact Angle Data for the Reaction of PCTFE with Grignard Reagents Containing Masked Hydroxyl Groups.

Substrate	Contact Angle Range (degrees) Advancing	Receding
PCTFE-PAA	89±2 to 96±1	35±1 to 47±2
Hydrolyzed PCTFE-PAA	81±2 to 85±2	34±1 to 37±2
PCTFE-PTHPE	84±1 to 105±1	45±1 to 75±1
Hydrolyzed PCTFE-PTHPE	67±1 to 90±2	21±10 to 48±6

A problem with this modification was that the same surface was not reproducibly prepared. This meant that, unless a large number of substrates were simultaneously prepared from the same solution, the reaction was not suitable for the preparation of surfaces suitable for surface studies.

Introduction of Aldehyde Groups.

Aldehyde groups were introduced using the Grignard prepared from 2-(2-bromoethyl)-1,3-dioxolane (BrMgEDO). Unlike the previous Grignard reagents, the BrMgEDO was easily prepared and reacted reproducibly to give the same surface repeatedly. The surface containing the protected aldehyde had an increased surface energy (advancing = $87 \pm 3^{\circ}$, receding = $50 \pm 1^{\circ}$). Upon deprotection the contact angle decreased further (adv = $80 \pm 1^{\circ}$, rec = 45 ± 1) which indicated that the surface was even more polar, consistent with the deprotection of the aldehydes. The film did not exhibit any visual changes; however, the XPS (Figure 1-3-9) does indicate that the surface was homogeneously modified with respect to the 50 Å sampled by the technique. The identification and quantitation of the amount of functionalization by XPS is not a trivial problem. The only observable changes are the decrease in fluorine and chlorine intensity and an increase in the oxygen intensity. If the assumption was made that the only source of oxygen introduced in the reaction arises from the introduction of the protected functional group, then XPS can be used to estimate the degree of functionalization. This assumption is not always valid; the oxygen intensity increased even when methyllithium was used. Although the surface appears to be a good

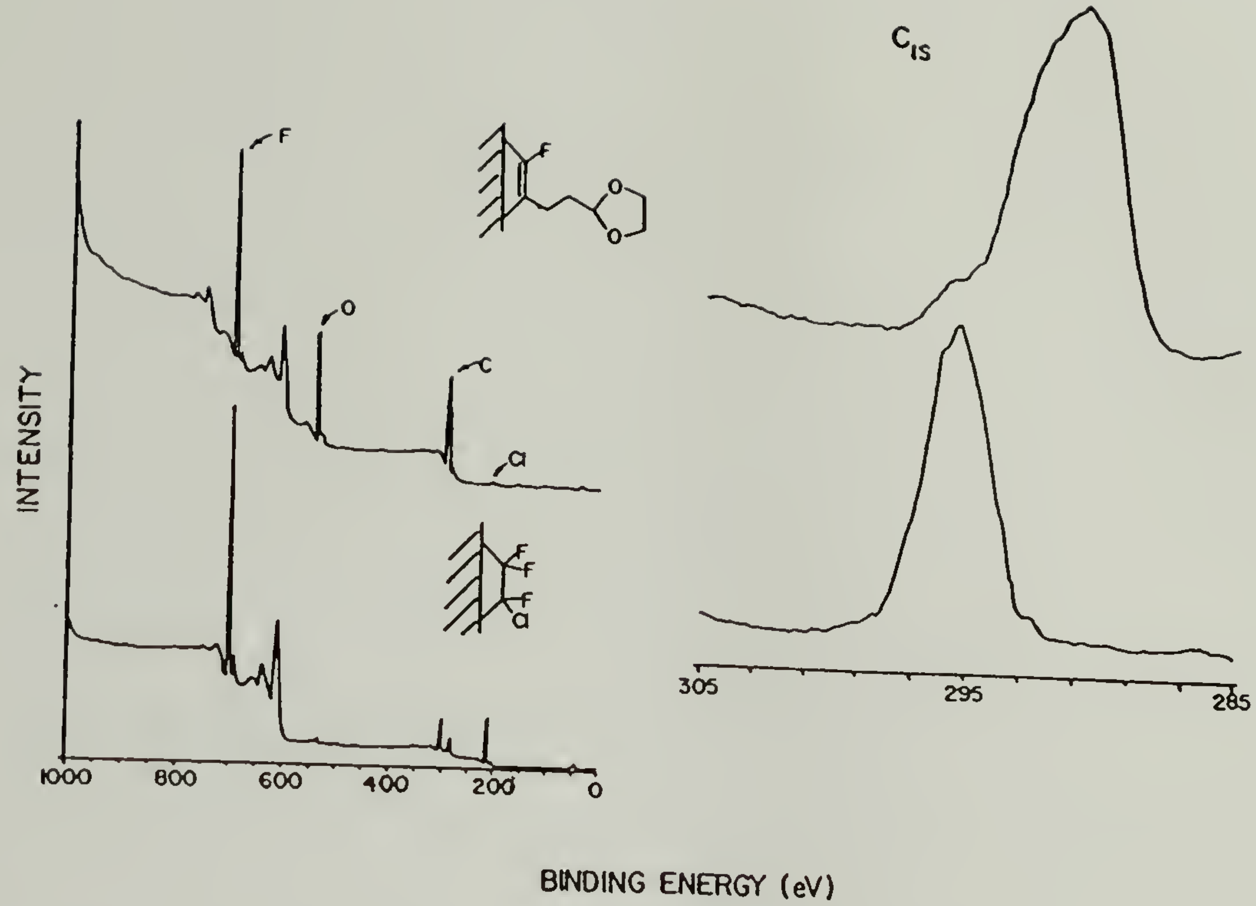


Figure 1-3-9. XP spectra of PCTFE film and PCTFE film after reaction with the Grignard prepared from 2-(2-bromoethyl)-1,3-dioxolane.

substrate for further study it does pose an uncertainty as to the quantitation of oxygen by XPS, and the presence of aldehydes cannot be unambiguously indicated. However the presence of aldehyde functionality can again be inferred from the analogous reaction on low molecular weight PCTFE oil in solution. The peaks in the IR spectrum at 2930, 2860 and 1465 cm^{-1} correspond to alkyl vibrations in the protected aldehyde and the broad absorbance (1600 - 1700 cm^{-1}) corresponds to C=C unsaturation. Upon deprotection a large peak corresponding to carbonyl groups was introduced at 1720 cm^{-1}. In addition the proton NMR exhibits resonances at (1.65 and 2.25 ppm broad overlapping (s), 3.25 ppm (d) and 4.50 ppm (s)) which are consistent with the introduction of the protected functionality. Upon deprotection a peak at 8.92 ppm, corresponding to the aldehylic proton, was observed.

Reaction of PCTFE With Organolithium Reagents.

Introduction.

The use of Grignard reagents to modify PCTFE was not entirely satisfactory. The major difficulties were: 1) The lack of a specific XPS label element; 2) the low solubility of the reagents in alkane solvents; 3) the long times required for the formation of the Grignard reagents; and 4) the low reactivity of Grignards at low temperatures. Lithium reagents were prepared with the same purpose in mind; to introduce functional groups in two steps. To facilitate XPS analysis the lithium reagents were chosen, where possible, to contain an element which can only be introduced through reaction with the reagent. Then, the removal of the protecting group will result in removal of the element as well as increase the oxygen content; these changes are readily monitored by XPS.

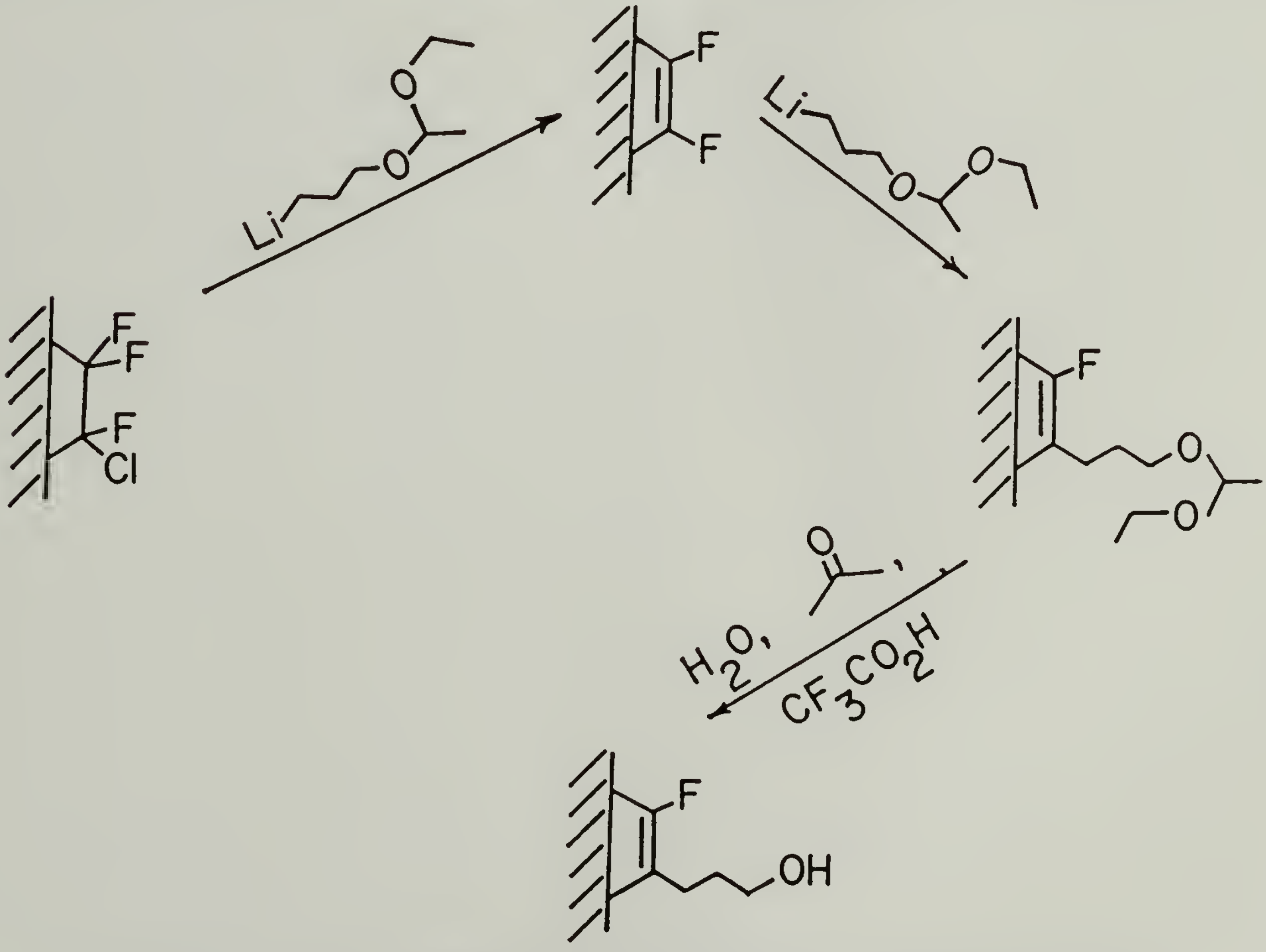
Lithium reagents have an added advantage in that they also retain much of their reactivity at low temperatures making possible a study of the temperature dependence of surface reactions. In addition many lithium reagents have some solubility in alkane solvents and this made possible the study of solvent effects on the surface reactions.

Results and Discussion.

Reaction of PCTFE With Lithiopropylethyl Acetaldehyde Acetal.

LiPAA was prepared using Eaton's procedure[14] as well as by lithium-halogen exchange in heptane at -78°C. The latter method was faster and more convenient. With this method it was possible to prepare

LiPAA solutions over a wide range of heptane-THF compositions, down to 50% THF (below which the solution is heterogeneous). When PCTFE film was reacted with excess LiPAA in THF and THF-heptane mixtures, contact angle data, XPS, UV-Vis and ATR-IR spectroscopies, and gravimetric analyses indicated that a reaction had taken place (Equation 1-3-5). The XP survey spectra (Figure 1-3-10) are consistent with the series of reactions presented in equation 1-3-5. Upon reaction with LiPAA there is a large relative decrease in fluorine (685 eV) as well as an increase in oxygen (532 eV). The relative intensities of oxygen to carbon (285 eV) change slightly upon deprotection. The change is not pronounced enough to unambiguously assign the oxygen and therefore the



Equation 1-3-5. Reaction of PCTFE with Lithiopropylethyl Acetaldehyde Acetal.

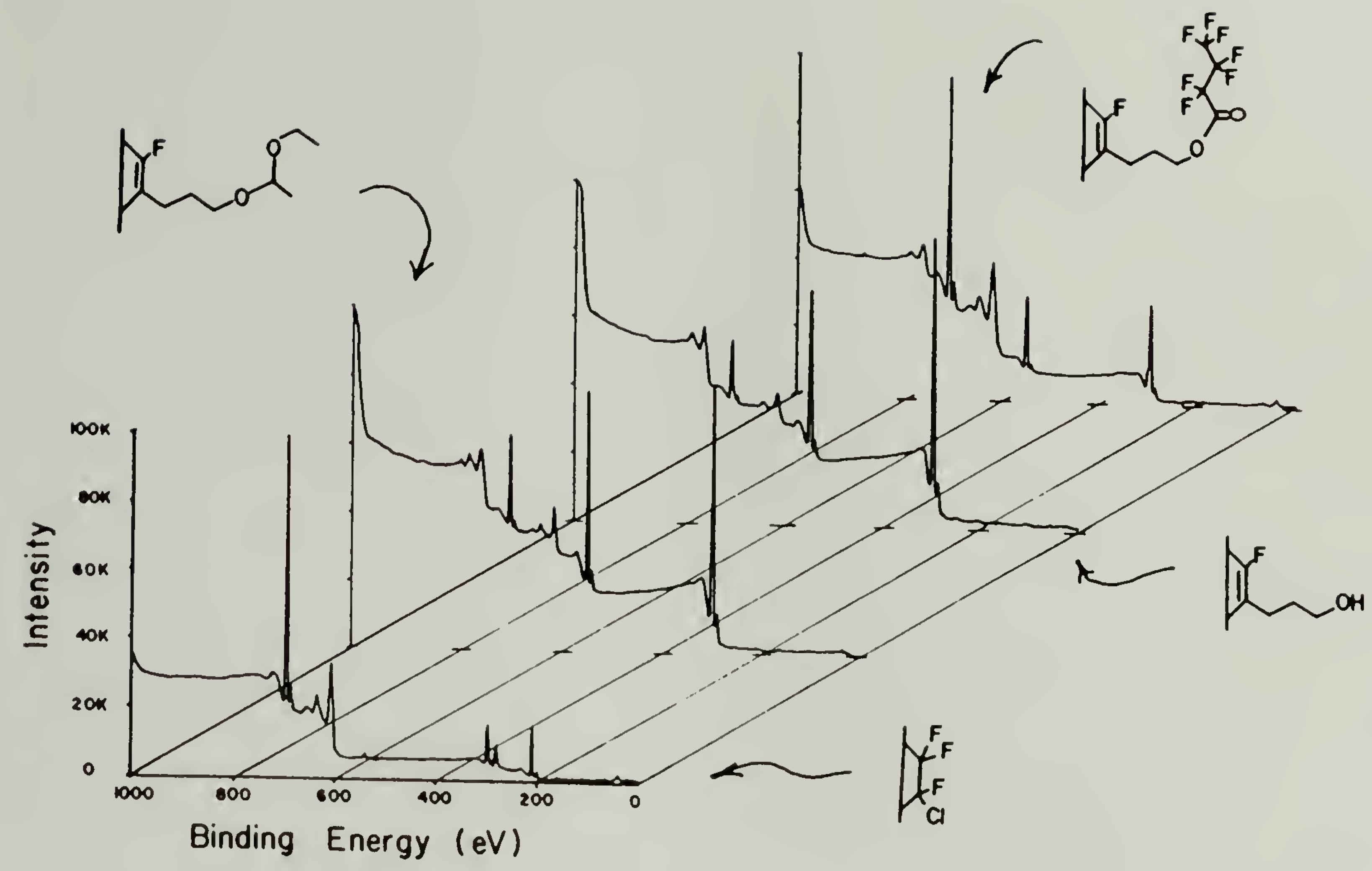


Figure 1-3-10. XPS Survey: Introduction of Hydroxyl Groups.

surface was derivatized with heptafluorobutyryl chloride. Reaction was indicated from the large increase in fluorine relative to the decrease in oxygen and carbon. These changes are more easily observed in the expanded C_{1s} region (Figure 1-3-11). The peak corresponding to the highly oxidized carbon (CF_2 and CFCl at 295 eV) was completely removed and a single complex peak to lower binding energy was observed (this peak is complex and contains unresolved alkyl carbon as well as olefin contributions). Upon reaction with the label, peaks corresponding to CF_3, CF_2 and an assymetric CH_2 peak are observed; the ratios of the areas correspond well to a surface which has been completely esterified with the heptafluorobutyryl chloride. These changes in the XPS are consistent with the introduction of both the protected hydroxyl

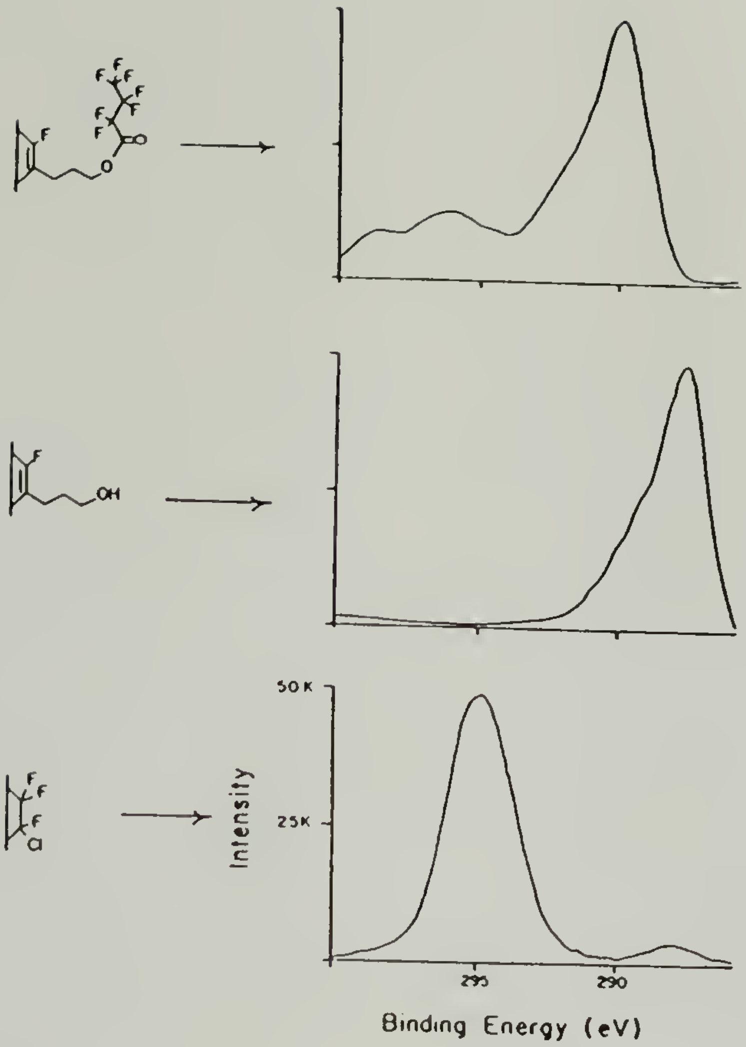


Figure 1-3-11. XPS C_{1s} Expanded Region for the PCTFE-OH Labelling Experiment.

and deprotected hydroxyl groups. Although XPS, when used in conjunction with another analytical method, is often helpful in determining the reaction depth, it was only possible to obtained a rough estimate for this surface. The C_{1s} expanded region was completely devoid of the peak at 295 eV for the surfaces produced at all temperatures except -78°C; therefore, the reaction depth has progressed beyond the XPS sampling depth (50 Å) for all except the reaction at -78°C. Contact angle data (Table 1-3-12) indicate that the surface was rapidly reacted and was homogeneous with regard to the sampling depth of this technique; the contact angles decrease upon reaction with the LiPAA and decrease further upon deprotection.

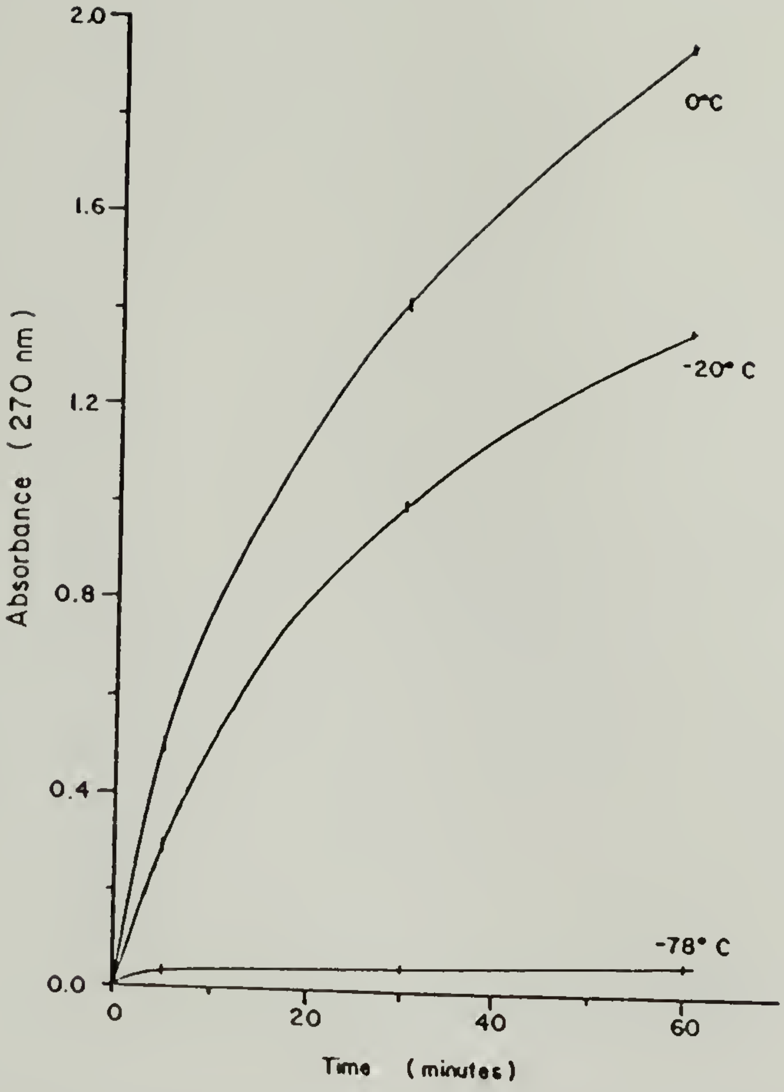


Figure 1-3-12. Plot of absorbance vs. reaction time for the reaction of PCTFE film with LiPAA.

UV-Vis spectroscopy when combined with XPS proved very useful for estimating the depth of the modifications. The relative amount of material reacted during the modification was obtained from the UV absorbance (270 nm). The graph in Figure 1-3-12 summarizes the UV results for the reactions at 0, -20 and -78^{o}C. The plots illustrate the temperature dependance of this reaction: The reaction progresses 30 times further at -20^{o}C than it does at -78^{o}C, and it increases further still upon raising the temperature to 0^{o}C. Additionally, it appears that the absorbance increases with reaction time for all temperatures; the longer the surface is reacted the deeper the reaction progresses. This increase in the depth of the reaction should be observable in the XPS for the reaction at -78^{o}C but it was not.

Table 1-3-12. Contact Angle Data for the Reaction of PCTFE with LiPAA.

Surface	Contact Angles (degrees) Obtained for the Reaction at:			
	$-78^{o}C$ and		$0^{o}C$	
	Advancing	Receding	Advancing	Receding
PCTFE+LiPAA (5 min)	78±2	49±2	95±3	0
after hydrolysis	71±2	20±2	64±2	19±2
PCTFE+LiPAA (30 min)	77±2	46±2	98±2	0
after hydrolysis	71±2	20±2	73±1	22±1
PCTFE+LiPAA (60 min)	73±1	42±1	98±3	0
after hydrolysis	69±1	19±1	66±3	20±3

Instead the small quantity of CF_2 observed after a reaction time of 5 minutes was still observed after a reaction time of 60 minutes and the fact that the UV-Vis absorbance increased 75% in the same time period strongly suggest that the reaction is not progressing in a uniform manner.

Based upon this information, the reaction depth obtained at $-78^{o}C$ was at least 50 Å, placing the reaction depth at $-20^{o}C$ at roughly 1500 Å (30 times the value obtained at $-78^{o}C$). This extensive modification should be readily observable using ATR-IR spectroscopy. The sampling depth (depth at which the evanescent wave decays to 90% of its value at the surface, $2d_p$) for the ATR-IR experiment using a germanium 45^{o} IRE at 3000 cm^{-1} is 420 nm. The spectra in Figure 1-3-13 indicate that indeed a very large quantity of the protected functionality was present when the surface was reacted at $-20^{o}C$ and that a much smaller quantity was introduced when the reaction was run at $-78^{o}C$. Another estimate for the reaction depth (at $-20^{o}C$) was

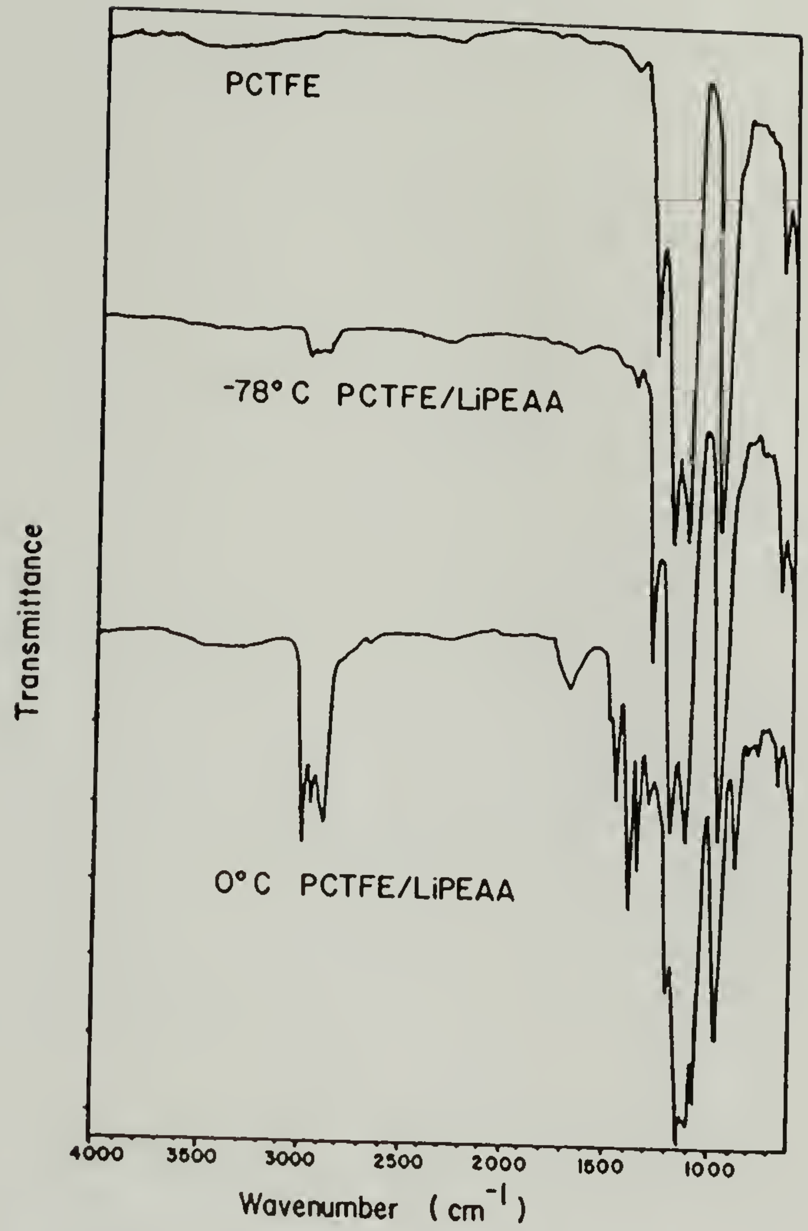


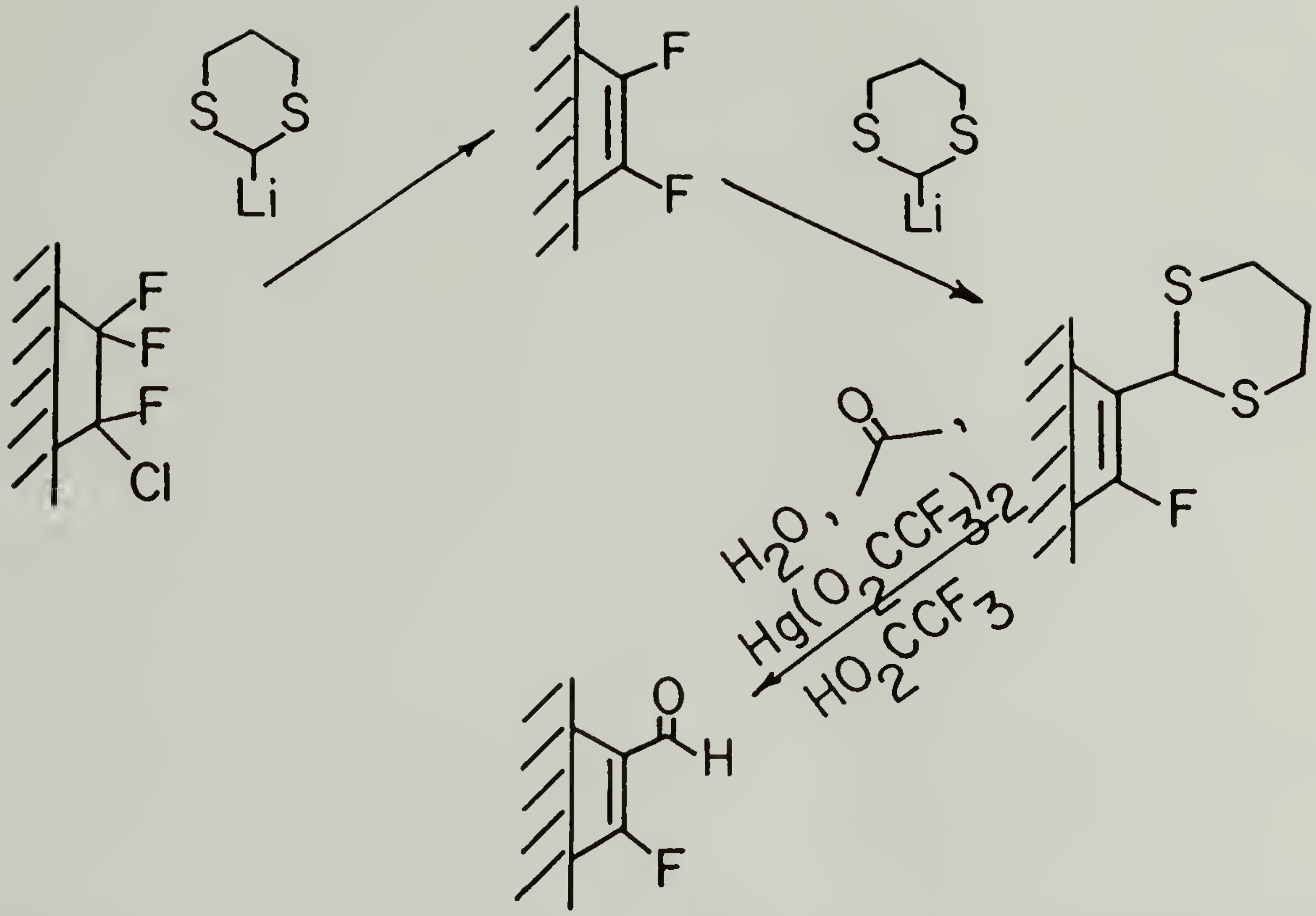
Figure 1-3-13. ATR-IR spectra for PCTFE film and PCTFE film reacted with Lithiopropylethyl Acetaldehyde Acetal.

obtained from the ATR-IR spectrum. The relative change in the C-Cl vibration at 900 cm^{-1} was calculated to be 20%. This value was related to the sampling depth at 900 cm^{-1} (1.4 micrometers) giving an estimate of 2800 Å. The film reacted at -78^{o}C did not observably change in the C-Cl region and this prevented the same method from being applied. However the UV-Vis data can help to provide an estimate; based upon the ATR-IR-obtained value for the reaction at -20^{o}C and the relative absorbance difference, the layer formed at -78^{o}C is roughly 30 times smaller or 93 Å. This value is reasonable and correlates pretty well with the XPS-derived result. It was also apparent from the combination of ATR-IR data and XPS data that the reaction at -78^{o}C did not progress in a uniform reaction path; the ATR-IR, which samples a much thicker layer than XPS, did change in intensity with reaction time while the XPS did not change indicating that again further reaction was occurring beyond the XPS sampling depth.

The experimental results indicate reaction depth can be dramatically affected by temperature. Also the results indicate that this reaction is not surface selective; changes are occurring into the bulk in an irregular fashion as the reaction time is increased. This method illustrates how analytical procedures, which combine reaction kinetics and direct observation, can be used to study reactions at surfaces. Also, this method exemplifies the problems of identification encountered when oxygen is the only distinguishing element introduced and used to identify the protecting group.

Introduction of Aldehyde Functionality Using 2-Lithio-1,3-dithiane.

The work presented in this thesis has for its objectives the preparation and characterization of two-dimensional arrays of polar functional groups. Prior work on the aldehyde surface involved the use of Grignard reagents. Though this reaction was facile, the characterization contained certain ambiguities, the most telling being the identification of the incorporated oxygen. This reaction overcomes this difficulty and presents a system which can be characterized completely. When PCTFE film was reacted with LiDT in THF and THF/Heptane mixtures, contact angle data, XPS, UV-Vis, ATR-IR and gravimetric analysis indicate that a surface selective reaction has occurred (Equation 1-3-6). The XPS survey (Figure 1-3-14) clearly



Equation 1-3-6. Reaction of PCTFE with 2-Lithio-1,3-dithiane.

show the incorporation of dithiane (sulfur at 164 eV) which upon reaction with mercuric salts, was removed and replace by oxygen (2S=10). The presence of the aldehyde functionality was indicated in this manner and, unlike the hydroxyl surface, it was not necessary to derivatize the aldehydes in order to demonstrate their presence.

That this reaction is surface selective is indicated by contact angles, XPS and UV-Vis kinetics. The contact angles reach their minimum value and minimum scatter after short reaction times (Table 1-3-13). Therefore the outer few angstroms are rapidly and uniformly reacted. UV-Vis spectroscopy samples the entire film and it too suggests that the surface has reacted completely after 5 minutes and no further increase in absorbance with time was observed. Variable angle XPS data is also consistent with a surface selective reaction.

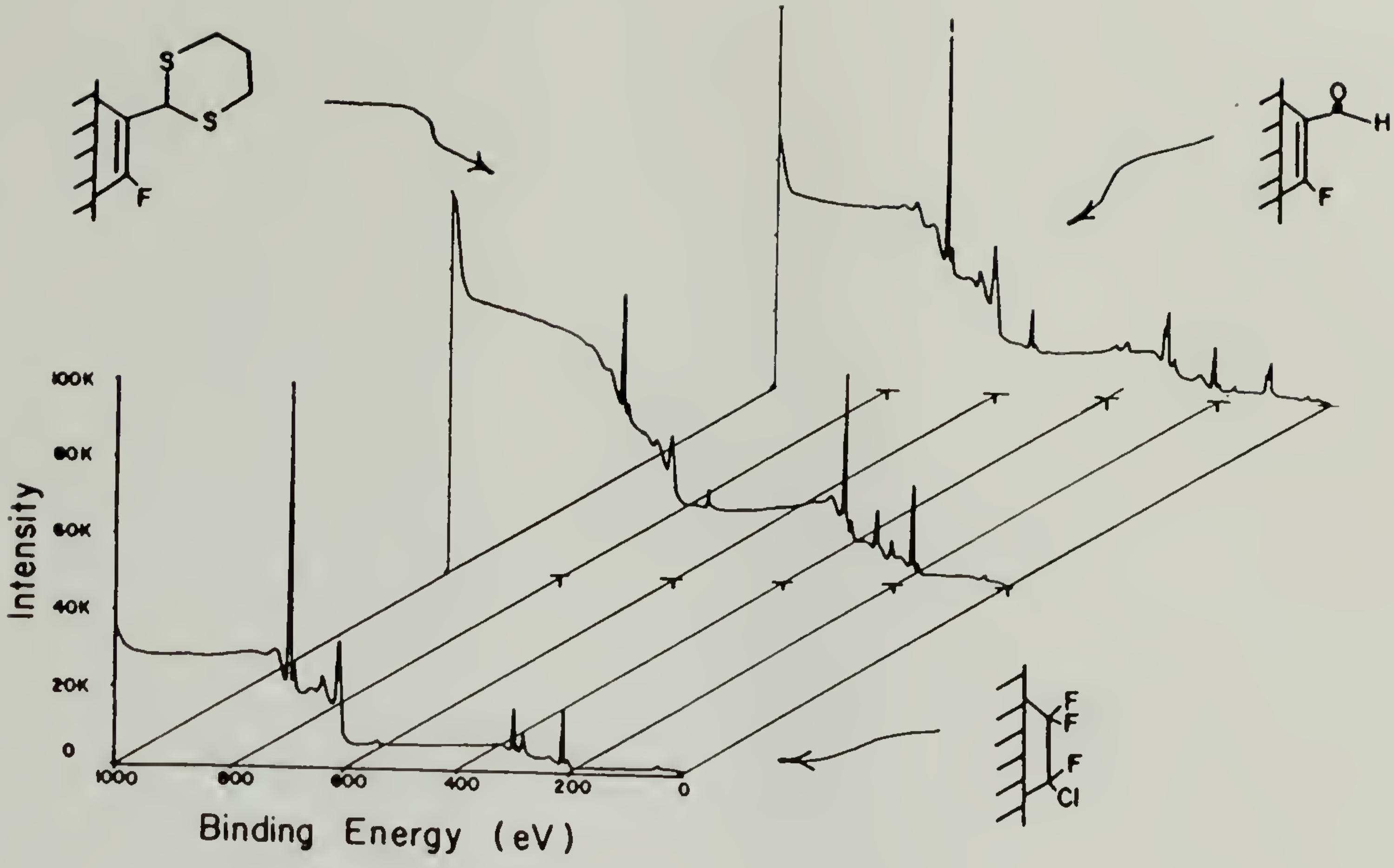


Figure 1-3-14. XPS Survey for the Introduction of Aldehyde Groups.

Table 1-3-13. Contact Angle Data for the Reaction of 2-Lithio-1,3-dithiane with PCTFE Film.

	Contact Angles (degrees) for the reaction at:			
	-78°C	and	0°C	
Surface	Advancing	Receding	Advancing	Receding
PCTFE+LiDT (5 min)	90±2	63±2	82±1	45±2
after deprotection	80±2	36±1	79±1	22±1
PCTFE+LiDT (30 min)	89±1	64±2	82±1	44±1
after deprotection	75±2	20±1	71±1	19±2
PCTFE+LiDT (60 min)	88±1	61±1	82±1	41±1
after deprotection	75±1	25±1	71±2	19±1

The atomic composition data (Table 1-3-14) indicate that changes are not occurring with time within the XPS sampling depth. It was also possible to use the expanded C_{1s} spectra (Figure 1-3-15) and the UV-Vis data to approximate the reaction depth. The XPS results indicate that

Table 1-3-14. XPS Atomic Composition Data (takeoff ∢=15° / 75°)for the Reaction of PCTFE with 2-Lithio-1,3-dithiane at:

	-78°C		and		-20°C	
Element	5 min.	30 min.	60 min.	5 min.	30 min.	60 min.
F	23.7	24.7	19.8	12.7	8.54	9.80
	34.8	32.3	29.7	20.0	15.5	15.8
O	3.57	3.82	6.25	5.75	5.83	7.58
	2.05	2.01	2.82	4.42	3.47	4.42
C	58.7	59.9	62.3	65.8	70.5	68.8
	49.8	51.8	53.0	60.3	65.5	64.3
Cl	4.37	4.57	2.60	1.61	1.20	1.11
	8.77	8.67	7.89	4.67	4.55	4.07
S	8.38	7.04	8.12	13.1	13.5	12.6
	4.57	4.42	5.36	10.1	10.5	11.4
Si	1.27	0.00	0.88	1.13	0.40	0.24
	0.00	0.84	1.24	0.58	0.00	0.00

nearly the entire XPS sampling depth was modified at 0°C and that the reaction at -78°C resulted in a modified layer that lies between 10 Å (15° takeoff angle) to 50 Å (75° takeoff angle). The area of the CF_2 region accounts for less than 20% of the total C_{1s} region and this would place the estimated depth at -78°C at roughly 30 - 40 Å. Combining this estimate with the relative UV-Vis absorbance (Figure 1-3-16) places the thickness of the layer formed at 0°C at 90 - 120 Å.

XPS was also invaluable for optimizing the deprotection step. The atomic composition was monitored before and after exposure of the PCTFE-DT film to conditions conducive to the deprotection of aldehydes. Removal of the dithiane protecting group is nontrivial especially when it is confined to the surface of a polymer. A number of methods were attempted (Table 1-3-15) the most successful resulted in the removal of

70 - 80% of the sulfur from the surface; it involved the use of trifluoroacetic acid, mercuric trifluoroacetate, acetone and water.

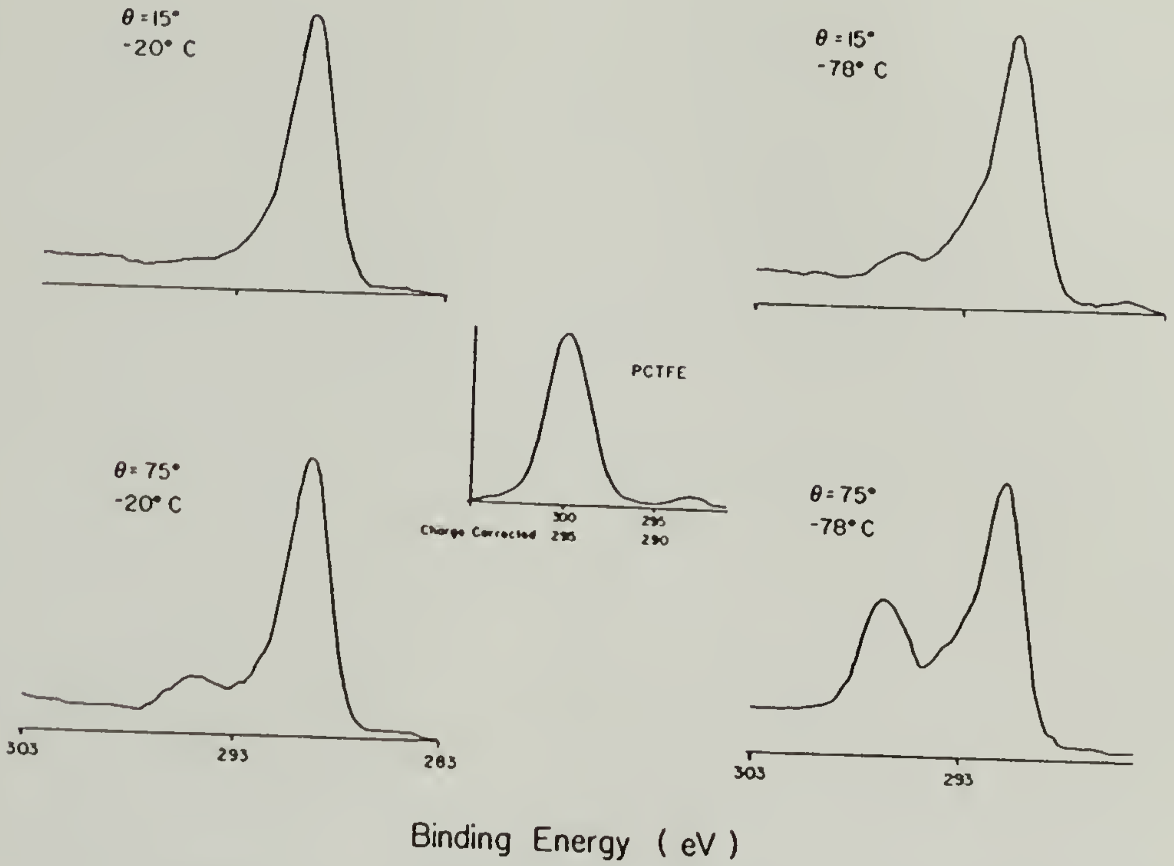


Figure 1-3-15. XPS C_{1s} expanded region for the reaction of PCTFE with 2-lithio-1,3-dithiane.

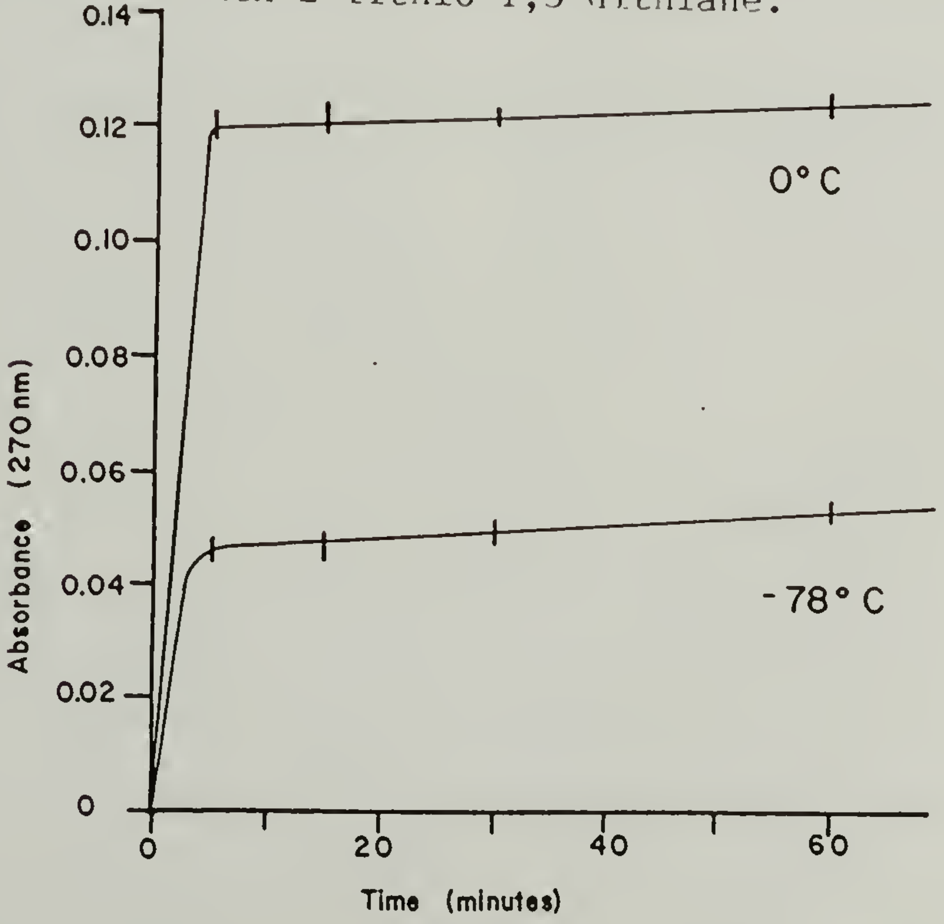


Figure 1-3-16. Plot of absorbance vs. time for the reaction of PCTFE with 2-lithio-1,3-dithiane.

Table 1-3-15. XPS Atomic Composition Data for the Deprotection of the PCTFE Aldehyde Surface.

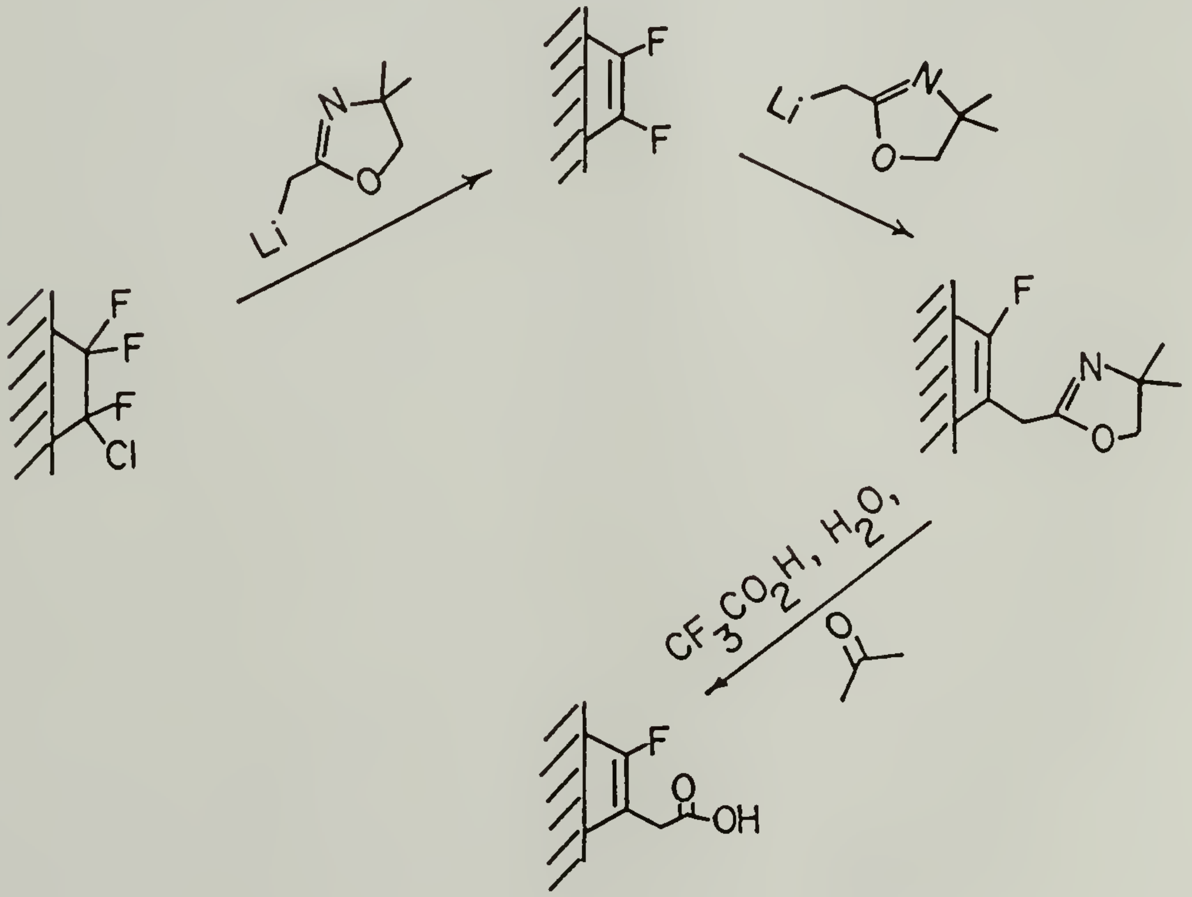
Deprotection Method	Atomic Composition (Percent) F	O	C	Cl	S	Si	Hg	I
None	12.7	5.75	65.8	1.61	13.1	1.13	0.00	-
$HgCl_2$	20.0	11.1	55.5	7.70	5.70	0.12	0.00	-
MeI	12.7	7.61	62.7	7.01	9.70	-	-	0.34
$Hg(O_2CCF_3)_2$	10.8	13.4	63.1	6.21	4.45	0.95	0.39	-

The reason for the success of this method probably lies with the higher solubility of the reagent in the polymer surface: Mercuric chloride is an inorganic salt and has limited solubility in the film, mercuric trifluoroacetate is an organic salt and is soluble in the film. The same is true for the acid, HCl is inorganic and insoluble, trifluoroacetic acid is organic and soluble. This reasoning does not explain the failure of methyl iodide to alkylate the surface; methyl iodide is soluble in the film. The reason for the failure of this method may be that the nonpolar surface presents a high activation barrier to the formation of polar sulfonium salts. If this is the case then alkylation reactions may not be useable for surface modifications. The ATR-IR spectra of the modified film did not exhibit any observable spectral changes. Also secondary electron images indicate that there is no change in microtopography at a resolution of 200 Å.

Together these results suggest a surface selective modification is possible using LiDT on PCTFE. The presence of both protected and deprotected functional groups was demonstrated using a combination of XPS, contact angle and UV-Vis. Gravimetric analysis indicated that this reaction produced mass changes which were at the detection limits of the method (± 1 microgram). Deprotection of the aldehyde required the use of reagents which could readily access the bulk polymer. The reaction was also sensitive to temperature; an increase in the temperature resulted in an increase in the depth of the modification. The presence of aldehydes was additionally confirmed from studies of the analogous reaction on low molecular weight PCTFE oil in solution. The IR spectrum of PCTFE-DT oil exhibits absorbances consistent with methylene groups (2930, 2870, and 1450 cm^{-1}) and unsaturation (broad multiple absorbances 1600 - 1700 cm^{-1}). Upon deprotection a large carbonyl appears at 1730 cm^{-1}. The proton NMR has a broad resonance from 1 - 2 ppm due to the protecting group and upon deprotection a resonance at 9.1 ppm due to the aldehylic proton was observed.

Introduction of Carboxylic Acid Groups Using 2-Lithio-2,4,4-trimethyl-2-oxazoline

This modification completes the extension of the organometallic method to include the incorporation of carboxylic acid groups onto the surface of PCTFE. Again the protecting group was specifically chosen because it permitted the unambiguous XPS characterization of the reaction. In this case the probe element is nitrogen (398 eV) and it is introduced only through reaction of the LiTMO. The reaction (Equation 1-3-7) theoretically will introduce equal amounts of oxygen and nitrogen thus their ratio should be 1:1. However experimentally the quantity of oxygen is always greater than the quantity of nitrogen. XPS survey spectra (Figure 1-3-17) are consistent with the series of reactions depicted in equation 1-3-7. When PCTFE film was allowed to react with LiTMO in THF and THF/heptane mixtures, the intensity of nitrogen and oxygen both increased. Upon deprotection, nitrogen was removed and the oxygen intensity underwent a corresponding increase. The same combination of analytical methods was applied to this surface. The contact angle data (Table 1-3-16) again rapidly assume their minimum values and decrease further upon deprotection. The UV-Vis data (Figure 1-3-18) suggest once again that this reaction is sensitive to



Equation 1-3-7. Reaction of PCTFE with 2-Lithio-2,4,4-trimethyloxazoline; introduction of carboxylic acid groups.

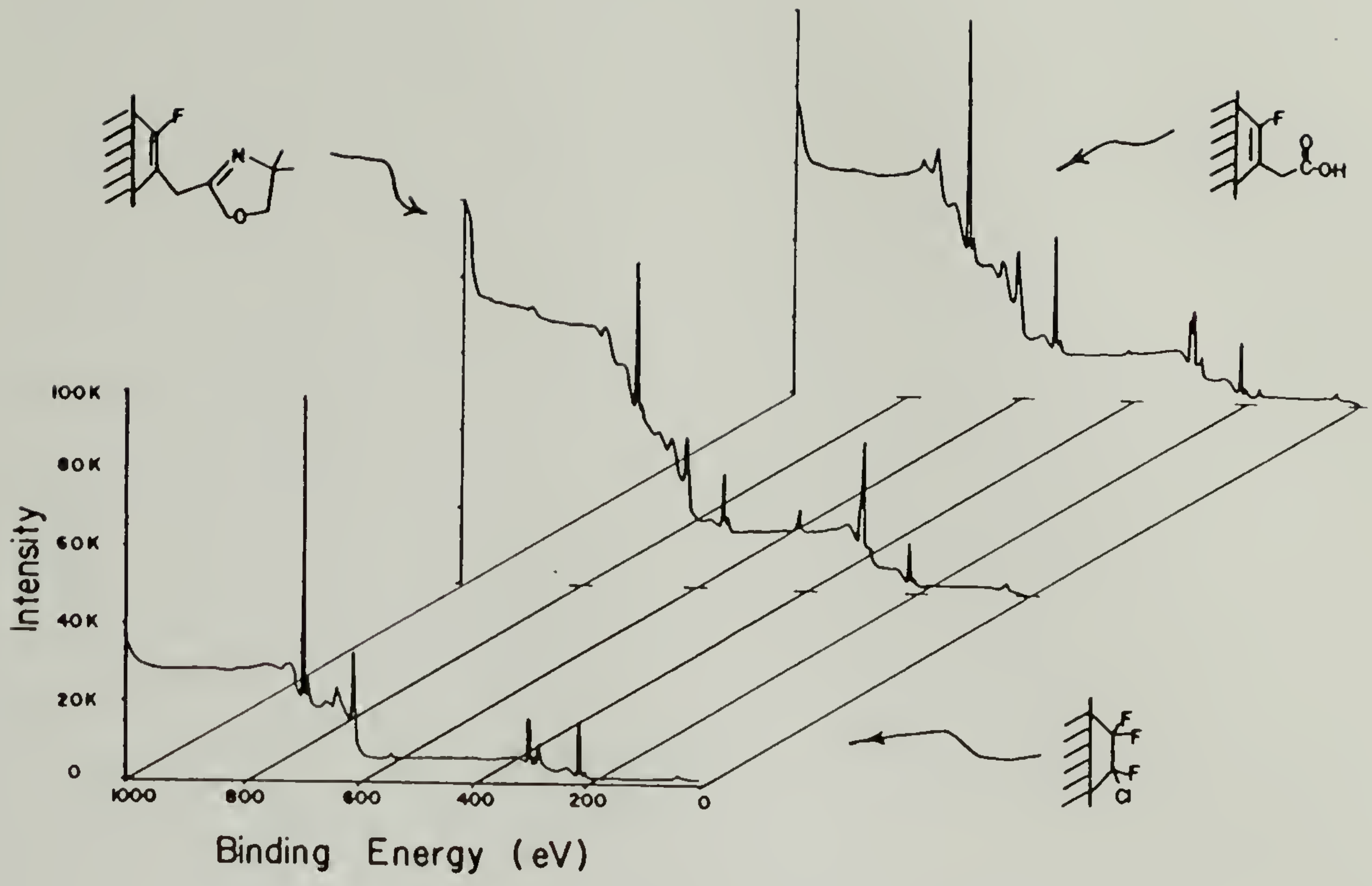


Figure 1-3-17. XPS survey for the reaction of PCTFE with 2-lithio-2,4,4-trimethyl-2-oxazoline.

Table 1-3-16. Contact Angle Data for the Reaction of LiTMO with PCTFE at:

	Contact Angles (degrees)			
	-78°C	and	0°C	
Surface	Advancing	Receding	Advancing	Receding
PCTFE+LiTMO (5 min)	89±2	45±2	75±1	37±2
after hydrolysis	75±3	10±2	70±2	10±1
PCTFE+LiTMO (30 min)	87±2	42±2	74±1	34±2
after hydrolysis	74±2	10±2	74±1	0
PCTFE+LiTMO (60 min)	88±1	43±2	74±1	34±1
after hydrolysis	71±1	0	72±1	0

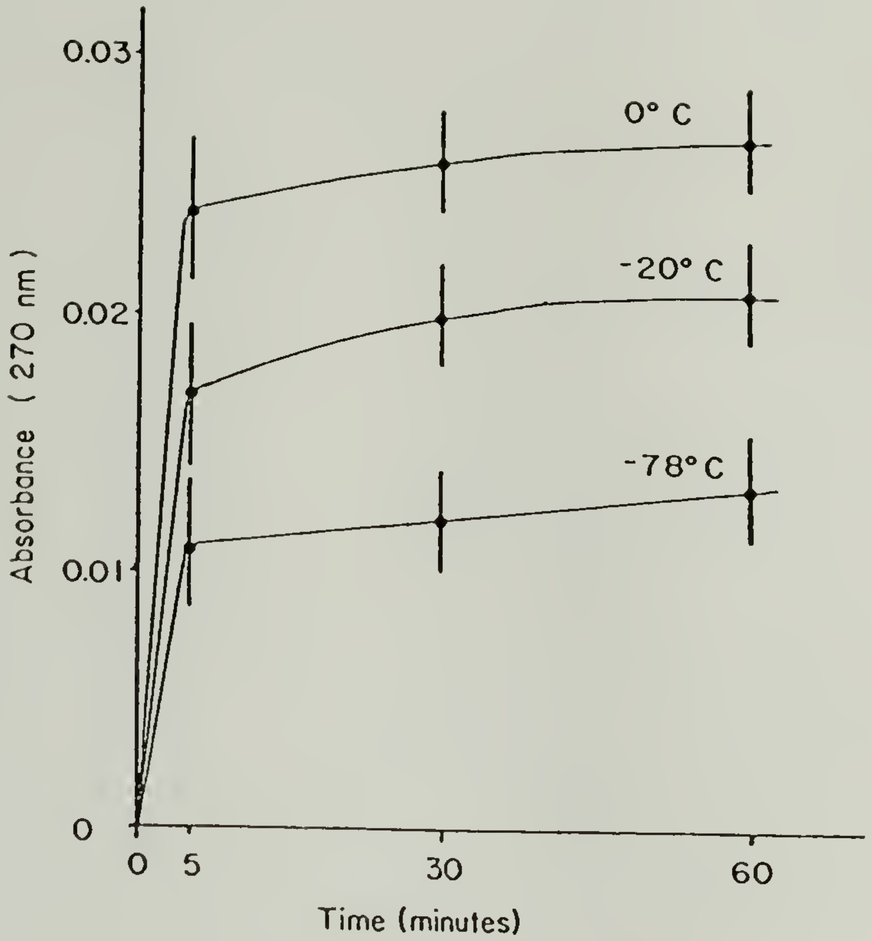


Figure 1-3-18. Plot of absorbance vs. time for the reaction of PCTFE film with LiTMO.

temperature and in addition the measured absorbance values are very low; the maximum value (that obtained at 0°C) being roughly the same as that obtained for the minimum for the other two reactions (both LiDT and LiPAA at -78°C). The XPS C_{1s} region (Figure 1-3-19) can again be used to estimate the depth of the modification. At -20°C the reaction has not progressed far beyond the 50 Å (75° takeoff angle) sampling depth and at -78°C the reaction was contained primarily within the 10 Å (15° takeoff angle) sampling depth. This would place the estimated depth at 10 - 15 Å for the reaction at -78°C and at 40 Å for the reaction at -20°C.

Once again XPS was used to find the optimum conditions for removing the protecting group. Several methods were attempted (Table 1-3-17) and the most efficient resulted in 75 - 90% removal of the

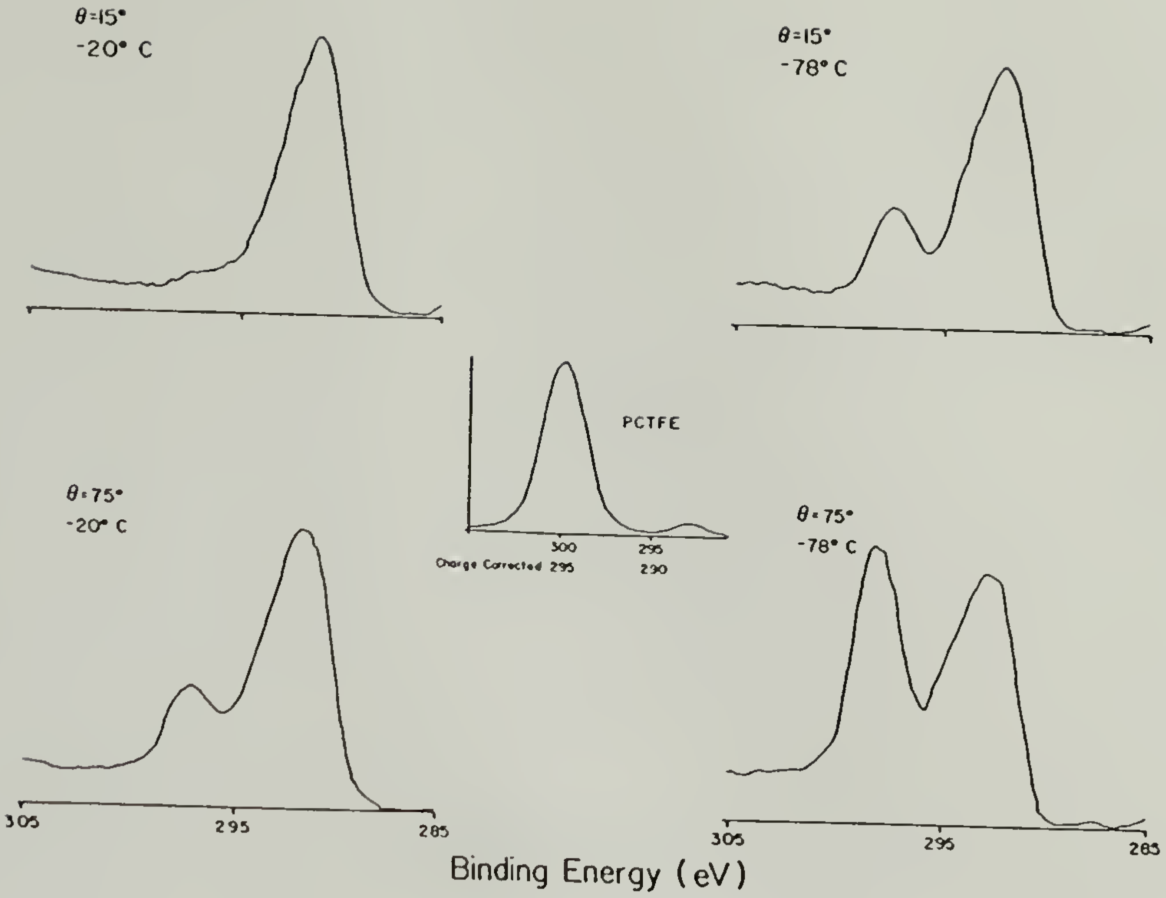


Figure 1-3-19. XPS C_{1s} expanded region for the reaction of PCTFE film with LiTMO.

Table 1-3-17. XPS Atomic Composition Data for the Deprotection of PCTFE-TMO film.

Element	PCTFE-TMO	PCTFE-TMO + CF_3COOH, H_2O, Acetone	PCTFE-TMO + HCl	PCTFE-TMO + MeI
F	7.66±3.6	21.2±4.2	11.5±2.2	13.3
O	12.6±2.1	14.8±2.9	14.7±2.3	11.4
N	7.29±1.2	1.94±0.70	5.50±1.9	5.00
C	66.7±4.2	53.2±3.2	61.0±3.1	58.6
Cl	4.21±2.5	6.62±1.6	7.30±1.7	11.4
Si	1.40±1.2	1.96±1.8	1.10±1.0	1.09
I	-	-	-	0.30

oxazoline. This method involved the use of trifluoroacetic acid, acetone and water. The other methods involving HCl or MeI were not successful probably for the reasons stated eariler. In addition the ratio of acetone to water was important, the optimum being 1:4. Apparently it is necessary to reduce the surface tension of the reaction solution enough to allow wetting while keeping the boiling point of the mixture high enough to effect hydrolysis.

The ATR-IR spectra of the modified film appeared unchanged and scanning electron microscopy indicated that there was no change in microtopography at a resolution of 200 Å. Gravimetric analysis indicated that the mass change upon reaction was at the limits of the technique (±1 microgram).

These results demonstrate that a surface selective modification of PCTFE is possible with LiTMO. The thickness of the layer can be controlled by changing the reaction temperature. The surface can be deprotected using trifluoroacetic acid and a mixture of acetone and water. The presence of the protected and deprotected carboxylic functionality was demonstrated using a combination of XPS, contact angles and UV-Vis. The introduction of carboxylic acid groups was also demonstrated using the analogous reactions on low molecular weight soluble PCTFE oil. The IR spectrum of PCTFE-TMO oil exhibits absorbances consistent with methyl (2960 and 2870 cm^{-1}) and methylene (2920 and 2850 cm^{-1}) groups as well as carbonyl (1720 cm^{-1}), C=C (broad multiple peak 1500 - 1600 cm^{-1}) and C=N at 1630 cm^{-1}. Upon deprotection a large carbonyl appeared at 1760 cm^{-1} and the position of this peak could be shifted to 1600 cm^{-1} by exposing it to triethylamine thereby forming a salt. The proton NMR of PCTFE-TMO exhibited resonances at (1.10 ppm (s), 1.65 ppm (s), 3.57 ppm (s)) and upon deprotection a resonance at 10 - 11 ppm corresponding to the carboxylic acid proton was observed only when the sample was completely free of 2-methyl-2-amino-1-propanol. Otherwise a band at 8.50 ppm was observed corresponding to the amine salt.

Solvent Dependence.

Each of the previous organolithium compounds exhibited reasonably large temperature dependent reactions with PCTFE film. The thermal dependence is a likely result of the changes in mobility which the surface experiences as the temperature is varied; higher temperatures favor more surface mobility and therefore more chains react, and low temperatures result in less mobility and a thinner modified layer results. However, this dependence is not merely affected by temperature changes; both the structure of the lithium reagent and the reaction solvent can also affect the reaction.

The surface which resulted upon reaction depended strongly upon which lithium reagent used. LiPAA is a primary lithium reagent and it resulted in extensive surface modification. It was a much more reactive lithium reagent than either LiDT (secondary and stabilized by two heteroatoms) or LiTMO (delocalized, resembling a benzylic lithium reagent). However, the observed reactivities should not be attributed to these structures alone. Since lithium reagents seldom exists as isolated molecules in solution; their aggregation and reactivity are dependent upon temperature and solvent. Thus reaction is also sensitive to the solvent used in the reaction. The modified layer is the most extensive when THF is the solvent and the layer decreases in thickness as the percentage of THF in the solution is decreased. This effect was monitored by following the relative changes in the UV-Vis absorbance as the composition of the solvent was varied (Figure 1-3-20). The results indicate that there is a direct relationship between the thickness of the layer and the amount of THF. High percentages of THF have the same effect as an increase in temperature. Whereas this effect forms an almost linear relationship for LiDT, the solvent effect appears to have reached a limiting value for the LiTMO; the depth is not as strong a function of THF concentration beyond a certain threshold value. The

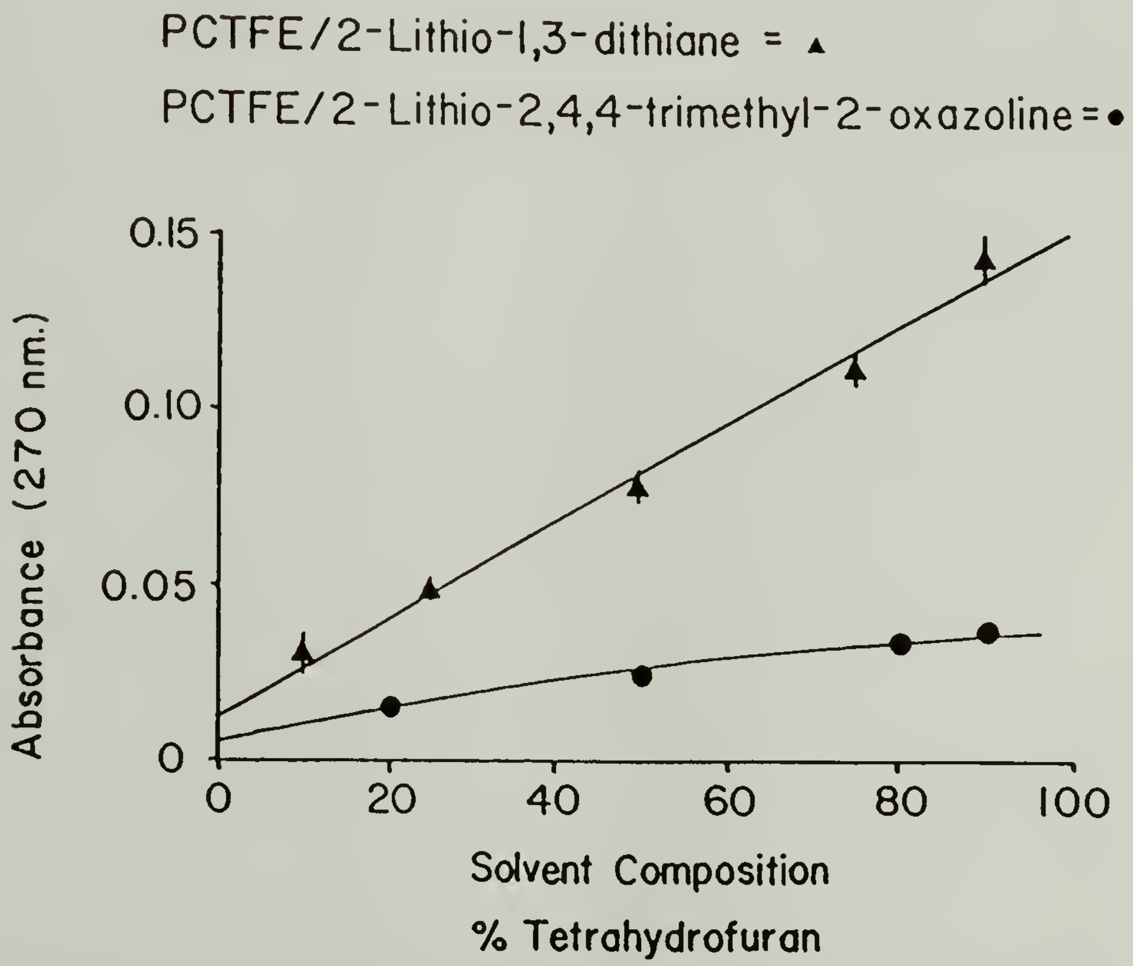


Figure 1-3-20. Plot of absorbance vs. solvent composition for the reaction of PCTFE film with LiDT and LiTMO.

origin of this dependence is not obvious: The surface of PCTFE may be swollen by THF more than by heptane (THF swells PCTFE at elevated temperatures and heptane does not). A second factor that could cause the observed changes is that the structure of the lithium reagent is altered by the solvent change. Coordinating solvets like THF favor isolated, solvated, monomeric types of structres and heptane would favor larger polymeric types of structures. In both cases it is obvious that the surface which is accessible to the lithium reagent is different for the different environments.

Reactions of PCTFE-COOH.

Esterification. The surface which best approximates a two-dimensional array of organic functional groups is the PCTFE-COOH surface. The kinetics as determined by XPS, contact angle and UV-Vis spectroscopy all indicate that the reaction is surface selective. The thickness of the modified layer prepared at -20°C was estimated to be 40 Å, and the XPS atomic composition was consistent with the incorporation of two TMO units for every three monomer units. The deprotection was estimated to be from 75 - 90% complete based by the nitrogen XPS atomic composition. Based upon these values the density of carboxylic acid groups is at least 1 for every two monomer units. This represents approximately $3x10^{-9}$ mole/cm^2 of carboxylic acid groups. This value is approximately three times that obtained for the closest packing value for fatty acid monolayers[15]. Therefore it was expected, based upon these values, that esterification reactions could be monitored with a variety of sensitive analytical equipment if the alcohols were chosen to contain suitable labels.

The initial alcohols used were chosen for specific analytical methods: 4-hydroxy-TEMPO as an ESR label; tribromoethanol for both XPS and electron-capture capillary GC; hexafluoroisopropanol, octanol and octadecanol for both contact angle and XPS. The methods which were used for the esterification of PCTFE-COOH all involve activation of the acid and then reaction with the alcohol. It was hoped that by altering the reaction conditions (changing from a nonswelling to a swelling solvent) functional groups in different locations in the surface could be reacted and comparisons to other methods of esterification (alkylation reactions) might give an indication about surface confined functional group reactivity.

The results which were obtained were very discouraging in that very little incorporation of the specified alcohols was observed. The two most promising methods for esterifying the surface were the use of thionyl chloride/DMF and carbonyldiimidazole. Attempts were made at using these reagents in both THF and $MeCl_2$, as well as mixtures of the two. The surfaces were analyzed by XPS prior to exposing them to the alcohol. The atomic composition data (Table 1-3-18) was consistent with the formation of the acyl imidazole (increased nitrogen) but did not provide convincing results for the formation of the acyl chloride. This may have been a result of the x-ray instability of the acid chloride or it may mean that the acid chloride was not formed in significant quantities to permit XPS analysis. These activated surfaces were then exposed to solutions of alcohols in THF and $MeCl_2$.

Table 1-3-18. XPS Atomic Composition Data for the CDI Esterification of PCTFE-COOH.

Element	PCTFE-TMO	PCTFE-COOH	CDI + PCTFE-COOH	PCTFE-COOH + CDI +		
				Octanol	Tribromo-ethanol	Hexafluoro-2-propanol
F	8.06	14.1	8.90	8.87	20.7	18.1
O	11.7	19.0	15.5	16.7	13.1	14.0
N	9.54	2.58	9.88	4.16	2.35	6.59
C	63.7	55.5	58.7	65.3	54.8	54.7
Cl	4.67	5.38	4.52	4.03	6.66	5.61
Si	2.11	3.43	1.74	0.95	0.72	1.01
Br	-	-	-	-	0.66	-

The best results, again were disappointing. The C_{1s} XP spectra at a 15^{o} angle showed the only observable changes for each of the alcohols. Typical results showed: 1) Slight increases to the high binding energy side of the CF_2 region when hexafluoroisopropanol was reacted. 2) Changes in the relative intensity of CF_2 to CH_2 when octanol and octadecanol were used (Figure 1-3-21). 3) Small increases (less than 0.5%) in the bromine atomic composition when tribromoethanol was used.

Some attempts were made to monitor the esterification using other analytical techniques. Gravimetric analysis was used to follow the esterification of PCTFE-COOH film with tribromoethanol. The area of the film involved in these determinations was 6 cm^2 and the mass increased $1x10^{-6}$ g which is the lower detection limit for the method.

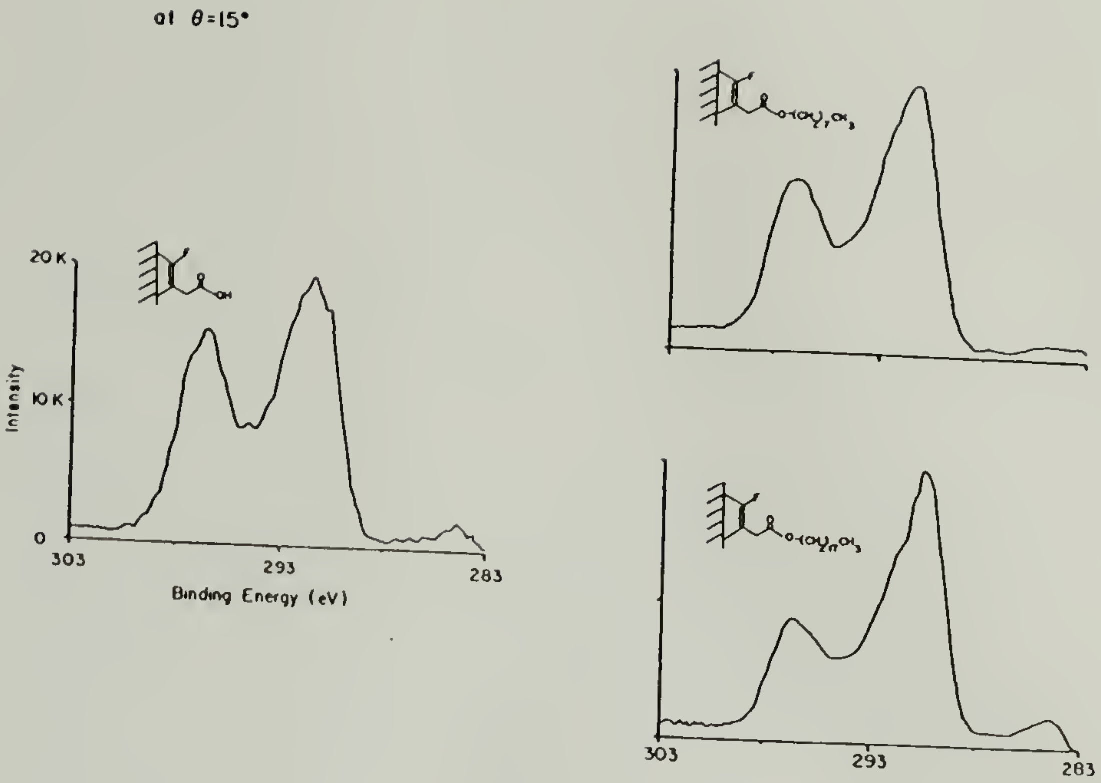


Figure 1-3-21. XPS C$_{1s}$ expanded region for PCTFE-COOH film and PCTFE-COOH film which was esterified with octanol and octadecanol.

The expected mass increase for 3×10^{-9} moles is 5.1×10^{-6} grams, thus if this value is correct only 20% of the carboxylic acid groups have reacted. Identically reacted films were refluxed in acidic ethanol to hydrolyze the esters and the hydrolysis solution was analyzed by ECD capillary GC along with standard solutions. The hydrolysis solution did show a small peak with the same retention time as tribromoethanol but the chromatograph also contained new peaks to either side which prevented integration. When a solution containing 1×10^{-7} g of tribromoethanol was placed through the same hydrolysis, the observed peak was free of overlapping peaks and the area could be determined. These results suggest that it is only possible to qualitatively identify low levels of tribromoethanol with ECD capillary GC.

Another analytical method which was attempted but which was also not successful is ESR. In this method the alcohol used was 4-hydroxyTEMPO; which contains a free spin and hence is ESR active. A standard sample containing $1x10^{-5}$ g of 4-hydroxyTEMPO along with a piece of PCTFE film was placed into the analysis cavity. The samples consisted of PCTFE-COOH films which was reacted (24 h) with thionyl chloride/DMF or carbonyldiimidazole in THF or $MeCl_2$. The film was then treated with a solution of 4-hydroxyTEMPO in THF or $MeCl_2$ before being dried under reduced pressure. The film was then placed into an ESR tube and analyzed. The standard sample containing 10^{-5} g of 4-hydroxyTEMPO gave a resonably large signal with the reciever gain set at 400. The sensitivity of the method was estimated from this sample to be 10^{-8} g. Analysis of the esterified film, however, exhibited no spins even when the reciever gain was set at $4x10^4$. This again indicates that either the esterification reaction does not work or that the number of functional groups present is low and this combined with low extents of reaction result in negative analytical results.

Determination of Functional Group Site Density

The value obtained from XPS for the functional group site density was appromiated at $3x10^{-9}$ mole/cm^2. This value has a number of uncertainties associated with it which include: The nonuniqueness of fit which is apparent when trying to relate the atomic composition data to an actual structure. This is one of the largest uncertainties and numerically the difference between 1 TMO unit every two monomer units and 2 TMO groups every three monomer units is roughly 25%. The second uncertainty arises from the estimation of the number of monomer units which are contained within the 40 Å of the modified surface. The method which was used for this calculation uses the macroscopic value for the density of PCTFE (2.1 g/cm^3). However on this scale density should be corrected for excluded volume, voids and surface topography. These corrections can be significant and the magnitude of this uncertainty is roughly 20%. A third uncertainty arises from the inability to remove all of the oxazoline protecting groups. The magnitude of this uncertainty is small relative to the other two and can be estimated from the standard deviations of the XPS analysis to be roughly 10%. Together these uncertainties in the functional group site density estimate reduce the value to, at best, an order of magnitude approximation.

Radiolabelling.

A much better value for the functional group site density was obtained through the combination of XPS and radioassay. The lithium reagent was prepared from [^{14}C]TMO and the increase in the radioactivity of the film is related directly to the amount of [^{14}C]TMO incorporation, and XPS then estimated the efficiency of the deprotection step which was then used to calculate the carboxylic acid group site density. The labelling of surfaces with radioactive isotopes is a widely practiced method for determining the functional group site density. This technique, in its currently practiced form, involves the reaction of surface functional groups with radioactive isotopes and measuring the radioactivity incorporated into the surface. As pointed out previously, this method actually measures the number of reacting functional groups. This value is only equal to the total number of functional groups if the reaction was quantitative as well as specific. The method presented here does not rely on the reaction of the functionality, instead the functional group itself contains the radioactive isotope.

The synthesis of [^{14}C]TMO was essentially that of Meyer[16] which was modified slightly to account for the necessarily small scale (5-6 mmole). The synthesis was repeated using unlabeled acetic acid until 60-70% yields were consistently obtained. Then the synthesis was repeated using 1-[^{14}C]acetic acid. The [^{14}C]TMO (0.45 g, 69% yield) was dissolved in heptane and stored under nitrogen in a Schlenk tube. The efficiency of the radioassay (80 %), liquid scintillation counting (LSC), method was established by measuring the radioactivity of a known quantity of [^{14}C]TMO and comparing the measured counts per minute to the true activity, decays per minute. The efficiency thus serves as the proportionality constant with which the experimentally determined CPM are converted into the true DPM. The PCTFE film used for these experiments was 25 micrometers thick. The average energy of the Beta particles emitted from the decaying ^{14}C is sufficient to pass through the entire thickness of the film to reach the fluor, where it interacts and the resulting fluoresence is measured by the detector. Since fluoresence is being monitored it is necessary to check for quenching by the film. That quenching was not significant was checked by LSC of a known amount of [^{14}C]TMO both with and without a film being present. The presence of the film reduced the number of counts by 0.5%. The

Li[^{14}C]TMO was then generated in a solution containing a 1:1 mixture of THF and heptane using the previously described method and reacted for the desired time at -20^{o}C and at -78^{o}C. The film was hydrolyzed with acetone, water and trifluoroacetic acid before being analyzed by LSC. The kinetics for the incorporation of TMO at -20^{o}C is well correlated to the formation of the fluoroolefin (Figure 1-3-22). Again it appears that after an initial rapid incorporation of TMO, the reaction rate decreases. Unlike the UV-Vis absorbance the TMO site density does not appear to have reached its maximum value. This suggests two possibilities: either the formation of the fluoroolefin proceeds at a faster rate than the incorporation of TMO or that the LiTMO is reacting

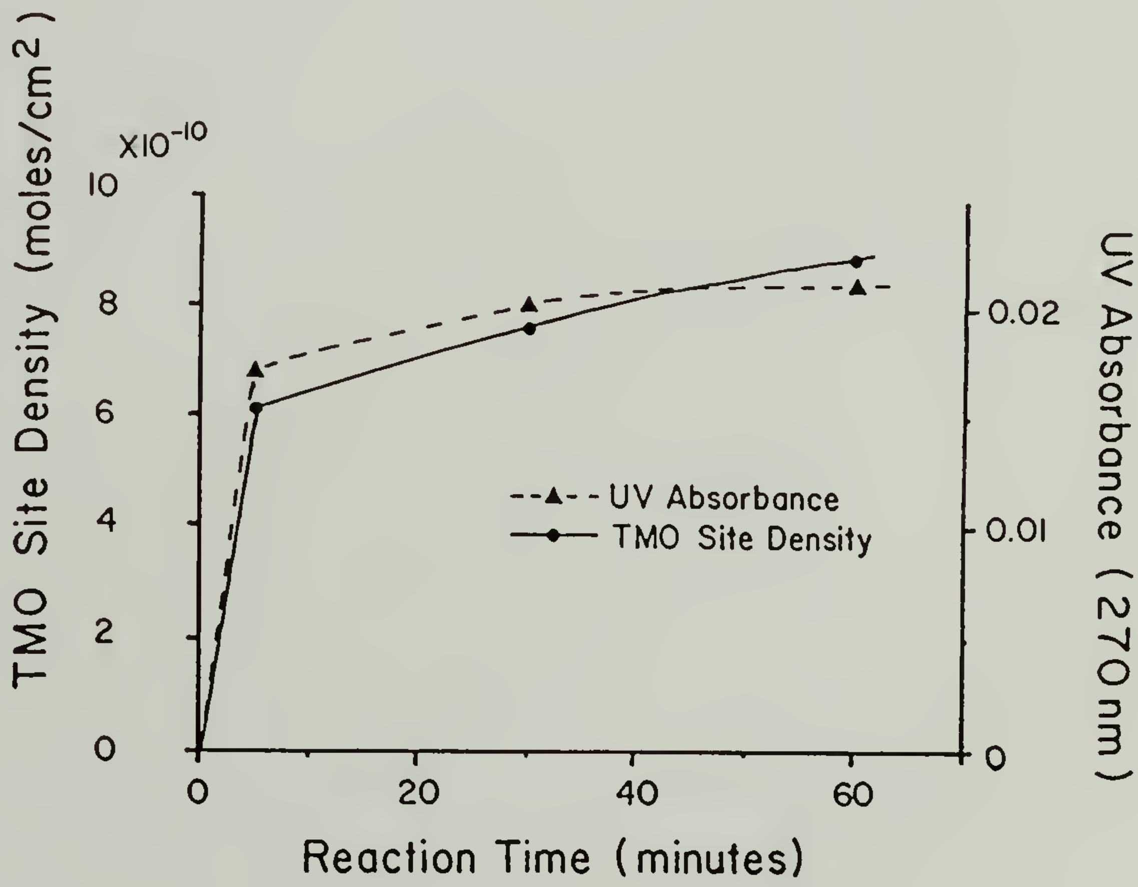


Figure 1-3-22. Plot of absorbance and ^{14}C determined PCTFE-TMO site density vs. time for the reaction of PCTFE with LiTMO.

with the substituted fluoroolefin to form the disubstituted product. The XPS data does not support the latter; this would require the nitrogen atomic composition to reach 11% which does not occur. That the XPS results do not support the former case may be a limitation of the XPS method. The XPS nitrogen atomic composition data for the -20°C reaction did not exhibit a change with reaction time; however, the nitrogen data for the reaction at -78°C did exhibit an increase as the reaction time was increased (4.74% after 5 minutes to 5.97% after 60 minutes). That the XPS atomic composition for the reaction at -20°C did not exhibit the same time dependence (9.22% after 5 minutes to 9.6% after 60 minutes) represents an artifact of the XPS analysis. The measured photoelectron intensity does not exhibit a linear dependance on depth but rather it exhibits the exponential decay presented earlier; as a result, the further the element of interest is away from the surface the lower the observed intensity. This loss of sensitivity of the XPS signal is apparent when the modification approached the XPS sampling depth. In addition the approximate XPS accuracy is 10%. Together these factors make it difficult to accurately define the changes that are occurring on the more extensively modified film.

Radioassay of the $[^{14}C]$TMO modified film provided a means for precisely obtaining the functional group site density. The reacted film was placed directly into the fluor solution; the dpm values were calculated from the efficiency and a correction was made for the background. The calculated dpm values were divided by the macroscopic surface area and converted, using the specific activity of the TMO, into moles/cm^2. The mean value obtained at -20°C for a 1 hour reaction was $(9.7\underline{+}0.6)\times10^{-10}$ moles/cm^2 (95% confidence based upon 8 measurements). The mean value obtained for a 1 hour reaction at -78°C was $(4.3\underline{+}1.0)\times10^{-10}$ moles/cm^2 (95% confidence based upon 3 measurements). These values represent the maximum TMO site density and therefore the maximum carboxylic acid site density. A better approximation to the true value is obtained by applying corrections for incomplete deprotection as well as corrections for adsorption of the TMO by the film.

When PCTFE film was exposed to [^{14}C]TMO for 1 hour at -20°C, exposed to the TMO hydrolysis conditions, extracted, dried, then analyzed by LSC, the film was found to contain radioactivity which corresponded to $(2.3\underline{+}0.6)\times10^{-10}$ moles/cm^2 (95% confidence based upon 5 measurements) This adsorbed material was not removed even after prolonged (3 days) heating at 90°C and 0.05 mm. The same was true of the control for the reaction at -78°C only in this case the radioactivity corresponded to 1.1×10^{-10} moles/cm^2. These values represent approximately 25% of the total radioactivity found in the Li[^{14}C]TMO treated film and introduces a large uncertainty into the accuracy of the functional group site densities. An additional correction had to be applied to the TMO data to obtain the carboxylic acid group site density. The XPS data indicates that upon hydrolysis 70 - 90% of the nitrogen was removed from the surface ($75\underline{+}12$%). Applying these corrections to the TMO site density gives an estimated carboxylic acid group density of $(5.6\underline{+}1.7)\times10^{-10}$ moles/cm^2 for the surface prepared at -20°C, and $(2.7\pm1.1)\times10^{-10}$ moles/cm^2 for the surface prepared at -78°C. The largest uncertainty, 25%, in this calculation was the correction for the adsorption of [^{14}C]TMO by the film. It was not obvious whether this control value accurately reproduces the experimental conditions nor whether PCTFE film will exhibit the same adsorption with Li[^{14}C]TMO. The deprotection step introduced an uncertainty of approximately 16% into the calculation, based upon the experimental standard deviation. The smallest uncertainty, 6%, involved the radioassay method itself. Thus while the radioassay method provides a precise method for determining relative amounts of [^{14}C]TMO incorporation as well as the maximum number of functional groups incorporated; it does not provide precise results when the absolute numbers of functional groups are required.

Esterification With Tritiated Ethanol.

The carboxylic acid site density was determined to be $(5.6\pm1.7)\times10^{-10}$ moles/cm^2 for the 1 hour reaction of Li[^{14}C] in heptane/THF at -20°C. These films were then esterified with [^{3}H]ethanol using three different esterification methods: acid catalysis, acid chloride formation and acyl imidazole formation. The films were then assayed by LSC. The energy of the Beta particle emitted from tritium is two orders of magnitude smaller than that emitted from [^{14}C]; therefore, it will not make it through the 25 micrometer thick film and geometry becomes important. Common practice is to multiply the obtained results by a factor of 2; the assumption being that 1/2 of the Beta particles are emitted back into the film and do not escape. This assumption was checked by reducing the PCTFECOOEt[^{3}H] film with Bu_3SnH and AIBN; this reductive dechlorination results in poly(trifluoroethylene) which is soluble in the fluor and LSC was obtained on the resulting solution.

The [^{3}H]EtOH was prepared by BH_3/THF reduction of a solution containing [^{3}H]sodium acetate, ethanol and acetic acid. The reduction was repeated using unlabeled sodium acetate until quantitative yields (>90%) were obtained. The reaction was then run with the labeled compound and the resulting [^{3}H]EtOH/THF solution was diluted with THF to 75 ml and stored under nitrogen. The solution was analyzed for alcohol content by reaction with 3,5-dinitrobenzoyl chloride/diaminopropane. The yield was 86% and the resulting specific activity was 0.179mCi/mmol. The LSC counting efficiency, 39.5%, was calculated from the measured cpm values of a known amount of [^{3}H]EtOH in the presence of a PCTFE film. The efficiency was reestablished for the polymer solutions at 28.7%. This time the efficiency was established from the cpm values that were obtained on a solution containing 2 ml of the reduced polymer solution, a known quantity of [^{3}H]EtOH and 3 ml of the fluor solution. This reproduces the quantities which were used to analyze the labelled film solutions by LSC.

The three methods of esterification which were examined using this method were: 1) sulfuric acid catalyzed esterification which consisted of refluxing the PCTFECOOH film in a solution containing [^{3}H]EtOH, THF, sulfuric acid and dichloromethane. Then the film was washed, extracted and dried before LSC. 2) Acyl chlorides were formed by reacting the PCTFE-COOH film with a solution containing thionyl chloride and DMF in methylene chloride. This solution was removed and replaced with a methylene chloride solution of the [^{3}H]EtOH/THF solution. The film was removed, washed, extracted and dried before LSC. 3) Acyl imidazoles were formed by reacting the PCTFE-COOH film with a $MeCl_2$ solution of 1,1'-carbonyldiimidazole (CDI). This solution was removed and replaced with a solution containing [^{3}H]EtOH/THF in $MeCl_2$. The film was removed, washed, extracted and dried before LSC. The results (Table 1-3-19) for the solid film indicate that only a small amount (10% or less) of the surface carboxylic acid groups were reacted. These

Table 1-3-19. Radioassay data for the esterification of PCTFE-COOH with [^{3}H]ethanol.

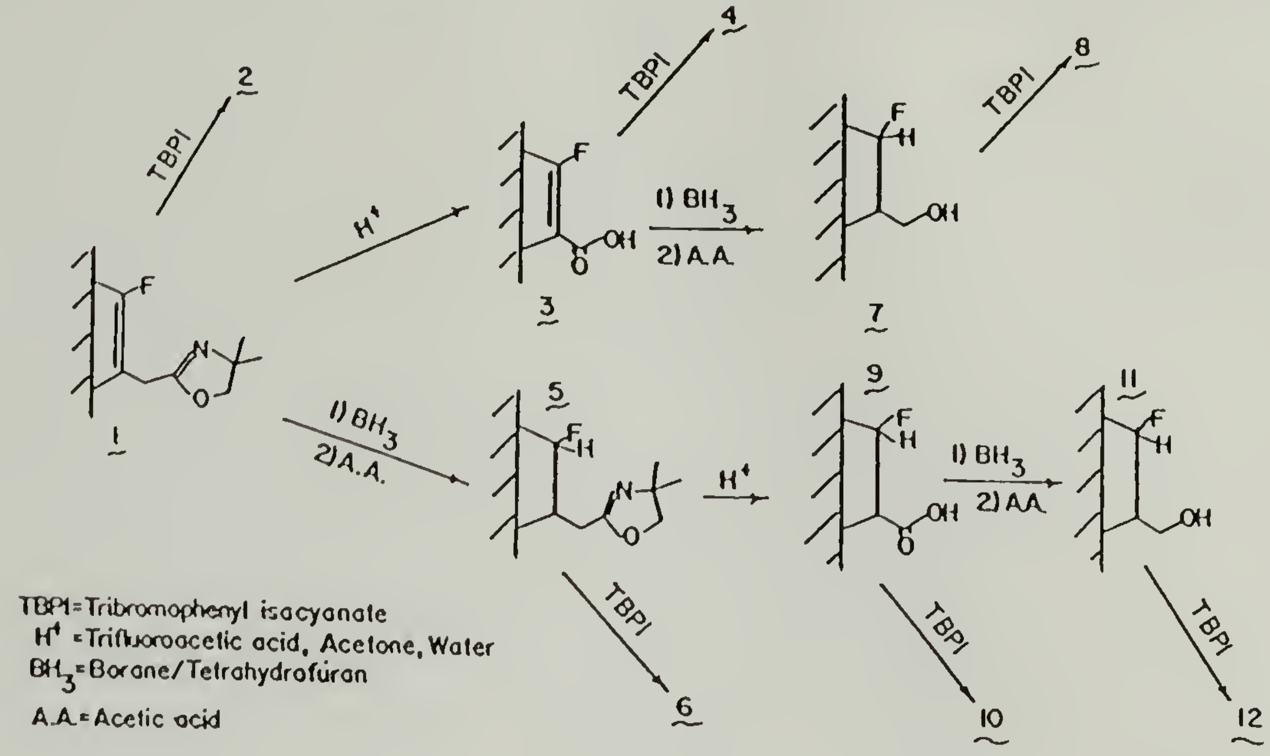
	Data obtained for solid PCTFE films		Data obtained for reduced PCTFE solutions	
Method	Activity moles/cm^2	percentage of COOH reacted	Activity moles/cm^2	percentage of COOH reacted
H_2SO_4	2.4×10^{-11}	4.3	5.8×10^{-11}	10.4
$SOCl_2$	5.7×10^{-11}	10.2	1.3×10^{-10}	23.2
CDI	5.1×10^{-11}	9.1	9.7×10^{-11}	17.3

are uncorrected for geometry and represent the functional groups which are near the surface and emitting Beta particles forward, out of the film. The films were then reacted at 60°C with Bu_3SnH and AIBN in THF. The resulting [^3H] labelled poly(trifluoroethylene) solution was diluted with THF to 4 ml and 2 ml of this solution was added to 3 ml of the fluor solution and subjected to LSC analysis. The results (Table 1-3-19) indicate that the values obtained in solution are roughly twice those obtained for the solid film. This supports the general practice of multiplying results obtained for solid film by 2. The results also indicate that not more than 30% of the surface carboxylic acid groups are esterified. Additionally, it appears that the sulfuric acid-catalyzed esterification is half as efficient as the other methods.

Reduction of PCTFE-COOH With Borane/Tetrahydrofuran.

Reactions involving BH_3/THF with carboxylic acids and olefins are known to be rapid and in most cases quantitative when conducted in solution. The resulting products, upon suitable hydrolysis, are alcohols and alkanes; therefore, BH_3/THF can be used as an efficient means of reducing both carboxylic acids and olefins. The application of this reaction to modified PCTFE represents an attempt to obtain information about organic transformation reactions and provides more information about surface structure-reactivity relationships. The surface of PCTFE prepared by reaction of LiTMO at -20°C contains both TMO functionality as well as unsaturation. When this surface is exposed to hydrolysis conditions nitrogen is removed from the surface and the XPS oxygen intensity increases. Oxygen intensity is expected to increase more than the nitrogen decreases because upon hydrolysis oxygen composes a higher percentage of atoms in the surface since carbon as well as nitrogen are removed upon deprotection. However there exists the possibility that hydrolysis of the conjugated backbone also occurs. That this does not occur was examined through chemical reactions; comparison of the PCTFE-TMO which was first reduced then hydrolyzed to the surface that was simply hydrolyzed should give an indication of the extent of double bond hydrolysis. The LiTMO modified surface was treated with tribromophenylisocyanate (TBPI) which was expected to react with any carboxyl or hydroxyl functionalities and then the surface was analyzed by XPS for bromine atomic composition. The PCTFE-TMO film was also reacted with BH_3/THF and then acetic acid/THF to give the hydrogenated surface PCTFE(H)TMO. That the surface was hydrogenated was indicated from the rapid visual color change; from yellow to colorless. Additionally the PCTFE-TMO film was reacted under hydrolysis conditions to give PCTFE-COOH. These two films were then reacted with TBPI and analyzed with XPS, again using the bromine atomic composition as an indication of hydroxyl and carboxylic acid groups. PCTFE(H)TMO was hydrolyzed to give PCTFE(H)COOH and this film and the PCTFE-COOH were reacted with BH_3/THF to give respectively PCTFE(H)CH_2OH and PCTFECH_2OH. These films were reacted with TBPI and again analyzed using XPS. This series of reactions is presented along with the XPS atomic composition and contact angles in Figure 1-3-23.

XPS atomic compostion data for this series indicate that this data cannot be used to support the claim that oxygen is introduced through hydrolysis of the conjugated backbone. If hydrolysis of the backbone



Sample	Contact Angle (degrees) Advancing	Contact Angle (degrees) Receding	XPS Percent Atomic Composition Data for Takeoff Angles 15°/75° Br	F	O	N	C	Cl	Si
1	72±1	25±2	0.37	14.8	10.4	5.98	64.1	2.87	1.55
			0.04	23.6	7.96	5.00	55.8	7.35	0.19
2	75±1	22±1	1.19	13.0	17.6	4.57	58.2	4.97	0.42
			1.14	17.9	13.3	5.19	54.7	7.45	0.33
3	62±1	5±1	0.00	24.3	13.1	1.15	54.9	6.47	0.16
			0.00	32.2	8.64	1.35	47.6	9.56	0.59
4	67±1	8±2	3.87	11.5	18.1	3.36	44.2	5.36	0.08
			3.12	16.1	13.6	3.16	42.5	8.50	0.00
5	75±1	31±1	0.00	23.4	10.9	4.58	55.4	5.31	0.55
			0.00	23.8	8.26	3.67	51.8	7.50	0.00
6	72±1	25±3	1.25	16.7	28.5	3.36	44.2	5.36	0.08
			0.62	24.0	21.2	3.16	43.5	8.50	0.00
7	78±1	35±2	0.00	36.0	10.3	0.29	40.5	10.8	1.99
			0.25	41.1	7.37	0.63	39.5	11.2	0.00
8	71±1	20±1	2.70	23.2	12.3	1.17	52.8	7.82	0.00
			1.37	34.4	9.12	1.40	43.2	10.3	0.20
9	74±1	28±2	0.02	30.4	12.8	1.16	45.0	9.65	1.79
			0.00	37.2	9.10	1.12	41.0	10.8	0.80
10	72±1	20±1	2.45	27.1	12.0	2.24	47.3	7.89	1.15
			1.24	34.8	8.20	1.51	41.9	10.3	1.99
11	78±1	35±1	0.00	38.7	10.7	1.55	38.4	9.50	1.08
			0.00	42.0	10.7	1.04	35.2	11.0	0.00
12	77±1	24±1	1.84	31.5	9.86	1.70	46.3	8.79	0.00
			1.21	37.0	8.25	1.56	40.3	10.1	1.64

Figure 1-3-23. XPS and contact angle data for the BH_3/THF reactions.

were to occur then PCTFE(H)COOH would have less oxygen introduced than PCTFECOOH; instead, the two values are not significantly different.

Likewise PCTFE(H)CH_2OH and PCTFECH_2OH should exhibit the same differences but again the XPS data indicated that the two have roughly the same oxygen intensities. The XPS data were consistent for those samples which were expected to have low levels of hydroxyl and carboxylic acid groups, PCTFETMO and PCTFE(H)TMO, which both had the lowest amount of bromine incorporated (1 %) upon exposure to the TBPI. XPS indicated surfaces exposed to hydrolysis then TBPI increased the amount of bromine incorporated, consistent with the introduction of carboxylic acid groups. It is also obvious from XPS atomic composition data that exposure of the surface to THF results in a large restructuring. That this restructuring occurs is most obvious from the increase in the fluorine atomic composition; PCTFECOOH was not exposed to THF and had the lowest fluorine content, PCTFE(H)CH_2OH was exposed to THF twice and it had one of the highest fluorine contents.

This series of reactions illustrates the difficulties encountered when studying reactions at a surface. The primary analytical tool, XPS, often does not have the capability, alone, to fully characterize a surface. When labelling methods are attempted they may not be specific, as in this case, for a single functional group. In addition when chemical reactions are executed at a surface the choice of reaction conditions must be made carefully; otherwise, as in this case, the solvent can induce structural reorganization. This can result in erroneous XPS interpretation, especially if the substrates being used are complex and not readily characterizable at the molecular level.

References

1. Dias, A.J.; McCarthy, T.J. **Macromolecules** 1984, 17, 2529

2. Starks, C.M.; Liotta, C. Phase Transfer Catalysis: Principles and Techniques, Academic Press: New York, 1978

3. Weber, W.P.; Gokel, G.W. Phase Transfer Catalysis in Organic Synthesis, Springer Verlag: Berlin, 1978

4. Kise., H.; Ogata, H. **J. Polym. Sci.: Polym. Chem. Ed.** 1983, 21, 3443

5. a) He, F.; Kise, H. **J. Polym. Sci.: Polym. Chem. Ed.** 1983, 21, 1729
   b) Kise, H. **J. Polym. Sci.: Polym. Chem. Ed.** 1982, 20, 3189

6. Schwartz, A.M. **J. Colloid Interface Sci.** 1980, 20, 3189

7. Kato, K. **J. Appl. Polym. Sci.** 1974, 18, 3087

8. Danielson, N.D.; Taylor, R.T.; Huth, J.A.; Siergiej, R.W.; Galloway, J.G.; Paperman, J.B. **Ind. Eng. Chem. Prod. Res. Dev.** 1983, 22, 303

9. Dias, A.J.; McCarthy, T.J. **Macromolecules** 1985, 18, 1826

10. Kobrich, G. **Angew. Chem. Int. Ed. Engl.** 1967, 6, 41

11. Cais, R.E.; Kometani, J.M. **Macromolecules** 1984, 17, 1932

12. Chambers, R.D.; Mobbs, R.H. **Adv. Fluorine Chem.** 1965, 4, 54

13. Greene, T.W. Protecting Groups in Organic Chemistry, Wiley-Interscience: New York, 1981

14. Eaton, P.E.; Cooper, G.F.; Johnson, R.C.; Mueller, R.H. **J. Org. Chem.** 1972, 37, 1947

15. Alexander, A.E.; Hibberd, G.E. in Weissberger, A.; Rossiter, B.W. eds. Techniques of Chemistry, Wiley Interscience: New York, 1972, Volume 1, Part V, p. 575

16. Meyer, A.I.; Temple, D.L.; Nolen, R.L.; Mihelich, E.D. **J. Org. Chem.** 1974, 39, 2778

CHAPTER IV: CONCLUSIONS AND SUGGESTIONS

This work represents the initial phase of an ongoing program involved with the study of polymer interfaces. Detailed fundamental experimental studies of polymer interfaces require well defined model surfaces: surfaces which are not available through currently practiced methods of polymer modification. This thesis has as a primary objective the preparation of well defined model surfaces on which further fundamental studies can be conducted. A second objective involves the development of analytical techniques which can characterize these surfaces at the molecular level. These two objectives cannot be approached independent of one another nor are they independent of the more fundamental objective of elucidating polymer surface structure-reactivity relationships.

Phase-transfer catalyzed dehydrofluorination of poly(vinylidene fluoride) was successfully employed to prepare a well characterized model surface. The eliminated surface was demonstrated, through a combination of analytical methods and reaction kinetics, to be a two-dimensional array (approximately 18 Å thick) of organic double bonds. Surface selectivity was the result of the sharp interface existing between the organic poly(vinylidene fluoride) film and the aqueous base; thus, phase transport limited the reaction to the surface. Temperature affected phase transport; high temperatures reduced the sharpness of the interface resulting in a thicker modified region and low temperatures sharpened the interface resulting in thinner modified layers. Reaction of the double bond surface resulted in new high energy surfaces; in this manner, two-dimensional arrays of polar functional groups were introduced into layers whose thickness was limited to the thickness of the eliminated layer. Not all reactions result in surfaces which are easily characterized: Reactions involving solid suspensions resulted in roughened surfaces making contact angle data difficult to interpret. Certain modifications were not specific to just the double bonds making gravimetric data ambiguous. Reactions which introduce oxygen into the surface require chemical derivatization in order to fully characterize them. This was illustrated for the hydrolysis of eliminated poly(vinylidene fluoride). It was possible to identify the oxygen species using a combination of direct analytical observation, XPS, and chemistry (reduction and labelling reactions). These experiments indicate that since the amount of label which was incorporated increased after reduction, more than one type of oxygen species was present: enolizable ketones, hydroxyl groups and nonenolizable ketones are possibilities.

Additional characterization work needs to be done if this substrate is to be used to study oxygen containing functional groups. The presence of more than one type of oxygen species was indicated, however this characterization was incomplete. Carboxylic acid groups may be present even though they did not show up in the attempted labelling studies. Their presence should additionally be checked by using BH_3 reduction and XPS labelling. This surface can be used for a variety of reactivity studies which do not involve just the introduction of oxygen. Preliminary work indicated that LiTMO reacted selectively with the brominated surface. As illustrated for PCTFE this method permits the flexible incorporation of a wide range of functionality; however, XPS characterization of the reacted surface needs to be done to assure that the expected reaction is occurring. Bromination was an effective reaction. Studies of displacement reactions involving Sn1 and Sn2 type mechanisms using this two-dimensional array of alkyl bromides should be facile and provide valuable information about this class of reactions when executed on surfaces. Initial investigations involving ammonia indicate that indeed bromine can be displaced resulting in surface amine groups.[1]

Poly(chlorotrifluoroethylene) was successfully reacted with a wide range of organometallic reagents. The reaction between PCTFE and organolithium reagents was examined with regard to both mechanism and products. Once this information was obtained, the reaction was extended to introduce a wide range of polar functional groups onto the PCTFE surface. The reaction of the functional organolithium reagents was shown, through a combination of analytical methods and chemical kinetics, to introduce functional groups into a layer whose thickness ranged from tens to thousands of angstroms. That this thickness is controllable is another asset of this modification method. It was observed, once again, that the sharpest interface was produced at the lowest temperatures and in this case the reactions at $-78^{\circ}C$ gave a surface whose thickness ranged from 10 to 50 Å. The most dramatic temperature dependence was observed for the introduction of hydroxyl groups using lithiopropylethyl acetaldehyde acetal. The origin of this dependence is not known. Future investigations aimed at this dependence might provide an explanation as to why some reactions exhibit autoinhibition and others do not. Solvent also affected the sharpness of the interface. High THF concentrations resulted in a thicker modified region, similar to an increase in temperature. This is a likely the result of two factors: the THF increases the mobility of the surface through swelling; and the lithium reagent is better solvated in a coordinating solvent like THF, hence it may be smaller and therefore have a higher rate of diffusion in PCTFE. Another area for future work is the determination of the more important influence. Understanding these factors may provide a useful tool for probing polymer surfaces.

The flexibility exhibited by this method of preparing model surfaces represents a major advantage over other methods of surface modification. This flexibility is highlighted in the studies involving the carboxylic acid surface. When relating surface structure to macroscopic properties it is necessary to characterize the surface quantitatively. The problem with current methods of quantitation is that they tend to rely on derivatization of the surface; therefore, what is actually being determined is the number of functional groups being reacted and this only represents the total number present when the derivatizations are quantitative and selective. The method of quantitation used in this thesis represents a new technique which does not rely on derivatization but instead quantitates the functional group site densities through the use of [^{14}C] labeled lithium reagents. In this method the functional groups themselves are the source of the radioactivity. The maximum number of carboxylic acid groups introduced using this method was determined to be $(9.7\underline{+}0.6)\times10^{-10}$ moles/cm^2 (95% confidence based upon 10 measurements). The actual number of carboxylic acid groups was approximated to be $(5.6\underline{+}1.7)\times10^{-10}$ moles/cm^2. These values were then used to monitor esterification reactions, much in the way functional groups are currently quantitated. The results indicate that no more than 30% of the PCTFECOOH groups are esterified. Differences in the esterification between methods were also observed: sulfuric acid catalyzed esterification resulted in only 10% esterification. This low extent of reaction presumably represents the groups which were accessible to the acid. A comparison between LSC data obtained on [^{3}H] labelled film and on the same film in solution indicated that roughly half the groups are counted in the former case; thus, the practice of doubling the radioactivities obtained for tritium labeled solids appears to be reasonable. Further applications of this "double" labelling method to include the other surfaces is straightfoward. Also a comparative study involving the same surface produced at two different temperatures should provide additional evidence for the accessibility of the reagents. For example, if the esterification is repeated utilizing the -78°C prepared surface and the reaction extents are found to increase, then it can be inferred that accessibility is the primary cause for the low reaction extents.

Another reaction which was examined was the BH_3/THF reduction of the modified PCTFE surface. These experiments demonstrate the application of chemistry to the solution of problems concerning functional group reactivity. In this case there exists the possibility that hydrolysis of the PCTFETMO surface to deprotect the carboxylic acid groups may also cause hydrolysis of the conjugated backbone. That this did not occur is indicated from the XPS atomic composition of a hydrolyzed PCTFETMO film and a BH_3/THF reduced (PCTFE(H)TMO) and hydrolyzed film; the two films had approximately the same oxygen atomic compositions. Another important finding is that THF induced structural reorganization of the surface which complicate the XPS data. Therefore future work should be focused at the study of functional group mobility induced by both temperature and solvent. Preliminary work suggests that this surface undergoes facile thermal rearrangement[2]. Additionally it would be useful to know the extent of reduction; this can be approached using this surface and its reaction with $[^3H]BH_3$ or through derivatization of the reduced surface with $[^3H]$ labeled reagents.

Application of this reduction to the other functionalized PCTFE surfaces would provide further data on functional group reactivity. Studies on the LiDT surface should be especially telling; the PCTFE-DT surface is relatively free of contaminating oxygen which complicated the PCTFE-TMO study. Therefore the analogous reduction-hydrolysis study should be facilitated. Additional studies of the reduced surface may also provide an explanation for some of the observed XPS results:

(the presence of mercury and residual sulfur) both may be present from secondary reactions with the unsaturation. A preliminary study indicated that BH_3/THF reacted with the unsaturation and not the dithiane protecting group. This investigation was complicated by the structural reorganization induced by the THF; therefore, additional studies should be conducted using solvents which do not cause the surface to reorganize.

References

1. Brennan, J.V.; McCarthy, T.J. This laboratory, unpublished results

2. Dias, A.J.; Cross, E. M.; McCarthy, T.J. This laboratory, unpublished results

PART II: MODIFICATION OF SYNTHETIC POLYMERS: PREPARATION OF SEMICONDUCTING POLYMERS

CHAPTER I: Introduction

Conducting polymers represent a major research area which contains diverse fundamental scientific issues as well as having the potential for commercial applications. Polymers with conjugated Pi-electron backbones display unique electronic and optical properties compared to conventional polymers. These properties include: low ionization potentials, low energy optical transitions and high electron affinities. Collectively these properties result in a class of polymers which can be reversibly oxidized or reduced more readily than conventional nonconjugated polymers. This oxidation or reduction is accomplished either electrochemically or through the use of charge-transfer additives (dopants) and in doing so the normally insulating polymer is converted into a conducting polymer. In many cases the electronic conductivity of these polymers is almost metallic. In addition to being used as subtrates for the study of electronic conductivity[1] these polymers possess interesting optical[2] and electrochemical[3] properties which are also currently being investigated.

Though research on conjugated polmers has been conducted for many decades[4], it has undergone a renaissance within only the last 10 or so years. Two of the key developments which served to ignite the current volume of research were the discovery by Ito _et al_[5] of a synthetic route to free-standing, high quality films of polyacetylene and the discovery by Shirakawa _et al_[6] that these films could be doped by electron donors or acceptors to conductivity levels (1000 S/cm) approaching those of some metals. Polyacetylene can be considered to be the archetypal conducting polymer. Much of what is known about conducting organic polymers has been obtained from a large number of both experimental and theoretical studies of polyacetylene[7].

An attractive goal for conducting polymers is to combine the processibility and other desirable properties of polymers with the electronic properties of metals or semiconductors. Unfortunately, the high density of conjugated Pi-bonds which are necessary for the desirable electronic and optical properties also makes the polymer chain rather stiff. Hence the polymers are usually less soluble and less fusible than nonconjugated polymers.

Many conjugated polymers are prepared directly from conventional polymerization processes: Ziegler-Natta, electrochemical coupling, Wittig, Friedal-Crafts and nucleophilic displacement generate such polymers as polyacetylene, polypyrrole, poly(phenylene vinylene), poly(p-phenylene), and poly(p-phenylene sulfide), respectively. Produced as above, these polymers are generally isolated as insoluble films. This lack of processibility tends to restrict the possible uses for these materials. The methods which have been examined as routes to processible conducting polymers include: copolymerization of the conjugated polymer with a block or grafts of a second soluble polymer, preparation of blends of conjugated polymers with processible polymers, polymer modification which involves the transformation of an existing nonconjugated polymeric precusor into the target conjugated polymer[8], and preparation of the conjugated polymer directly in a solvent which has the ability to solvate the polymer chains. What follows is a brief review of these alternative methods of preparing conjugated polymers placing emphasis on those aspects which pertain directly to the research presented in this dissertation.

Conducting Copolymers and Blends

Many copolymers of acetylene and substituted acetylenes have been prepared using Ziegler-Natta polymerization. Substituted acetylenes like methylacetylene and phenylacetylene are generally more soluble than polyacetylene. This has been attributed to the presence of side groups in the polymer which force the polymer to adopt a conformation which is unfavorable to the overlap of Pi-orbitals. Thus the effective degree of conjugation is reduced. If the fraction of the substituted acetylene in the copolymer is high enough, then the copolymer will be soluble. Generally these copolymers exhibit conductivities many orders of magnitude lower than polyacetylene homopolymer.

Graft copolymers of polyacetylene and insulating polymers have been prepared by exposure of negatively charged donor-doped polyacetylene to a variety of monomers including styrene, ethylene oxide, isoprene, butadiene and methyl methacrylate[9]. This approach of using doped polyacetylene as the polymerization catalyst results in highly colored, soluble graft copolymers. The alternative approach in which the nonconjugated polymer matrix is used as a catalyst for acetylene polymerization has also been shown for anionic polystyrene[10]. Two of the objectives for these block and graft copolymers are to impart solubility as well as environmental stability to the conducting fraction. However in forming these materials a dilution of the conductive material in the insulating matrix is also achieved. Thus the conductivities, if present at all, of these materials are greatly reduced.

Polyacetylene has also been blended with polybutadiene and polyisoprene[11]. These blends are synthesized by exposing the catalyst impregnated polymers to acetylene gas. These blends are two phase systems which contain microdomains of polyacetylene dispersed in the elastomer matrix. At high ratios of polyacetylene to elastomer (>40 % polyacetylene) the rubber loses its elasticity and resembles a highly filled rubber. This is a consequence of the rigidity of the microcrystalline domains of polyacetylene in the amorphous matrix. The doped conductivity of these filled elastomers is the highest (50 s/cm) when the elastomer is stretched prior to doping[11]. Thus the stress induces order in the polyacetylene domains which enhances the conductivity.

Electrochemical polymerizations have also been used to prepare a variety of conducting copolymers as well as conducting polymer blends. Copolymers are prepared using doped polyacetylene[12] as the electrode material. Pyrrole is oxidatively polymerized onto the conducting polyacetylene. The resulting structure exhibits improved air and water stability relative to polyacetylene homopolymer.

Interpenetrating networks of polypyrrole in swellable insulating plastic materials have also been produced electrochemically. The electrodes are coated with thin layers of insulating polymers like poly(vinyl alcohol) or poly(vinyl chloride) and exposed to a solution of pyrrole[13]. On diffusion through the insulating coating, pyrrole contacts the potential necessary for polymerization within the insulating polymer coating. The resulting composite blend of interpenetrating polypyrrole filaments in the insulating matrix exhibit good mechanical properties and only low levels of electronic conductivity.

Polymer Solutions

The solubilization of highly conjugated conducting polymers has long eluded researchers in the field. Preparation of soluble conducting polymers is sought for both fundamental scientific and commercial interest. In the solvated state the polymer is more amenable to obtaining better resolved analytical data, which would aid in the determination of molecular configurations and structure. Conducting polymer solutions would be important for commercial applications since polymer solutions are in a form which can be dealt with using modern conventional plastics processing technology. There are several reasons for the insolubility of conducting polymers: the rigidity of the conjugated backbone; the high concentration of free radicals, radical ions and ions which can participate in crosslinking reactions; and the crystallizability of the conjugated backbone. Collectively these serve to make the formed conjugated polymers insoluble. The list of solvent systems capable of dissolving certain conducting polymers is limited to two: molten iodine[14] and arsenic trifluoride[15]. These solvents have not yet been able to dissolve a free-standing polyacetylene film, but certain conducting polymers are soluble when prepared using I_2 and AsF_3 as polymerization solvents.

Molten iodine was used as a solvent for the synthesis and solubilization of conducting polycarbazoles[14]. The monomer that was used was the N-alkyldihalo derivative of carbazole which becomes doped during polymerization. Thus iodine serves as both solvent and dopant. The films cast from the solution displayed a conductivity of 1 s/cm. The resulting polymer had a THF soluble fraction and an insoluble, presumably crosslinked, fraction. The molecular weight of the soluble fraction was monitored by GPC. A range of molecular weights was found with the maximum estimated at 5×10^3.

AsF_3 was used as a solvent for a variety of conducting polymers: poly(p-phenylene sulfide), poly(p-phenylene oxide), polythiophenes and polyphenylenes[16]. Solutions of the nonconducting precursor polymers, poly(p-phenylene sulfide) and poly(p-phenylene oxide) are prepared in AsF_3, then an oxidant is added. In this manner a solution of the conducting form of the polymer is obtained. In the case of polythiophene and polyphenylene, AsF_3 solutions of the monomers and an oxidant are prepared. Thus polymerization and doping occur simultaneously in the solution. Although both arsenic trifluoride and molten iodine are exotic solvent systems, they do demonstrate that it is possible to dissolve certain conducting polymers.

These solutions can be diluted or concentrated to any concentration without the appearance of a sharp phase transition.

Reduction of the solvent volume under vacuum results in a free standing film. The film, once cast in this manner, is no longer soluble in AsF_3. This irreversible phase transition from solution to solid is a likely result of either crystallization or covalent bond formation within the polymer, both of which can be induced by removal of a stabilizing solvation sphere.

Polymer Modification

The modification of nonconjugated soluble polymers to form highly conjugated materials has been a major area of research for many years[17,18]. The modifications can be broadly classed into two types: pyrolytic modification in which the polymer is heated to high temperatures (350 - >600°C) either in vacuum or in air.[19-21] The resulting crosslinked aromatic (graphitic) polymer strucures are porous, lightweight, brittle and usually exhibit relatively good conductivities (20 s/cm). These resulting structures are not very well characterized. The chemical modification of nonconjugated polymers to form conducting polymers makes use of fast, high yield organic reactions which have precedence in low molecular weight compounds[22]. These reactions on polymers typically involve the thermally or chemically induced elimination of a small molecule from the polymer backbone. These reactions are used to produce a variety of conducting materials which again are usually insoluble. Their characterization is again limited. The structural information is inferred from knowledge about the reaction on small model organic compounds as well as from comparisons to the conjugated materials prepared directly from monomers. The highest conductivities obtained through this method are generally 1-2 orders of magnitude less than those obtained directly from polymerization of the monomer.

One of the most widely studied methods for modifying polymers to form highly conjugated polymers is dehydrohalogenation of poly(vinyl halides). One of the earliest synthesis of a conjugated polymer was achieved by Marvel et_al[4] who demonstrated that poly(vinyl chloride) could be eliminated to form a polyacetylene-like polymer. This same polymer was produced by Ostromysslenski at a much earlier date[4]. The thermal elimination of poly(vinyl halides) was found to be autocatalytic: allylic chlorine atoms are more labile[23] and the hydrohalic acid which forms catalyzes the elimination[24]. The thermal elimination thus propagates down the chain forming the insoluble product which contains a conjugated backbone.

The base catalyzed dehydrohalogenation of poly(vinyl chloride) has also been widely studied. These reactions were conducted with the polymer dissolved in THF. The dehydrochlorination was run with a variety of bases, among them were: phenoxides[8], amines[25], alkali metal amides[8], hydroxides[26], and alkoxides[8]. The extent to which chlorine atoms can be eliminated from a polymer is seldom complete. Flory calculated that on a statistical basis only 86%[27] of the chlorine could be removed reductively, as with zinc, however this value has often been wrongly quoted for base catalyzed dehydrohalogenation. For this value to be correct there would have to be a significant amount of cyclization occuring. However these eliminated polymers still contain low levels of saturated carbon. The presence of these saturated carbons restricts the electronic conductivity to low levels.

Poly(vinylidene halides) can also be eliminated to form conducting polymers. These polymers can be eliminated by reacting polymer solutions with the desired base. This time the resulting structure will contain both double and triple bonds. These polymers were also eliminated recently using a method involving the phase-transfer catalyzed dehydrohalogenation of solid poly(vinylidene halide) and poly(vinyl halide) polymers[28]. Thus the polymers could be cast into the desired form before the elimination reaction occurs. After the elimination the resulting polymers were insoluble and exhibited iodine doped conductivities of 1×10^{-5}s/cm. A drawback to this method is that the phase-transfer reaction is limited to the surface of the film, the true conductivity of the reacted material may be higher. Even when the polymer was reacted under more forcing conditions the resulting conductivity remained in the same order of magnitude. Thus though these conditions were capable of inducing complete elimination, they could also induce deleterious substitution reactions. This resulted in a sample which was thicker, but an inherently poorer conductor.

Objectives for This Work

This part of the dissertation has for its primary objective the extension of polymer modification reactions to preparing new conducting polymers. These methods as a secondary objective will present improved avenues for preparing "processable" conducting polymers. The most desirable modification method for meeting these objectives is one in which the precursor polymer is dissolved and isolated as a soluble highly conjugated conducting polymer. This has not yet been achieved and, as the results using AsF_3 and molten I_2 as solvents presented previously suggest, probably will not be achieved. Failing this, a modification method which allows the same degree of processibility as the AsF_3 solutions, but which replaces the exotic solvent with a more common solvent, was sought. Thus the base catalyzed dehydrofluorination of poly(vinylidene fluoride) and poly(trifluoroethylene) as well as the base catalyzed isomerization of polybutadiene were executed with the objectives of studying the variables which permit the preparation of conjugated polymer solutions.

References

1. Skotheim, T.A. ed. Handbook of Conducting Polymers, Marcel Dekker: New York, 1986, Volumes 1 & 2

2. a) Agrawal, G.P.; Cojan, C.; Flytzanis, C. **Phys. Rev.** 1978, B17, 778 b) Williams, D.J. ed. Nonlinear Optical Properties of Polymers, Americal Chemical Society: Washington, D.C., 1983

3. Chidsey, C.E.D.; Murray, R.W. **Science** 1986, 231, 25

4. Marvel, C.S.; Sample, J.H.; Roy, M.F. **J. Am. Chem. Soc.** 1939, 6, 3241 which comments on the earlier work by Ostromysslenski **Chem. Zentr.** 1913, 84II, 1187

5. Ito, T.; Shirakawa, H.; Ikeda, S. **J. Polym. Sci.: Polym. Chem. Ed.** 1974, 12, 11

6. Shirakawa, H.; Louis, E.J.; MacDiarmid, A.G.; Chiang, C.K.; Heegar, A.J. **J. Chem. Soc. Chem. Comm.** 1977, 578

7. Chien, JCW Polyacetylene, Wiley Intersciene: New York, 1984

8. Kise, H.; Ogata, H. **J. Polym. Sci.: Polym. Chem. Ed.** 1983, 21, 3443

9. Galvin, M.E.; Wnek, G.E. **Polym. Comm.** 1982, 23, 795

10. Baker, G.L.; Bates, F.S. **Macromolecules** 1984, 17, 2619

11. Rubner, M.; Tripathy, S.; Lee, K.; Georger, J.; Jopson, H.; Cholewa, P. **Division of Org. Coat. and Appl. Polym. Sci.** 1983, 48, 544

12. a) Ahlgren, G.; Krische, B. **J. Chem. Soc. Chem. Commun.** 1984, 946 b) Maxfield, M.; Wolf, J.F.; Miller, G.G.; Frommer, J.E.; Shachlet, L.W. **J. Electrochem. Soc.** 1986, 133, 117

13. a) Lindsay, S.E.; Street, G.B. **Syn. Met.** 1984, 10, 67 b) Niwa, O.; Tamamura, T. **J. Chem. Soc. Chem. Commun.** 1984, 817

14. Jenekhe, S.; Wellinghoff, S.; Reed, J. **Mol. Cryst. Liq. Cryst.** 1984, 105, 175

15. Frommer, J.E. **Acc. Chem. Rec.** 1986, 19, 2

16. Paushkin, Y.M.; Vishnyakova, T.P.; Lunin, A.F.; Nizova, S.A. in Organic Polymeric Semiconductors, Wiley Interscience: New York, 1974

17. Gibson, H.W. **Polymer** 1984, 25, 3

18. Grassie, N.; McNeil, J.C. **J. Polym. Sci.** 1959, 128, 312

19. Manassen, J.; Wallach, J. **J. Am. Chem. Soc.** 1965, 87, 2671

20. Bruck, S.D. **Polymer** 1965, 6, 319

21. March, J. Advanced Organic Chemistry, McGraw-Hill: New York, 1977

22. Campbell, J.E.; Rausher, W.H. **J. Polym. Sci.** 1955, 18, 461

23. a) Guyot, A.; Benevise, J.; Trambouse, Y. **J. Appl. Polym. Sci.** 1962, 6, 103 b) Troitskaya, L.S. **Chem. Abstr.** 68:3221

24. a) Matheson, L.A.; Boyer, R.F. **Ind. Eng. Chem.** 1952, 44, 867 b) Fuchs, N. **Makromol. Chem.** 1957, 22, 1

25. Bohrer, J. **Trans. NY Acad. Sci.** 1955, 2, 20 and also ibid. 1958, 5, 367

26. Marvel, C.S.; Sample, J.H.; Roy, M.E. **J. Am. Chem. Soc.** 1943, 65, 1716

27. Flory, P.J. **J. Am. Chem. Soc.** 1939, 61, 1518

28. a) Kise, H. **J. Polym. Sci.: Polym. Chem. Ed.** 1982, 20, 3189 b) He, F.; Kise, H. **J. Polym. Sci.: Polym. Chem. Ed.** 1983, 21, 1729 c) reference 8

CHAPTER II: EXPERIMENTAL SECTION.

Materials

Acetonitrile

2,2'-Azobis(2-methylpropionitrile) (AIBN) (A)

Barium oxide (F)

Benzene (A)

Benzene-d_6 (A)

Benzophenone (A)

Calcium hydride (A)

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (A)

Dicyclopentadiene (A)

Dimethylformamide (DMF) (A)

Dimethyl sulfoxide (DMSO) (A)

Dimethyl sulfoxide-d_6 (DMSO-d_6) (A)

Electrodag 502 (Ach)

Ethanol (F)

Heptane (F)

Hexane (F)

Iodine (F)

Lithium 2,2,6,6-tetramethylpiperidide (Harpoon) (Alfa)

Methanol (F)

2-Methyl-2-propanol (A)

Polybutadiene (SPP)

Poly(chlorotrifluoroethylene) (Af)

Poly(vinylidene fluoride) (PS)

Potassium *t*-butoxide (A)

Potassium hydride (A)

Potassium hydroxide (A)

Potassium fluoride (A)

2-Propanol (F)

R3-11 catalyst (C)

Sodium (A)

Tetrahydrofuran (F)

Tetramethylammonium hydroxide (A)

Tributyltin hydride (A)

Sources: A=Aldrich; Ach=Acheson; Af=Afton Plastics Molding Co. (Lakeland, Minnesota); Alfa=Alfa; C=Chemalog (S. Plainfield, N.J.); F=Fisher; PSS=Polysciences; SPP=Scientific Polymer Products

Material Handling.

Many of the materials used and the products whose preparation is described in this thesis are sensitive to air and water. Thus it was necessary to prepare and analyze these materials in carefully controlled anaerobic environments. The methods for obtaining suitable environments are well extablished in the literature and widely practiced, therefore these techniques will be discussed only briefly here[1].

The inert gas lines used were constructed out of 1/4" O.D. copper tubing and brass Swagelock fittings. The inert gas was either prepurified nitrogen or prepurified nitrogen passed through a column of R3-11 catalyst, to remove oxygen, and through a column of drierite, to remove water. Connections were made to the gas line using 1/4" I.D. Tygon tubing and the syringe needles were attached to male Luer lock to 1/4" I.D. tubing connectors.

The vacuum lines were constructed at the University of Massachusetts glass shop. The line (figure 1-2-1) was connected to a Precision vacuum pump through a liquid nitrogen cooled trap. The other end of the line was connected to a balast (1 liter). The vacuum was monitored using a Teledyne Hastings vacuum meter and gauge. Typical operating pressure for the vacuum line was 0.05 mm Hg.

Schlenk glassware was prepared at the University of Massachusetts glass shop. The distinguishing feature of Schlenk glassware is that it typically has two openings: one is a sidearm containing a 4mm straightbore Teflon stopcock and terminated in a 14/20 ₮ female connection; the other opening is a 24/40 ₮ male joint or a #25 O-ring connection (Figure 1-2-2). Using this glassware it was possible to flow nitrogen through the sidearm while adding or removing solids from the tube. Additionally, fluids were transported into and out of the tubes using cannula and a positive pressure of nitrogen.

Certain operations require the removal of the samples from the reaction vessels. When the operation involved only short time periods (1 - 2 minutes), they were carried out in polyethylene glovebags (I^2R) under a nitrogen atmosphere. Longer procedures were run in a Vacuum Atmosphere Company dry box.

Purification of Solvents and Reagents.

Distillations were performed through a 10 cm Vigreux column. Continuous distillations were run under nitrogen using a distillation head equipped with a overflow return tube at the bottom of the reservoir. Vacuum distillations were performed using a 10 cm Vigreux column; the pressure was monitored with a mercury manometer and regulated with a Manowatch (I^2R Company). Trap-to-trap distillations were performed using the apparatus depicted in part 1, figure 1-2-3 or using two vessels attached directly to the vacuum manifold. In this method the solvent is thoroughly degassed: freeze the solution with liquid nitrogen ($-195^{\circ}C$), open the frozen solution to the vacuum until the minimum pressure is observed, close the stopcock to the vessel and allow it to warm to room temperature. This freeze-pump-thaw cycle is repeated three times which removes the dissolved gases. The degassed solvent is again frozen and the vessel is evacuated until the minimum pressure is reached. If the distillation is run on the vacuum manifold then the stopcock to the vacuum is closed, the stopcock connecting the flasks is opened and a dewar containing liquid nitrogen is placed on the receiver flask. The dewar is removed from the flask containing the solvent and allowed to warm to room temperature. When the distillation is complete, the stopcock to the receiver is closed and the receiver is removed and placed under nitrogen. When the trap-to-trap apparatus is used, the dewar is removed from the flask containing the solvent and placed on the apparatus trap, without closing off the vacuum source. Upon completing the distillation, the stopcock is closed and the solvent is removed with a cannula and a positive pressure of nitrogen and stored under nitrogen.

Distillations from sodium benzophenone dianion necessitated special steps in order to achieve the deep purple color of the dianion rapidly: A new bottle, or one that has been suitably stored under nitrogen in a refrigerator, of HPLC grade solvent (uninhibited) was opened under a stream of nitrogen and quickly stoppered with a rubber septum; using a cannula and a positive pressure of nitrogen, the solvent was transferred into a nitrogen purged, septum stoppered Schlenk flask containing a magnetic stirring bar; the solvent was sparged with nitrogen (1 h) then benzophenone (2 g/L) and freshly cut sodium (1 g/L) were added to the flask under a stream of nitrogen. The mixture was stirred until the purple dianion color was achieved (3 - 6 h). The solvent was then ready for distillation.

<u>Acetonitrile</u> was HPLC grade and was distilled from calcium hydride

trap-to-trap and stored under nitrogen.

Benzene was HPLC grade and was continuously distilled from sodium benzophenone dianion.

Benzene-d_6 was Gold label and was distilled from calcium hydride trap-to-trap and stored under nitrogen.

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was vacuum distilled from calcium hydride (Bp 80°C, 0.6 mm).

Dicyclopentadiene was cracked to form cyclopentadiene which was collected in a -78°C trapped receiver and used immediately.

Dimethylformamide (DMF) was Spectrograde and was vacuum distilled from barium oxide (Bp 77°C, 40 mm) and stored under nitrogen.

Dimethyl sulfoxide (DMSO) was Gold label and was vacuum distilled from calcium hydride (Bp 70°C, 7 mm) and stored under nitrogen.

Dimethyl sulfoxide-d_6 (DMSO-d_6) was Gold Label and was vacuum distilled from calcium hydride (Bp 70°C, 7 mm) and stored under nitrogen.

Ethanol was degassed by three consecutive freeze-pump-thaw cycles prior to its use.

Heptane was HPLC grade and was continuously distilled from sodium benzophenone dianion.

Hexane was HPLC grade and was distilled from calcium hydride (Bp 69°C).

Iodine was dried by azeotropic distillation with benzene.

Methanol was refluxed overnight with magnesium turnings, then distilled and stored under nitrogen. It was further degassed by three consecutive freeze-pump-thaw cycles prior to use.

Polybutadiene (random cis-trans, 100,000 MW) was dried by swelling with benzene then removing the solvent by distillation.

2-Propanol was degassed by three consecutive freeze-pump-thaw cycles prior to use.

R3-11 Catalyst was activated by heating it to 160°C overnight in a stream of forming gas (Mateson 10% hydrogen, 90% nitrogen).

Tetrahydrofuran (THF) was HPLC grade and was distilled continuously from sodium benzophenone dianion.

Tetrahydrofuran-d_8 was distilled from calcium hydride trap-to-trap and stored under nitrogen.

2,2'-Azobis(2-methylpropionitrile) (AIBN); barium oxide; benzophenone; calcium hydride; Electrodag 502; Lithium 2,2,6,6-tetramethylpiperidide (Harpoon); 2-methyl-2-propanol; poly(chlorotrifluoroethylene) powder; poly(vinylidene fluoride) powder; potassium _t_-butoxide; potassium hydride (35 wt% dispersion in mineral oil); potassium hydroxide; sodium metal; tetramethylammonium hydroxide (2 _M_ in methanol); and tributyltin hydride were all used as obtained without further purification.

Measurements.

Infrared spectra of thin films cast on glass in vacuum and thin films cast on salt plates were recorded using a Perkin Elmer 283 spectrometer. UV-Vis spectra were obtained on polymer solutions using anaerobic cuvettes and a Perkin Elmer Lambda 3A spectrometer. UV-Vis spectra were obtained on thin films in a film holding attachment or by casting thin films directly on the cuvette wall. Titrations and pH measurements were obtained with Fisher pH and reference electrodes and a Fisher-Accumet pH meter. Fluoride analyses were obtained using a Corning fluoride selective electrode and the Accumet meter operating in the ion concentration mode. Proton NMR spectra of solutions prepared in sealed NMR tubes were recorded at 90MHz using a Perkin Elmer R32 spectometer. High field proton NMR and ^{19}F NMR were obtained on solutions in sealed NMR tubes using a Varian XL300 spectrometer. The specific electrical conductivity of the sample (σ) was determined by measuring the resistance (R) of a sample with known dimensions. The o can then be determined from:

$$\sigma = \frac{L}{R \times A}$$

Where L is the length between the electrodes and A is the cross-sectional area of the sample. The resistance was measured directly using a Fluka 8020B multimeter and the two probe mounting technique. In this method the sample is mounted in a glove box to two 0.1 mm diameter platinum wires using graphite paste (Electrodag 502). The apparatus (Figure 2-2-1) is then assembled and evacuated to 0.05 mm. Iodine doping entailed exposing the electrode mounted film to solid iodine for 4 h at room temperature (initial pressure 0.05 mm). Oxygen stability was examined by filling the apparatus with oxygen and monitoring the change in resistance. That the conductivity was electronic rather than ionic was shown through the absence of charge polarization: There was no decrease in the measured current with time; nor was there a large increase in current when the polarity of the

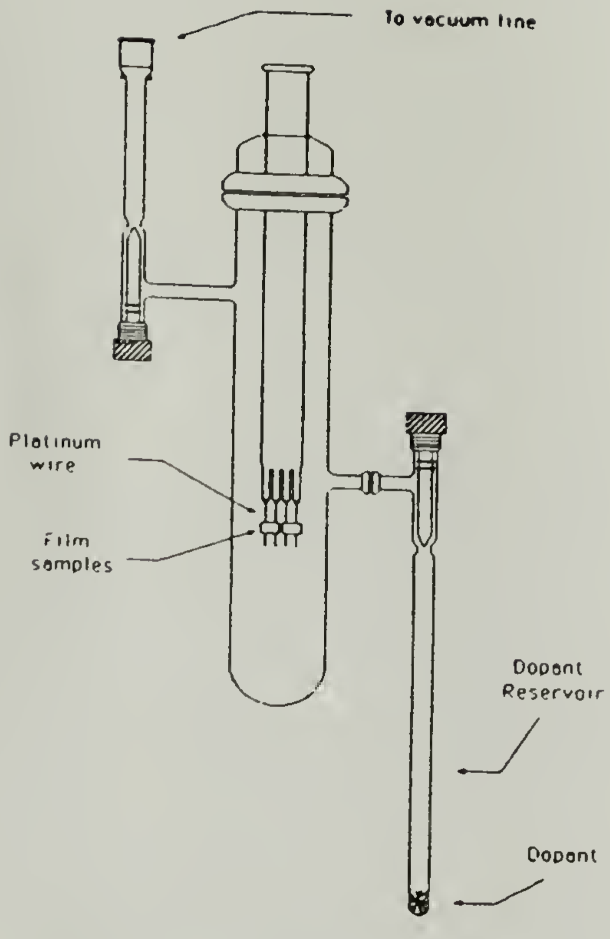


Figure 2-2-1. Conductivity apparatus.

voltage was reversed.

Preparation of poly(fluoroacetylene) (1:27, 40-43; 2:16, 18-20, 22, 24)

Poly(vinylidene fluoride) powder (0.200 g, 3.12×10^{-3} equivalents) was weighed into a clean, dry, degassed and tared Schlenk tube containing a Teflon-coated stirbar. The flask was capped, evacuated and flushed with nitrogen before introducing DMF (30 ml) via Hamilton airtight syringe. The mixture was stirred to dissolve the polymer. The tube was cooled to -23°C or alternatively room temperature, then the predetermined quantity of base was added dropwise via syringe over 15 minutes. The tube was kept at -23°C for 1 hour then removed and allowed to warm up to room temperature. The base concentration was determined by titration with 0.1<u>N</u> HCl to pH 6. The progress of the reaction was followed by titrating aliquots of the solution: all reactions were determined complete (total base consumption) in less than 24 h. The resulting mixture was centrifuged to remove the precipitated polymer and insoluble salts. Films were cast by transferring portions of the supernatant to tared vessels under nitrogen. These vessels were then evacuated with gradually decreasing pressure to constant mass. The eliminated polymer could also be isolated as a powder by adding 10 ml nitrogen sparged distilled water to the reaction mixture; followed by centrifugation-washing cycles using 5x20 ml water then 3x20 ml ethanol before drying at 25°C (0.05 mm) for 24 hours.

The concentration of the base used in this experiment was varied to alter the composition of the polymer. It was necessary to prepare the base solutions for the elimination: The calculated quantity of 2,2,6,6-tetramethylpiperidide (1.5<u>N</u> in ether) was transfered by cannula into a stoppered and purged Schlenk tube. The ether was removed under vacuum and DMF (10 ml) was added via cannula to the stirred HARPOON in its place. The required amount of tetramethylammonium hydroxide (2<u>M</u> in methanol) was added to a stoppered and purged Schlenk tube and the volume was brought up to 10 ml with DMF. A stock solution of KOH in 2-propanol (1.5<u>N</u>) was prepared by dissolving KOH (10 g) in a Schlenk tube with 2-propanol (100 ml). The calculated quantity of potassium <u>t</u>-butoxide was weighed in a glove box into a Schlenk tube containing a magnetic stirring bar. The tube was stoppered and DMF (10 ml) was added via cannula and the mixture was stirred to dissolve the base.

<u>Preparation of Poly(acetylene-co-ethylene)</u>. (2:23, 29, 46, 47, 51,

52, 55) Polybutadiene (1 g) was weighed into a clean, dry, tared and degassed Schlenk tube containing a Teflon-coated stirring bar. The flask was capped evacuated and then purged with nitrogen before THF (90 ml) was introduced via syringe. The mixture was stirred to dissolve the polymer. Potassium tert-butoxide (2.24 g) was dissolved in DMSO (10 ml) and was added dropwise via syringe to the stirred polymer solution. The reaction was monitored in the early stages by UV-Vis spectrophotometry of this reaction mixture in sealed cuvettes and by 90 MHz proton NMR in sealed 5 mm NMR tubes. Later stages were characterized by these methods and by analysis of the polymer obtained by precipitation with methanol. This procedure was followed at 0, 25 and 80°C. Isomerization reactions using other bases were executed in identical fashion: Potassium tert-butoxide was dissolved in tert-butanol. Potassium acetonitrilide was prepared from 2M potassium dimsyl and excess acetonitrile. Potassium dimsyl was prepared from potassium hydride and DMSO[2]. Potassium cyclopentadienide was prepared by adding 5 ml (excess) cyclopentadiene to an isomerization reaction initiated with potassium t-butoxide.

Preparation of Poly(trifluoroethylene). (3-11, 19)

PCTFE powder (2.0 g) was weighed into a clean, dry 100 ml flask that contained a magnetic stirring bar and a rubber septum stoppered condenser was attached. The apparatus was purged (15 min) with nitrogen before THF (50 ml) was introduced via cannula. Tributyltin hydride (10 g) and a solution containing 0.5 g AIBN in THF (10 ml) were also added via cannula. The mixture was placed in an oil bath at 65°C and stirred for 24 hours. At the end of this time period the PCTFE was completely in solution. The poly(trifluoroethylene) (PTF_3E) was precipitated with water/hexane (200 ml). The polymer was then extracted (24 h) with hexane in a Soxhlet extraction apparatus. The PTF_3E was then dried (24 h, 25°C, 0.05 mm) before IR, NMR and elemental analysis were obtained. Analysis:Calc. C:29.3; H:1.22; F:69.5 Found: C:29.6; H:1.28; F:69.1

Heterogeneous Preparation of Poly(difluoroacetylene). (3:15-17, 25-27) A film of poly(trifluoroethylene) (3 x 4 x 0.1 mm) was placed into a clean, dry, degassed and tared Schlenk tube. The tube was capped, evacuated and purged (15 min) with nitrogen before 10 ml of heptane was introduced via cannula. DBU (0.2 g) was then added to the tube via syringe. The tube was agitated with a Vortex Genie and allowed to stand 24 hours. After 24 hours the solution was removed via cannula and the film was washed consecutively with heptane (3x20 ml) and water (3x20 ml). The film was dried (24 h, 0.05 mm) before further analysis. The reaction was performed at 20°C and at 60°C. The film was characterized by IR, UV-Vis, electrical conductivity measurements and gravimetric determinations. Additionally the reaction mixtures were analyzed for fluorine content.

Homogeneous Preparation of Poly(difluoroacetylene). (3:15, 20, 26)

Poly(trifluoroethylene) (0.1 g) was weighed into a clean dry, degassed and tared Schlenk tube containing a Teflon-coated magnetic stirring bar. The tube was capped, evacuated and purged (15 min) with nitrogen before THF (10 ml) was introduced via cannula. The mixture was stirred to dissolve the polymer. DBU (0.19 g) in THF (10 ml) was added dropwise via cannula to the stirred polymer solution. The reaction was followed in the early stages by UV-Vis spectrophotometry of this reaction mixture in sealed cuvettes. Later stages of the reaction were characterized by this method, by analysis of the reaction solution for fluoride and by analysis of the polymer obtained by precipitation with water.

The kinetics of the elimination were also followed by ^{19}F NMR in sealed 5 mm NMR tubes. Poly(trifluoroethylene) (0.1 g) was placed in a purged, clean, dry and tared Schlenk tube containing a Teflon-coated magnetic stirring bar. The tube was capped, evacuated and purged (15 min) with nitrogen before THF (3 ml) was added. The mixture was stirred to dissolve the polymer. Sealed capillary tubes containing THF-d_8 and perfluorobenzene were prepared and added to the NMR tube to serve as both the external reference and deuterium lock. The polymer solution (0.5 ml) was placed via cannula into the NMR tube containing the reference capillary and the tube was sealed off under vacuum. DBU (0.2 g) was added to the remaining polymer solution and this was placed via cannula into another NMR tube along with a capillary, then this tube was also sealed under vacuum. The ^{19}F NMR was recorded within 1 hour and then every hour for 24 hours.

References.

1. Shriver, D.F. Manipulation of Air Sensitive Compounds, McGraw-Hill: New York, 1969

2. Brown, C.A. **J. Org. Chem.** 1974, 39, 3913

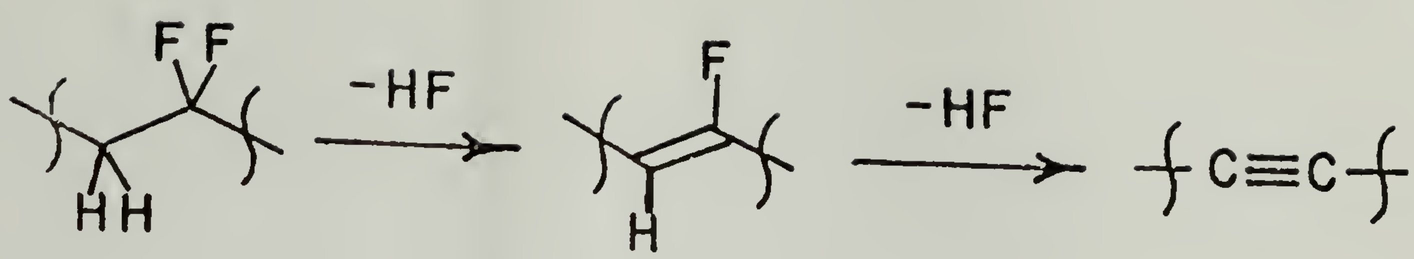
CHAPTER III: RESULTS AND DISCUSSION

Dehydrofluorination of Poly(vinylidene fluoride) in Dimethylformamide Solution.

The phase transfer catalyzed dehydrofluorination of solid poly(vinylidene fluoride) (PVF_2) has recently been reported[1,2] and in one of these Kise and Ogata report the electronic conductivity of an iodine-doped film sample to be $1.3x10^{-5}$ Scm^{-1}. Kise and Ogata also point out that since phase transfer catalyzed dehydrofluorination is limited to near the surface of the film, the true conductivity of the eliminated material may be higher. A film which was eliminated using more severe conditions (KOH in 2-propanol) exhibited a conductivity of $6.0x10^{-5}$ Scm^{-1} upon iodine doping[2]. These conditions induce substitution reactions which affect the conductivity, thus the sample may have been a thicker, but inherently poorer, conductor.

The research reported here examines the dehydrofluorination of PVF_2 in DMF solution using hindered bases (to impede substitution) and less severe conditions. This study will establish solubility, physical property and conductivity verses extent of reaction relationships for the dehydrofluorinated material.

When base is added to DMF solutions of PVF_2 under nitrogen, dehydrofluorination is effected (Equation 2-3-1) as evidenced by the neutralization of the base, the formation of fluoride salts, a color change from colorless to deep red-brown as well as corresponding changes in the infrared, visible and ultraviolet spectra. The choice of base causes observable structural differences in the eliminated



Equation 2-3-1. Dehydrofluorination of Poly(vinylidene fluoride) Using Potassium t-Butoxide in DMF Solution.

polymer. Table 2-3-1 summarizes the properties of the polymeric products for each base investigated.

Reaction with either potassium hydroxide in isopropanol or lithium 2,2,6,6-tetramethylpiperidide in ether produces gelatinous products prior to the completion of base addition. Small amounts of precipitate form when tetramethylammonium hydroxide in methanol is used. DMF solutions of potassium t-butoxide induce no observable precipitation. Explanations for these results are not obvious: the solvents used to solubilize the bases may contribute to precipitation, but they are not the sole factor. Neither the gels nor the granular precipitate formed in the reactions could be redissolved in DMF, so they are apparently (see below) crosslinked. The hydroxide base could substitute or add to fluoroolefins, then form ether crosslinks by either of these reactions. Infrared spectra do not indicate the presence of ether

Table 2-3-1. Properties of Films Cast From Solution Dehydrofluorinated Poly(vinylidene fluoride).

Base - Solvent Pair	Equivalents of Base	Weight % Precipitated Polymer	Film Quality	Conductivity (S/cm.)	
				Before I_2	After I_2
1.5 M KOH/i-PrOH	0.5	100 (gel)	Brittle	10^{-9}	10^{-9}
	1.0	100(gel)	Brittle	10^{-9}	10^{-9}
1.5 M Lithium 2,2,6,6-Tetramethylpiperidide/Ether	0.5	100 (gel)	Weak	10^{-9}	10^{-9}
	1.0	100 (gel)	Weak	10^{-9}	10^{-9}
2.0 M Tetramethylammonium hydroxide/Methanol	0.5	10	Brittle	10^{-9}	10^{-9}
	1.0	20	Brittle	10^{-9}	10^{-6}
1.5 M Potassium t-Butoxide/DMF	0.5	1	Flexible	10^{-9}	1.4×10^{-5}
	1.0	1	Flexible	10^{-9}	3.6×10^{-4}

crosslinks in any samples, but detection of small amounts of this functionality may be imposible: the broad and intense absorbance (1650 -1000 cm^{-1}) resulting from the conjugated double bonds and C-F (Figure 2-3-2) may prevent the identification of characteristic ether absorbances. These reactions were not studied further as DMF/potassium _t_-butoxide was a suitable alternative.

Figures 2-3-1 and 2-3-2 depict UV-Vis and infrared spectra of potassium _t_-butoxide eliminated samples. The UV-Vis spectra are of the reaction solutions; the infrared spectra are of cast films. As there is no fine structure to the UV-Vis spectrum, no reasonable estimates of the conjugation length are possible. The IR spectra indicate the presence of both conjugated double bonds (1500 - 1700 cm^{-1}) and triple

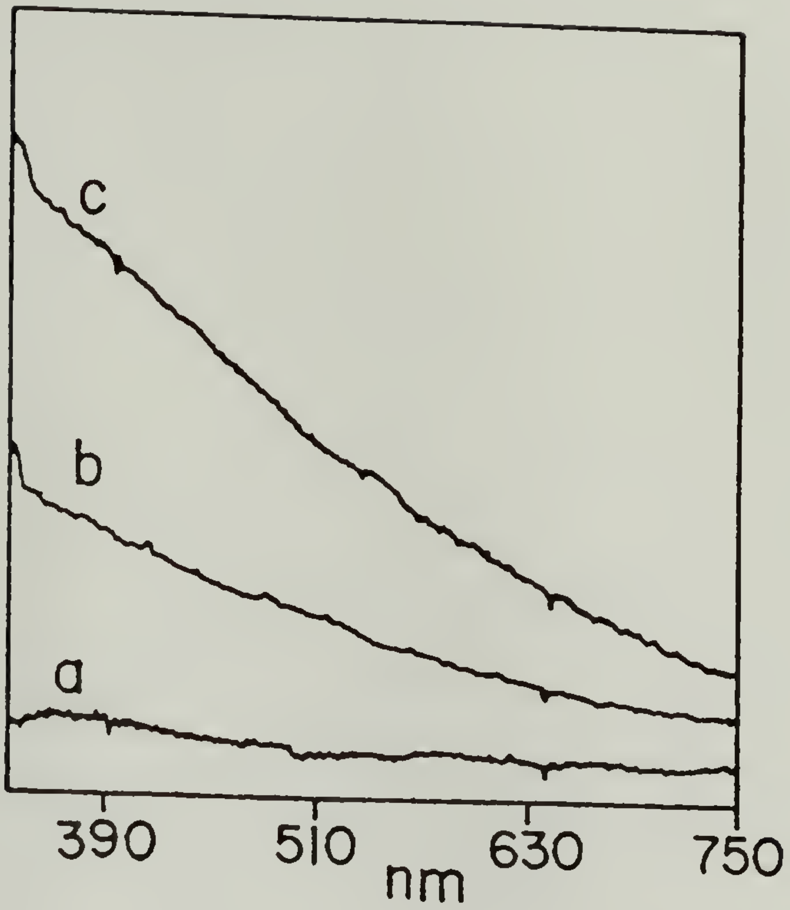


Figure 2-3-1. UV-Vis spectra of poly(vinylidene fluoride) which was eliminated with potassium t-butoxide in DMF solutions. a) PVF_2 b) PVF_2 after 0.5 equiv. of potassium t-butoxide c) PVF_2 after 1.0 equiv. base.

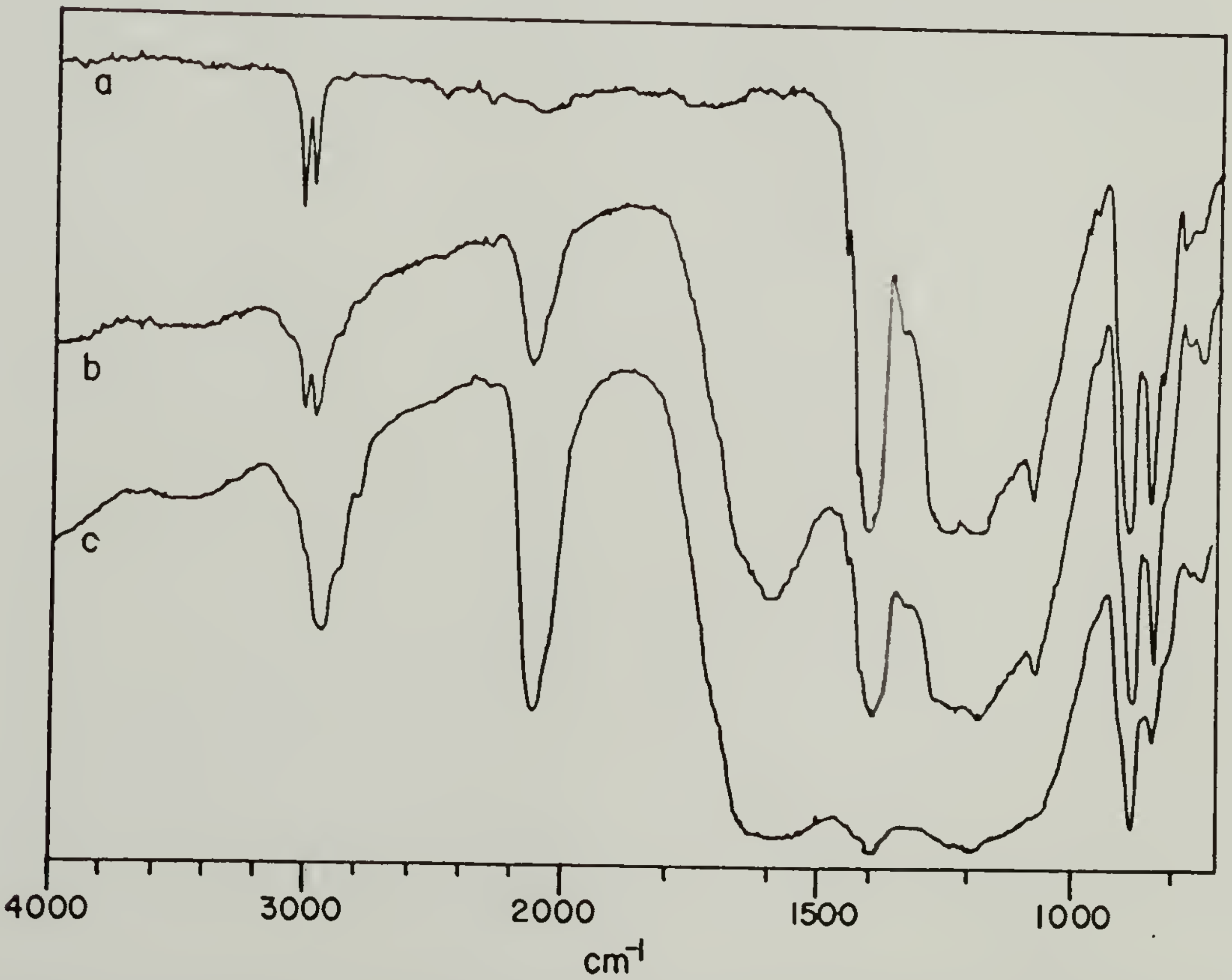


Figure 2-3-2. IR spectra of film which was cast from PVF_2 which was eliminated with potassium t-butoxide in DMF solution.

bonds (2050 - 2200 cm^{-1}) and that they form at competitive rates. A recent study by Percec[3] provides data which indicates that this absorbance may not be due to triple bonds; instead it is attributed to amine salts. When more than 1 equivalent of potassium t-butoxide per monomer unit (>100%) was added, large amounts of precipitation occurred. Complete precipitation was observed when two equivalents of base was approached.

The films formed from the potassium t-butoxide reaction exhibit limited conductivity, only slightly better than the results reported by Kise[2]. The conductivity of the sample was effected by oxygen exposure; the conductivity rapidly decrease with exposure time. Table 2-3-1 indicates a correlation between solubility and conductivity of I_2 doped eliminated poly(vinylidene fluoride). It is possible that crosslinking promotes both precipitation and interruption of conjugation. An interesting property of this material is that films cannot be redissolved in DMF after they are cast from DMF. This kinetic solubility is expected for highly solvated rigid polymers: crystallization occurs simultaneously with precipitation, inhibiting redissolution. Thus this material qualifies as an "operationally soluble" semiconducting polymer which becomes insoluble upon precipitation.

Isomerization of Polybutadiene to Form Poly(acetylene-co-ethylene).

Much effort has recently been directed toward syntheses of soluble polymers containing a conjugated polyene structure thus providing processible organic polymers which exhibit electronic conductivity.

From this vantage poly(1,3-butadiene) (Equation 2-3-2A) can be viewed

$$-\!\left(CH_2-CH_2-CH=CH\right)_n-$$

Equation 2-3-2A. Poly(1,3-butadiene).

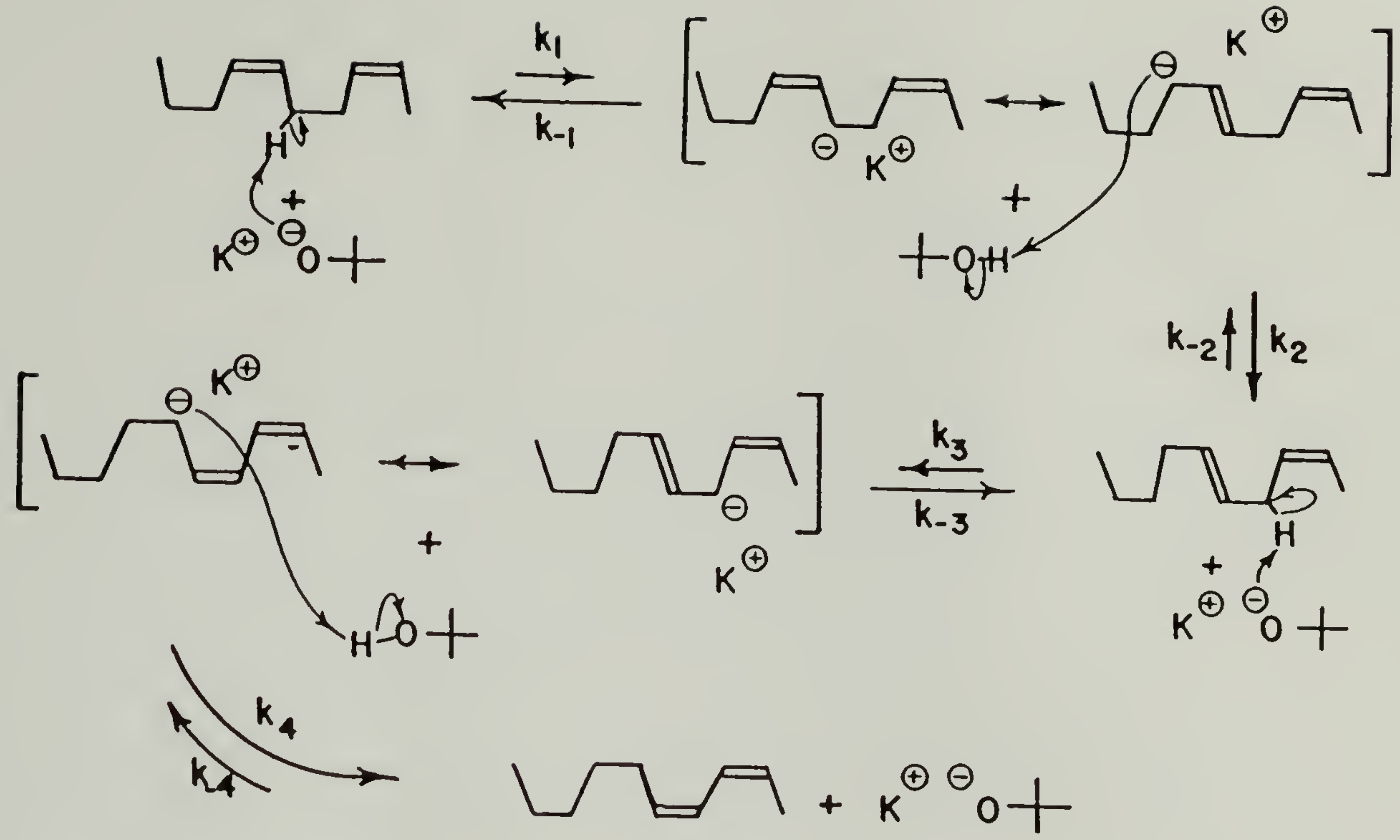
$$-\!\left[\left(CH_2-CH_2\right)_x\left(CH=CH\right)_y\right]_n-$$

Equation 2-3-2B. Poly(acetylene-co-ethylene).

as an alternating copolymer of acetylene and ethylene which, when reacted under suitable conditions, can be modified to a soluble conducting polymer.

Poly(1,3-butadiene) (Equation 2-3-2A) is enthalpically the least stable isomer of poly(acetylene-co-ethylene) (Equation 2-3-2B), and if a reaction coordinate were available via which positional isomerization of double bonds could occur, poly(1,3-butadiene) would isomerize to a more blocky poly(acetylene-co-ethylene). The resonance energy for conjugated dienes obtained from heats of combustion data is 3-4 kcal/mole[4]. Entropic factors should tend to randomize double bonds along the chain; thus the blockiness of the copolymer should be dependent on the temperature of the isomerization. Recently the alkaline-catalyzed isomerization of poly(butadiene) and its copolymers has been reported to yield polymers containing conjugation lengths of two and three units, thereby producing materials with superior drying characteristics[5-8].

Addition of potassium t-butoxide in DMSO to THF solutions of poly(1,3-butadiene) induces positional isomerization of the double bonds and formation of conjugated structures. The most obvious indication of conjugation is the visual change from a colorless to a blue-black solution; changes in proton NMR, infrared and UV-Vis spectra are also consistent with isomerization. Scheme 2-3-1 depicts the mechanism for this base-catalyzed isomerization. The vinyl groups present (8% by NMR) are not represented in this scheme; they undergo analogous isomerizations and do not interfere with the depicted process. An important requirement for this isomerization is the presence of DMSO[9]. When the base was added as a solution in t-butanol, no change in color or UV-Vis spectrum was observed after 24 h. With DMSO as the base solvent, a rapid coloration ensues. Figure 2-3-3 exhibits UV-Vis spectra of isomerization solutions. These spectra do not resemble the typical finger patterns of low molecular weight polyenes[10], although they do exhibit shifts to longer wavelengths and increasing intensity as the conjugation length increases. The majority of the absorbance is a result of the polyanion. If the solution is



Scheme 2-3-1. Mechanism for the Base Catalyzed Isomerization of Poly(1,3-butadiene).

exposed to oxygen, the blue color instantly discharges, leaving an orange solution and precipitated polymer. If the solution is quenched with methanol, the color becomes violet (Figure 2-3-3F). After isomerization for 74 hours, the UV-Vis spectrum of the methanol treated sample has a maximum absorbance at 230 nm, indicating that most of the conjugation is in the form of dienes and trienes, and a broad peak centered at 512 nm with an experimental extinction coefficient of 260 $M^{-1}cm^{-1}$.[11] This indicates that the polymer contains a range of conjugation lengths centered at 10 double bonds and approximately 0.2% have a length of 10 double bonds[10,11]. After 72 hours a further shift to longer wavelengths is not observed, but the intensity at 512 nm increases. The isomerized polymer is isolable as a violet air-

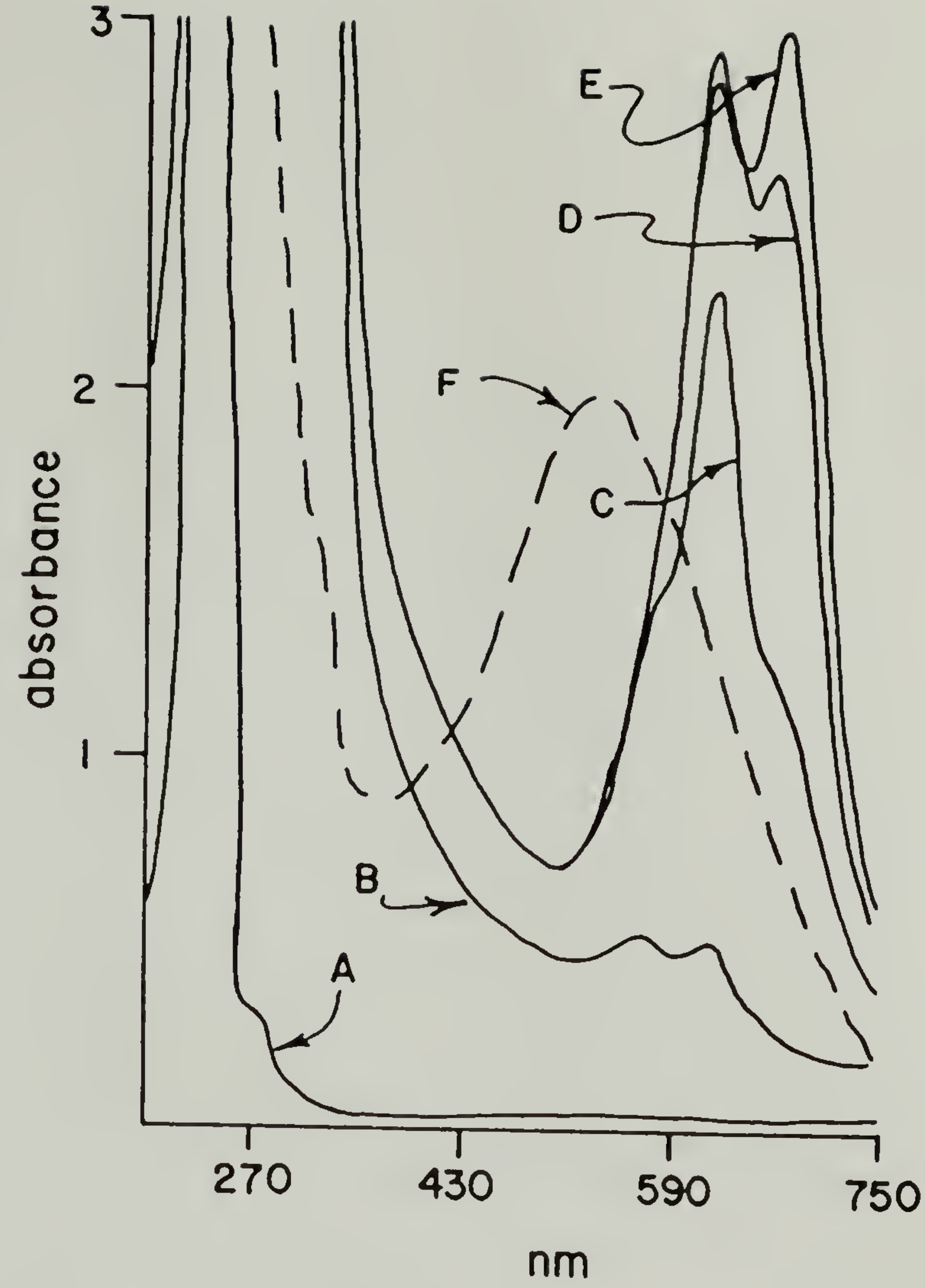


Figure 2-3-3. UV-Vis spectra of isomerization solutions (potassium t-butoxide in Me_2SO used as a base): A) t = 0 min; B) t = 5 min; C) t = 30 min; D) t = 120 min; E) t = 210 min; F) 72 h and then quenched with methanol.

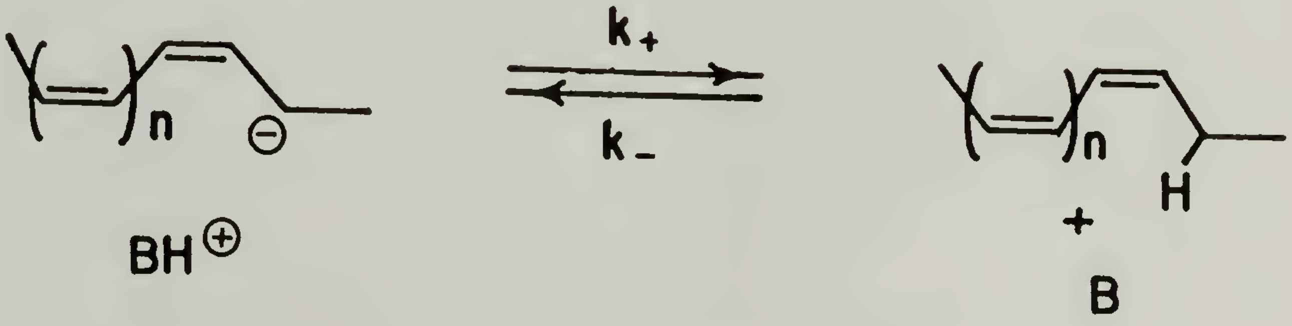
sensitive solid.

Proton NMR and infrared spectra also indicate isomerization. The ratio of benzene (proton impurities in NMR solvent - used as an internal standard) to allylic protons (centered at 1.87 ppm) decreases from 13.1 to 9.5 after 72 h at 80°C (the temperature was increased to increase the isomerization rate; see below). Four allylic hydrogens are lost for each unit of conjugation (see Scheme 2-3-1). The infrared spectra show the development of a broad asymetric shoulder to the long-wavelength side of the carbon-carbon double bond absorbance at

1630 cm^{-1}. This is indicative of conjugated double bonds.

The temperature was varied to test whether the conjugation length could be effected thermodynamically. UV-Vis spectra of reactions run at 0, 25 and 80°C exhibit identical absorbance positions; thus conjugation length is unaffected.

The equilibria depicted in Scheme 2-3-1 suggest that the length of conjugation should be affected by the strength of the base: isomerization should occur until the pK_b of the polyanion is equal to the pK_b of the base catalyst (Equation 2-3-3); thus a weaker base should render a longer length of conjugation. Figure 2-3-4 shows UV-Vis spectra of samples isomerized using potassium acetonitrilide (stronger base), potassium t-butoxide, and potassium cyclpentadienide (weaker base). The relative basicities have not been studied for this solvent system so the exact differences in basicity are not known. Potassium cyclopentadienide causes a 14 nm shift to longer wavelengths, and potassium acetonitrilide causes a >100 nm shift to shorter wavelengths.



Equation 2-3-3. Isomerization Equilibrium.

Conductivity was measured on films cast directly from the isomerization solutions under a nitrogen atmosphere. The resulting blue films were washed with methanol until all of the base was removed

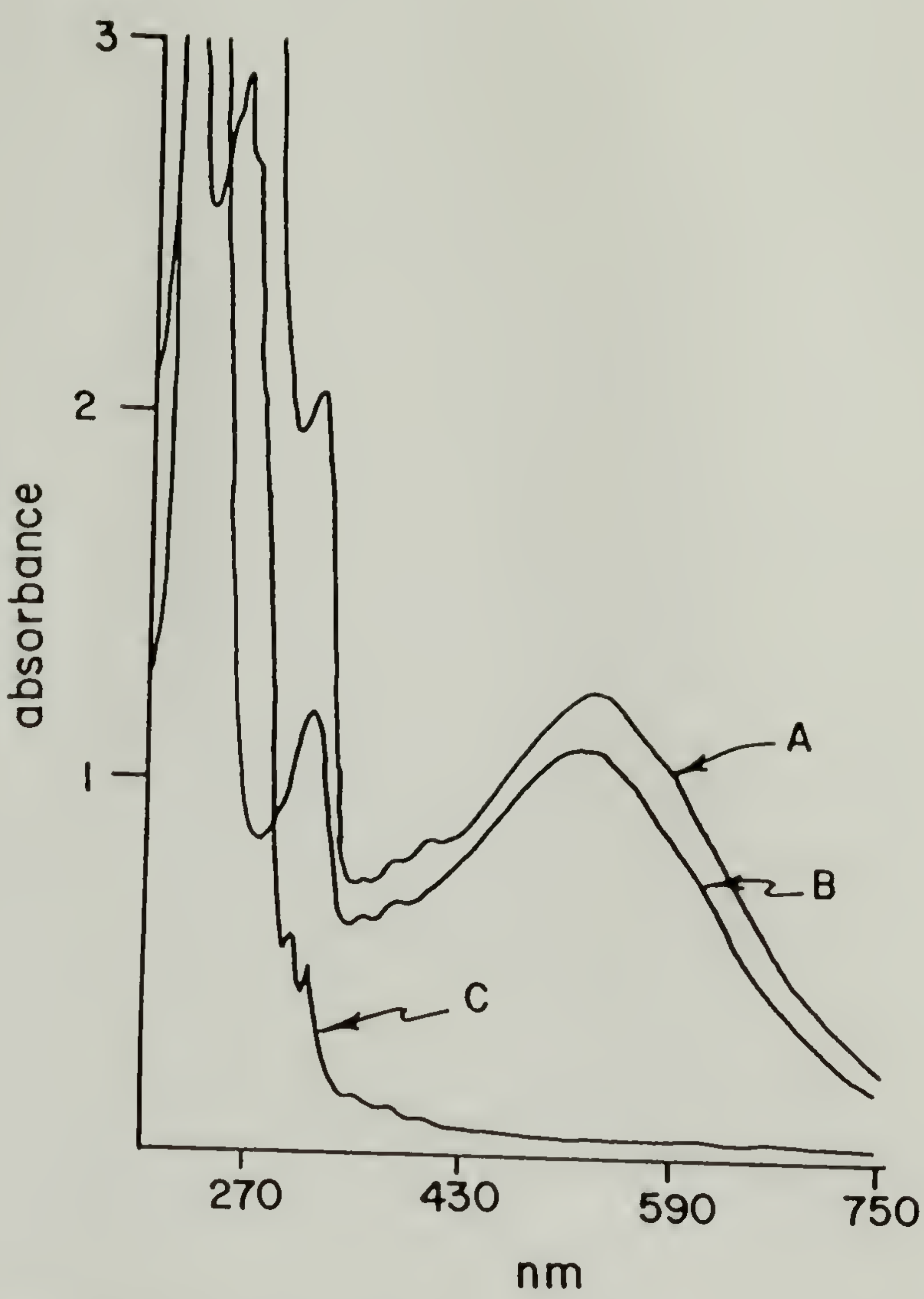


Figure 2-3-4. UV-Vis spectra of isomerized (24 h) samples after reaction with methanol: A) potassium cyclopentadienide; B) potassium t-butoxide; C) potassium acetonitrilide.

(phenolphthlein indicator). The resulting red films were dried at 80°C (0.05 mm) for 24 hours before they were mounted on electrodes. The films were from samples that were isomerized with potassium t-butoxide for various times, the longest being 7 days. Only this sample showed measurable electronic conductivity, $5 \times 10^{-7} Scm^{-1}$ after 4 hours of iodine doping (10^{-9} Scm^{-1} before I_2 doping). The value increases gradually and levels at this point. The sample was sensitive to oxygen and after 8 hours in oxygen the sample no longer exhibited any measurable conductivity.

Preparation of Poly(difluoroacetylene).

Much effort has recently been directed toward theoretic calculations for a variety of conducting polymers[12]. These theorists have calculated band gaps and ionization potentials for a variety of aromatic and polyacetylenic polymers. They have concluded that, based upon their molecular orbital calculations, that poly(difluoroacetylene) should be a better intrinsic conductor than polyacetylene. These theories have not been tested since it is not possible to prepare the polymer from the explosive difluoroacetylene monomer. Thus preparation of poly(difluoroacetylene) is possible only through polymer modification. The dehydrofluorination of poly(trifluoroethylene) to give poly(difluoroacetylene) using DBU as the base is reported here and represents a possible route to the theoretically interesting poly(difluoroacetylene).

Commercially prepared poly(trifluoroethylene) is prepared by free radical emulsion polymerization. This free radical polymerized material contains a large (approximately 14%) fraction of regio-irregular units. An alternate method of preparing poly(trifluoroethylene), used in this study, involves the tributyltin hydride reduction of poly(chlorotrifluoroethylene). Polymer prepared in this manner is highly regioregular (2 % head-to-head placement). Poly(trifluoroethylene) was dehydrofluorinated using two methods: Tetrahydrofuran solutions of poly(trifluoroethylene) were treated with DBU, and poly(trifluoroethylene) film was treated with a heptane solution of DBU in a two-phase reaction.

Poly(trifluoroethylene) was prepared in isolated and purified yields of 80% using tributyltin hydride and AIBN to reduce poly(chlorotrifluoroethylene). The undecoupled proton NMR exhibits a doublet at 5.53 ppm (J=41.5 Hz). The ^{19}F NMR spectrum has resonances in two regions: $-CF_2-$ and -CFH- at 115-125 ppm and 210-216 ppm repectively ($CFCl_3$ reference) having integrated areas of 2 to 1. The ^{19}F NMR of this polymer was studied extensively by Cais and Kometani[13] and the observed spectra are consistent with their assignments. The infrared spectrum is also consistent with the modified structure: alkyl stretch at 2920 cm^{-1} and no C–Cl at 950 cm^{-1}.

Addition of DBU to THF solutions of the poly(trifluoroethylene) results in dehydrofluorination and the formation of conjugated carbon-carbon double bonds. The most obvious indication of conjugation is the visual change from colorless to a red-brown solution; changes in ^{19}F NMR, infrared and UV-Vis spectroscopies, as well as the formation of fluoride salts are consistent with the formation of the eliminated material.

UV-Vis spectra which were recorded periodically during both the homogeneous and heterogeneous eliminations indicate the rapid formation of short lengths of conjugation giving an intense absorbance from 200 to 310 nm. In addition the spectra contain a shoulder at roughly 400 nm which increases in intensity and shifts to slightly longer wavelengths as the reaction progresses. Attempts at following, by UV-Vis spectroscopy, the heterogeneous elimination were unsuccessful. An attempt was made using thin films cast directly on the cuvettes. These films were typically less than 1 micrometer thick, yet the maximum absorbance (450 nm) could only be obtained by attenuation of the reference beam; hence, much noise is present in the spectrum.

Infrared spectra and ^{19}F NMR also indicated elimination. The ratio of F_6-benzene (external reference is a sealed capillary) to the -CFH- resonance at 217 ppm increased from 6.3 to 8.7 over a period of 8 hours. Thus it was possible to follow the elimination indicated by the change in this resonance. Attempts were made to use ^{19}F NMR to monitor the elimination through precipitation (16 hours); however, as the reaction progressed beyond 8 hours the magnetic properties of the sample changed sufficiently to distort the obtained spectra. The peaks could be observed but could not be phased well enough to allow accurate quantitation. In addition to the indicated decrease in the -CFH- intensity two new peaks appeared (Figure 2-3-5): A broad peak at 144 ppm corresponding to the fluoroolefin and a sharp peak at 122 ppm, which overlapped the $-CF_2-$ resonances, corresponding to the fluoride salt.

The infrared spectra (Figure 2-3-6) have a broad intense absorbance (1650-1000 cm^{-1}) resulting from conjugated double bonds and C-F. In addition absorbances observed at 2940 cm^{-1} and 2870 cm^{-1} (indicative of alkyl streching modes) and a broad peak at 3700 - 3100 cm^{-1} together suggest that the polymer contains residual DBU and DBU salts. These salts resisted all attempts at removal which included extraction with heptane, water and ethanol.

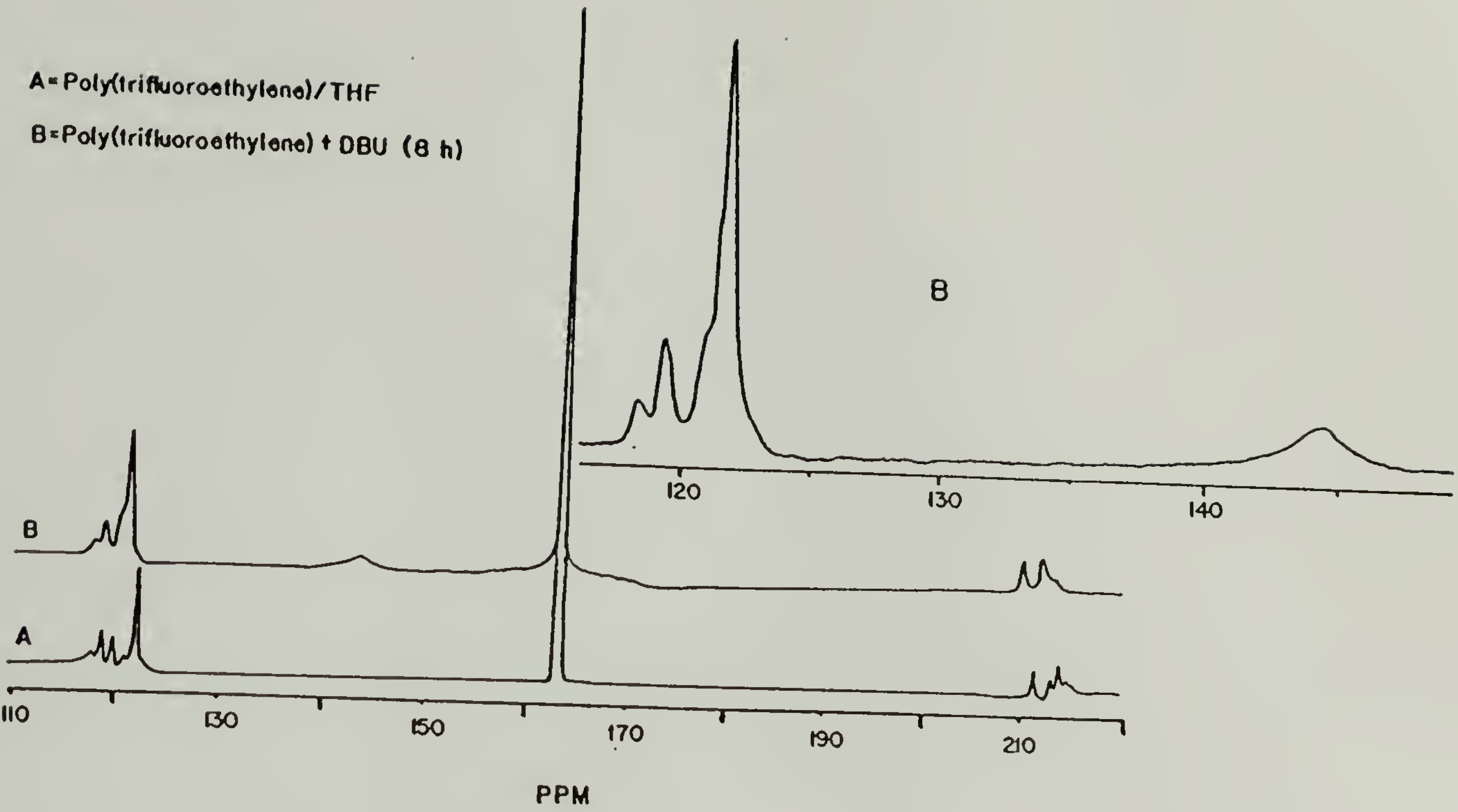


Figure 2-3-5. ^{19}F NMR for the reaction of poly(trifluoroethylene) with DBU in tetrahydrofuran solution.

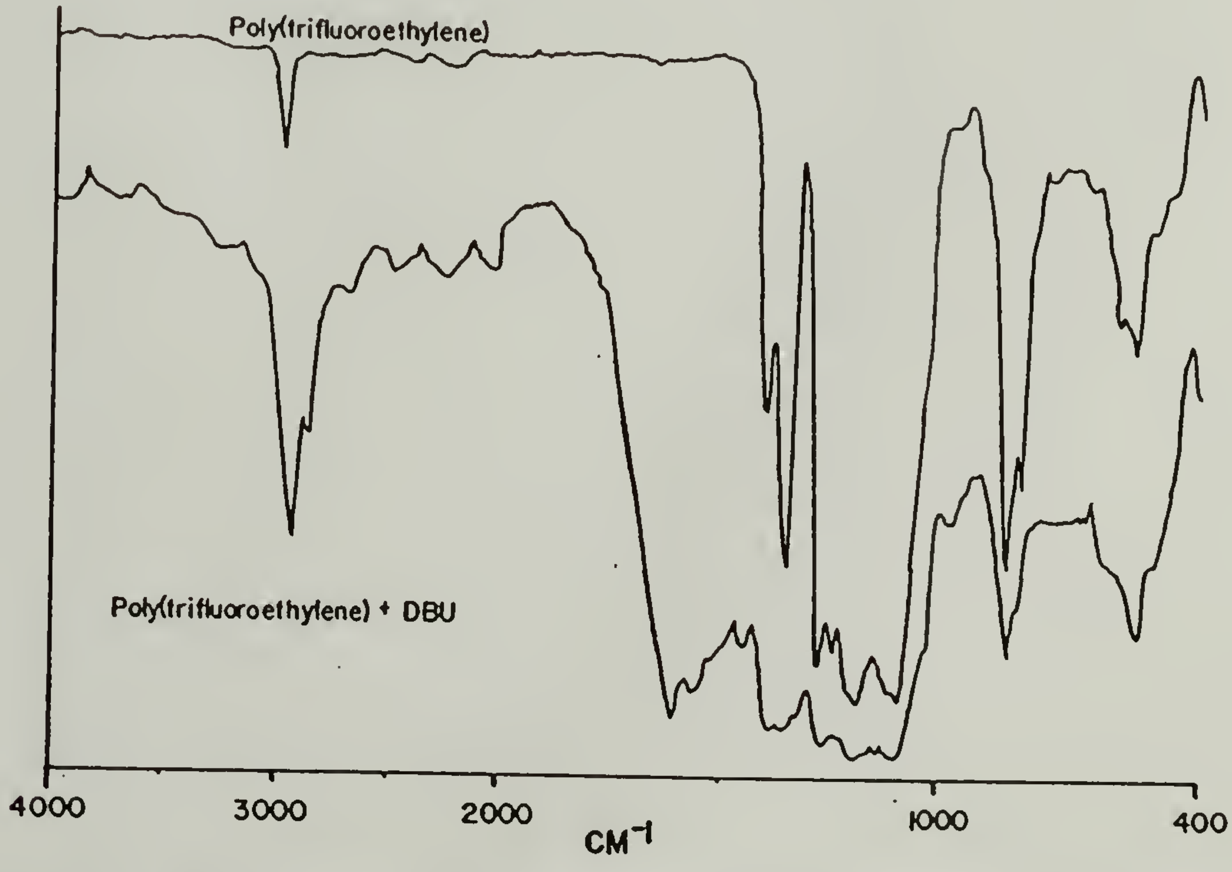


Figure 2-3-6. IR spectra of poly(trifluoroethylene) eliminated with DBU in Heptane.

Fluoride determination on the reaction mixtures from homogeneous elimination in THF indicates that nearly 90% of the calculated amount of fluoride was eliminated after 24 hours. Thus the precipitated polymer appears to be nearly completely eliminated. The results obtained for the films eliminated using the heterogeneous method were ambiguous: The values obtained indicate that more than 100% of the calculated amount of fluoride was present. The fluoride determination in this case involved using an extraction to remove fluoride from the film and from the heptane solution. Thus this method had added uncertainties. Recalibration of the method was accomplished by adding known amounts of potassium fluoride to the extraction procedure. These results indicated that the heterogeneous elimination was nearly complete (95 % of the calculated amount of the fluoride was found).

Conductivity was measured on eliminated films which were first extracted with heptane (8 h) and then with nitrogen sparged water (8 h). The resulting films were dried at 80°C (0.05 mm) for 24 hours before they were mounted on electrodes. The films had an average intrinsic conductivity of 5×10^{-5} S/cm^2 which decreased only slightly upon exposure to oxygen for 16 hours. The iodine doped samples had an average conductivity of 5×10^{-4} S/cm^{-1} which was very sensitive to oxygen exposure.

References

1. Dias, A.J.; McCarthy, T.J. **J. Polym. Sci.: Polym. Chem. Ed.** 1985, 23, 1057

2. Kise, H.; Ogata, H. **J. Polym. Sci.: Polym. Chem. Ed.** 1983, 21, 3443

3. Hahn, B.R.; Percec, V. **Polym. Prep., Am. Chem. Soc., Div. of Polym. Chem.**, New York National Meeting 1986, 27, 364

4. Purcell, W.P.; Singer, J.A. **J. Chem. Eng. Data** 1967, 12, 234

5. Otsuki, Y.; Ima, H.; Kaiya, A.; Horii, H. Ger. Offen. 2,357,001; **Chem. Abstr.** 1974, 81, p9243q

6. Kampf, W. Fr. Demande 2,459,251; **Chem. Abstr.** 1974, 81, P2431q

7. Kampf, W.; Herrman, C. Eur. Pat. Appl. EP86894; **Chem. Abstr.** 1983, 99, 213094q

8. Gatti, G.; Cancelleir, G.; Cavalli, L.; Andrenssi, P. **Conv. Ital. Sci. Macromol. 4th** 1979, 99

9. Ugelstad, J.; Rokstad, O.A.; Skarstein, J. **Acta. Chem. Scand.** 1963, 17, 208

10. Sondheimer, F.; Ben-Efraim, D.A.; Wolovsky, R. **J. Am. Chem. Soc.** 1961, 83, 1675

11. The extinction coefficient at 512 nm was obtained from the slope of a Beer's law plot using samples which were quenched with methanol and serially diluted. The concentration of these solutions was obtained by evaporating 5 ml in a tared beaker. The resulting residue was then washed with methanol until the base was removed and then dried 24 h at 50°C (0.05 mm) before reweighing. The value 0.2% is based on monomer units, or in other words, 0.2% of the double bonds are present in 10 double-bond conjugated units.

12. Boudreaux, D.S.; Chance, R.R.; Elsenbaumer, R.L.; Frommer, J.E.; Brédas, J.L.; Silbey, R. **Phys. Rev. B** 1985, 31, 652

13. Cais, R.; Kometani, J.M. **Macromolecules** 1984, 17, 1932

CHAPTER IV: CONCLUSIONS AND SUGGESTIONS.

This work demonstrates that it is possible to use polymer modification to produce new semiconducting polymers. The dehydrofluorination of poly(vinylidene fluoride) presented for the first time conditions which allow the preparation of a conducting polymer solution from which thin semiconducting films could be cast. Once cast these films could not be redissolved: crystallization or crosslinking occured simultaneously with precipitation. In addition there was an observed correlation between the structure of the dehydrofluorinated material and electronic conduction. Those films which were prepared from bases that caused gelation, presumably from crosslinking, generally gave brittle films which exhibited no measurable conductivity. No attempts were made at optimizing the observed conductivities. Future studies using other dopants and the direct addition of the dopant to the polymer solution may be worthwhile for optimizing this property.

Poly(acetylene-co-ethylene) was not a good semiconducting polymer. This result is not suprising since the total amount of extended conjugation is less than 1%; the majority of the conjugation remains as dienes and trienes. However this method does illustrate that base catalyzed isomerization can be induced on polymers and this should be considered whenever unsaturated polymers are exposed to basic conditions. Increasing the level of unsaturation in the polymer followed by isomerization may give materials which make better conductors. Exposure of polychloroprene to isomerization conditions resulted in rapid formation of a black crosslinked gel; thus, elimination and isomerization occur simultaneously resulting in the observed product. This reaction was not pursued but similar ideas could be applied to other functional polymers. Olefin metathesis polymerization is a good method for preparing new candidates for the isomerization reactions. It is possible to prepare polymers containing unsaturation as well as another functional group which could be eliminated. Thus the combination of isomerization and olefin metathesis polymerization represent a promising method for preparing new conducting materials.

The attempted synthesis of poly(difluoroacetylene) gave mixed results: Though the polymer could be prepared by DBU catalyzed dehydrofluorination in THF solution, it precipitated after 16 hours and it was therefore not possible to cast films from the solutions. Though the polymer could be prepared by heterogeneous elimination using DBU in heptane, it could not be freed of the resulting salt. Thus while the undoped conductivity was higher than that obtained for polyacetylene, it can not be said with any degree of certainty that this value represents the conductivity for pure poly(difluoroacetylene).

This illustrates an important consideration, it is generally not possible to get very pure materials when polymer modification is used to prepare a new polymer. Often these reactions are incomplete and the unreacted material usually cannot be removed from the product. This is especially true where products, like conducting polymers, are insoluble. Thus while these methods are capable of preparing new materials which are not attainable by other means, they usually contain other impurities. These materials may find useful applications, but they are not generally pure enough to allow direct theoretical comparisons.

APPENDIX

Disk 1

File(esca-)	Experiment	XPS Atomic Composition (Multiplex File) F O N C Cl S Si Br I
030.d (n)	JDIII-59	Survey PCTFE
034.d (n)	JDIII-59	
035.d (n)	JDIII-59-1	Survey PCTFE+LiTMO 5 min, -78°C
037.d (n)	JDIII-59-1	
038.d (n)	JDIII-59-1	
039.d (n)	JDIII-59-2	Survey PCTFE+LiTMO 30 min, -78°C
040.d (n)	JDIII-59-2	
041.d (n)	JDIII-59-2	
042.d (g)	JDIII-59-2	Survey
043.d (n)	JDIII-59-3	Survey PCTFE+LiTMO 60 min, -78°C
044.d (n)	JDIII-59-3	
045.d (n)	JDIII-59-3	
046.d (n)	JDIII-60-3	Survey PCTFE+LiTMO 60 m, -78°C, heptane
047.d (n)	JDIII-60-3	
048.d (g)	JDIII-60-3	Survey
049.d (n)	JDIII-60-1	Survey PCTFE+LiTMO 5 m, -78°C, heptane
050.d (n)	JDIII-60-1	
051.d (g)	JDIII-60-2	Survey PCTFE+LiTMO 30 m, -78°C, heptane
052.d (g)	JDIII-60-2	
054.d (n)	JDIII-59-1	Survey PCTFE-TMO + HCl
055.d (n)	JDIII-59-1	
056.d (n)	JDIII-59-2	Survey PCTFE-TMO + HCl
057.d (n)	JDIII-59-2	
058.d (n)	JDIII-59-3	Survey PCTFE-TMO + HCl
059.d (n)	JDIII-59-3	
065.d (n)	JDIII-61-1	Survey PCTFE+LiTMO 60 m, -78°C, heptane/THF
066.d (n)	JDIII-61-1	
067.d (n)	JDIII-61-1	
068.d (n)	JDIII-61-1	
069.d (n)	JDIII-61-1	Survey PCTFE-TMO + HCl
070.d (n)	JDIII-61-1	

Disk 2

File(esca-)	Experiment	XPS Atomic Composition (Multiplex File) F O N C Cl S Si Br I
072.d (n)	JDIII-62-3	Survey PCTFE+LiDT 60 m, -78°C, heptane/THF
073.d (n)	JDIII-62-3	
074.d (n)	JDIII-62-4	Survey PTFE+LiDT 60 m, rt, heptane/THF
075.d (n)	JDIII-62-4	
083.d (n)	JDIII-62-1	Survey PCTFE+LiDT 60 m, -78°C, heptane/THF
084.d (n)	JDIII-62-1	

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
085.d	(n)	JDIII-62-2	Survey PCTFE+LiDT 30 m, -78°C, heptane/THF								
086.d	(n)	JDIII-62-2									
087.d	(n)	JDIII-63-3	Survey PCTFE+LiPAA 60 m, -78°C, heptane,THF								
088.d	(n)	JDIII-63-3									
089.d	(n)	JDIII-63-1	Survey PCTFE+LiPAA 5 m, -78°C, heptane/THF								
090.d	(n)	JDIII-63-1									
091.d	(n)	JDIII-63-2	Survey PCTFE+LiPAA 30 m, -78°C, heptane/THF								
092.d	(n)	JDIII-63-2									
099.d	(n)	JDIII-62-2	Survey LiDT + $HgCl_2$								
100.d	(n)	JDIII-63-3	Survey PCTFE-PAA + HCl								
101.d	(n)	JDIII-63-3									
102.d	(n)	JDIII-64-1	Survey PTFE+LiTMO 60 m, 0°C, heptane/THF								
105.d	(n)	JDIII-64-1									
128.d	(n)	JDIII-62-5	Survey PCTFE+LiDT 120 m, -78°C, heptane/THF								
129.d	(n)	JDIII-62-5									
24	(n)	JDIII-73-1	Survey PCTFE+LiDT 5 m, -20°C, heptane/THF								
25	(n)	JDIII-73-1	22.3	5.50	0.60	64.9	-	6.70	-	-	-
Disk 3											
28	(n)	JDIII-75-1	Survey PCTFE+LiTMO (-78°, 5 min)+Br_2								
29	(n)	JDIII-75-1	11.2	5.10	1.80	74.8	4.30	-	-	3.80	-
30	(n)	JDIII-75-2	Survey PCTFE+LiTMO+Br_2+LiTMO								
31	(n)	JDIII-75-2	14.4	4.50	1.30	72.5	6.80	-	-	0.50	-
32	(n)	JDIII-76-1	Survey PCTFE+LiDT 60 m, -78°C								
33	(n)	JDIII-76-1	17.2	2.40	-	74.4	5.30	0.70	-	0.00	-
34	(n)	JDIII-76-2	Survey PTFE+LiDT 60 m, -78°C								
35	(n)	JDIII-76-2	4.00	5.80	-	89.5	-	0.60	-	0.00	
72	(n)	JDIII-77-1	9.10	10.0	7.30	67.5	5.80	-	-	-	-
73	(g)	JDIII-77-1	Survey PCTFE+LiTMO								
74	(g)	JDIII-77-1	10.0	13.8	8.50	67.6	5.10	-	-	-	-
79	(n)	JDIII-77-1	Survey PCTFE-TMO + HCl								
80	(n)	JDIII-77-1	24.3	11.4	3.70	50.2	10.4	-	-	-	-
85	(n)	JDIII-77-1	Survey PCTFE-TMO,HCL + Br_3EtOH								
86	(n)	JDIII-77-1	8.50	18.8	4.90	57.6	7.51	-	2.70	0.00	-
87	(n)	JDIII-77	Survey PCTFE control								
88	(n)	JDIII-77	54.1	1.40	0.00	29.9	14.6	-	-	-	-
90	(n)	JDIII-65-3	9.50	10.0	7.50	68.1	4.90	-	-	-	-

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
91	(n)	JDIII-65-3	8.60	10.6	7.40	68.9	4.50	-	-	-	-
94	(n)	JDIII-65	Survey PCTFE + HCl Control								
95	(n)	JDIII-65	52.2	2.80	0.00	29.8	15.2	-	-	-	-
96	(n)	JDIII-65-3	Survey PCTFE-TMO + HCl								
97	(n)	JDIII-65-3	14.8	14.3	4.90	57.3	8.70	-	-	-	-
98	(n)	JDIII-65-3	Survey PCTFE-TMO + HCl								
99	(n)	JDIII-65-3	11.5	14.7	5.50	61.0	7.30	-	-	-	-
Disk 4											
102	(n)	JDIII-65-2	Survey PCTFE+LiTMO, 30 m, 0°C								
103	(n)	JDIII-65-2	33.6	6.80	2.90	45.7	11.0	-	-	-	-
104	(n)	JDIII-65-1	Survey PCTFE+LiTMO, 5 m, 0°C								
105	(n)	JDIII-65-1	40.3	6.70	2.20	38.8	12.1	-	-	-	-
125	(n)	JDIII-65-3	Survey PCTFE-TMO + EtI								
126	(n)	JDIII-65-3	8.80	10.6	6.40	64.9	9.30	-	-	-	-
143	(n)	JDIII-65-3	Survey PCTFE-TMO + EtI								
144	(n)	JDIII-65-3	7.70	12.2	6.00	63.2	10.8	-	-	-	0.10
153	(n)	JDIII-65-3	Survey PCTFE-TMO + MeI								
154	(n)	JDIII-65-3	13.3	11.4	5.00	58.6	11.4	-	-	-	0.30
155	(n)	JDIII-66-1	Survey PCTFE+LiDT 5 m, 0°C								
156	(n)	JDIII-66-1	13.6	6.60	-	63.6	7.50	8.80	-	-	-
163	(n)	JDIII-66-3	Survey PCTFE+LiDT 60 m, -78°C								
164	(g)	JDIII-66-3	Survey								
165	(n)	JDIII-66-3	32.2	6.30	-	44.0	12.3	5.30	-	-	-
166	(n)	JDIII-66-1	Survey PCTFE+LiDT 5 m, 0°C								
167	(n)	JDIII-66-1	8.50	9.50	-	69.0	4.60	8.40	-	-	-
168	(n)	JDIII-66-2	Survey PCTFE+LiDT 30 m, 0°C								
169	(n)	JDIII-66-2	11.5	7.60	-	64.4	6.80	9.80	-	-	-
170	(n)	JDIII-66-4	Survey PCTFE+LiDT 120 m, 0°C heptane/THF								
171	(n)	JDIII-66-4	25.8	6.90	-	50.3	10.7	6.40	-	-	-
172	(n)	JDIII-66-4	Survey PCTFE-DT + $HgCl_2$								
173	(n)	JDIII-66-4	24.8	12.9	-	50.5	8.60	3.30	-	-	-
174	(n)	JDIII-66-1	Survey PCTFE+LiDT 5 m, -78°C								
Disk 5											
175	(n)	JDIII-66-1	17.3	6.10	-	63.0	5.80	7.90	-	-	-
176	(n)	JDIII-66-2	Survey PCTFE+LiDT 30 m, -78°C								
177	(n)	JDIII-66-2	20.6	5.00	-	60.5	6.70	7.30	-	-	-
178	(n)	JDIII-66-3	Survey PCTFE+LiDT 60 m, -78°C								
179	(n)	JDIII-66-3	18.6	4.30	-	63.8	6.00	7.30	-	-	-
181	(n)	JDIII-66-4	17.6	7.10	-	61.1	6.40	7.90	-	-	-
194	(n)	JDIII-66-3	Survey PCTFE-DT + MeI								
195	(n)	JDIII-66-3	12.7	7.60	-	62.7	7.00	9.70	-	-	0.34
196	(n)	JDIII-66	Survey PCTFE + MeI control								
197	(n)	JDIII-66	49.0	1.56	-	36.1	13.3	0.00	-	-	0.00

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
198	(n)	JDIII-66-3	Survey PCTFE-DT + $HgCl_2$								
199	(n)	JDIII-66-3	9.10	12.8	-	63.9	6.00	8.20	-	-	-
200	(g)	JDIII-66-3	Survey PCTFE-DT + $HgCL_2$								
201	(g)	JDIII-66-3	12.8	14.6	-	59.2	6.10	7.20	-	-	-
202	(n)	JDIII-65-3	Survey PCTFE+LiTMO 60 m, -78°C								
203	(n)	JDIII-65-3	43.7	2.90	1.20	40.0	12.2	-	-	-	-
204	(n)	JDIII-65-4	Survey PCTFE+LiTMO 120 m, 0°C								
205	(n)	JDIII-65-4	27.2	6.40	3.90	51.9	10.6	-	-	-	-
206	(n)	JDIII-65-3	Survey PCTFE+LiTMO 60 m, 0°C								
207	(n)	JDIII-65-3	30.1	9.90	3.60	45.8	10.5	-	-	-	-
208	(n)	JDIII-66-3	Survey PCTFE+LiDT 60 m, 0°C								
209	(n)	JDIII-66-3	9.60	10.7	-	64.7	4.70	10.3	-	-	-
210	(g)	JDIII-66-3	Survey								
211	(n)	JDIII-66-3	Survey PCTFE-DT + $HgCl_2$								
212	(n)	JDIII-66-3	20.5	11.6	-	56.0	8.20	3.70	-	-	-
224	(n)	JDIII-66-4	Survey PCTFE+LiDT 120 m, -78°C								
225	(n)	JDIII-66-4	38.0	1.50	-	44.7	10.5	5.50	-	-	-
226	(n)	JDIII-66-4	Survey PCTFE+LiDT 120 m, 0°C								
227	(n)	JDIII-66-4	13.6	5.00	-	60.8	8.60	12.0	-	-	-
228	(g)	JDIII-66-4	Survey PCTFE+LiDT 120 m, 0°C								
229	(g)	JDIII-68-3	Survey PCTFE+LiTMO 60 m, -78°C								
Disk 6											
230	(g)	JDIII-68-3	22.3	11.9	5.40	53.3	7.10	-	-	-	-
231	(n)	JDIII-68-3	Survey								
232	(n)	JDIII-68-3	44.6	2.60	1.60	39.0	12.2	-	-	-	-
233	(n)	JDIII-68	Survey PCTFE + TMO control								
234	(n)	JDIII-68	51.1	3.00	0.40	33.9	11.7	-	-	-	-
235	(g)	JDIII-68-3	Survey PCTFE+LiTMO 0°C								
236	(g)	JDIII-68-3	for reorganization								
237	(n)	JDIII-68-3	reorganization								
238	(g)	JDIII-68-3	reorganization								
239	(g)	JDIII-68-3	24.0	6.90	4.50	55.9	8.60	-	-	-	-
240	(g)	JDIII-68-3	C_{1s} of 239 after aquisition								
241	(g)	JDIII-68-3	C_{1s} after 15 min with source on								
242	(g)	JDIII-67-3	Survey PCTFE-DT MeI/Acetone								
243	(g)	JDIII-67-3	multiplex Si contam.								
244	(n)	JDIII-67-3	Survey PCTFE-DT MeI/Acetone								
245	(n)	JDIII-67-3	12.7	8.00	-	62.2	6.90	9.70	-	-	0.50
246	(g)	JDIII-69-3	Survey PCTFE+LiDT 120 m, 0°C								
247	(g)	JDIII-69-3	9.70	7.00	-	65.1	1.00	17.3	-	-	-
248	(n)	JDIII-69-3	Survey								

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
249	(n)	JDIII-69-3	12.9	4.60	-	64.4	4.00	14.2	-	-	-
250	(g)	JDIII-68-2	Survey PCTFE-TMO + HCl								
251	(n)	JDIII-68-2	Survey								
252	(n)	JDIII-68-2	23.5	17.9	3.20	45.2	7.90	-	2.30	-	-
255	(g)	JDIII-70-1	Survey PCTFE+LiTMO for reorganization								
256	(g)	JDIII-70-1									
257	(g)	JDIII-70-1	after heating								
258	(g)	JDIII-70-1	after heating								
259	(g)	Polyacetylene									
260	(g)	Polyacetylene									
261	(g)	Polyacetylene									
262	(n)	JDIII-69-3	Survey PCTFE-DT + $Hg(O_2CCF_3)$								
263	(n)	JDIII-69-3	10.0	10.8	-	64.3	7.20	7.50	-	-	-
Disk 7											
264	(n)	JDIII-70-4	Survey PCTFE-TMO H_2O reflux								
267	(n)	JDIII-69-2	Survey PCTFE-DT + $Hg(O_2CCF_3)_2$								
268	(n)	JDIII-69-2	6.60	10.4	-	72.0	3.10	7.80	-	-	-
269	(g)	JDIII-69-2	Heat, check for reorganization								
270	(g)	JDIII-69-2	31.7	9.40	-	43.8	7.30	7.90	-	-	-
271	(g+30°)	JDIII-69-2	31.1	5.80	-	47.0	9.20	6.90	-	-	-
272	(g+60°)	JDIII-69-2	31.0	5.60	-	46.2	10.9	6.20	-	-	-
284	(g)	JDIII-71-1	Survey PCTFE+LiPAA 60 m, 0°C								
285	(g)	JDIII-71-1	8.90	19.9	-	71.2	0.10	-	-	-	-
286	(g+30°)	JDIII-71-1	7.20	18.3	-	74.3	0.20	-	-	-	-
287	(g+60°)	JDIII-71-1	7.40	18.0	-	74.5	0.20	-	-	-	-
288	(n)	JDIII-71-1	Survey PCTFE+LiPAA 60 m, 0°C								
289	(g)	JDIII-72-1	Survey PCTFE+LiDT 60 m, 0°C heptane								
290	(g)	JDIII-72-1	17.1	10.6	-	56.1	3.10	13.1	-	-	-
291	(g+30°)	JDIII-72-1	14.6	6.30	-	60.6	7.70	10.9	-	-	-
292	(g+60°)	JDIII-72-1	17.2	4.80	-	57.5	10.8	9.80	-	-	-
293	(n)	JDIII-72-1	Survey PCTFE+LiDT 60 m, 0°C heptane								
294	(g)	JDIII-73-1	Survey PCTFE-DT -78° + $Hg(O_2CCF_3)_2$								
295	(g)	JDIII-73-1									
296	(g)	JDIII-73-1									
297	(g+30°)	JDIII-73-1									
298	(g+60°)	JDIII-73-1	30.7	3.50	-	53.0	6.50	6.30	-	-	-
299	(n)	JDIII-73-1	Survey PCTFE-DT -78°C + $Hg(O_2CCF_3)_2$								

300	(g)	JDIII-71-1	Survey PCTFE-PAA + H^+								
301	(g)	JDIII-71-1	9.00	22.6	-	67.5	0.90	-	-	-	-
302	(g+30°)	JDIII-71-1	8.30	21.8	-	69.2	0.80	-	-	-	-
303	(g+60°)	JDIII-71-1	7.80	21.6	-	69.9	0.70	-	-	-	-
304	(n)	JDIII-71-1	Survey PCTFE-PAA + H^+								
305	(g)	JDIII-74-1	Survey PCTFE+LiPAA 60 m, -78°C								
306	(g)	JDIII-74-1	10.2	14.6	-	74.7	0.50	-	-	-	-
307	(g+30°)	JDIII-74-1	12.2	13.8	-	67.3	2.90	-	-	-	-
308	(g+60°)	JDIII-74-1	15.5	12.3	-	67.3	4.90	-	-	-	-
309	(n)	JDIII-74-1	Survey PCTFE+LiPAA 60 m, -78°C								
Disk 8											
310	(g)	JDIII-74-1	Survey PCTFE-PAA + F_7butyryl chloride								
311	(g)	JDIII-74-1	34.6	11.6	-	52.7	1.1	-	-	-	-
312	(g+30°)	JDIII-74-1	35.1	11.2	-	51.4	2.3	-	-	-	-
313	(g+60°)	JDIII-74-1	36.3	11.2	-	48.9	3.70	-	-	-	-
314	(n)	JDIII-74-1	Survey PCTFE-PAA + F_7butyryl chloride								
315	(g)	JDIII-71-3	Survey PCTFE-PAA + F_7butyryl chloride								
316	(g)	JDIII-71-3	33.4	13.3	-	52.5	0.90	-	-	-	-
317	(g+30°)	JDIII-71-3	30.8	13.4	-	55.5	0.40	-	-	-	-
318	(g+60°)	JDIII-71-3	30.3	13.6	-	55.7	0.40	-	-	-	-
319	(n)	JDIII-71-1	Survey PCTFE-PAA + F_7butyryl chloride								
327	(g)	JDIII-73-3	Survey PCTFE-DT + Hg THF/H_2O								
328	(g)	JDIII-73-3	21.5	11.8	-	55.9	6.00	4.00	-	-	-
329	(n)	JDIII-73-3	28.5	9.00	-	50.5	8.33	3.20	-	-	-
330	(n)	JDIII-73-3	Survey PCTFE-DT + Hg THF/H_2O								
331	(g)	JDIII-71-3	Survey PCTFE + LiPAA 0°C								
332	(g)	JDIII-71-3	5.10	18.1	-	76.2	0.60	-	-	-	-
333	(n)	JDIII-71-3	5.80	16.9	-	75.2	2.10	-	-	-	-
334	(n)	JDIII-71-3	Survey PCTFE + LiPAA 0°C								
339	(g)	JDIV-1-1	Survey PCTFE + LiTMO								
340	(g)	JDIV-1-1	14.2	12.3	6.60	64.7	2.20	-	-	-	-
341	(n)	JDIV-1-1	21.6	7.60	5.20	57.7	7.90	-	-	-	-
342	(n)	JDIV-1-1	Survey PCTFE + LiTMO 0°C								
343	(n)	JDIV-1-1	High Si								
344	(n)	JDIV-1-1	after $MeCl_2$, still high Si								
345	(n)	JDIV-1-1	High Si								
366	(g)	JDIV-1-1	PCTFE-TMO + CF_3COOH, H_2O; High Si								
367	(g)	JDIV-1-1	High Si								
368	(n)	JDIV-1-1	High Si								
Disk 9											
e321	(g)	JDIV-15a	Survey PCTFE LiDT 5 m, -20°C								

e322	(g)	JDIV-15a	13.9	8.37	-	59.1	2.43	16.2	-	-	-
e323	(n)	JDIV-15a	20.9	3.33	-	58.5	6.10	11.2	-	-	-
e324	(n)	JDIV-15a		Survey							
e325	(g)	JDIV-15b		Survey	PCTFE LiDT 30 m, -20°C						
e326	(g)	JDIV-15b	23.3	8.19	-	54.4	3.41	10.7	-	-	-
e327	(n)	JDIV-15b	32.1	2.13	-	50.8	8.34	6.61	-	-	-
e328	(n)	JDIV-15b		Survey							
e329	(g)	JDIV-15c		Survey	PCTFE LiDT 60 m, -20°C						
e330	(g)	JDIV-15c	23.0	5.28	-	57.8	3.60	10.3	-	-	-
e331	(n)	JDIV-15c	33.3	1.84	-	49.4	8.51	6.96	-	-	-
e332	(n)	JDIV-15c		Survey							
420	(g)	JDIV-3-1		Survey	PCTFE LiDT 0°C, 5 m						
421	(g)	JDIV-3-1	6.50	13.7	-	69.7	0.00	10.1	-	-	-
422	(n)	JDIV-3-1		Survey							
423	(n)	JDIV-3-1	9.20	10.0	-	64.3	5.00	11.7	-	-	-
434	(g)	JDIV-3-2		Survey	PCTFE LiDT 0°C (90% THF)						
435	(g)	JDIV-3-2	12.6	9.80	-	63.9	0.00	13.8	-	-	-
436	(n)	JDIV-3-2		Survey							
437	(n)	JDIV-3-2	14.3	5.90	-	62.0	5.40	12.5	-	-	-
442	(g)	JDIV-3-3		Survey	PCTFE LiDT 0°C (90% heptane)						
443	(g)	JDIV-3-3	9.40	12.0	-	64.2	3.80	10.8	-	-	-
444	(n)	JDIV-3-3		Survey							
445	(n)	JDIV-3-3	26.8	5.10	-	49.8	11.5	6.80	-	-	-
446	(g)	JDIV-3-4		Survey	PCTFE LiDT 0°C (75% heptane)						
447	(g)	JDIV-3-4	6.50	11.1	-	68.3	1.90	12.3	-	-	-
448	(n)	JDIV-3-4	19.9	5.90	-	54.4	11.0	8.70	-	-	-
449	(n)	JDIV-3-4		Survey							
450	(g)	JDIV-3-5		Survey	PCTFE LiDT 0°C (50% heptane)						
451	(g)	JDIV-3-5	15.1	11.5	-	57.5	4.40	11.6	-	-	-
452	(n)	JDIV-3-6		Survey	PCTFE LiDT 0°C (25% heptane)						
453	(n)	JDIV-3-6	19.5	7.20	-	54.9	8.60	9.90	-	-	-

Disk 10

e189	(g)	JDIV-13-a		Survey	LiTMO/Tosic Acid						
e190	(g)	JDIV-13-a	11.4	16.1	1.37	66.6	4.60	-	-	-	-
e191	(n)	JDIV-13-a		Survey	LiTMO/Tosic Acid						
e192	(n)	JDIV-13-a	23.4	10.6	1.55	55.6	8.88	-	-	-	-
e203	(g)	JDIV-13		Survey	LiTMO/CF_3COOH						
e204	(g)	JDIV-13	18.3	13.2	2.19	58.7	7.37	0.31	-	-	-
e205	(n)	JDIV-13	30.4	8.68	0.71	49.5	10.7	0.09	-	-	-
e206	(n)	JDIV-13		Survey							
e207	(g)	JDIV-13-b		Survey	PCTFE/Tosic Acid						
e208	(g)	JDIV-13-b	25.7	12.1	1.79	51.8	8.62	0.00	-	-	-
e209	(n)	JDIV-13-b	35.7	8.55	0.89	42.8	11.6	0.48	-	-	-
e210	(n)	JDIV-13-b		Survey							
e219	(g)	JDIV-13-b2		Survey	CsOH/PCTFE-COOH						
e220	(g)	JDIV-13-b2	no Cs								
e221	(n)	JDIV-13-b2	no Cs								

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
e44	(g)	JDIV-14-1		Survey PCTFE-COOH, Br_3EtOH							
e45	(g)	JDIV-14-1	14.4	10.8	2.87	66.9	2.63	-	-	2.39	-
e46	(n)	JDIV-14-1		Survey PCTFE-COOH, Br_3EtOH							
e47	(n)	JDIV-14-1	24.0	10.7	3.74	54.3	5.98	-	-	1.33	-
e48	(g)	JDIV-14		Survey PCTFE, Br_3EtOH control							
e49	(g)	JDIV-14	53.6	0.43	0.31	30.7	15.0	-	-	0.00	-
e50	(n)	JDIV-14		Survey							
e51	(n)	JDIV-14	56.0	0.00	0.00	31.0	13.0	-	-	0.00	-
e52	(n)	JDIV-14		C_{1s} for control							
e78	(g)	JDIV-11-a		Survey PCTFE-TMO + MeI							
e79	(g)	JDIV-11-a	14.7	15.4	3.70	59.9	6.30	-	-	-	0.00
e80	(n)	JDIV-11-a		Survey							
e81	(n)	JDIV-11-a	28.1	10.6	1.54	49.2	10.6	-	-	-	0.00
e82	(g)	JDIV-11-a		Survey PCTFE-TMO + Tosic Acid							
e83	(g)	JDIV-11-a	14.5	14.1	3.95	61.2	5.31	0.92	-	-	-
e84	(n)	JDIV-11-a		Survey PCTFE-TMO+Tosic Acid							
e85	(n)	JDIV-11-a	22.9	10.1	3.48	53.7	9.35	0.54	-	-	-
Disk 12											
f166	(n)	JDIV-25-d		Survey PCTFE-TMO + CF_3COOH							
f197	(n)	PPV		Survey							
f198	(g)	PPV		Survey							
f199	(n)	PPV									
f200	(n)	PPV		Al source							
f201	(n)	PPV									
f202	(g)	PPV									
f203	(g)	PPV									
f204	(g)	JDIV-25-e	20.8	14.2	1.80	51.8	11.4	0.00	-	-	-
f205	(n)	JDIV-25-e	33.9	7.24	2.76	39.7	15.4	1.03	-	-	-
f206	(g)	JDIV-25-e		Survey PCTFE-COOH+$SOCl_2$/DMF							
f207	(n)	JDIV-25-e		Survey							
f217	(g)	JDIV-28-a	54.0	2.01	0.72	43.1	-	-	0.09	-	-
f218	(n)	JDIV-28-a	55.0	0.86	0.35	43.6	-	-	0.19	-	-
f219	(g)	JDIV-28-a		Survey PVF_2							
f220 through f224 PVF_2 F_{1s} and F_{2s} at (15°, 30°, 45°, 60° and 75°)											
f225	(g)	JDIV-27-al	10.6	13.4	6.34	58.5	9.30	0.36	1.51	-	-
f226	(n)	JDIV-27-al	24.2	11.4	3.65	47.9	12.1	0.72	0.00	-	-
f227	(g)	JDIV-27-al		Survey PCTFE-TMO -20°C, THF/heptane							
f228	(n)	JDIV-27-al		Survey							
f229	(g)	JDIV-27-a	Si								
f230	(g)	JDIV-27-a	6.97	15.7	4.31	63.6	8.79	-	0.59	-	-
f231	(n)	JDIV-27-a	13.4	10.9	5.96	58.3	10.6	0.25	0.67	-	-
f232	(n)	JDIV-27-a		Survey PCTFE after $MeCl_2$							

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
f233	(n)	JDIV-27-a	Al source								
f234	(g)	JDIV-25-f	18.9	19.1	3.39	51.3	5.18	0.00	2.17	-	-
f235	(n)	JDIV-25-f	26.1	13.8	1.63	47.2	9.65	0.00	1.54	-	-
f235	(n)	JDIV-25-f	Survey PCTFE-TMO + CF_3COOH								

Disk 12

f1 through f4 angular XPS data for PCTFE at 15°, 30°, 45° and 75°

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
f10	(n)	JDIV-18-a									
f11	(n)	JDIV-18-a	Survey PCTFE+LiTMO -10°C, (80% Heptane)								
f12	(g)	JDIV-18-a	Survey Check for reorganization								
f13	(g)	JDIV-16-b	Survey PCTFE-TMO+Tosic Acid								
f14	(g)	JDIV-16-b	18.3	15.9	3.06	54.6	8.20	-	-	-	-
f15	(n)	JDIV-16-b									
f16	(n)	JDIV-16-b	Survey								
f17	(g)	JDIV-16-b	33.3	7.89	2.63	45.7	10.7	-	-	-	-
f18	(g)	JDIV-16-b	Survey, check for reorganization								
f19	(g)	JDIV-16-b	Survey								
f20	(n)	JDIV-16-c	Survey								
f21	(n)	JDIV-16-c	1.60	12.1	0.00	85.2	0.73	-	-	0.42	-

f52 through f56; PCTFE angular XPS data for 15°, 30°, 45°, 60° and 75°

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
f57	(g)	JDIV-18-b	Survey PCTFE-TMO+MeOH/BF_3								
f58	(g)	JDIV-18-b	14.9	14.7	5.05	60.4	4.99	-	-	-	-
f59	(n)	JDIV-18-b	27.6	10.1	2.46	50.7	9.16	-	-	-	-
f111	(g)	JDIV-24	19.8	14.1	4.38	54.0	7.65	-	-	-	-
f112	(n)	JDIV-24	29.7	12.8	1.67	45.1	10.7	-	-	-	-
f113	(g)	JDIV-24	Survey PCTFE control								
f127	(g)	JDIV-24c	21.5	17.2	0.00	60.5	0.70	-	-	-	-
f128	(g)	JDIV-24c	Survey PCTFE-RMgDioxolane								
f129	(n)	JDIV-24c	23.0	15.4	0.72	60.3	0.62	-	-	-	-
f130	(g)	JDIV-24d	Survey PCTFE-RMgDioxolane								
f131	(n)	JDIV-24d									

Disk 13

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
f290	(n)	JDIV-27b	29.3	11.0	3.65	46.0	9.74	0.00	0.43	-	-
f60	(n)	JDIV-18b	Survey MeOH/BH_3								
f61	(g)	JDIV-18b	23.3	11.0	6.35	53.0	5.40	-	-	0.96	-
f62	(n)	JDIV-18b	32.2	10.4	3.38	44.1	9.14	-	-	0.71	
f63	(g)	JDIV-19a	23.5	8.37	4.47	56.4	7.27	-	-	-	-
f64	(n)	JDIV-19a	37.1	5.13	3.14	43.7	10.9	-	-	-	-

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
f65	(g)	JDIV-19a	Survey PCTFE+p-phenylenesulfide								
f66	(n)	JDIV-19a	Survey								
f67	(g)	JDIV-20a	Survey PCTFE+maleic anhydride								
f68	(g)	JDIV-20a	48.3	4.30	0.36	33.1	13.9	-	-	-	-
f69	(g)	JDIV-21a	27.5	9.49	4.13	50.3	8.52	-	-	-	-
f70	(n)	JDIV-21a	38.9	5.80	2.27	40.9	12.2	-	-	-	-
f71	(g)	JDIV-21a	Survey PCTFE 8 h, -20°C								
f72	(n)	JDIV-21a	C_{1s} after all scans								
f73	(g)	JDIV-21b	26.4	11.4	3.26	50.5	8.34	-	-	-	-
f74	(n)	JDIV-21b	38.3	7.26	1.70	40.9	11.8	-	-	-	-
f75	(g)	JDIV-21b	Survey PCTFE+LiTMO 1 h, -20°C								
f76	(g)	JDIV-22	9.52	15.1	5.40	67.7	2.23	-	-	-	-
f77	(n)	JDIV-22	19.2	11.9	3.91	57.8	7.22	-	-	-	-
f78	(g)	JDIV-22	Survey PCTFE+LiTMO								
f79	(g)	JDIV-24	Survey Kel-F 82 film								
f80	(g)	JDIV-24	43.1	8.32	0.00	34.5	14.1	-	-	-	-
f81	(n)	JDIV-24	47.6	2.36	0.78	36.2	13.0	-	-	-	-
f88	(g)	JDIV-23b	24.9	17.7	1.34	46.6	9.46	-	-	-	-
f89	(n)	JDIV-23b	39.6	7.20	1.18	39.8	12.3	-	-	-	-
f90	(g)	JDIV-23b	Survey PCTFE-TMO+CF_3COOH								
f91	(n)	JDIV-23b	Survey								
f92	(g)	JDIV-23c	28.4	12.3	3.03	46.7	9.35	-	-	-	0.27
f93	(n)	JDIV-23c	42.0	8.77	1.07	33.6	14.4	-	-	-	0.13
f94	(n)	JDIV-23c	Survey PCTFE-TMO+MeI								
Disk 14											
f132	(g)	JDIV-24d	15.3	22.7	0.00	61.9	0.10	-	-	-	-
f133	(n)	JDIV-24d	21.4	17.9	0.00	60.0	0.78	-	-	-	-
f134	(n)	JDIV-24d	Survey PCTFE+BrMgDioxolane								
f139	(g)	JDIV-25a	6.98	15.3	7.35	66.7	3.66	-	-	-	-
f140	(n)	JDIV-25a	12.8	8.58	4.91	66.4	7.27	-	-	-	-
f141	(g)	JDIV-25a	Survey PCTFE+LiTMO								
f142	(n)	JDIV-25a	Survey								
f143	(g)	JDIV-25b	16.3	12.7	5.38	59.0	6.69	-	-	-	-
f144	(n)	JDIV-25b	26.6	12.0	3.35	47.5	10.5	-	-	-	-
f145	(g)	JDIV-23b	Survey PCTFE-TMO + CF_3COOH								
f146	(g)	JDIV-23b	19.8	13.4	4.53	54.0	8.24	-	-	-	-
f147	(n)	JDIV-23b	27.6	13.0	2.41	45.6	11.4	-	-	-	-
f148	(g)	JDIV-23b	Survey PCTFE-COOH+oxalyl chloride								

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
f159	(g)	JDIV-25c	15.6	15.3	4.18	59.5	5.42	-	-	-	-
f160	(n)	JDIV-25c	26.4	8.92	1.92	51.8	11.0	-	-	-	-
f161	(g)	JDIV-25c	Survey PCTFE-TMO+CF$_3$COOH								
f162	(n)	JDIV-25c	Survey								
f163	(g)	JDIV-25d	18.2	13.0	3.87	59.1	5.83	-	-	-	-
f164	(n)	JDIV-25d	29.0	7.10	2.33	50.4	11.2	-	-	-	-
f165	(g)	JDIV-25d	Survey PCTFE+CF$_3$COOH								
Disk 15											
f237	(n)	JDIV-25f	Survey Al source								
f238	(g)	JDIV-25f	49.7	5.40	29.6	15.2	0.00	0.22	-	-	-
f239	(g)	JDIV-25f	Survey PCTFE control								
f240	(g)	JDIV-25f	Survey PCTFE control Al source								
f241	(n)	JDIV-25f	Survey PCTFE control Al source								
f242	(g)	JDIV-25f	12.6	16.4	3.32	54.3	9.04	0.70	3.60	-	-
f244	(n)	JDIV-25f	21.9	15.0	2.21	49.5	11.1	0.00	0.24	-	-
f245	(n)	JDIV-25g	Survey PCTFE-COOH+SOCl$_2$/DMF								
f246	(g)	JDIV-28b	39.6	8.35	1.50	50.0	-	-	0.43	-	-
f247	(n)	JDIV-28b	45.3	2.07	0.81	51.9	-	-	0.00	-	-
f248	(g)	JDIV-28b	Survey eliminated PVF$_2$								
f249	(g)	JDIV-28c	25.0	10.5	0.50	62.6	-	-	1.33	-	-
f250	(n)	JDIV-28c	32.5	7.56	0.99	58.2	-	-	0.77	-	-
f252 through f256 PPV											
Disk 16											
f257	(n)	PPV	C_{1s} Region								
f277	(g)	JDIV-30a	8.15	14.0	7.76	66.3	1.21	0.45	2.11	-	-
f278	(n)	JDIV-30a	16.3	10.4	5.59	61.2	5.58	0.93	0.00	-	-
f279	(g)	JDIV-30a	Survey PCTFE+LiTMO								
f280	(n)	JDIV-30a	Survey								
f290	(g)	JDIV-27b	20.8	13.7	4.69	54.9	5.34	0.00	0.49	-	-
f291	(n)	JDIV-27b	29.3	11.0	3.65	46.0	9.74	0.00	0.43	-	-
f292	(g)	JDIV-27b	Survey PCTFE-TMO+CF$_3$COOH								
f293	(n)	JDIV-27b	Survey								
f294	(g)	JDIV-25H	Survey PCTFE-COOH+SOCl$_2$/DMF								
f295	(n)	JDIV-25H	survey								
f296	(g)	JDIV-31a	2.75	10.8	7.75	76.7	1.52	0.04	0.47	-	-
f297	(n)	JDIV-31a	12.9	7.22	7.02	66.5	5.34	0.91	0.16	-	-
f298	(g)	JDIV-31a	Survey PCTFE+LiTMO								
f299	(n)	JDIV-31a	Survey								

File(esca-)	Experiment	F	O	N	C	Cl	S	Si	Br	I
f300 (g)	JDIV-27c	11.7	14.3	10.4	58.0	3.99	0.38	1.12	-	-
f301 (n)	JDIV-27c	23.6	11.2	6.61	48.4	8.37	0.28	1.57	-	-
f302 (g)	JDIV-27c			Survey PCTFE-COOH+CDI						
f303 (n)	JDIV-27c			Survey						
f304 (g)	JDIV-30b	16.4	19.4	3.28	54.4	5.17	0.15	1.31	-	-
f305 (n)	JDIV-30b	27.8	12.3	3.12	46.4	9.15	0.00	0.71	-	-
f306 (g)	JDIV-30b			Survey PCTFE-TMO + CF_3COOH						
f307 (n)	JDIV-30b			Survey						
f308 through f312 PPV + AsF_5 dopant										
Disk 17										
f313 (g)	PPV/AsF_5									
f314 (g)	JDIV-32a	8.06	11.7	9.54	63.7	4.67	0.16	2.11	-	-
f315 (n)	JDIV-32a	9.54	13.6	5.93	61.6	7.32	0.50	1.55	-	-
f316 (g)	JDIV-32a			Survey PCTFE+LiTMO						
f317 (n)	JDIV-32a			Survey						
f322 (g)	JDIV-31b	19.9	14.7	1.15	57.5	6.37	0.35	0.08	-	-
f323 (n)	JDIV-31b	33.8	7.22	1.43	46.5	11.0	0.00	0.00	-	-
f324 (g)	JDIV-31b			Survey PCTFE-TMO+CF_3COOH						
f325 (n)	JDIV-31b			Survey						
f326 through f329 PCTFE-COOH + F_6-2-propanol: Ca contamination										
f339 (g)	JDIV-27d1	8.87	16.7	4.16	65.3	4.03	0.00	0.95	-	-
f340 (n)	JDIV-27d1	19.6	14.4	3.20	53.8	8.82	0.16	0.00	-	-
f341 (g)	JDIV-27d1			Survey PCTFE-COOH+Octanol						
f342 (n)	JDIV-27d1			Survey						
f343 (g)	JDIV-27d2	6.43	17.5	4.13	68.9	1.50	0.00	1.55	-	-
f344 (n)	JDIV-27d2	15.7	12.4	3.85	59.5	7.27	0.52	0.72	-	-
f345 (g)	JDIV-27d2			Survey PCTFE-COOH+Octadecanol						
f346 (n)	JDIV-27d2			Survey						
f347 through f350 JDIV-30-aw Si contaminated										
f351 (g)	JDIV-33a	2.03	14.2	6.08	66.5	4.47	1.92	4.76	-	-
f352 (n)	JDIV-33a	6.72	13.6	6.31	62.2	6.96	1.65	2.53	-	-
f353 (g)	JDIV-33a			Survey PCTFE-TMO+CF_3COOH						
f354 (n)	JDIV-33a			Survey						
Disk 18										
f359 (g)	JDIV-30c	23.4	12.5	4.08	50.5	5.43	1.18	2.90	-	-

File(esca-)	Experiment	F	O	N	C	Cl	S	Si	Br	I
f360 (n)	JDIV-30c	28.1	9.34	2.74	48.8	9.24	0.40	1.39	-	-
f361 (g)	JDIV-30c			Survey PCTFE-COOH+Ph_3PCl_2						
f362 (n)	JDIV-30c			Survey						
f363 (g)	JDIV-32b	14.1	19.0	2.58	55.5	5.38	0.00	3.43	-	-
f364 (n)	JDIV-32b	25.2	13.9	2.70	45.5	10.5	0.00	2.32	-	-
f365 (g)	JDIV-32b			Survey PCTFE-TMO+CF_3COOH						
f366 (n)	JDIV-32b			Survey						
f377 (g)	JDIV-31c-b	21.5	10.1	2.80	48.6	6.82	0.23	0.00	-	-
f378 (n)	JDIV-31c-b	35.5	6.52	1.41	45.9	10.6	0.00	0.12	-	-
f379 (g)	JDIV-31c-b		Survey PCTFE-COOH+F_7Butyryl chloride							
f380 (n)	JDIV-31c-b		Survey							
f381 (g)	JDIV-30-d1	17.0	14.3	3.78	55.8	8.65	0.02	0.73	-	-
f382 (n)	JDIV-30-d1	39.4	9.99	4.73	29.2	15.2	0.42	1.03	-	-
f383 (g)	JDIV-30-d1		Survey PCTFE-COOH+Octanol							
f384 (n)	JDIV-30-d1		Survey							
f385 (g)	JDIV-30-d2	19.7	11.0	3.61	56.1	9.23	0.28	0.00	-	-
f386 (n)	JDIV-30-d2	28.4	7.94	1.93	49.4	11.8	0.56	0.00	-	-
f387 (g)	JDIV-30-d2		Survey PCTFE-COOH+Octadecanol							
f388 (n)	JDIV-30-d2		Survey							
f389 (g)	JDIV-31-d	22.4	10.2	3.27	56.8	6.77	0.28	0.20	-	-
f390 (n)	JDIV-31-d	33.0	7.49	2.13	47.9	9.29	0.15	0.07	-	-
f391 (g)	JDIV-31-d		Survey PCTFE-COOH+DMF/$COCl_2$ & $NaBH_4$							
f392 (n)	JDIV-31-d		Survey							
f393 (g)	JDIV-32c	8.90	15.5	9.88	58.7	4.52	0.76	1.74	-	-
f394 (n)	JDIV-32c	20.5	10.4	7.91	51.4	8.84	0.19	0.77	-	-
f395 (g)	JDIV-32c		Survey PCTFE-COOH + CDI							
f396 (n)	JDIV-32c		Survey							
f397 (g)	JDIV-31d2	31.4	11.1	2.13	49.4	4.92	0.03	1.11	-	-
Disk 19										
f398 (n)	JDIV-31d2	30.8	8.84	2.71	47.5	9.07	0.00	1.13	-	-
f399 (g)	JDIV-31d2	Survey PCTFE-COOH+$COCl_2$/DMF&$NaBH_4$+F_7ButyrylCl								
f400 (n)	JDIV-31d2	Survey								
f416 (g)	JDIV-32d			C_{1s}						
f417 (n)	JDIV-32d			C_{1s}						
f418 (g)	JDIV-32d	18.1	14.0	6.59	54.7	5.61	0.00	1.01	-	-
f419 (n)	JDIV-32d	28.7	9.19	4.75	46.3	9.82	0.61	0.67	-	-
f420 (g)	JDIV-32d		Survey PCTFE-COOH+CDI+F_6-2-propanol							
f421 (n)	JDIV-32d		Survey							

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
f430	(g)	JDIV-36b	18.0	17.7	1.96	53.1	3.76	0.93	4.56	-	-
f431	(n)	JDIV-36b	26.4	11.2	1.60	49.4	9.68	0.00	1.80	-	-
f432	(g)	JDIV-36b		Survey PCTFE-TMO+CF_3COOH							
f433	(n)	JDIV-36b		Survey							
f434	(g)	JDIV-32d2		C_{1s} HiRes							
f435	(n)	JDIV-32d2		C_{1s} HiRes							
f445	(g)	JDIV-37b	18.6	18.2	2.38	51.2	5.34	0.22	4.08	-	-
f446	(n)	JDIV-37b	31.1	8.37	1.72	46.9	10.6	0.20	1.12	-	-
f447	(g)	JDIV-37b		Survey PCTFE-TMO+CF_3COOH							
f448	(n)	JDIV-37b		Survey							
f449	(g)	JDIV-36c3		C_{1s} Hi Res							
f450	(n)	JDIV-36c3		C_{1s} Hi-Res							
f451	(g)	JDIV-36c3	21.9	11.6	2.19	53.4	9.01	1.83	0.10	-	-
f452	(n)	JDIV-36c3	30.9	7.47	1.89	47.0	11.9	0.38	0.41	-	-
f453	(g)	JDIV-36c3		Survey PCTFE-COOH+$SOCl_2$/DMF							
f454	(n)	JDIV-36c3		Survey							
f455	(g)	JDIV-36c2	20.7	13.1	2.35	54.8	6.66	1.01	0.72	0.66	-
f456	(n)	JDIV-36c2	33.0	8.52	1.98	44.2	12.3	0.01	0.00	0.00	-
f457	(g)	JDIV-36c2		Survey PCTFE-COOH+$SOCl_2$/DMF							
f458	(n)	JDIV-36c2		Survey							
f459	(g)	JDIV-36c1		C_{1s} Hi-Res							
f460	(n)	JDIV-36c1		C_{1s} Hi-Res							
f461	(g)	JDIV-36c1	20.2	11.7	0.90	56.6	8.00	1.29	1.33	-	-
f462	(n)	JDIV-36c1	32.8	6.34	0.48	48.5	11.3	0.51	0.08	-	-

Disk 20

f463	(g)	JDIV-36c1		Survey PCTFE-COOH+$SOCl_2$/DMF							
f464	(n)	JDIV-36c1		Survey							
f465	(g)	JDIV-37c	26.5	10.1	7.03	49.8	6.63	0.00	0.00	-	-
f466	(n)	JDIV-37c	32.3	7.76	4.75	44.8	10.4	0.05	0.00	-	-
f467	(g)	JDIV-37c		Survey PCTFE-COOH+CDI							
f468	(n)	JDIV-37c		Survey							
f469	(g)	JDIV-46a	11.7	13.9	4.40	61.2	4.63	0.83	3.38	-	-
f470	(n)	JDIV-46a	23.0	8.94	4.55	52.8	9.47	0.00	1.24	-	-
f471	(g)	JDIV-46a		Survey PCTFE+LiTMO							
f472	(n)	JDIV-46a		Survey							
f473	(g)	JDIV-37c		C_{1s} Hi Res							
f474	(n)	JDIV-37c		C_{1s} Hi Res							
f475	(g)	JDIV-37c	26.1	11.0	4.62	49.4	7.40	0.00	1.45	-	-
f476	(n)	JDIV-37c	35.1	7.67	2.72	42.1	10.6	0.00	1.86	-	-
f477	(g)	JDIV-37c		Survey PCTFE-COOH+CDI							

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
f478	(n)	JDIV-37c			Survey						
f479	(g)	JDIV-37c1	21.2	11.4	5.13	53.5	8.69	0.13	0.00	-	-
f480	(n)	JDIV-37c1	31.7	8.76	3.82	44.0	11.7	0.00	0.00	-	-
f481	(g)	JDIV-37c1			Survey PCTFE-COOH+CDI						
f482	(n)	JDIV-37c1			Survey						
f483	(g)	JDIV-37c2	20.1	12.7	3.68	55.8	6.03	0.00	1.57	0.00	-
f484	(n)	JDIV-37c2	30.0	8.32	3.51	47.6	10.2	0.00	0.18	0.16	-
f485	(g)	JDIV-37c2			Survey PCTFE-COOH+CDI						
f486	(n)	JDIV-37c2			Survey						
f487	(g)	JDIV-37c4	32.2	11.1	5.45	38.0	11.3	0.42	1.53	-	-
f488	(n)	JDIV-37c4	32.8	8.84	3.15	43.6	11.7	0.00	0.00	-	-
f489	(g)	JDIV-37c4			Survey PCTFE-COOH+CDI						
f490	(n)	JDIV-37c4			Survey						
f491	(g)	JDIV-40b	24.1	12.2	2.86	50.1	7.86	0.00	2.86	-	-
f492	(n)	JDIV-40b	34.2	9.28	1.68	42.6	12.2	0.00	0.00	-	-

Disk 21

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
f493	(g)	JDIV-40b			Survey PCTFE-TMO+CF_3COOH						
f494	(n)	JDIV-40b			Survey						
f495	(g)	JDIV-48a	45.9	5.90	0.77	27.5	16.1	0.00	3.77	-	-
f496	(n)	JDIV-48a	54.4	3.85	0.86	23.1	17.1	0.02	0.67	-	-
f497	(g)	JDIV-48a			Survey PCTFE control						
f498	(n)	JDIV-48a			Survey						
f499	(g)	JDIV-38c	24.3	11.6	0.97	53.6	8.27	0.00	1.29	-	-
f500	(n)	JDIV-38c	36.3	8.01	0.33	42.4	12.1	0.00	0.92	-	-
f501	(g)	JDIV-38c			Survey PCTFE-COOH+BH_3						
f502	(n)	JDIV-38c			Survey						
f503	(g)	JDIV-38c2	20.2	13.0	2.26	58.0	6.58	0.00	0.00	-	-
f504	(n)	JDIV-38c2	32.9	7.95	0.99	46.1	10.3	0.20	1.58	-	-
f505	(g)	JDIV-38c2			Survey PCTFE-TMO+BH_3						
f506	(n)	JDIV-38c2			Survey						
f507	(g)	JDIV-38c3	67.9	3.50	0.00	13.4	15.2	0.00	0.00	-	-
f508	(n)	JDIV-38c3	56.3	3.32	0.00	26.7	13.2	0.00	0.00	-	-
f509	(g)	JDIV-38c3			Survey PCTFE+BH_3 control						
f510	(n)	JDIV-38c3			Survey						
f511	(g)	JDIV-46b	27.6	11.8	2.52	47.1	8.90	0.82	1.22	-	-
f512	(n)	JDIV-46b	39.9	8.82	2.20	35.9	13.3	0.00	0.00	-	-
f513	(g)	JDIV-46b			Survey PCTFE-TMO+CF_3COOH						
f514	(n)	JDIV-46b			Survey						
f515	(g)	JDIV-48b	4.29	6.94	1.02	75.3	1.59	6.94	3.95	-	-
f516	(n)	JDIV-48b	9.67	4.72	0.00	76.3	2.55	6.73	0.00	-	-
f517	(g)	JDIV-48b			Survey PCTFE+LiDT						

File(esca-)	Experiment	F	O	N	C	Cl	S	Si	Br	I
Disk 22										
f519 (g)	JDIV-48b2	4.38	1.50	0.00	78.8	0.92	11.2	3.25	-	-
f520 (n)	JDIV-48b2	8.01	3.17	0.00	72.8	3.73	12.3	0.00	-	-
f521 (g)	JDIV-48b2	Survey PCTFE+LiDT -20°								
f522 (n)	JDIV-48b2	Survey								
g202 (A)	JDIV-64a3	45.4	4.76	0.26	47.9	0.57	0.00	1.12	-	-
	Angle	50.2	3.01	0.26	45.7	0.17	0.12	0.50	-	-
g203 (g)	JDIV-64a3	Survey PVF$_2$ + trichloroacetylisocyanate								
g204 (A)	JDIV-64a3	42.4	5.72	0.47	48.4	1.51	0.33	1.11	-	-
		44.6	4.67	0.23	49.5	0.80	0.28	0.00	-	-
g205 (g)	JDIV-64a3	Survey PVF$_2$+LiAlH$_4$+Cl$_3$AI								
g228 (g)	JDIV-64Br	43.6	4.37	-	49.9	0.08	-	0.59	1.46	-
g229 (g)	JDIV-64Br	Survey PVF$_2$E+Br$_2$								
g230 (g)	JDIV-64Br	46.0	4.90	-	47.9	0.09	-	0.32	0.77	-
g236 (A)	JDIV-71									
g237 (g)	JDIV-71	Survey PCTFE+Bu$_3$SnH 0°C, hv								
g251 (g)	JDIV-64Br2	33.0	9.38	-	55.5	-	-	1.46	0.76	-
g252 (g)	JDIV-64Br2	Survey PVF$_2$E+Br$_2$+NaOH								
g253 (g)	JDIV-64Br3	32.7	12.2	-	50.8	0.48	-	3.45	0.41	-
g254 (g)	JDIV-64Br$_3$	Survey PVF$_2$E+Br$_2$+NaCl								
Disk 23										
g106 (A)	JDIV-56-3b	24.2	16.1	1.08	49.7	7.93	0.05	0.97	-	-
		36.0	8.84	1.15	41.2	11.9	0.25	0.69	-	-
g107 (g)	JDIV-46-c3	41.9	9.65	-	48.5	-	-	-	-	-
g108 (n)	JDIV-46c3	48.1	6.20	-	45.7	-	-	-	-	-
g109 (g)	JDIV-46-c3	Survey PCTFECOOH+CDI+Octanol								
g110 (g)	JDIV-26-c1	42.9	10.9	-	46.2	-	-	-	-	-
g111 (n)	JDIV-26-c1	47.8	5.92	-	46.2	-	-	-	-	-
g112 (g)	JDIV-26-c1	Survey PCTFECOOH+CDI+F$_6$-2-propanol								
g113 (g)	JDIV-26-c2	50.6	12.9	-	36.3	-	-	-	0.22	-
g114 (n)	JDIV-26-c2	48.9	6.65	-	44.4	-	-	-	0.06	-
g115 (g)	JDIV-26-c2	Survey PCTFECOOH+CDI+Br$_3$EtOH								
g124 (A)	JDIV-50	No N increase for PCTFECOOH+diisopropylamine								
g125 (g)	JDIV-52-1									
g126 (n)	JDIV-52-1	PCTFE-TMO+BF$_3$, F$_6$-2-propanol								
g127 (g)	JDIV-52-2									
g128 (n)	JDIV-52-2	PCTFE-TMO+BF$_3$, octanol								
g129 (g)	JDIV-52-3									
g130 (n)	JDIV-52-3	PCTFE-TMO+BF$_3$, Br$_3$EtOH								

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
g131	(A)	JDIV-57-1	25.3	9.19	2.15	54.4	7.19	0.00	1.18	0.58	-
			36.5	5.76	1.34	45.0	10.1	0.04	0.95	0.31	-
g71	(A)	JDIV-58-1	23.9	10.3	4.74	54.4	4.89	0.26	1.55	-	-
			35.1	6.10	2.84	45.4	9.79	0.00	0.77	-	-
g72	(g)	JDIV-58-1	C_{1s} for PCTFETMO 5 min, -78°C								
g73	(A)	JDIV-58-2	23.2	12.3	3.13	53.1	5.84	0.00	2.49	-	-
			34.5	5.22	2.33	47.3	9.95	0.00	0.73	-	-
g74	(g)	JDIV-58-2	C_{1s} for PCTFETMO 30 m, -78°C								
g75	(A)	JDIV-58-3	20.5	10.5	5.97	57.0	4.84	0.26	0.88	-	-
			30.4	6.75	3.95	49.3	8.77	0.00	0.79	-	-
g76	(g)	JDIV-58-3	C_{1s} for PCTFETMO 60 m, -78°C								
g81	(A)	JDIV-57-2	20.2	11.8	5.32	57.5	5.18	0.00	0.00	-	-
			27.3	8.69	2.45	51.8	7.91	0.03	1.89	-	-
g29	(A)	JDIV-49c									
g30	(g)	JDIV-49c	PCTFE+LiDT+Hg(O_2CCF_3)$_2$ Si con.								
g31	(n)	JDIV-49c	Survey								

g32 through g48 PCTFE, PCTFE-TMO, PCTFECOOH contaminated with Si
Examined the contamination in g43 (PDMS) and g44 - 48 (SiO_2)

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
g52	(A)	JDIV-57-1	9.30	12.3	9.70	67.1	1.47	0.00	0.13	-	-
			15.0	7.82	6.86	64.5	5.75	0.00	0.00	-	-
g53	(g)	JDIV-57-1	C_{1s}								
g54	(g)	JDIV-57-1	Survey PCTFE+LiTMO								
g55	(n)	JDIV-57-1	Survey								
g56	(A)	JDIV-56-3	Si contaminated								
g57	(g)	JDIV-56-3	C_{1s}								

Disk 25

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
g132	(g)	JDIV-57-1	Survey PCTFECOOH+BH_3+TBPI								
g133	(A)	JDIV-57-2	16.9	12.3	5.42	56.6	6.80	0.00	1.52	0.48	-
			28.0	9.24	3.27	49.5	9.52	0.00	0.14	0.34	-
g134	(A)	JDIV-57-3	25.5	11.1	2.23	51.9	7.34	0.00	0.90	1.05	-
g134	(g)	JDIV-57-3	Survey PCTFETMO+BH_3+TBPI								
g150	(A)	JDIV-64	53.5	1.11	0.00	45.1	0.00	0.34	-	-	-
			52.1	2.35	0.11	45.3	0.01	0.16	-	-	-
g151	(g)	JDIV-64	Survey PVF_2 control								
g152	(A)	JDIV-64-1	43.7	4.17	0.51	50.7	-	0.24	0.65	-	-
			49.0	2.17	0.07	48.3	-	0.00	0.40	-	-
g153	(g)	JDIV-64-1	Survey eliminated PVF_2								
g154	(A)	JDIV-64-2	41.8	7.09	1.32	49.4	-	0.42	0.00	-	-
			46.7	4.38	0.68	47.9	-	0.30	0.02	-	-

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
g155	(g)	JDIV-64-2	Survey eliminated and hydrolyzed PVF$_2$								
g178	(A)	JDIV-64-a2	38.3	6.54	0.50	51.9	-	0.00	2.72	-	-
			43.5	3.55	0.00	51.8	-	0.21	1.00	-	-
g179	(g)	JDIV-64-a2	Survey PVF$_2$E+LiAlH$_4$								
g180	(A)	JDIV-64-a2	Si contaminated								
g181	(g)	JDIV-64-a2	Survey PVF$_2$E+H$^+$+LiAlH$_4$								
g194	(A)	JDIV-64-c3	25.5	12.9	3.12	53.0	4.42	0.00	1.02	-	-
			34.9	8.28	1.59	52.0	2.73	0.52	0.00	-	-
g195	(g)	JDIV-64-c3	Survey PVF$_2$E+H$^+$+LiAlH$_4$+Cl$_3$AI								
g196	(A)	JDIV-64-c3	27.7	16.0	2.50	48.5	1.77	2.63	0.96	-	-
			35.8	11.9	1.98	47.6	1.47	0.38	0.86	-	-
g197	(g)	JDIV-64-c3	Survey PVF$_2$E+H$^+$+Cl$_3$AI								
g198	(A)	JDIV-64-b3	37.0	9.91	1.32	49.0	1.44	1.35	0.00	-	-
			42.5	7.07	0.96	47.7	0.63	0.80	0.28	-	-
g199	(g)	JDIV-64-b3	Survey PVF$_2$E+Cl$_3$AI								
g200	(A)	JDIV-64-b3	23.8	13.6	2.78	52.7	5.17	1.15	0.92	-	-
			32.9	9.11	1.83	52.7	2.85	0.45	0.19	-	-
g201	(g)	JDIV-64-b3	Survey PVF$_2$E+LiAlH$_4$+Cl$_3$AI								
Disk 26											
g261	(A)	JDIV-72-1	23.7	3.57	-	58.7	4.37	8.38	1.27	-	-
			34.8	2.05	-	49.8	8.77	4.57	0.00	-	-
g262	(g)	JDIV-72-1	C$_{1s}$ HiRes								
g263	(g)	JDIV-72-1	Survey PCTFE+LiDT 5 m, -78°C								
g264	(A)	JDIV-72-2	24.7	3.82	-	59.9	4.57	7.04	0.00	-	-
			32.3	2.01	-	51.8	8.67	4.42	0.84	-	-
g265	(g)	JDIV-72-2	Survey PCTFE+LiDT 30 m, -78°C								
g266	(A)	JDIV-72-3	19.8	6.25	-	62.3	2.60	8.12	0.88	-	-
			29.7	2.82	-	53.0	7.89	5.36	1.24	-	-
g267	(g)	JDIV-72-3	Survey PCTFE+LiDT 60 m, -78°C								
g268	(A)	JDIV-72-1b	12.7	5.75	-	65.8	1.61	13.1	1.13	-	-
			20.0	4.42	-	60.3	4.67	10.1	0.58	-	-
g269	(g)	JDIV-72-1b	Survey PCTFE+LiDT 5 m, -20°C								
g295	(g)	JDIV-64-c1	48.9	11.0	-	36.7	3.42	0.00	0.00	-	-
g296	(n)	JDIV-64-c1	49.2	8.19	-	40.8	1.70	0.00	0.12	-	-
g297	(g)	JDIV-64-c1	Survey PVF$_2$E+H$^+$+NaBH$_4$+Cl$_3$AI								
g298	(g)	JDIV-64-c2	47.9	6.74	-	42.0	2.20	0.00	1.20	-	-
g299	(n)	JDIV-64-c2	49.6	4.61	-	44.8	1,01	0.00	0.00	-	-
g300	(g)	JDIV-64-c2	Survey PVF$_2$E+NaBH$_4$+Cl$_3$AI								
g301	(g)	JDIV-64-c3	47.2	3.41	-	48.5	0.65	0.00	0.23	-	-
g302	(n)	JDIV-64-c3	51.9	2.28	-	45.5	0.34	0.00	0.00	-	-
g303	(g)	JDIV-64-c3	Survey PVF$_2$+NaBH$_4$+Cl$_3$AI								
g336	(A)	JDIV-65-1	12.6	20.4	-	65.7	0.42	-	0.95	-	-
			13.5	19.7	-	66.5	0.19	-	0.00	-	-
g337	(g)	JDIV-65-1	Survey PCTFE+LiPAA -20°C								

File(esca-)	Experiment	F	O	N	C	Cl	S	Si	Br	I
g338 (n)	JDIV-65-1	Survey PCTFE+LiPAA -20°C								
g352 (A)	JDIV-65-1b	17.1	15.2	-	66.4	0.88	-	0.40	-	-
		20.8	11.0	-	66.1	2.17	-	0.00	-	-
g353 (g)	JDIV-65-1b	Survey PCTFE+LiPAA -78°C, 5 m								
g354 (n)	JDIV-65-1b	Survey								
g355 (A)	JDIV-65-1b2	14.3	16.7	-	67.5	0.30	-	1.29	-	-
		19.3	11.6	-	66.6	2.45	-	0.00	-	-
g356 (g)	JDIV-65-1b2	Survey PCTFE+LiPAA -78°C, 60 m								
g357 (n)	JDIV-65-1b2	Survey								
g358 (A)	JDIV-65-1E	44.9	11.5	-	43.5	0.16	-	0.00	-	-
		42.0	11.3	-	46.6	0.08	-	0.04	-	
g359 (g)	JDIV-65-1E	Survey PCTFEPAA+F_7Butyryl chloride								
g360 (n)	JDIV-65-1E	Survey								
Disk 27										
g361 (A)	JDIV-65-1NE	16.1	20.8	3.16	57.5	1.51	-	0.78	-	-
		16.1	16.8	2.34	63.3	0.40	-	0.13	-	-
g362 (g)	JDIV-65-1NE	Survey PCTFEPAA+dinitrobenzoyl chloride								
g363 (n)	JDIV-65-1NE	Survey								
g400 (A)	JDIV-66-1	24.3	13.1	1.15	54.9	6.47	-	0.16	0.00	-
		32.2	8.64	1.35	47.6	9.56	-	0.59	0.00	-
g401 (g)	JDIV-66-1	Survey PCTFE+LiTMO+CF_3COOH								
g402 (A)	JDIV-66-2	14.8	10.4	5.98	64.1	2.87	-	1.55	0.37	-
		23.6	7.96	5.00	55.8	7.38	-	0.19	0.04	-
g403 (g)	JDIV-66-2	Survey PCTFETMO								
g404 (A)	JDIV-66-3	23.4	10.9	4.58	55.4	5.31	-	0.55	0.00	-
		23.8	8.26	3.67	51.8	7.50	-	0.00	0.00	-
g405 (g)	JDIV-66-3	Survey PCTFETMO+BH_3								
g420 (A)	JDIV-66-4	13.0	17.6	4.57	58.2	4.97	-	0.42	1.19	-
		17.9	13.3	5.19	54.7	7.45	-	0.33	1.14	-
g421 (g)	JDIV-66-4	Survey PCTFE								
g422 (n)	JDIV-66-4	Survey PCTFETMO+TBPI								
g423 (A)	JDIV-66-5	11.5	18.1	4.07	57.2	4.18	-	1.10	3.87	-
		16.1	13.6	3.61	55.6	6.69	-	1.36	3.12	-
g424 (g)	JDIV-66-5	Survey PCTFECOOH+TBPI								
g425 (A)	JDIV-66-6	16.7	28.5	3.36	4.42	5.36	-	0.08	1.76	-
		24.0	21.2	3.10	42.5	8.50	-	0.00	0.62	-
g426 (g)	JDIV-66-6	Survey PCTFETMO+BH_3+TBPI								
g434 (A)	JDIV-66-7	30.4	12.0	1.16	45.0	9.65	-	1.79	0.02	-
		37.2	9.10	1.12	41.0	10.8	-	0.80	0.00	-
g435 (g)	JDIV-66-7	Survey PCTFETMO/BH_3/H^+								
g436 (A)	JDIV-66-8	36.0	10.3	0.29	40.5	10.8	-	1.99	0.00	-
		41.1	7.37	0.63	39.5	11.2	-	0.00	0.25	-
g437 (g)	JDIV-66-8	Survey PCTFE/H^+/BH_3								
g453 (A)	JDIV-66-9	23.2	12.3	1.17	52.8	7.82	-	0.00	2.70	-
		34.4	9.12	1.40	43.2	10.3	-	0.20	1.37	-

File(esca-)		Experiment	F	O	N	C	Cl	S	Si	Br	I
g454	(g)	JDIV-66-9	Survey PCTFETMO/H^+/BH_3/TBPI								
g455	(A)	JDIV-66-10	27.1	12.0	2.24	47.3	7.89	-	1.15	2.45	-
			34.8	8.20	1.51	41.9	10.3	-	1.99	1.24	-
g456	(g)	JDIV-66-10	Survey PCTFETMO/BH_3/H^+/TBPI								
g480	(A)	JDIV-66-11	31.5	9.86	1.70	46.3	8.79	-	0.00	1.84	-
			37.0	8.25	1.56	40.3	10.1	-	1.64	1.21	-
g481	(g)	JDIV-66-11	Survey PCTFETMO/BH_3/H^+/BH_3/TBPI								
g482	(A)	JDIV-66-12	38.7	10.7	1.55	38.4	9.51	-	1.08	0.00	-
			42.0	10.7	1.04	35.2	11.0	-	0.00	0.00	-

Disk 29

g537 through g560 PPV analyzed for atomic compostion as well as an attempt at obtaining valence XPS data.

BIBLIOGRAPHY

Adamson, A Physical Chemistry of Surfaces 4th ed. Wiley: N.Y., 1982

Agrawal, G P; Cojan, C; Flytzanis, C. **Phys. Rev.** 1978, B17, 778

Ahlgren, G; Krishe, B **J. Chem. Soc. Chem. Comm.** 1984, 946

Aldrich Catalog/Handbook of Fine Chemicals 1986

Alexander, A E; Hibberd, G E in Weissberger, A; Rossiter, B W eds. Techniques of Chemistry Wiley: N.Y. 1972, 1, 575

Amouroux, J; Goldman, M; Revoil, M F **J. Polym. Sci: Polym. Chem. Ed.** 1982, 20, 1373

Astumian, R D; Schelly, Z A **J. Am. Chem. Soc.** 1984, 106, 304

Baker, G L; Bates, F S **Macromolecules** 1984, 17, 2619

Barker, D J; Brewis, D M; Dahm, R H **J. Mat. Sci.** 1979, 14, 749

Baszkin, A; Ter-Minassian-Saraga, L **J. Polym. Sci., Part C** 1971, 243

Batich, C D; Wendt, R W Abstr. Amer. Chem. Soc., Div. Polym. Chem. Houston National Meeting, 1980, 179

Bell, A T; Hollahan, J R Techniques and Applications of Plasma Chemistry Wiley: N.Y., 1974

Blais, P; Day, M; Wiles, D M **J. Appl. Polym. Sci.** 1973, 17, 875

Blythe, A R; Briggs, D; Kendall, C K; Rance, D G; Zichy, V J I **Polymer** 1979, 19, 1273

Bohrer, J **Trans. N. Y. Acad. Sci.** 1955, 2, 20; 1958, 5, 367

Bonafini, J A; Dias A J; Guzdar, Z A; McCarthy, T J **J. Polym. Sci.: Polym. Lett. Ed.** 1985, 23, 33

Bonafini, J A; McCarthy, T J Master of Science Degree Thesis University of Massachusetts: Amherst, Massachusetts 1984

Borisova, T K; Kiselev, A V; Korolev, A Y; Lygin, V I; Solomonova, I N **Kolloidn. Zh.** 1966, 28, 792

Boudreaux, D S; Chance, R R; Elsenbaumer, R L; Frommer J E; Brédas, J L; Silbey, R **Phys. Rev. B** 1985, 31, 652

Briggs, D in Brewis, D M ed. Surface Analysis and Pretreatments of Plastics and Metals Applied Science: London, 1982

Briggs, D; Brewis, D M; Konieczko, M B **J. Mat. Sci.** 1979, 14, 1344

Briggs, D; Kendall, G K **Polymer** 1979, 20, 1053

Briggs, D; Zichy, V J I; Brewis, D M; Comyn, J; Dalm, R H; Green, M A; Konieczko, M B **Surface Interface Analysis** 1980, 2, 107

Brown, C A **J. Org. Chem.** 1974, 39, 3913

Bruck, S D **Polymer** 1965, 6, 319

Bussher, H J; Van Pelt, A W J; DeBoer, P; DeJong, H P; Arends, J **J. Colloids and Surfaces** 1984, 9, 319

Cais, R E; Kometani, J M **Macromolecules** 1984, 17, 1932

Campbell, J E; Rausher, W H **J. Polym. Sci.** 1955, 18, 461

Chambers, R D; Mobbs, R H **Adv. Fluorine Chem.** 1965, 4, 54

Charlesby, A Atomic Radiation and Polymers Pergamon Press: N.Y., 1960, Chapter 22

Chein, J C W Polyacetylene Wiley: N. Y., 1984

Chidsey, C E D; Murray, R W **Science** 1986, 231, 5

Clark, D T in Briggs, D ed. Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy Heyden and Sons: London, 1977

Clark, D T in Ivin, K J ed. Structural Studies of Macromolecules by Spectroscopic Means Wiley: London, 1979

Clark, D T; Dilks, A **J. Polym. Sci.: Polym. Chem. Ed.** 1977, 15, 2321

Clark, D T; Feast, W J Polymer Surfaces Wiley: N. Y., 1978

Clark, D T; Peeling, J; O'Malley, J M **J. Polym. Sci.: Polym. Chem. Ed.** 1976, 14, 543

Clark, D T; Thomas, H R **J. Polym. Sci.: Polym. Chem. Ed.** 1977, 15, 2843

Clark, D T; Wilson, R J **J. Polym. Sci.: Polym. Chem. Ed.** 1983, 21, 837

Collins, G C S; Lowe, A C; Nickolas, D **Eur. Polym. J.** 1973, 9, 1173

Corey, E J; Seebach, D **Angew. Chem. Int. Ed.** 1965, 4, 1075

Costello, C A; McCarthy, T J **Macromolecules** 1984, 17, 2529

Danielson, N D; Taylor, R T; Huth, J A; Siergiej, R W; Galloway, J G; Paperman, J B **Ind. Eng. Chem. Prod. Res. Dev.** 1983, 22, 303

Dias, A J; McCarthy, T J **Macromolecules** 1984, 17, 2529

Dias, A J; McCarthy, T J **Macromolecules** 1985, 18, 1826

Dias, A J; McCarthy, T J **J. Polym. Sci.: Polym. Chem. Ed.** 1985, 23, 1057

Dohany, J E; Robb, L E Kirk-Othmer Encyclopedia of Chemical Technology Wiley: N. Y., 1980, volume 11, page 64

Dwight, D W; Riggs, W M **J. Colloid Interface Sci.** 1974, 47, 650

Eaton, P E; Cooper, G F; Johnson, R C; Mueller R H **J. Org. Chem.** 1972, 37, 1947

Einstein, A **Ann. Phys.** 1905, 17, 132

Everhart, D S; Reilley, C N **Surface Interface Anal.** 1981, 3, 126

Flory, P J **J. Am. Chem. Soc.** 1939, 61, 1518

Fluorney, P A; Shaffers, W J **Spectrochim. Acta** 1966, 22, 5

Frommer, J E **Acc. Chem. Res.** 1986, 19, 2

Fuchs, N. **Makromol. Chem.** 1957, 22, 1

Gagnon, D R; McCarthy, T J **J. Appl. Polym. Sci.** 1984, 29, 4335

Galvin, M E; Wnek, G E **Polym. Comm.** 1982, 23, 795

Gatti, G; Concelleir, G; Cavalli, L; Andrenssi, P **Conv. Ital. Sci. Macromol. 4th** 1979, 79

Gibson, H W **Polymer** 1984, 25, 3

Grassie, N; McNeil, J C **J. Polym. Sci.** 1959, 128, 312

Gugot, A; Benevise, J; Trambouse, Y **J. Appl. Polym. Sci.** 1962, 6, 103

Hahn, B R; Percec, V Polym. Prepr., Am. Chem. Soc., Div. of Polym. Chem. New York National Meeting **1986**, 27, 364

Hannah, R W **Appl. Spectrosc.** 1963, 17, 23

Hanson, W N **Anal. Chem.** 1963, 35, 765

Harrick, N J Internal Reflection Spectroscopy Wiley: N. Y., 1967

Harrick, N J **J. Opt. Soc. Am.** 1965, 55, 851

Harrick, N J, duPré, F K **Appl. Opt.** 1966, 5, 1739

He, F; Kise, H **J. Polym. Sci.: Polym. Chem. Ed.** 1983, 21, 1729

Henke, B L **Adv. X-ray Anal.** 1969, 13, 1

Hoffman, J D; Weeks, J J **J. Chem. Phys.** 1962, 37, 1723

Holm, R; Storp, S **Surface Interface Anal.** 1980, 2, 96

Holmes-Farley, S R; Remey, R H; McCarthy, T J; Deutch, J; Whitesides, G M **Langmuir** 1985, 1, 725

Huh, C; Mason, S G **J. Colloid Interface Sci.** 1977, 60, 11

Huth, J A; Danielson, N D **Anal. Chem.** 1982, 54, 930

Jenekhe, S; Wellinghoff, S; Reed, J **Mol. Cryst. Liq. Cryst.** 1984, 105, 175

Johnson, R E; Dettre, R H **J. Phys. Chem.** 1964, 68, 1744

Joy, D C; Hren, J J; Golstein, J T eds. Introduction to Analytical Electron Microscopy Plenum Press: N. Y., 1979

Kaelble, D H; Cirlin, E H **J. Polym. Sci. Part A** 1971, 29, 363

Kampf, W **Fr. Demande 2,459,251; Chem. Abstr. 1974, 81p2431q**

Kampf, W; Herman, C **Eur. Pat. Appl. EP86894; Chem. Abstr. 1983, 99:213094q**

Kato, K **J. Appl. Polym. Sci.** 1974, 18, 3087

Kavan, W; Dousek, F P **Carbon** 1986, 1, 61

Kel-F 81 Engineering Manual 3 M Company: St. Paul, Minnesota

Kise, H **J. Polym. Sci.: Polym. Chem. Ed.** 1982, 20, 3189

Kise, H; Ogata, H **J. Polym. Sci.: Polym. Chem. Ed.** 1983, 21, 3443

Kobrich, G **Angew. Chem. Int. Ed.** 1967, 6, 41

Lazare, S; Hoh, P D; Baker, J M; Srinivasian, R **J. Am. Chem. Soc.** 1984, 106, 4288

Lindsay, S E; Street, G B **Syn. Metals** 1984, 10, 67

Manassen, J; Wallach, J **J. Am. Chem. Soc.** 1965, 87, 2671

March, J Advanced Organic Chemistry McGraw-Hill: N. Y., 1977

Marvel, C S; Sample, J H; Roy, M F **J. Am. Chem. Soc.** 1939, 6, 3241

Marvel, C S; Sample, J H; Roy, M F **J. Am. Chem. Soc.** 1943, 65, 1716

Matheson, L A; Boyer, R F **Ind. Eng. Chem.** 1952, 44, 867

Maxfield, M; Wolf, J F; Miller, G G; Frommer, J E; Shachlet, L W **J. Electrochem. Soc.** 1986, 133, 117

Meyer, A I; Temple, D L; Nolen, R L; Mihelich, E D **J. Org. Chem.** 1974, 39, 2778

Mirabella, F M **J. Polym. Sci.: Polym. Phys. Ed.** 1982, 20, 2309

Neumann, A W; Good, R J **J. Colloid Interface Sci.** 1972, 38, 341

Niwa, O; Tamamura, T **J. Chem. Soc. Chem. Comm.** 1984, 817

Nuzzo, R G; Smolinsky, G **Macromolecules** 1984, 17, 1012

Oster, G; Shibata, O **J. Polym. Sci.** 1957, 26, 233

Otsuki, Y; Ima, H; Kaija, A; Horii, H **Ger. Offen. 2,357,001; Chem. Abstr.** 1974, 81p9243q

Owen, E. Degradation and Stabilization of Poly(vinyl chloride) Appl. Sci. Pub: London, 1984

Pauskin, Y M; Vishnyakova, T P; Lunin, A F; Nizova, S A Organic Polymeric Semiconductors Wiley: N. Y., 1974

Peeling, J; Clark, D T **Polym. Degradation Stab.** 1981, 3,92

Pfeifer, P; Avnir, D **J. Chem. Phys.** 1983, 79, 3558

Purcell, W P; Singer, J A **J. Chem. Eng. Data** 1967, 12, 234

Rasmussen, J R; Bergbreiter, D E; Whitesides, G M **J. Am. Chem. Soc.** 1977, 99, 4746

Rasmussen, J R; Stedronsky, E R; Whitesides, G M **J. Am. Chem. Soc.** 1977, 99, 4736

Riggs, W; Dwight, D J **J. Electron Spectr.** 1974, 5, 447

Rossman, K **J. Polym. Sci.** 1956, 19, 141

Rubner, M; Tripathy, S; Lee, K; Georger J; Jopson, H; Cholewa, P Division of Org. Coat. and Appl. Polym. Sci. 1983, 48, 544

Rukenstein, K; Gourisanhar, S **J. Colloid Int. Sci.** 1985, 107, 488

Seki, S; Sato, K; Sasakowa, A **Chem. Abstr.** 1976, 76:p73362y

Shirakowa, H; Louis, E J; MacDiarmid, A G; Chiang, C K; Heegar, A J **J. Chem. Soc. Chem. Comm.** 1977, 578

Shriver, D F Manipulations of Air Sensitive Compounds McGraw-Hill: New York, 1969

Skotheim, T A ed. Handbook of Conducting Polymers Marcel Dekker: New York, 1986 volumes 1 & 2

Somorjai, G A Principles of Surface Chemistry Prectice-Hill: Englewood Cliffs, New Jersey, 1972

Sondheimer, F; Ben-Efraim D A; Wolovsky, R **J. Am. Chem. Soc.** 1961, 83, 1675

Srinivasian, R; Leigh, W J **J. Am. Chem. Soc.** 1982, 104, 6784

Starks, C M; Liotta, C Phase Transfer Catalysis: Principles and Techniques Academic Press: New York, 1978

Swartz, A M **J. Colloid Interface Sci.** 1980, 20, 3189

Ugelstad, J; Rokstad, O A; Skarstein, J **Acta Chem. Scand.** 1963, 17, 208

Vogel, A I A Textbook of Quantitative Inorganic Analysis Longmans-Green & Co.: London, 1961 page 267

Wenzel, R N **Ind. Eng. Chem.** 1936, 28, 988

Weber, W P; Gokel, G W Phase Transfer Catalysis in Organic Synthesis Springer-Verlag: Berlin, 1978

West, A C in Kirk-Othmer Encyclopedia of Chemical Technology Wiley: New York, 1980, volume 11, page 49