ABSTRACT

FORMATION OF C-C COVALENT BOND ON THE SURFACE OF POLY (CHLOROTRIFLUOROETHYLENE) BY SUBSTITUTION

by Wafa Abdulrazaq Mazi

Previous work by our group showed the poly (chlorotrifluoroethylene) can be functionalized by one electron reduction followed by radical trapping. Several new methods for such reduction were examined including Cu / phenanthroline in dimethyl sulfoxide (DMSO), NaS₂O₄, in DMSO, Zn/Pd in tetrahydrofuran (THF), chloro (pyridine) cobaloxime (III) with Mg in THF, and NiCl₂, Mg⁰ or Cu/ PPh₃ in dimethylformamide (DMF) or acetonitrile.

The most promising systems were found to be NiCl₂, Mg⁰/ PPh₃, but the choice of trapping agent and solvent was crucial. Trapping with acrylonitrile, dihydropyran, butyl acrylate, and styrene were successful. Further reactions of styrylated PCTFE were carried out.
FORMATION OF C-C COVALENT BOND ON THE SURFACE OF POLY (CHLOROTRIFLUOROETHYLENE) BY SUBSTITUTION

A Thesis

Submitted to the
Faculty of Miami University
in partial fulfillment of
the requirements for the degree of
Master of Science - Arts & Science
Department of Chemistry and Biochemistry

by
Wafa Abdulrazaq Mazi
Miami University
Oxford, Ohio
2010

Advisor____________________________________
(Dr. Richard Taylor)

Reader____________________________________
(Dr. James W. Hershberger)

Reader____________________________________
(Dr. James Cox)

Reader____________________________________
(Dr. Neil D. Danielson)
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Acknowledgment

I would like to gratefully acknowledge my thesis advisor, Dr. Richard Taylor, for his guidance, enthusiasm, and support during my studies. He has encouraged, helped, and advised me a lot. I appreciate being a member of his research group, and working independently in his laboratory. Also, I would like to thank him for his patience on answering my questions, and for his generous support. Special thanks are given to my committee members Dr. James W. Hershberger, Dr. James Cox, and Dr. Neil D. Danielson for their generosity and insights.

I appreciate the friendship and support from the many friends I have made here and my friends back home; there are too many to list here.

I would like to dedicate my success to my greatest parents, siblings, best friend Muhammad Bakr, and country. I would like to thank them for loving, supporting, encouraging, and standing beside me. Great thanks are given to King Abdullah Al Saud, for the opportunity to study abroad and the financial support.
Chapter-1

Introduction

The importance of solid-phase reagents in modern organic synthesis

A heterogeneous reaction that occurs at the interface of the two phases with the reagents bound to solid materials in a solution is known as a solid-phase organic synthesis. The solid-phase technique was first presented in 1963 by Merrifield\textsuperscript{1,2}. Generally, three steps are required for this technique to be used. First, an organic substrate is linked to the solid phase by a covalent bond, then selective reactions are carried out to afford some or all products on the solid support. Finally, a cleavage process is carried out to yield the final product\textsuperscript{1}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{solid-phase_synthesis.png}
\caption{Solid-phase organic synthesis\textsuperscript{1}}
\end{figure}

Every step in the procedure is carried out on the same solid support. Solid supports have been used as catalysts and reagents for single step syntheses. The advantage of the single step transformation is that it should be much easier than that of the multi-step syntheses on solid-phase supported reagents, since they do not require a high yield to be achieved\textsuperscript{3}.

The ease of separation of by-products from a reaction mixture and the use of a reagent in a continuous process makes solid-phase synthesis a favorable technique, not only in modern organic synthesis, but also in other fields of chemistry such as combinatorial chemistry, green chemistry, and medicinal chemistry. Combinatorial chemistry is coupled with solid phase supported reagents because the solid supported reagent is an easy procedure that leads to a high
yield of products with excess of reagents, and it is an iterative process which can be used to produce huge numbers of products\(^4\). In addition, the waste reagents can be regenerated and used again with excess of starting materials to start a new cycle of synthesis, which allows the technique to meet the requirements of modern environmentally friendly chemistry\(^2\).

**Polystyrene the dominant polymer-support**

Although polystyrene and its derivatives have been widely used as a solid-support, the need for other resins is still in place. Reasons for this need include: the difficulty of analyzing of functional groups, the compatibility of the appropriate organic solvent with the support, and improvement of the solvent–solid phase interface to minimize the drawbacks that could occur due to phase transformation. Because of these drawbacks Si(dimethylsilyl), a silica gel derivative, was an option.

One of silica gel features is the ability to be treated with organic solvents. For example, unlike polystyrene, it neither swells nor shrinks in organic solvents. Since Si(dimethylsilyl) derivatized silica gel is only surface functionalized, it has a high capacity with loading of functional groups. Si(dimethylsilyl) derivatized silica gel averages 1.5 mmol/ g loading compare to 1.0 mmol/ g of polystyrene resin. Although silica gel based silane resins have many useful applications, it has drawbacks that include the overlapping of functional groups peaks in the IR spectrum, making analysis difficult\(^2\).

**Previous Work**

Previous work by our group focused on polystyrene-based reagents. It was reported by our group that polystyrene could be mercurated and converted into polystyrene seleninic acid (a versatile oxidizing agent) \(^5,6,7\). Another oxidation agent was produced by treating the intermediate compound of mercurated polystyrene with I\(_2\) in THF, which then undergoes oxidation. (Scheme 1, 2).
Due to the reactivity of the benzylic protons present in polystyrene toward oxidation, polystyrene-based reagents were found to be unsuitable for repeated recycle. To overcome this problem, our group started a new project to investigate poly (fluorocarbon) species. One of the important features of this species is its inertness to reaction under a variety of conditions such as oxidizing agents, high temperature and strong acids and bases, because of the high fluorine content. Although there are many uses of the modified fluorocarbon polymers and their derivatives in the area of materials science, the effective chemical modification of such preformed fluorocarbon polymers is limited by their natural stability, which presents a synthetic challenge.

There are number of poly (fluorocarbons) that are applicable for further modifications. These include: Teflon a homopolymer of poly ( trifluoroethylenat) (PTFE), Kel-F and Neoflon, homopolymers of chlorotrifluoroethylenet (PCTFE), and Nafion, a copolymer of PTFE and perfluoro[2- (fluorosulfonylethoxy) propylvinyl ether]. Our choice was PCTFE. The reason for choosing this polymer was the prediction that the chlorine atoms would be sufficiently reactive to allow chemical modifications (schema 3). However, the unreacted sites would not present any difficulties in further reactions.
Scheme 3: General equation of the substitution of Cl atom by a group of interest

The substitution of chlorine atom by other organic groups was achieved by our research group and others. This substitution was obtained by treating PCTFE with organolithium and organomagnesium reagents (scheme 4). However, side reactions, such as formation of functionalized fluoroalkene and oxygen incorporation, took place, as analyzed by IR spectroscopy.

Scheme 4: Reaction of PCTFE with organolithium or organomagnesium

To explain the results, we proposed that the PCTFE was undergoing a two-electron transfer mechanism, which involved reduction-elimination-addition reactions. This indicates a metal-halogen (LiCl) exchange followed by elimination of metal-fluoride, and finally, the addition of organic group (scheme 5).
Cais\textsuperscript{18} was able to form poly (trifluoroethylene) (PTF) by reducing PCTFE using tin hydride. One of the features of tin radical is the ability to select the chlorine atom instead of the fluorine atom. Moreover, the resulting PCTFE radical was trapped by hydride prior to any further elimination or rearrangement. Following this procedure our group started to investigate a new technique to form the PCTFE radical, and succeeded in trapping with other radical scavengers. Our group succeeded in substituting the chlorine atom by other organic groups applying the mechanism of one-electron transfer. By treating PCTFE with chloro (pyridine) cobaloxime (III)/magnesium redox in which chloro (pyridine) cobaloxime (III) acted as a catalyst, allylated PCTFE was obtained with a high degree of functionalization \textasciitilde50\% (Scheme 6). Also, phenethylated PCTFE was achieved with 30\% in yield by the reaction of PCTFE with styrene under these conditions (Scheme 7).
Although we were able to form carbon-carbon covalent bond, we were not able to prepare a system with no benzylic hydrogens, which remains sensitive toward oxidation.

Additionally, a sulfinate PCTFE was prepared via SET by the reaction of PCTFE with Zn/ SO\(_2\) in DMF without degradation of polymer backbone and no apparent of side reaction\(^\text{30}\).

Research Goal

The ultimate goal of our group is to investigate new methods for expanding the scope of PCTFE functionalization. The main objective of this thesis is to develop a method to substitute the chlorine atom of PCTFE with efficient organic groups that can undergo further reactions or be used as a catalyst in other organic syntheses.

Method used to characterize modified PCTFE

In our laboratory three types of PCTFE have been studied: Kel-F 6061 (solid), PCTFE oil, and PCTFE film. Most of our experiments were run in both Kel-F 6061 (solid) and PCTFE film. We used IR spectroscopy to analyze PCTFE products by comparing their spectra with the native PCTFE spectra (Figure 2). There is no absorption in the region of 3000- 2800 cm\(^{-1}\) due to the
absence of C-H bonds. The bands between 1000-1400 cm$^{-1}$ are due to C-F stretches while the strong band at 961.34 is assigned to the C-Cl stretches. In a successful reaction the C-Cl stretch diminishes and peaks of functional groups are added.

Figure 2: IR absorption of the native PCTFE film
Chapter -2

Results and Discussion

Substitution reactions of perfluoroalkyl halides are an important topic for many scientists. Organofluorine compounds have received a great attention due to the applications of the resulting products in pharmaceutical and materials sciences\(^{19,20}\). In order for the substitution to occur, a perfluoroalkyl radical must be produced. There are several ways to produce R\(_F^*\) including: photolysis or thermolysis of perfluoroalkanesulfonyl chlorides and organometallic compounds containing perfluoroalkyl substituents, thermal decomposition of perfluorinated acyl peroxides of the general formula (C\(_n\)F\(_{2n} \pm 1\)COO)\(_2\), and electrolysis of perfluoroalkanecarboxylic acids\(^{21}\). The nucleophilic substitution of perfluoroalkyl halides with aromatic or heteroaromatic compounds can be obtained by using metal or metal complexes, or applying electrochemical induced via S\(_\text{RN}1\) mechanism in aprotic solvents\(^{19}\). The S\(_\text{RN}1\) mechanism is favorable for perfluoroalkyl halides, because the latter manifest very low reactivity in nucleophilic reactions of the S\(_\text{N}1\) and S\(_\text{N}2\) type\(^{21}\).

In addition, it was reported by Uneyama that the functionalization of fluoroalkyl halides can be achieved via single electron transfer reaction of benzene chalcogens with perfluoroalkyl halides, where the radicals of R\(_F^*\) – X are provided by SET reaction, which undergoes addition to alkenes or alkynes to produce the corresponded perfluoroalkyl-chalcogenated compounds\(^{20}\).

An improved method to functionalize PCTFE was developed by our group by applying single-electron transfer mechanisms. To generate the PCTFE radical, a transition metal in a reduced oxidation state agent provides an electron that finally generates the PCTFE radical. Common metals were used by our group were Co, Cr, and Zn\(^{24}\). In the following sections, our attempts to modify PTCFE with these and others metals will be discussed.

Reactions of PCTFE with Cu and phenanthroline

Shreeve and coworkers\(^{22}\) were successful in using a recyclable ionic liquid synthesized from 2,2’ bipyridine in a polar aprotic solvent, which improved the copper-catalyzed cross-coupling reactions between perfluoroalkyl halides and iodo compounds. In order to functionalize PCTFE we followed their method using phenanthroline instead of 2,2’ bipyridine and electron rich iodo
compounds applying experimental procedure and conditions presented in the paper published by Kemmitt\textsuperscript{23} which proposed successful reactions of rich electron iodo compounds with fluorous ponytails. We conducted the reaction using these experimental conditions in attempts to modify PCTFE.

**Reaction of PCTFE (powder) with 1-bromo-4-iodobenzene**

![Scheme 9: Reaction of PCTFE with 1-bromo-4-iodobenzene](image)

Reaction of PCTFE with 1-bromo-4-iodobenzene, Cu, and phenanthroline in the presence of DMSO for 8 days at 80°C resulted in a greenish dusty residue. Analysis of IR spectrum (Appendix, Spectrum 4) showed that the C-Cl peak located at 955 cm\(^{-1}\), did not diminish or change. A peak at 1619 cm\(^{-1}\) associated with C=O appeared. However, the regions associated with C-H bond did not include any peaks, indicating that the desired reaction did not occur.

**Reaction of PCTFE (powder) with 1(4-iodoacetophenone)**

![Scheme 10: Reaction of PCTFE with 1(4-iodoacetophenone)](image)

Reaction of PCTFE with 1(4-iodoacetophenone), Cu, and phenanthroline in the presence of DMSO for 8 days at 80°C resulted in a greenish dusty residue. Analysis of the IR spectrum (Appendix, Spectrum 5) showed that the C-Cl stretch is diminished and shifted to 959 cm\(^{-1}\). A strong peak at 1668 cm\(^{-1}\) associated with C=O appeared. Also a strong stretch at 814 cm\(^{-1}\) due to \(=\text{CH}\) out of plan appeared. Many other peaks presented in the IR spectrum indicated a high level of side reactions, but not substitution.
**Reaction of PCTFE (powder) with 4-Iodoanisole**

A light brownish residue resulted from the reaction of the PCTFE with 4-Iodoanisole, Cu, and phenanthroline in the presence of DMSO for 8 days at 80°C. Analysis of the IR spectrum (Appendix, Spectrum 6) presented no change of the IR spectrum from the native PCTFE, indicating no reaction.

**Reaction of PCTFE (powder) with 4-Iodoaniline**

The IR spectrum (Appendix, Spectrum 7) of the reaction of PCTFE with 4-Iodoanisole, Cu, and phenanthroline in the presence of DMSO for 8 days at 80°C resulted in a colorless product with some greenish impurities, and presented the same spectrum as native PCTFE. This result indicated that our attempted to modify the PCTFE by the reactants mentioned above was not successful.

**Reactions of PCTFE with NaS\textsubscript{2}O\textsubscript{4}**

It is reported by Furin\textsuperscript{21,28} that the preparation of the perfluoroalkanesulfinic acid can be achieved by reacting R\textsubscript{F-}X with the reducing agent NaS\textsubscript{2}O\textsubscript{4}. The reaction occurs via SET to form the radicals that undergo the S\textsubscript{RN1} mechanism. Moreover, Wang\textsuperscript{29} was able to form polyfluoroalkylated 3-iodoalkyldenetetrahydrofuran-2-one by the reaction of R\textsubscript{F*} generated from the reaction of R\textsubscript{F-}X with NaS\textsubscript{2}O\textsubscript{4}. In addition, as Br and I represented in R\textsubscript{F} are easily substituted and produced the desirable products in a good to high yield\textsuperscript{21}, we attempted to use this reducing agent to modify our polymer.
Reaction of PCTFE (powder) with 4-Iodotoluene

The reaction of the PCTFE with 4-iodotoluene, NaS₂O₄, and 3,4,7,8-tetramethyl-1,10-phenanthroline in the presence of DMSO for 7 days at 80°C resulted in a dark dusty brownish residue. Analysis of the IR spectrum (Appendix, Spectrum 8) showed that the C-Cl stretch located at 961 cm⁻¹ still existed. All other peaks presented in the native polymer appeared in the spectrum, with a slightly broad peak appearing located at 3412.69 cm⁻¹ which indicates that the resulting product is contaminated with OH. The data analysis indicates that the reaction was limited and no substitution occurred.

Reaction of PCTFE (powder) with 4-Iodoaniline

A dark purple residue resulted from the reaction of PCTFE with 4-iodoaniline and NaS₂O₄ in DMSO for 6 days at 80°C. The IR spectrum for the product (Appendix, Spectrum 9) is typical to the native PCTFE, indicating that the reaction did not occur.

Reaction of PCTFE (powder) with 4-Iodoacetophenone

Scheme 13: Reaction of PCTFE with 4-Iodotoluene and NaS₂O₄

Scheme 14: Reaction of PCTFE with 4-iodoaniline and NaS₂O₄

Scheme 15: Reaction of PCTFE with 4-iodoacetophenone and NaS₂O₄
The reaction of the PCTFE with 4-iodoacetophenone and NaS₂O₄ in DMSO, for 5 days at 80°C, resulted in a white dusty residue. The IR spectrum (Appendix, Spectrum 10) indicated that the reaction did not occur since the spectrum was not different from the native PCTFE.

**Reaction of PCTFE (powder) with 4-Iodoanisole**

Scheme 16: Reaction of PCTFE with 4-iodoanisole and NaS₂O₄

The analysis of the IR spectrum of the oily sugary residue resulting from the reaction of PCTFE with 4-iodoanisole and NaS₂O₄ in DMSO for 5 days at 80°C, showed peaks at 3404.76 cm⁻¹ OH stretch, 3015.87 cm⁻¹, and 2924.60 cm⁻¹ CH stretch (Appendix, Spectrum 11.1) and many other stretches indicate a contamination of the residue. The residue was mixed with tetrahydrofuran, and stirred for 30 min. The mixture was filtered using a Buchner funnel and washed with ethyl ether. The residue was air-dried and the IR spectrum (Appendix, Spectrum 11.2), was recorded. Analysis indicated that the peaks are located at 3404.76 cm⁻¹ and 3015.87 cm⁻¹ appeared with more intensity. Additionally, a carbonyl stretch at 1617.40 cm⁻¹ appeared. The slimy residue was mixed with 15 mL of water and 1.053g CaOCl, calcium hypochlorite. The mixture was stirred again for 30 min and then it was filtered and washed in sequence with methanol, acetone, and ethylether. The light brown residue was air-dried and the IR spectrum was recorded (Appendix, Spectrum 11.3). Analysis indicated that although peaks at 3531.74 cm⁻¹ and 3392.85 cm⁻¹ appeared, the C-Cl stretch located at 961 cm⁻¹ was not diminished, thus, the reaction failed to achieve our goal.

**Reaction of PCTFE (powder) with 4-vinylbenzoic acid**

Scheme 17: Reaction of PCTFE with 4-vinylbenzoic acid and NaS₂O₄
The reaction of PCTFE with 4-vinylbenzoic acid and NaS$_2$O$_4$ in DMSO for 4 days at 80°C gave a white dusty residue. The analysis of the IR spectrum (Appendix, Spectrum 12) indicated that some side reactions occurred resulted in peaks stretches at the region of > 1000 cm$^{-1}$. However, the C-Cl stretch was still intense which indicated that the addition of 4-vinylbenzoic acid to the PCTFE was not successful.

**Reactions of PCTFE with Zn/ Pd**

It is reported by Ishikawa$^{25}$ that a cross-coupling reaction of perfluoroalkyl iodides with allyl, vinyl, or aryl halides in the presence of Zn/Pd catalyst in THF give the corresponding allyl, vinyl, or aryl perfluoroalkylides in good yield. It was found that Pd$^0$ that is formed from PdCl$_2$ or Pd(PPh$_3$)$_2$Cl$_2$ by Zn is the actual catalyst. Our attempts to modify PCTFE using Zn/Pd catalyst is presented in the following section.

**Reaction of PCTFE (powder) with 4-Iodoaniline**

![Image of Scheme 18: Reaction of PCTFE with 4-iodoaniline and Zn/ Pd (PPh$_3$)$_4$ in toluene.]

The cross-coupling reaction of PCTFE with 4-iodoaniline in the presence of Zn/ Pd (PPh$_3$)$_4$ in toluene at 80°C for 8 days resulted in a gold brownish residue with some amounts of Zn. Therefore, to remove the Zn THF and HCl was added to the residue, which was then filtered and washed in sequence with water, acetone, methanol, and ethyl ether. The residue was air-dried and the IR spectrum was recorded. The IR (Appendix, Spectrum 13) spectrum presented the starting materials.

**Reaction of PCTFE (powder) with 4-Iodoaniline**

![Image of Scheme 19: Reaction of PCTFE with 4-iodoaniline and Zn/ PdCl$_2$, PPh$_3$ in toluene.]

The light brown residue resulting from the reaction of the PCTFE with 4-iodoaniline and Zn/PdCl$_2$, PPh$_3$ in toluene for 8 days at 80°C was mixed with 10ml THF and 10ml HCl. The mixture was filtered using a Buchner funnel and the residue was washed in sequence with water, acetone, methanol, and ethylether. The IR spectrum (Appendix, Spectrum 14) indicated that the reaction did not occur since the spectrum is identical to the native PCTFE.

**Reactions of PCTFE with Co (III)/ THF**

Bromo (pyridine) bis (dimethyl-gloyoximato) cobalt (III) and zinc constituted a redox couple that has been reported$^{26}$ to be highly effective for promoting the perfluoroalkylation reactions of electron deficient alkenes. Perfluoroalkyl iodides or bromides were reacted with ethyl acrylate, ethyl methacrylate, ethyl crotonate, acrylonitrile, and methyl vinyl ketone in the presence of (bromo (pyridine) cobaloxime (III)). These reactions were reported to occur via the addition of R$_F$ to a double bond. Zn was used as reducing agent to reduce Co (III) to Co (II). Our research group was successful in modifying the PCTFE using a catalytic amount of chloro (pyridine) cobaloxime (III) with Mg in THF$^7$. In the following section our recent attempts to modify PCTFE are presented.

**Reaction of PCTFE (powder) with Styrene**

\[
\begin{array}{c}
\begin{array}{c}
\text{F} \\
\text{C} \\
\text{F}
\end{array}
\end{array} + \begin{array}{c}
\begin{array}{c}
\text{C} \\
\text{Cl}
\end{array}
\end{array} \rightarrow \begin{array}{c}
\begin{array}{c}
\text{F} \\
\text{C} \\
\text{Cl}
\end{array}
\end{array}
\]

Scheme 20: Reaction of PCTFE with styrene and Co (III) / Mg$^0$ in THF

The reaction of the PCTFE with styrene, Co (III) and Mg$^0$ in THF for 4days at 60°C produced a colorless residue. The IR spectrum (Appendix, Spectrum 15) showed no change in the spectrum of the starting polymer, indicating no reaction.

The same reaction as above was carried out for 2 days at 65°C. A light green residue was produced. The IR spectrum (Appendix, Spectrum 16) showed that the starting materials were recovered. Thus, the reaction did not occur.
The reaction of PCTFE with styrene Co (III) and Mg\textsuperscript{0} in THF for 2 days at 65°C carried out again a liquid sample of PCTFE. The product was a yellow brownish residue. The IR spectrum (Appendix, Spectrum 17) showed peaks at 2980cm\textsuperscript{-1}, 2960.31 cm\textsuperscript{-1}, and 2869 cm\textsuperscript{-1} which associated with –CH alkane stretches. In addition, the intensity of the C-Cl peaks did not diminish and many other peaks appeared in the spectrum which indicates that side homogenous reaction occurred. Thus, the reaction of the oil PCTFE using Co (III) failed.

**Reaction of PCTFE (liquid) with 4-Iodoaniline**

![Reaction Scheme 21: Reaction of PCTFE (Oil) with 4-iodoaniline and Co (III) / Mg\textsuperscript{0} in THF](image)

Reacting 4-iodoaniline with the PCTFE, Co (III) and Mg\textsuperscript{0} in THF for 4 days at 65°C gave a black residue. Analysis of the IR spectrum (Appendix, Spectrum 18) showed that some peaks in the region of alkenes (3067.46 cm\textsuperscript{-1}, 3035.71 cm\textsuperscript{-1}) presented, also the region of alkane includes some stretches (2960.31 cm\textsuperscript{-1}, 2876.98 cm\textsuperscript{-1}), however, the C-Cl stretch was still intense. Some other peaks appeared in the spectrum due to a homogeneous reaction in the solution itself and not in the polymer.

**Reaction of PCTFE (powder) with 4-vinylbenzoic acid**

![Reaction Scheme 22: Reaction of PCTFE with 4-vinylbenzoic acid and Co (III) / Mg\textsuperscript{0} in THF](image)

The white residue produced from the reaction of PCTFE with 4-vinylbenzoic acid and Co (III) / Mg\textsuperscript{0} in THF for 4 days at 65°C was mixed with HCl and THF to remove the excess Mg. After filtering and washing as detailed in the general method, the IR spectrum (Appendix, Spectrum 19) showed very weak peaks at 2980.15 cm\textsuperscript{-1} and 2861.11 cm\textsuperscript{-1} that might be associated with
–CH stretches, however, the peak at 967.18 cm\(^{-1}\) associated with C-Cl remained very intense. Thus, the reaction was not completely successful.

**Reaction of PCTFE (powder) with 4-Iodoaniline**

\[
\begin{align*}
\text{PCTFE} & \quad \text{Co(II) / Mg}^0 \quad \text{THF} \\
& \quad \text{Substitution did not occur}
\end{align*}
\]

Scheme 23: Reaction of PCTFE with 4-iodoaniline and Co (III) / Mg\(^0\) in THF

The greenish residue (mixed with Mg) that resulted from the reaction of PCTFE with 4-Iodoaniline was treated with HCl and THF to remove the Mg. The IR spectrum (Appendix, Spectrum 20) displayed only the PCTFE peaks. Therefore, the reaction of the PCTFE with 4-iodoaniline and Co (III) / Mg\(^0\) in THF for 4 days at 65°C was not successful.

**Reaction of PCTFE with 4-Iodoanisole**

\[
\begin{align*}
\text{PCTFE} & \quad \text{Co(III) / Mg}^0 \quad \text{THF} \\
& \quad \text{Substitution did not occur}
\end{align*}
\]

Scheme 24: Reaction of PCTFE with 4-iodoanisole and Co (III) / Mg\(^0\) in THF

The reaction of the PCTFE with 4-iodoanisole and Co (III) / Mg\(^0\) in THF for 4 days at 65°C resulted in a light green residue. The residue was contaminated with Mg. HCl and THF was added to the residue to release the Mg, the mixture was filtered again and washed in sequence with water, acetone, methanol, and ether. The IR spectrum (Appendix, Spectrum 21) of the residue showed a broad medium peak at 3412.69 cm\(^{-1}\) associated with OH stretch. However, the C-Cl was still intense, indicating that the reaction failed.

**Reactions of PCTFE with NiCl\(_2\)/ PPh\(_3\)**

Treating perfluoroalkyl (bromides or iodides) with alkenes, alkynes, or aromatics applying one electron transfer mechanism in the presence of metals, transition metals, inorganic reductants, and redox systems give the corresponding perfluoroalkylated products in good yields. However,
perfluoroalkyl chlorides cannot give the corresponding perfluoroalkylated products under the same conditions because of the strong carbon-chloride bond.

The use of DMSO as a solvent instead of CH$_3$CN/ H$_2$O in Na$_2$SO$_4$/NaHCO$_3$ could convert perfluoroalkyl chlorides and other fluoroalkyl chlorides and nonfluoroalkyl chlorides to their corresponding sulfinate salts or alkylate alkenes, alkynes and aromatics. The reaction of α-ω chlorofluoroalkyl iodides with olefins in the presence of Raney nickel in ethanol at 80° C gives high yields of the iodine adducts. Chen and colleagues$^{27}$ showed that the ω-chlorofluoroalkylation of amine, aniline, furan, thiophene and pyrrole with the resulting iodides can occur in the presence of tetrakis (triphenylphosphine) nickel. When DMF used as a solvent the functionalization the perfluoroalkyl chloride in the presence of Zn/ NiCl$_2$ at 80°C was efficient.

It was found that perfluoroalkyl chlorides can react not only with electron-rich alkenes but also with electron-poor alkenes in the presence of Zn/ NiCl$_2$ PPh$_3$ in DMF under the same conditions of time (6-8h) and temperature (95-100°C), under nitrogen. Similarly, a corresponding mixture of E/Z alkenes is produced when alkynes are treated with perfluoroalkyl chloride under the same conditions. In addition, the regioselectivity of products are produced from the treatment of aromatic electron-rich compounds with perfluoroalkyl chloride under same condition depends on the starting materials$^{27}$. Below, we report our attempts to use these reaction conditions to modify PCTFE.

**Reaction of PCTFE (liquid) with N, N-Dimethyl aniline**

![Scheme 25: Reaction of PCTFE (oil) with N, N-Dimethylaniline, NiCl$_2$, Zn$^0$, and PPh$_3$ in DMF](image)

The reaction of the PCTFE oil with N, N-Dimethylaniline, NiCl$_2$, Zn$^0$, and PPh$_3$ in DMF for 3days at 100°C under N$_2$ resulted in a black residue. The IR spectrum (Appendix, **Spectrum 22**) showed a complete substitution of Cl that is clearly observed in the disappearance of C-Cl stretch at ~963 cm$^{-1}$. Also, two medium peaks at 2861.11 cm$^{-1}$ and 2936.50 cm$^{-1}$ associated with alkane. However, many other peaks appeared, such as a carbonyl stretch at 1659.03 cm$^{-1}$ due to the
difficulty of separating the liquid polymer from the solvent. It would appear that reaction with DMF rather than the aniline occurred.

**Reactions of PCTFE with NiCl₂/ PPh₃ and Allyltributyltin**

![Chemical structure](image)

Scheme 26: General reaction of PCTFE with Allyltributyltin, NiCl₂, Zn or Mg⁰, and PPh₃ in DMF or acetonitrile

In order to functionalize PCTFE, we applied the conditions proposed by Chen²⁷ using allyltributyltin. The use of allyltributyltin as a trapping agent in the presence of Co (III) with the reducing agent Mg, which is reduced the cobalt to Co (II), provided a clean modification of the PCTFE²⁴. In the following the section, we present our attempted to functionalize the PCTFE applying both methods stated above.

**Reaction of PCTFE with Allyltributyltin**

The reaction of the PCTFE film with allyltributyltin, NiCl₂, Mg⁰, and PPh₃ in DMF, could result in different products based on the time, temperature, and solvent. We repeated the experiment several times changing the conditions mentioned above. A black breakable residue was produced when the reaction was carried out for 3 days at 100°C. The IR spectrum (Appendix, Spectrum 23) analysis indicated the disappearance of C-Cl stretch at ~963 cm⁻¹. Additionally, a broad peak associated with OH stretch appeared at 3365 cm⁻¹ and medium peak at 2960.31 cm⁻¹ associated with –CH stretch appeared. However, other peaks associated to allyl group at 3020 and 3010 cm⁻¹ were not shown in the spectrum. The conclusion that can be drawn is that this reaction destroyed all reactants and that the reaction with DMF referenced above may be occurring. Also, the color may indicate two electron reduction reactions, resulting in elimination reaction on the backbone.

However, a light yellow residue was obtained when the reaction was carried out at 50°C for one day. The IR spectrum (Appendix, Spectrum 24) analysis indicated that an intense peak at 965
cm\(^{-1}\) associated with C-Cl stretch remained. Peaks located at 296.34 cm\(^{-1}\) associated with –CH alkane and at 1688.76 cm\(^{-1}\) associated with C=C appeared. Although, peaks assigned above were shown, we conclude that the reaction did not occur, although some reaction with DMF may be indicated.

Changing the temperature to 90\(^\circ\)C for one day gave a black residue. The IR spectrum (Appendix, Spectrum 25) showed –OH stretch at 3333. cm\(^{-1}\), -CH alkane stretch at 2956.34 cm\(^{-1}\), and C=O stretch at 1670.92 cm\(^{-1}\). C-Cl stretch located at 963.21 cm\(^{-1}\) is still intense which indicates a low percentage of functionalize. In addition, running the reaction for two days at 90\(^\circ\)C again gave a black breakable residue. The IR spectrum (Appendix, Spectrum 26) indicated that the C-Cl stretch disappeared completely. A broad peak at 3400.79 cm\(^{-1}\) due to –OH stretch appeared. The IR data also showed two peaks one at 1615.10 cm\(^{-1}\) associated with C=O cm\(^{-1}\) the second peak is associated with –CH aliphatic at 2960.31 cm\(^{-1}\). We conclude that at 90\(^\circ\)C for two days the reaction destroyed all reactants, with some incorporation of DMF.

We assumed that the solvent could affect the functionalization of the polymer; thus, we used acetonitrile instead of DMF. The temperature and time were the same as the previous experiment. From the IR data (Appendix, Spectrum 27) there is no change in the spectrum except for two peaks at 2952.38 and 2924.60 cm\(^{-1}\), which are associated with alkane –CH stretch. These peaks could be related to methyl group in the solvent. Therefore, the reaction failed. As the reaction was repeated; however, a different IR spectrum was recorded (Appendix, Spectrum 28.1, 28.2) in two areas of the product (light and dark). A broad peak at 3404.76 cm\(^{-1}\) due to –OH stretch was clearly seen in the dark area of the spectrum. In the light area a weak band at 2960.31 cm\(^{-1}\) appeared. The remaining peaks in both areas of the product are related to the starting polymer which concluded that the reaction failed. Running the reaction again at 80\(^\circ\)C for 4 days gave a different IR spectrum (Appendix, Spectrum 29). Analysis of the IR data indicated a total disappearance of C-Cl stretch at 963 cm\(^{-1}\), an appearance of alkane stretches at 2960.31 and 2892.85 cm\(^{-1}\), C=C stretch at 1651.10 cm\(^{-1}\), and a weak –OH stretch at ~ 3300 cm\(^{-1}\). However, we conclude that the reaction failed because the IR spectrum did not match the allylated PCTFE published previously by our group\(^{24}\).

Since we ran the previous reactions on the PCTFE film, we thought running them in the powder might gave a better functionality, thus we repeated the reaction carried out at 80\(^\circ\)C for 4 days on
a solid PCTFE sample in DMF. Unfortunately, the result was disappointing especially that the allyltributyltin was able to functionalize the PCTFE in our previous work. The IR spectrum (Appendix, Spectrum 30) showed an intense peak at 963.38 cm\(^{-1}\) corresponded to C-Cl stretch. A broad slightly intense band corresponded to –OH at 3363.16 cm\(^{-1}\) appeared. Additionally, a peak stretch at 2956.34 cm\(^{-1}\) associated with alkane appeared. Thus, we concluded that reaction of the PCTFE with allyltributyltin under various time, temperature, and solvent conditions, was not a successful choice to functionalize PCTFE.

**Reactions of PCTFE with NiCl\(_2\)/ PPh\(_3\) and Various Reactants**

The reaction of PCTFE with different electron-rich compounds may provide our desired goal. Thus, reactions of PCTFE with NiCl\(_2\)/ PPh\(_3\) in DMF with different monomers were carried out at 80\(^{\circ}\)C for 4 days. The reaction of PCTFE with acrylonitrile was carried out on both the film and solid sample. However, the products for the both reactions were totally different. While the IR spectrum (Appendix, Spectra 31, 32) of the film showed an intense peak associated with C-Cl at 963.95 cm\(^{-1}\), the C-Cl peak at 966.01 cm\(^{-1}\) in the solid diminished. Another difference is appears in the region of > 1200 cm\(^{-1}\) of the spectrum. While the film sample showed some nitrile incorporation at 2244.97 cm\(^{-1}\), the solid sample gave no reaction. A slightly strong peak associated with –CH alkane at 2956.96 cm\(^{-1}\) in the solid sample, the peak at 2932.53 cm\(^{-1}\) was medium in the film. The film spectrum had a broad peak appeared at 3418.99 cm\(^{-1}\) corresponding to –OH stretch, which was missing in the solid sample. Thus, we concluded that the reaction of PCTFE with acrylonitrile was not successful.

Using butylacrylate produced a promising functionality clearly shown in the IR spectrum (Appendix, Spectrum 33). A clear diminished of C-Cl stretch at 950.84 cm\(^{-1}\), strong –CH alkane stretches at 2951.89 and 2865.82 cm\(^{-1}\) appeared. However, very intense stretches were shown in the spectrum one at 1724.43 cm\(^{-1}\) associated with ester C=O, second one at 1160.67 cm\(^{-1}\) associated with ester C-O. We conclude that a successful substitution occurs.

When methyl vinyl ketone was submitted to the same conditions of time, temperature and solvent, the IR spectrum (Appendix, Spectrum 34) included –OH stretch at 3398.65 cm\(^{-1}\), alkane medium band at 2972.22 cm\(^{-1}\), and C=O stretch at 1666.86 cm\(^{-1}\). However, C-Cl stretch at
964.13 cm\(^{-1}\) showed no change in intensity, which indicates either a low percentage of functionality or no functionality at all, and some incorporation of DMF.

Dihydropyran was reacted with both film and solid sample of the PCTFE. The IR spectra (Appendix, Spectra 35, 36) for both samples are similar to each other. Both solid and film sample have \(\text{–OH}\) stretch at 3372.15 cm\(^{-1}\); however, the stretch in the film sample is more intense than the one appeared in the solid sample. The \(\text{–CH}\) alkane stretch located at 2962.02 cm\(^{-1}\) appeared in both sample but the peak appeared in the solid sample is more smooth and intense. Also, the intensity of the C-Cl stretch diminished in the both samples; but the one in the film has less intense than that in the solid. The C=C alkene stretch located at 1648.59 cm\(^{-1}\) is less intense in the soil PCTFE. It could be seen the reaction of the PCTFE with dihydropyran resulted in the similar IR spectrum of both the solid and the film sample. The peak at >1000cm\(^{-1}\) is indicative of C-O incorporation into the polymer.

The IR spectrum (Appendix, Spectrum 37) of the PCTFE reaction with trichloroethylene showed two weak peaks located at 2921.51 and 2850.63 cm\(^{-1}\) which corresponded to \(\text{–CH}\) alkane stretch. The C-Cl stretch appeared at 960.95 cm\(^{-1}\) did not diminish, and a broad \(\text{–OH}\) peak at 3350 cm\(^{-1}\) was evident in the spectrum. The conclusion was that the reaction did not occur as proposed.

**Reactions of PCTFE and Styrene**

![Scheme 27: General reaction of the PCTFE with styrene, NiCl\(_2\) or Cu, Mg\(^0\), and PPh\(_3\) in DMF or acetonitrile or \(\alpha,\alpha,\alpha\)-trifluorotoluene](image)

Our research group previously demonstrated a successful addition of PCTFE to styrene. As mentioned earlier, the reaction was carried out in the presence of Mg and catalytic amount of
chloro (pyridine) cobaloxime (III) in THF\textsuperscript{7}. Following the section presents our attempts to modify PCTFE by treating it with styrene in the presence of either NiCl\textsubscript{2} or Cu.

Reaction of PCTFE with Cu/ PPh\textsubscript{3} and styrene

The reactions were carried out with variations in time, temperature, and solvent. Also a blank (no styrene) experiment was run as well. When the reaction was run at 90\textdegree C for 4 days, the analysis of the IR spectrum (Appendix, Spectrum 38) indicated a diminution of C-Cl at 979.07 cm\textsuperscript{-1} and appearance of –CH alkane stretches at 2932.53 and 2813.49 cm\textsuperscript{-1}. Moreover, the spectrum included many other peaks, which are indicated a high level of side reaction. Additionally, when comparing the peaks to the blank IR spectrum (Appendix, Spectrum 39), we found that a low percentage of functionalization did occur with side reactions as mentioned earlier. Changing the temperature to 60\textdegree C and the time to 4 days resulted in no change in the IR spectrum (Appendix, Spectrum 40) from the native polymer except a weak band at 1440 which might be for C-N group, CH\textsubscript{2}, or CH\textsubscript{3}. When α,α,α- trifluorotoluene under the same conditions of time and temperature as the previous experiment, three new weak peaks appeared in the IR spectrum (Appendix, Spectrum 41), which are located at 2932.53 cm\textsuperscript{-1} associated with –CH alkane, 1442.95 cm\textsuperscript{-1} which might be for CH\textsubscript{2}, or CH\textsubscript{3}, and 1716.51 cm\textsuperscript{-1}. We concluded that the desired reaction did not occur.

Reaction of PCTFE with NiCl\textsubscript{2}/ PPh\textsubscript{3} and styrene

Styrene reacted with PCTFE in the presence in NiCl\textsubscript{2} and PPh\textsubscript{3}, under different conditions of time, temperature, and solvent. When acetonitrile was used as a solvent at 90\textdegree C for 2 days resulted in a brownish product that has two areas (dark and light). The IR spectrum for the dark area (Appendix, Spectrum 42.1) showed an intense C-Cl stretch at 961.23 cm\textsuperscript{-1}, and a weak peak appeared in alkene =C-H region at 3023.80 cm\textsuperscript{-1}, medium to weak –OH stretch at 3690.47 cm\textsuperscript{-1}, and stretch band at 1438.98 cm\textsuperscript{-1} which might be for CH\textsubscript{2}, or CH\textsubscript{3}. The spectrum (Appendix, Spectrum 42.2) for the light area is totally different from the previous spectrum. A peak at 3369.04 cm\textsuperscript{-1} corresponded with –OH stretch is broad and intense. A new medium peak at 1645.15 cm\textsuperscript{-1} appeared which might be for C=C stretch, and the peak corresponded with the C-Cl stretch being diminished. Comparison between the two areas of the reaction product indicated that the reaction failed.
When the previous reaction was repeated in DMF for 4 days, the product was black and the IR spectrum (Appendix, Spectrum 43) showed many peaks in the alkene regions. Also, a broad –OH stretch at 3373 cm\(^{-1}\), and a weak stretch at 2928.57 cm\(^{-1}\) associated with –CH alkane stretch appeared. Moreover, the C-Cl stretch at 965 cm\(^{-1}\) diminished; however, side reaction took place. A blank experiment was run in DMF for 2 days at 90°C. The IR spectrum (Appendix, Spectrum 44), showed a broad peak at 3384.92 cm\(^{-1}\) associated with –OH stretch. Also, a C=O stretch at 1647.13 cm\(^{-1}\), many other peaks appeared in regions between the carbonyl stretch and 1000 cm\(^{-1}\) which is indicated a reaction between the solvent and the polymer. It is worth to mentioning that the C-Cl stretch diminished.

When the reaction was carried out at 60°C for 4 days in DMF, some functionalization did occur. However, high levels of side reactions also occurred. The interpretation of the IR spectrum (Appendix, Spectrum 45), indicated alkane –CH stretch at 2920.63 cm\(^{-1}\), C-H aromatic stretch located at 3031.74 cm\(^{-1}\), and C-C aromatic stretches at 1490.52, 1448.89, and a385.46 cm\(^{-1}\). Additionally, a broad stretch band related to –OH appeared at 3428.57 cm\(^{-1}\) and an intense C=O peaks at 1657.04 cm\(^{-1}\) showed too. The intensity of C-Cl peak at 963.21 cm\(^{-1}\) did not diminish, leading to the conclusion that the functionalization did occur in low percent but side reaction happened too. Using α,α,α trifluorotoluene as a solvent instead of DMF under same conditions resulted in no functionalization of the polymer. The IR spectrum (Appendix, Spectrum 46), included a broad band appeared at 3369.04 cm\(^{-1}\) associated with –OH stretch, and peak at 1649.11 cm\(^{-1}\) appeared which is for C=O . Moreover, the peak at 965.19 cm\(^{-1}\) associated with C-Cl diminished, but the desired reaction did not occur.

Since the oil sample is easier to react, the reaction of PCTFE oil sample was carried out at 60°C for 4 days in DMF. The IR spectrum (Appendix, Spectrum 47) showed a complete disappearance of C-Cl stretch, and appearance of C-H alkane stretches at 2968.25, 2932.53, and 2880.95 cm\(^{-1}\). Other peaks related to OH and C=O appeared which are due to DMF presented in the product. We concluded that some functionality of PCTFE did occur but with some level of side reaction. Running a blank experiment produced an IR spectrum, (Appendix, Spectrum 48), that has peaks related to the DMF. In addition, the C-Cl located at 963.21 cm\(^{-1}\) appeared to be very intense, which meant the reaction carrying on at 60°C for 4 days resulted in low functionality with some level of side reaction.
Changing a reaction environment could result in different products. Thus, we carried out the reaction of PCTFE with styrene in the presence of NiCl$_2$, Mg$^0$, and PPh$_3$ in DMF at 80$^\circ$C for 4 days. The IR spectrum, (Appendix, Spectrum 49), showed a clear decreasing in the C-Cl stretch at 958.42 cm$^{-1}$. In addition to C-H alkane stretches at 2921.51 and 2840.50 cm$^{-1}$ an aromatic C-H stretch at 3012.65 cm$^{-1}$ appeared as well. Moreover, C-C aromatic stretches appeared at 1491.85 and 1451.40 cm$^{-1}$. We concluded that the reaction carried out at 80$^\circ$C for 4 days was successful in functionalizing the PCTFE film. We treated a small piece of the styrylated PCTFE with nitromethene, concentrated H$_2$SO$_4$, and concentrated HNO$_3$. The IR spectrum, (Appendix, Spectrum 50), of the final product showed new peaks at 1517.13 and 1350.28 cm$^{-1}$ associated with nitro group. A C-C aromatic stretch at 1600.56 cm$^{-1}$ appeared as well, demonstrating that further reaction of the styryl groups could be carried out.

Repeating the reaction again in a solid sample of PCTFE tested the efficiency of the new temperature and time conditions. The IR spectrum, (Appendix, Spectrum 51), of the resulting styrylated PCTFE was satisfactory. Aromatic C-H stretches appeared at 3087.30, 3063.49, and 3027.77 cm$^{-1}$ and C-C aromatic bands appeared too at 1599.55, 1450.52, and 1450.88 cm$^{-1}$. Additionally, peaks at 2924.60 and 2849.20 cm$^{-1}$ associated with C-H alkane stretches. Also, the C-Cl stretch at 901.76 cm$^{-1}$ was clearly diminished, which indicated a complete substitution occurred.

The reaction was carried out again at 95$^\circ$C for 4 days on a larger amount of solid PCTFE in the purpose of further reactions. The IR spectrum, (Appendix, Spectrum 52), showed both aromatic C-H stretch at 3012.65 cm$^{-1}$ and alkyl C-H at 2921.51 cm$^{-1}$. Also, C-C aromatic appeared at 1600.56, 1494.38, and 1451.40 cm$^{-1}$. It is worth mentioning that although the peak at 963.48 cm$^{-1}$ did not diminish, the styrylated polymer was reacted with nitromethene, concentrated H$_2$SO$_4$, and concentrated HNO$_3$. The IR spectrum showed lots of noise and background; but no new peaks associated to a succeed reaction appeared. Thus, the product was washed with CH$_2$Cl$_2$ and purified with high vacuum system. The noise in the IR spectrum, (Appendix, Spectrum 53), did not disappear and no change in the spectrum was recorded.

The reaction was carried out again at 80$^\circ$C for 4 days on a larger amount of film PCTFE. The PCTFE was cut out in six small squares, the IR spectrum (Appendix, Spectrum 54-1, 54-2, 54-3, 54-4, 54-5, 54-6), for the six squares have alkyl (>2900 cm$^{-1}$) and aromatic (>3010 cm$^{-1}$) C-H
stretches. The spectra have also the C-C aromatic stretch between 1490 -1450 cm\(^{-1}\). However, although the C-Cl stretch did not diminish; we concluded that the functionalization did occur.

It was proposed by our research group\(^{28}\) that mercurated polystyrene could be formed by treatment of cross-linked polystyrene with mercuric trifluoroacetate. Electrophilic addition to the mercurated polystyrene proposed to be achieved in fair to excellent in nonacetic environment. Thus, our attempt to mercurate the styrylated PCTFE will be discussed herein.

The reaction of styrylated PCTFE with Hg (II) O in trifluoroacetate resulted in mercurated styrylated PCTFE. This functionalization is presented in the IR spectrum, (Appendix, Spectrum 55), as evidenced by strong peak at 1676.76 cm\(^{-1}\) \(^{28}\). Attempts to electrophilic substitution reaction to mercurated PCTFE were carried out. The reaction of mercurated PCTFE (film) with I\(_2\) was not successful proved as no change in the IR spectrum (Appendix, Spectrum 56). Phosphorus oxychloride was added to mercurated PCTFE. Unfortunately, the addition failed (Appendix, Spectrum 57). To sum up, the styrylated PCTFE was successfully converted to mercurated PCTFE; however, the mercurated PCTFE was not reactive enough to undergo electrophilic addition.

The reaction with the nitrosonium ion was carried out on both styrylated PCTFE and mercurated PCTFE. The reaction carried out after the analysis of the IR spectrum, (Appendix, Spectrum 58), for the nitrosonium, as evidence in a strong nitro group at 1507.02 cm\(^{-1}\). Both reaction either with styrylated PCTFE or mercurated PCTFE did not occur. While the IR spectrum, (Appendix, Spectrum 59), of mercurated PCTFE treated with nitrosonium has a weak peak at 2920.71 cm\(^{-1}\) associated with alkyl C-H stretch, the peaks associated with alkyl C-H stretches located at 2954.45 and 2853.62 cm\(^{-1}\) in the IR spectrum, (Appendix, Spectrum 60), of styrylated PCTFE are too strong. We concluded that the addition of nitrosonium to both styrylated and mercurated PCTFE failed. It would appear that the mercurated polymer undergoes protodemercuration, a well known side reaction when acidic conditions are used.
Chapter- 3

Experimental

General procedure:

All reactions were carried out using temperatures controlled by a Carousel reactor fitted with a magnetic stir bar. Time, temperature, and solvent were varied among the individual reactants. Reaction mixtures were filtered using a Buchner funnel and the residue washed sequentially with acetone, methanol, and water. Some residues were purified with Soxhlet cleaning process. Products were air-dried and IR spectra recorded on FT-IR Spectrometer.

Reaction of PCTFE with Cu and phenanthroline

Reaction of PCTFE with 1-bromo-4-iodobenzene

Following the general procedure (1.17g, 10mmol) PCTFE powder, (4.23g, 15mmol) 1-bromo-4-iodobenzene, (0.32 g, 5mmol) Cu, (0.9g, 15mmol) phenanthroline, and 50 mL DMSO were heated to 80°C for 8 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 4). Analysis indicated that the desired products did not form.

Reaction of PCTFE with 1(4-iodoacetophenone)

Following the general procedure (1.3g, 11mmol) PCTFE powder, (3.81g, 15.48mmol) 1(4-iodoacetophenone), (0.325g, 5.078mmol) Cu, (0.914g, 15mmol) phenanthroline, and 50 mL DMSO were heated to 80°C for 8 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 5). Analysis indicated that the peak at 963 cm⁻¹ associated with C-Cl stretch diminished, peaks in other regions appeared.

Reaction of PCTFE with 4-Iodoanisole

Following the general procedure (1.4g, 12mmol) PCTFE powder, (3.4g, 14.52mmol) 4-Iodoanisole, (0.325g, 5.078mmol) Cu, (0.911g, 15mmol) phenanthroline, and 50 mL DMSO were heated to 80°C for 8 days. The mixture was filtered using a Buchner funnel and washed as
detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 6). Analysis indicated that the expected product did not form.

**Reaction of PCTFE with 4-Iodoaniline**

Following the general procedure (1.196g, 10.26mmol) PCTFE powder, (3.3g, 15.06mmol) 4-Iodoaniline, (0.5g, 7.81mmol) Cu, (0.91g, 15mmol) phenanthroline, and 52 mL DMSO were heated to 80°C for 8 days. Mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 7). Analysis indicated that the reaction did not occur.

**Reaction of PCTFE with NaS₂O₄**

**Reaction of PCTFE with 4-Iodotoluene**

Following the general procedure (1.187g, 10.188mmol) PCTFE powder, (3.258g, 14.9mmol) 4-Iodotoluene, (5.24g, 34.67mmol) NaS₂O₄, (0.868g, 15mmol) 3, 4, 7, 8-tetramethyl-1, 10-phenanthroline, and 52 mL DMSO were heated to 80°C for 7 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded. Analysis indicated that the reaction did not occur. (Appendix, Spectrum 8)

**Reaction of PCTFE with 4-Iodoaniline**

Following the general procedure (1.22g, 10.47mmol) PCTFE powder, (3.3g, 14.71mmol) 4-Iodoaniline, (5.22g, 30mmol) NaS₂O₄, and 52 mL DMSO were heated to 80°C for 6 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 9). Analysis indicated that the reaction did not occur.

**Reaction of PCTFE with 4-Iodoacetophenone**

Following the general procedure (1.17g, 10mmol) PCTFE powder, (3.62g, 16.52mmol) 4-Iodoacetophenone, (5.25g, 30.17mmol) NaS₂O₄, and 52 mL DMSO were heated to 80°C for 5 days. The mixture was filtered using Buchner funnel and washed as detailed in the general
method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 10). Analysis indicated that the reaction did not take place.

**Reaction of PCTFE with 4-Iodoanisole**

Following the general procedure (1.15g, 9.87mmol) PCTFE powder, (3.23g, 13.8mmol) 4-Iodoanisole, (5.25g, 30.17mmol) NaS₂O₄, and 50 mL DMSO were heated to 80°C for 5 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 11). Analysis indicated that the reaction did not take place; however, some peaks appeared in the region of > 3000 cm⁻¹.

**Reaction of PCTFE with 4-vinylbenzoic acid**

Following the general procedure (1.17g, 10.mmol) PCTFE powder, (1.048g, 7mmol) 4-vinylbenzoic acid, (5.12g, 29.42mmol) NaS₂O₄, and 50mL DMSO were heated to 80°C for 4 days. The mixture was filtered using Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 12). Analysis indicated that side reactions took place.

**Reaction of PCTFE with Zn/ Pd**

**Reaction of PCTFE with 4-Iodoaniline**

Following the general procedure (1.20g, 10.3mmol) PCTFE powder, (6.453g, 29.42mmol) 4-Iodoaniline, (3.24g, 49.54mmol) Zn, (0.052g) Pd(PPh₃)₄ and 52 mL toluene were heated to 80°C for 8 days. The mixture was filtered using a Buchner funnel and washed methanol and CH₂Cl₂. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 13). Analysis indicated that the reaction did not take place.

**Reaction of PCTFE with 4-Iodoaniline**

Following the general procedure (1.17g, 10mmol) PCTFE powder, (6.547g, 29.85mmol) 4-Iodoaniline, (3.31g, 50.61mmol) Zn, (0.043g) PdCl₂, (0.038g) PPh₃, and 50 mL toluene were heated to 80°C for 8 days. The mixture was filtered using a Buchner funnel and washed as
detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 14). Analysis indicated that the reaction did not take place.

**Reaction of PCTFE with Co (III)/ THF**

**Reaction of PCTFE with Styrene**

Following the general procedure (1.28g, 10.98mmol) PCTFE powder, (1.94g, 18.62mmol) styrene, (0.402g, 1mmol) chloro (pyridine) bis (dimethyl-gloyoximato) cobalt (III), (0.971g, 39.9mmol) Mg, and 10 mL THF were heated to 60°C for 4 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 15). Analysis indicated that the starting materials were recovered.

**Reaction of PCTFE with Styrene**

Following the general procedure (1.28g, 10.98mmol) PCTFE powder, (1.94g, 18.62mmol) styrene, (0.41g, 1mmol) chloro (pyridine) bis (dimethyl-gloyoximato) cobalt (III), (0.96g, 39.48mmol) Mg, and 50 mL THF were heated to 65°C for 2 days. The mixture was filtered using Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 16). Analysis indicated that the starting materials were recovered.

**Reaction of PCTFE (liquid) with Styrene**

Following the general procedure (2.2g, 18.88mmol) PCTFE liquid, (1.5g, 14.4mmol) styrene, (0.4g, 1mmol) chloro (pyridine) bis (dimethyl-gloyoximato) cobalt (III), (0.98g, 40.31mmol) Mg, and 50 mL THF were heated to 65°C for 2 days. The mixture was filtered using conical beaker and funnel. The solution mixed with 300mL water and extracted in a separatory funnel with 100mL CH₂Cl₂ for three times. The organic layers of CH₂Cl₂ were collected and extracted with 200mL water. Small amount of MgSO₄ was added to dry the solution. The solution was filtered and dried in rotary evaporator. The IR spectrum was recorded, (Appendix, Spectrum 17). Analysis indicated that side reactions took place.
**Reaction of PCTFE (liquid) with 4-Iodoaniline**

Following the general procedure (1.5g, 12.87mmol) PCTFE liquid, (3.95g, 18mmol) 4-Iodoaniline, (0.413g, 1mmol) chloro (pyridine) bis (dimethyl-gloyoximato) cobalt (III), (0.97g, 39.9mmol) Mg, and 50 mL THF were heated to 65°C for 4 days. The mixture was filtered using conical beaker and funnel. The solution mixed with 300mL water and extracted in a separatory funnel with 100mL CH₂Cl₂ for three times. The organic layers of CH₂Cl₂ were collected and extracted with 200mL water. Small amount of MgSO₄ was added to dry the solution. The solution was filtered and dried in rotary evaporator the IR spectrum was recorded, (Appendix, Spectrum 18). Analysis indicated that side reactions took place.

**Reaction of PCTFE with 4-vinylbenzoic acid**

Following the general procedure (1.17g, 10.04mmol) PCTFE powder, (2.7g, 18.22mmol) 4-vinylbenzoic acid, (0.45g, 1.1mmol) chloro (pyridine) bis (dimethyl-gloyoximato) cobalt (III), (0.933g, 38.37mmol) Mg, and 50 mL THF were heated to 65°C for 4 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 19). Analysis indicated that the reaction did not occur.

**Reaction of PCTFE with 4-Iodoaniline**

Following the general procedure (1.25g, 10.72mmol) PCTFE powder, (3.83g, 17.46mmol) 4-Iodoaniline, (0.403g, 1mmol) chloro (pyridine) bis (dimethyl-gloyoximato) cobalt (III), (0.98g, 42mmol) Mg, and 49 mL THF were heated to 65°C for 4 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 20). Analysis indicated that the reaction did not occur.

**Reaction of PCTFE with 4-Iodoanisole**

Following the general procedure (1.22g, 10.47mmol) PCTFE powder, (3.8g, 16.23mmol) 4-Iodoanisole, (0.41g, 1mmol) chloro (pyridine) bis (dimethyl-gloyoximato) cobalt (III), (0.96g, 41.18mmol) Mg, and 50 mL THF were heated to 65°C for 4 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and
the IR spectrum was recorded, (Appendix, Spectrum 21). Analysis indicated that the reaction did not take place.

**Reaction of PCTFE (liquid) with NiCl₂/ PPh₃ N, N-Dimethyl aniline**

Following the general procedure (0.903, 7.75mmol) PCTFE liquid, (1.22g, 10.06mmol) N, N-Dimethyl aniline, (0.579g, 8.8mmol) Zn, (0.631g, 4mmol) NiCl₂, (0.63g, 2.4mmol) PPh₃, and 10 mL DMF were heated to 65°C for 4 days. The mixture was filtered using a conical beaker and funnel. The solution mixed with 300 mL water and extracted in a separatory funnel with 100 mL CH₂Cl₂ for three times. The organic layers of CH₂Cl₂ were collected and extracted with 200 mL water. Small amount of MgSO₄ was added to dry the solution. The solution was filtered and dried in a rotary evaporator. The IR spectrum was recorded, (Appendix, Spectrum 22). Analysis indicated that the peak at 963 cm⁻¹ diminished some peaks appeared in other regions.

**Reaction of PCTFE with NiCl₂/ PPh₃ and Allyltributyltin**

**Reaction of PCTFE (sheet) with Allyltributyltin**

Following the general procedure (0.042g, 0.36mmol) PCTFE, 3ml allyltributyltin, (1g, 41.13mmol) Mg, (0.617g, 3.9mmol) NiCl₂, (0.64g, 2.44mmol) PPh₃, and 10 mL DMF were heated to 100°C for 3 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 23). Analysis indicated that the reaction at 100°C resulted in wide spread decomposition.

**Reaction of PCTFE (sheet) with Allyltributyltin**

Following the general procedure (0.045g, 0.386mmol) PCTFE, 4ml allyltributyltin, (1.018g, 41.87mmol) Mg, (0.7g, 4.44mmol) NiCl₂, (0.731g, 2.78mmol) PPh₃, and 10 mL DMF were heated to 50°C for a day. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 24). Analysis indicated that side reactions occurred.
Reaction of PCTFE (sheet) with Allyltributyltin

Following the general procedure (0.039g, 0.334mmol) PCTFE, 4ml allyltributyltin, (1.1g, 45.24mmol) Mg, (0.74g, 4.69mmol) NiCl$_2$, (0.77g, 2.93mmol) PPh$_3$, and 10 mL DMF were heated to 90°C for a day. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air-dried and the IR spectrum was recorded, (Appendix, Spectrum 25). Analysis indicated that side reactions took place.

Reaction of PCTFE (sheet) with Allyltributyltin

Following the general procedure (0.062g, 0.53mmol) PCTFE, 4ml allyltributyltin, (1.06g, 43.6mmol) Mg, (0.514g, 3.26mmol) NiCl$_2$, (0.653g, 2.48mmol) PPh$_3$, and 10 mL DMF were heated to 90°C for 2 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 26). Analysis indicated that side reactions occurred although C-Cl stretch at 963 cm$^{-1}$ disappeared.

Reaction of PCTFE (sheet) with Allyltributyltin

Following the general procedure (0.063g, 0.54mmol) PCTFE, 4ml allyltributyltin, (1.11g, 45.66mmol) Mg, (0.521g, 3.31mmol) NiCl$_2$, (0.53g, 2.02mmol) PPh$_3$, and 10 mL acetonitrile were heated to 90°C for 2 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 27). Analysis indicated that side reactions occurred.

Reaction of PCTFE (sheet) with Allyltributyltin

Following the general procedure (0.055g, 0.472mmol) PCTFE, 4ml allyltributyltin, (0.91g, 37.433mmol) Mg, (0.612g, 3.88mmol) NiCl$_2$, (0.603g, 2.29mmol) PPh$_3$, and 10 mL acetonitrile were heated to 90°C for 2 days. The mixture was filtered using Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 28). Analysis indicated that side reactions occurred.
**Reaction of PCTFE (sheet) with Allyltributyltin**

Following the general procedure (0.0523g, 0.448mmol) PCTFE, 5 mL Allyltributyltin, (1g, 41.13mmol) Mg, (0.682g, 4.327mmol) NiCl₂, (0.523g, 1.99mmol) PPh₃, and 10 mL DMF were heated to 80°C for 4 days. The mixture was filtered using Buchner funnel and washed as detailed in the general method. The residue was air dried and purified with Soxhlet cleaning process at 65 V for two days. The IR spectrum was recorded, (Appendix, Spectrum 29). Analysis indicated that side reactions occurred.

**Reaction of PCTFE (powder) with Allyltributyltin**

Following the general procedure (1.639g, 14.06mmol) PCTFE, 3.8 mL Allyltributyltin, (1.04g, 42.78mmol) Mg, (0.62g, 3.93mmol) NiCl₂, (0.63g, 2.4mmol) PPh₃, and 10 mL DMF were heated to 80°C for 4 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and purified with Soxhlet cleaning process at 68 V for two days. The IR spectrum was recorded, (Appendix, Spectrum 30). Analysis indicated that side reactions occurred.

**Reaction of PCTFE with NiCl₂/ PPh₃ and Various Reactants**

**Reaction of PCTFE (Sheet) with Acrylonitrile**

Following the general procedure (0.077g, 0.66mmol) PCTFE, 4 mL acrylonitrile, (1.06g, 43.6mmol) Mg, (0.624g, 3.95mmol) NiCl₂, (0.715g, 2.7mmol) PPh₃, and 11.5 mL DMF were heated to 80°C for 4 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and purified with Soxhlet cleaning process at 75 V for two days. The IR spectrum was recorded, (Appendix, Spectrum 31). Analysis indicated that side reactions occurred.

**Reaction of PCTFE (Powder) with Acrylonitrile**

Following the general procedure (1.0g, 8.58mmol) PCTFE, 2.5 mL acrylonitrile, (1.11g, 45.66mmol) Mg, (0.602g, 3.82mmol) NiCl₂, (0.675g, 2.57mmol) PPh₃, and 11.5 mL DMF were heated to 80°C for 5 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and purified Soxhlet cleaning process at
75 V for two days. The IR spectrum was recorded, (Appendix, Spectrum 32). Analysis indicated that side reactions occurred although the intensity of the peak at 963 cm\(^{-1}\) associated with C-Cl stretch decreased.

**Reaction of PCTFE (Sheet) with Butylacrylate**

Following the general procedure (0.092 g, 0.789 mmol) PCTFE, 2.5 mL butylacrylate, (1.12 g, 46.07 mmol) Mg, (0.59 g, 3.74 mmol) NiCl\(_2\), (0.54 g, 2.05 mmol) PPh\(_3\), and 10 mL DMF were heated to 80\(^\circ\)C for 4 days. The mixture was filtered using a Buchner funnel and washed as mentioned in the general method. The residue was air dried and purified with Soxhlet cleaning process at 75 V for two days. The IR spectrum was recorded, (Appendix, Spectrum 33). Analysis indicated that the intensity of the peak at 963 cm\(^{-1}\) associated with C-Cl stretch decreased; however, some peaks appeared in other regions.

**Reaction of PCTFE (Sheet) with Methylvinylketone**

Following the general procedure (0.12 g, 1 mmol) PCTFE, 2.5 mL methylvinylketone, (1.02 g, 41.9 mmol) Mg, (0.5 g, 3.17 mmol) NiCl\(_2\), (0.47 g, 1.79 mmol) PPh\(_3\), and 14 mL DMF were heated to 80\(^\circ\)C for 4 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and purified with Soxhlet cleaning process at 75 V for two days. The IR spectrum was recorded, (Appendix, Spectrum 34). Analysis indicated that side reactions took place.

**Reaction of PCTFE (Sheet) with Dihydropyran**

Following the general procedure (0.7 g, 6 mmol) PCTFE, 3 mL dihydropyran, (1.1 g, 45.24 mmol) Mg, (0.55 g, 3.49 mmol) NiCl\(_2\), (0.73 g, 2.78 mmol) PPh\(_3\), and 10 mL DMF were heated to 80\(^\circ\)C for 4 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and purified with Soxhlet cleaning process at 75 V for two days. The IR spectrum was recorded, (Appendix, Spectrum 35). Analysis indicated that some side reactions took place beside the diminution of C-Cl peak intensity located at 963 cm\(^{-1}\).
Reaction of PCTFE (powder) with Dihydropyran

Following the general procedure (2.062g, 17.69mmol) PCTFE, 3 mL dihydropyran, (1.048g, 43.10mmol) Mg, (0.675g, 4.28mmol) NiCl₂, (0.635g, 2.42mmol) PPh₃, and 10 mL DMF were heated to 80°C for 4 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and purified with Soxhlet cleaning process at 75 V for two days. The IR spectrum was recorded, (Appendix, Spectrum 36). Analysis indicated that side reactions occurred.

Reaction of PCTFE (Sheet) with Trichloroethylene

Following the general procedure (0.102g, 0.87mmol) PCTFE, 3 mL trichloroethylene, (1.1g, 45.24mmol) Mg, (0.683g, 4.33mol) NiCl₂, (0.62g, 2.36mmol) PPh₃ and 10 mL DMF were heated to 80°C for 4 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 37). Analysis indicated that the reaction did not occur.

Reaction of PCTFE with and styrene

- Reaction of PCTFE with Cu/ PPh₃ styrene

Reaction of PCTFE (sheet) with Styrene

Following the general procedure (0.059g, 0.506.mmol) PCTFE, (1.021g, 9.8mmol) styrene, (0.383g, 5.98mmol) Cu, (1.08g, 44.42mmol) Mg, (0.518g, 1.97mmol) PPh₃, and 12 mL DMF were heated to 90°C for 4 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 38). Analysis indicated that side reactions occurred.

Reaction of PCTFE (sheet) (Blank)

Following the general procedure (0.071g, 0.609mmol) PCTFE, (0.5g, 7.81mmol) Cu, (1.1g, 45.24mmol) Mg, (0.67g, 6.43mmol) PPh₃ and 12 mL DMF were heated to 90°C for 2 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 39). Analysis indicated that side reactions occurred.
**Reaction of PCTFE (sheet)**

Following the general procedure (0.06g, 0.515mmol) PCTFE, (0.51g, 7.96mmol) Cu, (1.2g, 49.36mmol) Mg, (0.56g, 2.13mmol) PPh\textsubscript{3}, and 11 mL DMF were heated to 60\(^\circ\)C for 4 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 40). Analysis indicated that the reaction did not occur.

**Reaction of PCTFE (sheet) with Styrene**

Following the general procedure (0.074g, 0.635mmol) PCTFE, (1g, 9.6mmol) styrene, (0.56g, 8.75mmol) Cu, (1g, 41.13mmol) Mg, (0.544g, 2.07mmol) PPh\textsubscript{3}, and 10 mL \(\alpha,\alpha,\alpha\), trifluorotoluene were heated to 60\(^\circ\)C for 4 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 41). Analysis indicated that side reactions took place.

- **Reaction of PCTFE with NiCl\textsubscript{2}/ PPh\textsubscript{3} with styrene**

**Reaction of PCTFE (sheet) with Styrene**

Following the general procedure (0.036g, 0.309mmol) PCTFE, (1.215g, 12mmol) styrene, (1g, 41.1mmol) Mg, (0.596g, 3.78mmol) NiCl\textsubscript{2}, (0.601g, 2.29mmol) PPh\textsubscript{3}, and 10 mL acetonitrile were heated to 90\(^\circ\)C for 2 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 42). Analysis indicated that side reactions occurred.

**Reaction of PCTFE (sheet) with Styrene**

Following the general procedure (0.057g, 0.489mmol) PCTFE, (1.07g, 10.27mmol) styrene, (1.1g, 45.24mmol) Mg, (0.673g, 4.27mmol) NiCl\textsubscript{2}, (0.518g, 1.97mmol) PPh\textsubscript{3}, and 10 mL DMF were heated to 90\(^\circ\)C for 4 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, Spectrum 43). Analysis indicated that side reactions occurred.
**Reaction of PCTFE (sheet) (Blank)**

Following the general procedure (0.085g, 0.729mmol) PCTFE, (0.812g, 33.4mmol) Mg, (0.477g, 3mmol) NiCl₂, (0.49g, 1.86mmol) PPh₃, and 11 mL DMF were heated to 90°C for 2 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded. (Appendix, Spectrum 44). Analysis indicated that side reactions occurred.

**Reaction of PCTFE (sheet) with Styrene**

Following the general procedure (0.073g, 0.626mmol) PCTFE, (1.11g, 10.65mmol) styrene, (0.331g, 2.1mmol) NiCl₂, (1.1g, 45.24mmol) Mg, (0.802g, 3.05mmol) PPh₃, and 10 mL DMF were heated to 60°C for 4 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded. (Appendix, Spectrum 45). Analysis indicated that side reactions occurred.

**Reaction of PCTFE (sheet) with Styrene**

Following the general procedure (0.079g, 0.678mmol) PCTFE, (1.01g, 9.69mmol) styrene, (0.585g, 3.7mmol) NiCl₂, (1.2g, 49.36mmol) Mg, (0.6g, 2.28mmol) PPh₃, and 12 mL α,α,α, trifluorotoluene were heated to 60°C for 4 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded. (Appendix, Spectrum 46). Analysis indicated that side reactions occurred.

**Reaction of PCTFE (liquid) with Styrene**

Following the general procedure (0.746, 6.403mmol) PCTFE liquid, (1.06g, 10.17mmol) styrene, (1.02g, 41.95mmol) Mg, (0.569g, 3.61mmol) NiCl₂, (0.53g, 2.02mmol) PPh₃, and 10 mL DMF were heated to 60°C for 4 days. The mixture was filtered using conical beaker and funnel. The solution mixed with 300 mL water and extracted in a separatory funnel with 100 mL CH₂Cl₂ for three times. The organic layers of CH₂Cl₂ were collected and extracted with 200 mL of diluted HCl. Small amount of MgSO₄ was added to dry the solution. The solution was filtered and dried in rotary evaporator. The IR spectrum was recorded. The mixture was extracted again with 25 mL ether, and 20ml water was added for 5 times. The solution was dried by adding MgSO₄,
filtered, and evaporated again and the IR spectrum was recorded, (Appendix, **Spectrum 47**). Analysis indicated that side reactions occurred.

**Reaction of PCTFE (sheet) (Blank)**

Following the general procedure (0.065g, 0.557mmol) PCTFE, (1.03g, 42.36mmol) Mg, (0.5g, 3.17mmol) NiCl₂, (0.68g, 2.59mmol) PPh₃, and 10 mL DMF were heated to 60°C for 4 days. The mixture was filtered using a Buchner funnel and washed as detailed in the general method. The residue was air dried and the IR spectrum was recorded, (Appendix, **Spectrum 48**). Analysis indicated that side reactions occurred.

**Reaction of PCTFE (sheet) with Styrene**

Following the general procedure (0.071g, 0.609mmol) PCTFE, (1.15g, 11.04mmol) styrene, (1.01g, 41.54mmol) Mg, (0.612g, 3.88mmol) NiCl₂, (0.491g, 1.87mmol) PPh₃, and 10 mL DMF was heated to 80°C for 4 days. Mixture was filtered using Buchner funnel and washed as detailed in the general method. The residue was air dried and purified with Soxhlet cleaning process at 68 V for two days. The IR spectrum was recorded, (Appendix, **Spectrum 49**). Analysis indicated that side reactions occurred.

**Preparation of nitrostyrylated PCTFE:**

Small piece of styrylated PCTFE was suspended in 8ml nitromethene in ice bath, 1 mL of concentrated H₂SO₄, and 0.8 mL of concentrated HNO₃ was added. The resulting mixture was stirred for an hour in an ice bath, then for 4 days at room temperature. The resulting polymer was filtered using a Buchner funnel and washed with hexane, acetone, methanol, water, and methanol. The residue was air dried and purified Soxhlet cleaning process for one day. The IR spectrum was recorded, (Appendix, **Spectrum 50**). Analysis indicated that stretches associated with nitro group appeared.

**Reaction of PCTFE (powder) with Styrene**

Following the general procedure (1.98g, 16.99mmol) PCTFE, 2.50 mL styrene, (1.08g, 44.42mmol) Mg, (0.5g, 3.17mmol) NiCl₂, (0.556g, 2.11mmol) PPh₃, and 10 mL DMF were heated to 80°C for 4 days. The mixture was filtered using a Buchner funnel and washed as
detailed in the general method. The residue was air dried and purified with Soxhlet cleaning
process at 68 V for two days. The IR spectrum was recorded, (Appendix, Spectrum 51).
Analysis indicated that although C-Cl stretch diminished clearly side reactions occurred.

Reaction of PCTFE (powder) with Styrene

Following the general procedure (2.85g, 24.46mmol) PCTFE, 2ml styrene, (1.083g, 43.06mmol)
Mg, (0.617g, 3.9mmol) NiCl₂, (0.636g, 2.42mmol) PPh₃, and 11 mL DMF were heated to 95°C
for 6 days. The mixture was filtered using a Buchner funnel and washed as detailed in the
general method. The residue was air dried and purified with Soxhlet cleaning process at 75 V for
2 days. IR was recorded, (Appendix, Spectrum 52). Analysis indicated that the intensity of the
peak located at 963 cm⁻¹ diminished.

Preparation of nitrostyrilated PCTFE:

0.27g styratated PCTFE was suspended in 8ml nitromethene in ice bath, 1 mL of concentrated
H₂SO₄, and 0.8 mL of concentrated HNO₃ was added. The resulting mixture was stirred for an
hour in an ice bath, then for 4 days at room temperature. The resulting polymer was filtered
using a Buchner funnel and washed with hexane, acetone, methanol, water, and methanol. The
residue was air dried and purified Soxhlet cleaning process for one day. The IR spectrum was
recorded, (Appendix, Spectrum 53). Analysis indicated peaks associated to a succeed reaction.

Reaction of PCTFE (Sheet) with Styrene

Following the general procedure (0.662g, 5.68mmol) PCTFE (six squares), 1.977ml styrene,
(1.338g, 55mmol) Mg, (0.72g, 4.5mmol) NiCl₂, (0.773g, 2.94mmol) PPh₃, and 13 mL DMF were
heated to 80°C for 4 days. The mixture was filtered using a Buchner funnel and washed as
detailed in the general method. The residue was air dried and purified with Soxhlet cleaning
process at 75 V for 2 days. The IR spectrum was recorded, (Appendix, Spectrum 54-1, 54-2, 54-
3, 54-4, 54-4, 54-5, and 54-6). Analysis indicated that peaks at other regions appeared.

Reaction of Styrylated PCTFE (Sheet) with 4-methylphenyldiazonium

In a conical beaker was added (1.033g, 9.6mmol) P-toluidine, 10 mL (2M) HCl. The mixture
was cooled to 0°C, and then (0.716g, 10.37mmol) NaNO₂. The mixture was stirred for 5 min,
and then it was filtered and washed with excess of CH$_2$Cl$_2$. The solution was extracted in a separatory funnel, and the organic layer was evaporated. The IR spectrum was recorded. Analysis indicated the appearance of N-H stretch at 1507 cm$^{-1}$. The resulting slurry was reacted with 0.123g styrated PCTFE in 25ml CH$_2$Cl$_2$. The mixture was stirred for 6 days. The polymer was washed as detailed in the general procedure and air dried. The IR spectrum was recorded.

**Reaction of Styrylated PCTFE (Sheet) with Hg (II)O**

Two squares of styrylated polymer was treated with 50ml CH$_2$Cl$_2$, (0.76g, 3.5mmol) Hg (II)O, 10 mL trifluoro acetic acid, and 35 mL CH$_2$Cl$_2$. The reactants were stirred for 22 hours. Then mercurated polymer was filtered and was washed with methanol in the general procedure. The IR spectrum was recorded, (Appendix, Spectrum 55). Analysis indicated that the corresponded to the functionalization appeared.

**Reaction of Mercurated PCTFE (Sheet) with I$_2$**

0.106 g mercurated PCTEF was reacted with (0.178g) I$_2$, in 25 mL of CH$_2$Cl$_2$. The mixture was stirred for 2 hours, and then it was filtered and washed with ether, ethyl acetate, acetone, methanol, and water, and vice versa. The IR spectrum was recorded, (Appendix, Spectrum 56).

**Reaction of Mercurated PCTFE (Sheet) with POCl$_3$/DMF**

0.107g mercurated PCTFE was react with10ml Phosphorus oxychloried (POCl$_3$) in 15 mL DMF. The mixture was stirred for one night, and then it was washed with ether, ethyl acetate, acetone, methanol, and water, and vice versa. The IR spectrum was recorded, (Appendix, Spectrum 50).

**Reaction of mercurated PCTFE (Sheet) with P-toluidine**

In a conical beaker was added (1.033g, 9.6mmol) P-toluidine, 10 mL (2M) HCl. The mixture was cooled to 0$^\circ$C, and then (0.716g, 10.37mmol) NaNO$_2$. The mixture was stirred for 5 min, and then it was filtered and washed with excess of CH$_2$Cl$_2$. The solution was extracted in a separatory funnel, and the organic layer was evaporated. The IR spectrum was recorded, (Appendix, Spectrum 58). Analysis indicated the appearance of N-H stretch at 1507 cm$^{-1}$. The resulting slurry was reacted with 0.122g mercurated PCTFE in 25ml CH$_2$Cl$_2$. The mixture was
stirred for 4 days. The polymer was washed as detailed in the general procedure and air dried. The IR spectrum was recorded, (Appendix, Spectrum 60).
Conclusion and further investigation

Conclusion

Substitution reactions of PCTFE are complicated by the interplay of several variables. PCTFE oil is not a good model for reactions with solid since reaction of the solid occur at a phase interface. In reactions of the solid, the best solvents are DMF and acetonitrile, but side reactions with the solvent limits the selection of viable trapping agent.

The most promising reactions for further investigations are styrene, butylacrylate, dihydropyran, and acrylonitrile. A success substitution of chlorine atom with C-O appears in the reaction of PCTFE with both butylacrylate and dihydropyran in the presence of NiCl₂, Mg⁰, and PPh₃ in DMF for 4days at 80°C. In addition, under same conditions a nitrile group appears in the region of ( >2200 cm⁻¹) when PCTFE reacts with acrylonitrile. The reaction of PCTFE with styrene resulted in a clear functionalization occurred.

Recommendation for further work

Styrene appears to be the most promising for further reaction. A powerful electrophile such as NO₂ must be present for a successful reaction. An alternate route to further functionalization of styrylated PCTFE lies in reduction of the nitro compounds to the aniline, followed by diazotization and substitution. Reaction on the acrylic ester and nitrile derivatives should also be pursued.
Scheme 28: Proposed further reaction of styrylated PCTFE with NO₂

Scheme 29: Proposed further reaction of acrylonitrile PCTFE
Scheme 30: Proposed further reaction of butylacrylate PCTFE
Appendix

1: IR absorption of the native PCTFE film
2: IR absorption of the native PCTFE oil
3: IR absorption of the native PCTFE solid
4: Product of the reaction of PCTFE with 1-bromo-4-iodobenzene, Cu, and phenanthroline in the presence of DMSO
5: Product of the reaction of PCTFE with 1(4-iodoacetophenone), Cu, and phenanthroline in the presence of DMSO
6: Product of the reaction of PCTFE with 4-Iodoanisole, Cu, and phenanthroline in the presence of DMSO
7: Product of the reaction of PCTFE with 4-Iodoaniline, Cu, and phenanthroline in the presence of DMSO
8: Product of the reaction of PCTFE with 4-iodotoluene, NaS₂O₄, and 3,4,7,8-tetramethyl-1,10-phenanthroline in the presence of DMSO
9: Product of the reaction of PCTFE with 4-iodoaniline and NaS\textsubscript{2}O\textsubscript{4} in the presence of DMSO
10: Product of the reaction of PCTFE with 4-idoacetophenone and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4} in the presence of DMSO
11-1: Product of the reaction of PCTFE with 4-iodoanisole and NaS₂O₄ in the presence of DMSO
11-2: Product of the reaction of the PCTFE with 4-iodoanisole and NaS$_2$O$_4$ in the presence of DMSO

(After treating with 19mL tetrahydrofuran, and stirred for 30 min)
11-3: Product of the reaction of PCTFE with 4-iodoanisole and NaS$_2$O$_4$ in the presence of DMSO

(After treating with water and calcium hypochlorite, and stirred for 30 min)
12: Product of the reaction of PCTFE with 4-vinylbenzoic acid and NaS$_2$O$_4$ in the presence of DMSO
13: Product of the reaction of PCTFE with 4-iodoaniline and Zn/ Pd (PPh₃)₄ in toluene
14: Product of the reaction of PCTFE with 4-iodoaniline and Zn/ PdCl$_2$, PPh$_3$ in toluene
15: Product of the reaction of PCTFE with styrene Co (III) and Mg0 in THF (4 days, at 60°C)
16: Product of the reaction of PCTFE with styrene Co (III) and Mg0 in THF (2 days, at 65°C)
17: Product of the reaction of PCTFE (oil) with styrene Co (III) and MgO in THF (2 days, at 65°C)
18: Product of the reaction of PCTFE (oil) with 4-iodoaniline Co (III) and Mg0 in THF (4 days, at 65°C)
19: Product of the reaction of PCTFE with 4-vinylbenzoic acid Co (III) and Mg0 in THF (4 days, at 65°C)
20: Product of the reaction of PCTFE with 4-iodoaniline Co(III) and Mg0 in THF (4 days, at 65°C)
21: Product of the reaction of PCTFE with 4-iodoanisole Co (III) and Mg0 in THF (4 days, at 65°C)
22: Product of the reaction of PCTFE (oil) with N, N-Dimethylaniline, NiCl₂, Zn⁰, and PPh₃ in DMF
23: Product of the reaction of PCTFE with allyltributyltin, NiCl$_2$, Mg$^0$, and PPh$_3$ in DMF (4 days-100° C)
24: Product of the reaction of PCTFE with allyltributyltin, NiCl$_2$, Mg$^0$, and PPh$_3$ in DMF (1 days-50° C)
25: Product of the reaction of PCTFE with allyltributyltin NiCl$_2$, Mg$^0$, and PPh$_3$ in DMF (1 days-90° C)
26: Product of the reaction of PCTFE with allyltibutyltin, NiCl$_2$, Mg$^0$, and PPh$_3$ in DMF (2 days-90$^\circ$ C)
27: Product of the reaction of PCTFE with allyltributyltin, NiCl₂, Mg⁰, and PPh₃ in Acetonitrile
(2 days-90° C)
28.1: Product of the reaction of PCTFE with allyltributyltin, NiCl₂, Mg⁰, and PPh₃ in Acetonitrile (2 days-90°C) dark area
28.2: Product of the reaction of PCTFE with allyltributyltin, NiCl₂, Mg⁰, and PPh₃ in Acetonitrile (2 days-90° C) light area
29: Product of the reaction of PCTFE with allyltributyltin, NiCl₂, Mg⁰, and PPh₃ in Acetonitrile (4 days-80⁰ C)
30: Product of the reaction of PCTFE (powder) with allyltributyltin, NiCl$_2$, Mg$^0$, and PPh$_3$ in DMF (4 days-80$^\circ$ C)
31: Product of the reaction of PCTFE (film) with acrylonitrile, NiCl$_2$, Mg$^0$, and PPh$_3$ in DMF (4 days-80$^\circ$ C)
32: Product of the reaction of PCTFE (solid) with acrylonitrile, NiCl$_2$, Mg$^0$, and PPh$_3$ in DMF (4 days-80$^0$ C)
33: Product of the reaction of PCTFE with butylacrylate, NiCl$_2$, Mg$^0$, and PPh$_3$ in DMF (4 days-80° C)
34: Product of the reaction of PCTFE with methylvinylketone, NiCl₂, Mg⁰, and PPh₃ in DMF (4 days-80⁰ C)
35: Product of the reaction of PCTFE (film) with dihydropyran, NiCl₂, Mg⁰, and PPh₃ in DMF (4 days-80⁰ C)
36: Product of the reaction of PCTFE (powder) with dihydropyran, NiCl$_2$, Mg$^0$, and PPh$_3$ in DMF (4 days-80° C)
37: Product of the reaction of PCTFE (film) with trichloroethylene, NiCl₂, Mg⁰, and PPh₃ in DMF (4 days-80° C)
38: Product of the reaction of PCTFE (film) with styrene, Cu, Mg\(^0\), and PPh\(_3\) in DMF (2 days-90° C)
39: The blank IR Spectrum for the reaction of PCTFE (film) with Cu, Mg$^0$, and PPh$_3$ in DMF (2 days-90° C)
40: Product of the reaction of PCTFE (film) with styrene, Cu, Mg$^0$, and PPh$_3$ in DMF (4 days-60°C)
41: Product of the reaction of PCTFE (film) with styrene, Cu, Mg⁰, and PPh₃ in α,α,α-trifluorotoluene (4 days-60°C)
42.1: Product of the reaction of PCTFE (film) with styrene, NiCl$_2$, Mg$^0$, and PPh$_3$ in acetonitrile
(2 days-90° C) dark area
42.2: Product of the reaction of PCTFE (film) with styrene, NiCl₂, Mg₀, and PPh₃ in acetonitrile (2 days-90°C) light area
43: Product of the reaction of PCTFE (film) with styrene, NiCl$_2$, Mg$^0$, and PPh$_3$ in DMF (4 days-90$^\circ$ C)
44: Product of the reaction of PCTFE (film) with NiCl$_2$, Mg$^0$, and PPh$_3$ in DMF (2 days-90$^\circ$ C)
45: Product of the reaction of PCTFE (film) with NiCl$_2$, Mg$^0$, and PPh$_3$ in DMF (4 days-60$^\circ$ C)
46: Product of the reaction of PCTFE (film) with NiCl₂, Mg⁰, and PPh₃ in α,α,α, trifluorotoluene (4 days-60⁰ C)
47: Product of the reaction of PCTFE (oil) with styrene NiCl$_2$, Mg$^0$, and PPh$_3$ in DMF (4 days - 60$^\circ$ C)
48: Product of the reaction of PCTFE with NiCl$_2$, Mg$^0$, and PPh$_3$ in DMF (4 days-60$^\circ$ C)
49: Product of the reaction of PCTFE (film) with styrene NiCl₂, Mg⁰, and PPh₃ in DMF (4 days-80° C)
50: Product of the reaction of the styrared PCTFE with nitromethene, concentrated H$_2$SO$_4$, and concentrated HNO$_3$
51: Product of the reaction of PCTFE (powder) with styrene NiCl$_2$, Mg$^0$, and PPh$_3$ in DMF (4 days-80$^\circ$ C)
52: Product of the reaction of PCTFE (powder) with styrene NiCl$_2$, Mg$^0$, and PPh$_3$ in DMF (4 days-95$^\circ$ C)
53: Product of the reaction of the styrated PCTFE with nitromethene, concentrated H$_2$SO$_4$, and concentrated HNO$_3$
54-1: Product of the reaction of PCTFE (film) with styrene NiCl₂, Mg⁰, and PPh₃ in DMF (4 days-80° C)
54-2: Product of the reaction of PCTFE (film) with styrene NiCl₂, Mg⁰, and PPh₃ in DMF (4 days-80⁰ C)
54-3: Product of the reaction of PCTFE (film) with styrene NiCl₂, Mg⁰, and PPh₃ in DMF (4 days-80° C)
54-4: Product of the reaction of PCTFE (film) with styrene NiCl₂, Mg⁰, and PPh₃ in DMF (4 days-80° C)
54-5: Product of the reaction of PCTFE (film) with styrene NiCl\(_2\), Mg\(^0\), and PPh\(_3\) in DMF (4 days-80\(^o\) C)
54-6: Product of the reaction of PCTFE (film) with styrene NiCl₂, Mg⁰, and PPh₃ in DMF (4 days-80⁰ C)
55: IR spectrum of mercurated PCTFE
56: Product of the reaction of mercurated PCTFE with I$_2$
57: Product of the reaction of mercurated PCTFE with POCl₃/ DMF
58: The IR spectrum of nitration reaction
59: Product of the reaction of mercurated PCTFE with nitrosonium
60: Product of the reaction of styrlated PCTFE with nitrosonium
Thesis references