# A Green Catalytic Methodology for Polymerization Activators

## Abstract

Polyolefins are pervasive in today's society. Trash/shopping bags, packaging films, lawn furniture, toys, and automotive components (body panels, engine parts, weather stripping) are common items constructed of polyolefins.[1] Their widespread use results from superior properties (good chemical resistance, weatherability, toughness, and low-density) and low cost. Polyolefins represent 60% of all polymers sold worldwide.[2] In terms of volume and contribution to the world's economy the numbers are staggering (110 million tons[3] at €110 billion[4] per year). What is even more amazing is that polyolefins are relative newcomers to the polymer field; production started in the 1960s.[1,5]

The development of Ziegler-Natta catalysts (ZNCs) enabled commercialization of polyolefins.[5] ZNCs do not always produce polyolefins with the best possible physical properties and may also generate off-spec materials with no utility.[5] Removal/disposal of these materials is detrimental to the environment and wasteful of valuable petro-feedstocks. In the 1980s a major breakthrough in polyolefin production was the discovery of single site catalysts (SSCs).[6] SSCs allow for the production of designer grades of polyolefins with superior physical properties without generating off-spec polymers. SSCs are formed by the reaction of a transition metal compound (TMC) with an activator.

Despite these advantages, SSCs have not yet taken much market share due to high activator cost.[7] The two main types of activators are methylaluminoxane[8] (MAO) and perfluoroarylated Lewis acids[9] (PFLAs). MAO has serious drawbacks including limited shelf-life, it is spontaneously flammable with air (pyrophoric), and it must be used in large excess. PFLAs are storage stable, not pyrophoric, and effective on an equimolar basis. Due to low yields, expensive precursors, unstable/toxic intermediates, requisite use of polluting solvents, and energy intensive reaction conditions, manufacture of PFLAs is costly, dangerous, and damaging to the environment.[10]

Improved ways of making PFLAs in a cost-effective, safe, and environmentally acceptable manner is a critical need in the polyolefins industry. The research effort proposed herein will utilize an innovative adaptation of a well-established method (transmetallation) for the synthesis of PFLAs. This process will incorporate the following.

1. *Cheap precursors*.
2. *Process itself will be catalyzed*.
3. *Improved safety*.
4. *Minimal or no solvents*.
5. *Components not consumed are recycled*.

Optimum reactions conditions will be determined on a small scale in Phase I. Phase II will focus on kiloscale production to provide polyolefin manufacturers with pilot plant quantities of PFLAs. Licenses of the technology will then be made available to these manufacturers for implementation worldwide.

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***Abbreviations***

eq. = equivalent
EPDM = ethylene propylene diene monomer
FTIR = Fourier transform infrared
GC = gas chromatography
HDPE = high-density polyethylene
HPLC = high precision liquid chromatography
IP = intellectual property
LLDPE = linear low-density polyethylene
MAO = methylaluminoxane
NMR = nuclear magnetic resonance
PFLA = perfluoroarylated Lewis acid
PP = polypropylene
QA = quality assurance
QC = quality control
SSC = single site catalyst
ST = Stewart's Technologies
THF = tetrahydrofuran

TMC = transition metal compound
USPTO = US patent and trademark office
UV/Vis = ultraviolet/visible
VT = Virginia Tech
ZNC = Ziegler-Natta catalyst

## 1. Identification and Significance of the Problem or the Opportunity

In the 1960s a renaissance in the polymer industry occurred with the advent of ZNCs making the production of polyolefins economically feasible.[5,6] Polyolefins (Table 1) are a class of polymers derived from the polymerization of α-olefins (especially ethylene) with versatility and economy matched by few materials. As a result, polyolefins make up 60% of total polymer production and continue to grow at a rate of 6-9% per year.[2,3] This translates to 110 million tons,[3] enough to build 44 polyolefin replicas of Kufu's great pyramid at Giza,[7d] every year. With a current market price of €1,000 ($1,400) per ton polyolefins contribute greatly to the world's economy (€110 billion {$150 billion} per year).[3] ZNCs are far from ideal as they possess a number of ill-defined catalytic sites with differing activities.[5] This results in the production of complicated mixtures of polyolefins. Off-spec polymer molecules that are invariably produced downgrade the ultimate properties of the final resin. In some cases off-spec polymers (*e.g.* atactic PP or leachable, low-molecular weight fractions) have such a deleterious effect that they must be removed to yield a useful resin. This generates waste products, is energy intensive, and is costly.

Table 1. Polyolefins and Their Uses[1]

| Polyolefin | Common Uses |
|---|---|
| High-density polyethylene (HDPE) | Packaging containers (*e.g.* milk, detergent, food); housewares; pipe/conduit (*e.g.* water, gas, electrical); bags (*e.g.* refuse, shopping); toys. |
| Linear low-density polyethylene (LLDPE) | Packaging films (*e.g.* food and non-food); housewares; appliances; bags (*e.g.* refuse); toys. |
| Polypropylene (PP) | Automotive (*e.g.* external/internal body panels, engine components); microwaveable food containers; housewares; appliances; toys. |
| Ethylene propylene diene monomer (EPDM) | Weather stripping/insulation; automotive hoses; roofing membranes. |

The most significant advance in polyolefin production in the last 30 years was the discovery of SSCs in the 1980s.[6] SSCs have well-defined catalytic centers that produce more uniform resins with higher tensile/puncture/impact strengths, better clarity, and lower odor/taste characteristics.[5] SSCs can be fine-tuned to produce specific grades of polymers and can be adapted to operate in solution, slurry, or gas-phase polymerization processes.[5] SSCs comprise a TMC (*e.g.* metallocene) and a Lewis acid activator (*e.g.* MAO[8] or PFLA[9]). Widespread use of SSCs has been hampered by the cost of the activator[7] and although growth of SSCs is 15-20% a year[7b,c] they currently represent only 5%[7b,c] of the catalysts used for polyolefin production. As an activator, MAO possesses significant drawbacks. It has an ill-defined structure, it is pyrophoric (requiring special handling), it must be used in large excess (>1,000 eq. for each eq. TMC), and it has a limited shelf-life (forms unreactive gels).[8] PFLAs are superior activators.[9] They have discrete structures, are storage stable, and are very efficient in terms of atom economy (1 eq. per eq. TMC).

Large scale use of PFLAs has been hampered by difficulties experienced in their manufacture. Three main strategies have been used for the synthesis of these compounds each possessing drawbacks.[10] One strategy involves the preparation of a (pentafluorophenyl)magnesium halide (Grignard reagent) in an ethereal solvent followed by reaction with a Group 13 or 15 metal halide (Scheme 1).

$$3\ BrMgC_6F_5 + MX_3 \xrightarrow[\substack{\text{M = Group13 or 15}\\ \text{X = halogen}}]{Et_2O} 3\ BrMgX + M(C_6F_5)_3$$

Scheme 1

These reactions are inefficient (low yields). The Grignard reagent is thermally unstable in the absence of an ethereal solvent and requires special handling.[11] The ethereal solvent also forms a "poisoning" chemical bond with the product and its removal is difficult, inefficient, and energy intensive. Another method involves the use of pentafluorophenyllithium ($C_6F_5Li$) instead of the Grignard reagent in the displacement reaction with the Group 13 or 15 metal halide, with improved product yields (Scheme 2).

$$3\ C_6F_5Li + MX_3 \xrightarrow[\substack{\text{M = Group13 or 15}\\ \text{X = halogen}}]{-78\ ^\circ C} 3\ LiX + M(C_6F_5)_3$$

Scheme 2

Pentafluorophenyllithium is very thermally unstable. As a solid it is a treacherous, shock-sensitive explosive. It *must* be prepared and reacted at low temperatures (*i.e.* < -40 °C).[11] Whether using lithium or magnesium reagents, the reaction is also typically conducted an ethereal solvent that must be removed from the end product, generally with great difficulty.

A third approach for the synthesis of (pentafluorophenyl) Group 13 and 15 metal compounds is transmetallation (Scheme 3). This involves reaction of a precursor pentafluorophenyl metal compound (typically mercury, cadmium, or tin) with a Group 13 or 15 metal halide.[11] In some cases yields are good and the compounds are stable, but the metals present prohibitive chemical hygiene and environmental hazards, in addition to considerable synthetic challenges. A recent provisional patent filing by Stewart's Technologies[12] (ST) discloses a unique transmetallation strategy that can be used to prepare a number of Group 13 and 15 pentafluorophenyl compounds. This new methodology is unique in that the precursor pentafluorophenyl metal compound does not contain a toxic metal and transmetallation can be affected in the absence of solvent in many cases. The main drawback associated with this new technology is that the materials used to prepare the precursor pentafluorophenyl metal compound are relatively expensive.

$$3/2\ M'(C_6F_5)_2 + MX_3 \xrightarrow[\substack{\text{M = Group13 or 15}\\ \text{M' = Hg, Cd, Sn}\\ \text{X = halogen}}]{} 3/2\ HgX_2 + M(C_6F_5)_3$$

Scheme 3

**The goal of this research effort is development of a synthetic route to PFLAs with improved safety characteristics and reduced environmental impact exhibiting the following criteria.**

1. Uses the *least expensive* precursors (*e.g.* hexafluorobenzene, $C_6F_6$, and/or pentafluorobenzene, $HC_6F_5$).
2. The *process itself will be catalyzed* to reduce the overall energy consumption.
3. Does *not* use toxic, energetic, or unstable intermediates.
4. Reaction requires *minimal or no* polluting solvents.
5. With the exception of the precursors all reaction components are *recyclable*.

The benefits of such a process would have a cascading effect as the availability of low-cost PFLAs will spur additional growth of SSC polymerizations greatly reducing the overall environmental impact of polyolefin production.

## 2. Phase I Objectives

The ultimate goal of Phase I is the development of a process for producing PFLAs that possess the following characteristics.

1. Hexafluorobenzene and/or pentafluorobenzene can be used as feedstocks.
2. The process will operate in a catalytic manner so as to reduce both energy and material consumption.
3. No toxic metals or energetic or unstable materials will be involved.
4. The process will not use coordinating ethereal solvents or chlorinated solvents and if possible can be conducted in the complete absence of any solvents.
5. Any by-product that is produced will be of value and can be used either in the preparation of the fluorinated feedstocks or as an energy source.

In order to achieve this goal the project will be conducted through successive stages each with its own goal as follows.

*Stage 1*

The objective of this stage is the synthesis of four catalysts, each containing a different transition metal (Fe, Cu, Rh, Pd) using existing procedures detailed in the chemical literature. If possible improvements will be made in the synthesis of these compounds.

*Stage 2*

The purpose of this stage is to screen each catalyst for activity in PFLA production using hexafluorobenzene and pentafluorobenzene as feedstocks to determine which catalysts have the highest potential for use in an industrial setting.

*Stage 3*

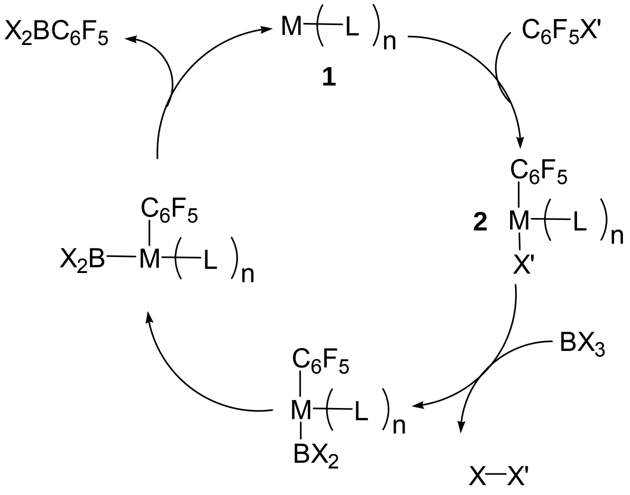
The two most promising catalysts are further investigated in detail for the gram scale preparation of the PFLA, tris(pentafluorophenyl)boron. Detailed cost analysis of the two systems will be conducted and the most promising system will be explored on a pilot plant scale in Phase II. All findings will be summarized and a provisional patent filing will be made covering the developed IP.

## 3. Phase I Work Plan

Due to the proprietary nature of the chemical processes to be developed the following is a generalized description of work to be done in Phase I. The purpose for doing this is to provide maximum protection to the IP while in its developmental stage. Once provisional patent protection has been obtained a full description of the technologies developed in Phase I will be disclosed in both the final report and Phase II proposal.

Recent work conducted at ST and filed by ST[12b] with the US patent and trademark office (USPTO) showed/demonstrated/suggested that transmetallation was a highly effective yet underutilized method for the preparation of PFLAs. Three factors have prevented wide-scale adoption of the transmetallation technique. First, the number of known perfluoroaryl metal transfer agents has been limited to few compounds that typically bear toxic metals (*i.e.* Hg, Cd, Sn). Second, the utility of the remaining perfluoroaryl metal transfer agents bearing less toxic metals (*e.g.* Cu, Ag) has been limited by difficulties encountered in their synthesis and/or their low reactivity in transmetallation to form PFLAs.

The transmetallation chemistry recently developed by ST circumvents most of these difficulties and allows for the production of a number of PFLAs in an economical yet more environmentally friendly manner. The main drawback associated with this new technology is the high cost of the precursors used in the synthesis of the perfluoroaryl metal transfer agent used in this process. These findings led to an epiphany; the most economical method for producing PFLAs under greener conditions could be realized by developing a *catalyst* (**1**) to convert the cheapest feedstocks ($C_6F_6$ or $HC_6F_5$) into the desired *pentafluorophenyl metal transfer agent* (**2**). In its ultimate configuration the $C_6F_5$ metal transfer agent (**2**) generated in this process would itself be an intermediate chemical derivative of the catalyst (**1**) used and any by-products would themselves be valuable either in the production of the precursors (*i.e.* KF, HF) or as fuel (*i.e.* $H_2$). One example of such a process is depicted in Scheme 4.



M = Fe, Cu, Pd, Rh
L = unspecified type of ligand
X = halogen or H
X' = H or F

Scheme 4

Four organometallic compounds, each based on a different transition metal (*i.e.* Fe, Cu, Rh, and Pd), have been selected as potential candidates as catalysts for this process. All of the compounds are known and methods for their preparation and characterization have been detailed extensively in the chemical literature. Two of these compounds (those based on Cu and Pd) have also been prepared and used by Professor Deck's group for other research purposes. Dr. Deck's working knowledge of these compounds specifically and organometallic chemistry in general will allow for facile and efficient synthesis of these catalysts in a short time frame.

The Phase I work load required to develop a process that meets all of the stated goals for this project will be distributed in a carefully optimized manner. Each task will be assigned by taking into consideration the time required, the degree of complexity, and the special talents possessed by each individual involved. As such the experimental work will be conducted jointly by ST and Professor Mathers whereas Professor Deck will certify results as an objective observer on a consultancy basis as part of the quality assurance (QA) and quality control (QC) program.

Dr. Mathers will be responsible for the synthesis of both the Fe and Cu containing catalysts. These tasks are assigned to Dr. Mathers for the following reasons.

1. Neither compound is complicated or time consuming to prepare. Dr. Mathers can thus readily synthesize these compounds in the limited amount of time that he has committed to the project.
2. Dr. Mathers can readily follow the progress of these reactions qualitatively using simple techniques such as thin layer chromatography or quantitatively using instrumentation that he has available in his laboratory (*e.g.* Fourier transform infrared spectroscopy {FTIR}, ultraviolet and visible absorbance spectroscopy {UV/Vis}, high precision liquid chromatography {HPLC}, and gas chromatography {GC}).
3. Both catalysts are stable to air and ambient moisture and do not require special handling techniques or storage methods. As such, these catalysts lend themselves to manufacture at locations other than where they will be tested.

Dr. Mathers will conduct the synthesis of both Fe and Cu containing catalysts on a modest scale (about one gram) in his laboratory facilities. The project team will discuss synthetic procedures by conference call to maximize efficiency and safety. Dr. Deck will review the analytical data from this work and handle all spectroscopic analysis and characterization due to his experience. Should Dr. Mathers encounter difficulties during the synthesis of either catalyst Dr. Deck will provide guidance on how to resolve these issues.

Dr. Lewis is responsible for synthesizing the Pd and Rh based catalysts based on the following rationale.

1. The Pd and Rh catalysts are more difficult and time consuming to prepare. As the PI, Dr. Lewis is able to devote the required work hours necessary to synthesize these compounds.
2. These catalysts are best analyzed using advanced instrumentation such as nuclear magnetic resonance (NMR) spectroscopy. Dr. Lewis has walk up access to this instrumentation at Virginia Tech (VT) 7 days a week.
3. The Rh catalyst is air-sensitive and thus has special handling and storage requirements. The laboratories at ST are equipped with all of the necessary glassware and glove box facilities.

Dr. Lewis will conduct the synthesis of these catalysts on a gram scale in his laboratory and conduct analysis of these compounds at the VT analytical facilities. All air-sensitive manipulations will be conducted using standard Schlenk and vacuum line techniques. Air-sensitive compounds will be stored in a dry box in Dr. Lewis' laboratory prior to usage to prevent their decomposition. Dr. Lewis will discuss all synthetic procedures with Dr. Deck prior to implementation for additional input. Dr. Deck will be in charge of the interpretation of all analytical data collected by Dr. Lewis and will make suggestions on how to optimize the synthesis of each catalyst.

Dr. Lewis is further charged with the task of screening each catalyst's potential for the production of PFLAs given the following.

1. These experiments will require a substantial commitment of time and as a result must be conducted by the PI.
2. These reactions are of a highly proprietary nature and should be conducted at ST. Conducting these most sensitive and novel experiments on a public university campus could compromise our IP positions.
3. These reactions need to be monitored using analytical instrumentation that is only available through VT. Since Dr. Lewis is trained in the use of these instruments and has walkup access to them it is most logical to conduct these experiments at ST which is within the vicinity of VT. Using VT instruments does not compromise IP because all spectra are obtained on a fee-for-service basis.
4. The proximity of ST and VT (about 5 minutes by car) greatly facilitates interactions such as consultations with Prof. Deck and the use of VT instrumentation, both of which will help us reach our desired outcomes more quickly.

All experimental work on catalyzed PFLA synthesis will be conducted by Dr. Lewis in his laboratory facilities. Analysis of the product mixtures will be carried out at VT by Dr. Lewis. Dr. Deck will review all written procedures and discuss them with Dr. Lewis beforehand. Dr. Deck will interpret all of the analytical data collected and give advice on how to improve specific reaction sequences.

The following procedure is given as a general description of how such experiments will be conducted and is not meant to be all inclusive.

Inside a nitrogen glove box a 250 mL Schlenk flask fitted with a high vacuum PTFE stopcock is charged with 0.100 g (0.250 mmol) of a Rh catalyst, and 0.400 g (2.25 mmol) tetrafluoro-*p*-xylene as an internal standard. A Teflon-coated magnetic stirring bar is added, and the flask is capped with a rubber septum, removed from the glove box, and attached to a Schlenk line (vacuum/nitrogen dual manifold) via butyl rubber tubing. Then, 5.0 mL (0.045 mol) of pentafluorobenzene (previously dried by distillation from $CaH_2$) is injected using a syringe. With stirring, 15.0 mL (0.015 mol) of a commercial 1.0 M solution of $BH_3$ in tetrahydrofuran (THF) is injected drop-wise, watching cautiously for hydrogen evolution. Following complete addition of $BH_3$ the contents of the Schlenk flask are stirred for one hour after which a 0.050-mL aliquot is withdrawn using a gas-tight syringe and injected into a septum-sealed 5-mm NMR tube containing an appropriate pre-dried solvent (*e.g.* $C_6D_6$). $^{19}F$ NMR spectroscopy is then conducted on the sample at VT (Varian Unity, 300 K, 376.29 MHz). The sample is analyzed for signals characteristic of the desired PFLA, $B(C_6F_5)_3$. Conversion to product is determined by comparison of the integrated values for the peak for the F atoms of the internal standard to the value for the peak corresponding to the ortho F atoms of pentafluorobenzene.

In this manner each catalyst will be screened for activity in the preparation of PFLAs from both hexafluorobenzene and pentafluorobenzene. The results of these screening reactions will be tabulated and catalysts will be ranked by activity and the overall calculated cost per gram of PFLA afforded by each system. The research team will review the results of these screening reactions and determine which system(s) are most promising for the industrial synthesis of PFLAs and suggest how to optimize these processes. Follow up experiments focusing on fine tuning systems deemed by the research team as being useful industrially will be conducted. A report summarizing all of the key findings for both catalyst synthesis and their application to PFLA synthesis will be produced jointly by Dr. Mathers and Dr. Lewis. Dr. Deck will certify all of the analytical data as a final QA measure.

## 4. Related Research or R&D

This section summarizes key work that has been done on the synthesis of Group 13 and 15 pentafluorophenyl compounds. Given the breadth of research that has been conducted in this area the following is not meant to be comprehensive. It should be noted that the known Group 15 pentafluorophenyl compounds can be viewed as weak Lewis bases. Their chemistry is included as ST has recently filed a provisional patent[12b] detailing the synthesis of acidic versions of these compounds and the methodology to be developed in the current project will be extended to these new matters of composition (that is Group 15 PFLAs) in addition to the known Group 13 PFLAs.

Tris(pentafluorophenyl)boron, $B(C_6F_5)_3$, was first prepared by Massey and Park via reaction of pentafluorophenyllithium and boron trichloride ($BCl_3$) in pentane at –78 °C (Scheme 5).[10a] Not only is this chemistry inherently dangerous to conduct but yields were reported to range only from 30-50%. The reaction suffers from a bizarre hazard in which accidental interruption of magnetic stirring results in compaction of the shock-sentitive $C_6F_5Li$ intermediate – when this occurs the reaction must be quenched immediately. Nevertheless, closely analogous chemistry is embodied in a number of patents.[10b] Due to the thermal instability of pentafluorophenyllithium subsequent investigators used pentafluorophenylmagnesium bromide ($BrMgC_6F_5$) in conjunction with the diethyl etherate complex of boron tifluoride $\{BF_3{\cdot}O(CH_2CH_3)_2\}$ for the preparation of $B(C_6F_5)_3$ (Scheme 6).[10c] This procedure gives rise to improved yields (c.a., 80%) and also forms the basis of a number of patents.[10d] Although safer from an operational standpoint removal of the ethereal solvents used in this method requires additional steps such as azeotropic distillation or sublimation and is energy intensive and time consuming.

$$3\ C_6F_5Li\ +\ BCl_3\ \xrightarrow[\text{pentane}]{-78\ °C}\ 3\ LiCl\ +\ B(C_6F_5)_3$$

Scheme 5

$$3\ BrMgC_6F_5\ +\ BF_3{\cdot}O(CH_2CH_3)_2\ \xrightarrow{Et_2O}\ 3\ BrMgCl\ +\ B(C_6F_5)_3$$

Scheme 6

Following the discovery of $B(C_6F_5)_3$ several (pentafluorophenyl) Group 15 compounds were prepared. The first (pentafluorophenyl) Group 15 compounds, tris(pentafluorophenyl)phosphine $\{P(C_6F_5)_3\}$ and tris(pentafluorophenyl)phosphine oxide $\{OP(C_6F_5)_3\}$ were reported by Pummer and coworkers.[10e] $P(C_6F_5)_3$ was prepared in 39.5% yield by reaction of phosphorus trichloride ($PCl_3$) with $BrMgC_6F_5$ in ether (Scheme 7). This method suffers from low yields. $OP(C_6F_5)_3$ was prepared in 97.1%

$$3\ BrMgC_6F_5 + PCl_3 \xrightarrow{Et_2O} 3\ BrMgCl + P(C_6F_5)_3$$

Scheme 7

yield by oxidation of $P(C_6F_5)_3$ with sodium dichromate ($Na_2Cr_2O_7$) in a mixture of sulfuric and acetic acids (Scheme 8). Christoph and coworkers subsequently detailed the preparation of both

$$P(C_6F_5)_3 \xrightarrow[H_2SO_4/HOAc]{Na_2Cr_2O_7} OP(C_6F_5)_3$$

Scheme 8

tris(pentafluorophenyl)arsenic {$As(C_6F_5)_3$} and tris(pentafluorophenyl)antimony {$Sb(C_6F_5)_3$} in addition to $P(C_6F_5)_3$.[10f] This was accomplished by reaction of $C_6F_5MgBr$ with $AsCl_3$, $SbCl_3$, and $PSCl_3$ in diethyl ether respectively (Scheme 9). This method suffers from low product yields {25% for $P(C_6F_5)_3$, 39% for $As(C_6F_5)_3$, and 32% for $Sb(C_6F_5)_3$}. Subsequent researchers substituted pentafluorophenyllithium in place of the Grignard reagent for the preparation of these compounds (Scheme 10).[10g] This resulted in improved product yields {85% for $P(C_6F_5)_3$, 75% for $As(C_6F_5)_3$, and 75% for $Sb(C_6F_5)_3$}. Due to the thermal instability of the lithium reagent these reactions had to be conducted at –78°C. The synthesis of tris(pentafluorophenyl)amine {$N(C_6F_5)_3$} proved to be more difficult than the other aforementioned (pentafluorophenyl) Group 15 compounds. Tatlow and coworkers were able to prepare $N(C_6F_5)_3$ by reaction of $HN(C_6F_5)_2$ with hexafluorobenzene in the presence of the strong base *p*-tolylsodium (Scheme 11).[10h] Reaction was conducted at 230°C for 42 hours to afford $N(C_6F_5)_3$ in 24% yield. This procedure suffers from drastic reaction conditions and low yields.

$$3\ BrMgC_6F_5 + MCl_3 \xrightarrow[M\,=\,PS,\ As,\ Sb]{Et_2O} 3\ BrMgCl + P(C_6F_5)_3,\ As(C_6F_5)_3,\ Sb(C_6F_5)_3$$

Scheme 9

$$3\ C_6F_5Li + MCl_3 \xrightarrow[M\,=\,PS,\ As,\ Sb]{-78\ ^\circ C} 3\ LiCl + P(C_6F_5)_3,\ As(C_6F_5)_3,\ Sb(C_6F_5)_3$$

Scheme 10

$$C_6F_6 + HN(C_6F_5)_2 \xrightarrow[230\ ^\circ C/\ 48hrs]{p\text{-tolylsodium}} N(C_6F_5)_3$$

Scheme 11

Preparation of the diethyl etherate adduct of tris(pentafluorophenyl)gallium {$Ga(C_6F_5)_3{\cdot}O(CH_2CH_3)_2$} from reaction of gallium trichloride ($GaCl_3$) and $BrMgC_6F_5$ in diethyl ether was reported as early as the mid 1960s (Scheme 12).[10c] Although this procedure gives rise to $Ga(C_6F_5)_3{\cdot}O(CH_2CH_3)_2$ in 65% yield these researchers were unable to remove the coordinated diethyl ether. The synthesis of base free $Ga(C_6F_5)_3$ was not possible until much later. The first disclosure of a method for making base free $Ga(C_6F_5)_3$ involved the reaction elemental iodine with $Ga(C_6F_5)_3{\cdot}O(CH_2CH_3)_2$ to form uncomplexed $Ga(C_6F_5)_3$ and an iodine-diethyl ether adduct the later being removed by distillation under reduced pressure.[10i] No information on the yield of uncomplexed $Ga(C_6F_5)_3$

$$3\ BrMgC_6F_5 + GaCl_3 \xrightarrow{Et_2O} 3\ BrMgCl + Ga(C_6F_5)_3{\cdot}O(CH_2CH_3)_2$$

Scheme 12

as produced by this method was provided. This method suffers from the use of environmentally unfriendly iodine. A second method for the preparation of uncomplexed $Ga(C_6F_5)_3$ involves the exchange reaction between $B(C_6F_5)_3$ and trimethylgallium $\{Ga(CH_3)_3\}$ (Scheme 13).[10j] This strategy purportedly gives rise to high yields of

$$B(C_6F_5)_3 + Ga(CH_3)_3 \longrightarrow B(CH_3)_3 + Ga(C_6F_5)_3$$

Scheme 13

uncomplexed $Ga(C_6F_5)_3$ but involves the requisite use of expensive and pyrophoric $Ga(CH_3)_3$ in addition to consuming valuable $B(C_6F_5)_3$.

Synthesis of the diethyl etherate complex of tris(pentafluorophenyl)indium $\{In(C_6F_5)_3{\cdot}Et_2O\}$ was reported by Pohlmann and Brinckmann.[10c] This involved the reaction of $BrMgC_6F_5$ with indium trichloride in diethyl ether to give $In(C_6F_5)_3{\cdot}Et_2O$ in 34% yield. No method for removing the complexed diethyl ether was provided (Scheme 14). This method suffers from low yields and the inability to form uncomplexed

$$3\ BrMgC_6F_5 + InCl_3 \xrightarrow{Et_2O} 3\ BrMgCl + In(C_6F_5)_3{\cdot}O(CH_2CH_3)_2$$

Scheme 14

$In(C_6F_5)_3$. The preparation of uncomplexed $In(C_6F_5)_3$ was first reported by Deacon and Parrott.[10k] These researchers developed three different strategies for manufacture of this compound. The first involved direction reaction of neat $IC_6F_5$ with excess In metal (Scheme 15). $In(C_6F_5)_3$ was isolated in a low yield of

$$IC_6F_5 + \text{excess In} \longrightarrow In(C_6F_5)_3$$

Scheme 15

31% via sublimation from the reaction mixture. The second method involved reaction of pentafluorophenylmagnesium chloride with indium trichloride in THF followed by treatment of the crude product with dioxane/ether to yield the complex $In(C_6F_5)_3{\cdot}$dioxane in 41% yield. Despite the increased yield no means of obtaining uncomplexed $In(C_6F_5)_3$ was described. A third procedure involved transmetallation of In metal with $Hg(C_6F_5)_2$ (Scheme 16). This resultant product mixture was

$$3/2\ Hg(C_6F_5)_2 + In \longrightarrow 3/2\ Hg + In(C_6F_5)_3$$

Scheme 16

contaminated with metallic mercury and purification required fractional sublimation to ultimately afford $In(C_6F_5)_3$ in 53% yield. This method suffers from the toxicity of the precursor mercury compound.

Synthesis of the diethyl ether adduct of tris(pentafluorophenyl)aluminum $\{Al(C_6F_5)_3{\cdot}O(CH_2CH_3)_2\}$ from reaction of aluminum trichloride ($AlCl_3$) and pentafluorophenylmagnesium bromide ($BrMgC_6F_5$) in diethyl ether was reported as early as the mid 1960s (Scheme 17).[10c] Attempts at removing the

$$3\ BrMgC_6F_5 + AlCl_3 \xrightarrow{Et_2O} BrMgCl + Al(C_6F_5)_3{\cdot}O(CH_2CH_3)_2$$

Scheme 17

coordinated ether resulted in explosion. The synthesis of base free $Al(C_6F_5)_3$ was not possible until much later. The first disclosure of a method for making base free $Al(C_6F_5)_3$ was given by Schmidt and coworkers in 1995.[10l] This was accomplished by reaction of $Me_2AlCl$ with $C_6F_5Li$ in hexanes to initially form $Me_2AlC_6F_5$ which is then heated to 180°C in vacuo to liberate $AlMe_3$ and generate crude $Al(C_6F_5)_3$ (Scheme 18). Recrystallization of the crude reaction product from THF gave the adduct $THF{\cdot}Al(C_6F_5)_3$ in

$$C_6F_5Li + ClAl(CH_3)_2 \xrightarrow[\text{hexanes}]{-78\ ^\circ C} LiCl + Me_2AlC_6F_5 \xrightarrow{180\ ^\circ C} 2/3\ AlMe_3 + 1/3\ Al(C_6F_5)_3$$

Scheme 18

64% yield. This procedure is dangerous to conduct as $C_6F_5Li$ is thermally unstable and the produced $Al(C_6F_5)_3$ is energetic and exploded on occasion. An alternative route for the synthesis of $Al(C_6F_5)_3$ involves the exchange reaction between $B(C_6F_5)_3$ and trimethylaluminum which is typically conducted in an aromatic hydrocarbon (*i.e.,* toluene; Scheme 19).[10j] This strategy purportedly gives rise to high yields

$$B(C_6F_5)_3 + Al(CH_3)_3 \xrightarrow{\text{toluene}} B(CH_3)_3 + Al(C_6F_5)_3{\cdot}\text{toluene}$$

Scheme 19

of base free $Al(C_6F_5)_3$ (stable in toluene) but involves the requisite use of pyrophoric $Al(CH_3)_3$ in addition to consuming valuable $B(C_6F_5)_3$.

The synthesis of $Bi(C_6F_5)_3$ was first disclosed by Royo and Uson[12m] in 1969 followed by Deacon and Johnson[10n] in 1972. Both sets of investigators prepared this compound from the reaction of $C_6F_5MgBr$ with bismuth trichloride ($BiCl_3$) in diethyl ether (Scheme 20). Yields of $Bi(C_6F_5)_3$ obtained from

$$3\ BrMgC_6F_5 + BiCl_3 \xrightarrow{Et_2O} Bi(C_6F_5)_3$$

Scheme 20

this method were low (*c.a.,* 30%). Naumann and coworkers then prepared $Bi(C_6F_5)_3$ via transmetallation of bismuth tribromide ($BiBr_3$) with $Cd(C_6F_5)_2{\cdot}$diglyme in acetonitrile (Scheme 21).[10o] Although this

$$3/2\ Cd(C_6F_5)_2{\cdot}\text{diglyme} + BiBr_3 \xrightarrow{MeCN} 3/2\ CdBr_2 + Bi(C_6F_5)_3{\cdot}\text{diglyme} \xrightarrow{\Delta,\ \text{vac}} Bi(C_6F_5)_3$$

Scheme 21

procedure improved product yields (71%) it suffers from the use of toxic cadmium compounds. Isolation of uncoordinated $Bi(C_6F_5)_3$ from this method also requires distillation of diglyme from the product under reduced pressure, a process that is time consuming and energy intensive.

ST[12] recently disclosed a unique transmetallation strategy (in a provisional patent filing) that can be used to prepare a number of Group 13 and 15 pentafluorophenyl compounds. This strategy is unique in that the precursor pentafluorophenyl metal compound does not contain a toxic metal, no coordinating solvents are involved, and transmetallation can be affected in the absence of solvent in many cases. The main drawback associated with this new technology is that the materials used to prepare the precursor pentafluorophenyl metal transfer agent are relatively expensive.

From the foregoing it is clear that there is a need for an improved process for preparing uncomplexed (pentafluorophenyl) Group 13 and 15 metal compounds in a highly efficient manner with improved industrial applicability. Ideally, such a process would be safe to operate and have reduced impact on the environment. The project is directed to these, as well as other, important needs.

## 5. Key Personnel and Bibliography of Directly Related to Work

***Stewart P. Lewis*, Ph.D.**

Dr. Lewis established a specialty catalyst manufacturing and consulting business (Stewart's Technologies, LLC.)[12], which supports the polymer industry. As Principal Investigator, Dr. Lewis brings experience in design, development, and marketing of catalysts for specific chemical production needs (*e.g.* polymer production under environmentally friendly conditions). He will lead the research effort in Phase I of this project.

## PROFESSIONAL EMPLOYMENT

**Ferrum College**
Adjunct Professor of Chemistry *January 2008-present*

**MapTech, Inc. (Energy Alternatives Division)** *April 2007 - present*
Research Scientist

**Innovative Science, Inc. (Formerly Stewart's Technologies)** *January 2005 - present*
Founder and President

**The University of Akron** *January 1997 - December 2004*
Graduate Research Assistant

**Virginia Polytechnic Institute and State University** *January 1995 - December 1996*
Undergraduate Research Assistant

## EDUCATION

| | | |
|---|---|---|
| **Ph.D.** | Polymer Science, The University of Akron | 2004 |
| **M.S.** | Polymer Science, The University of Akron | 2000 |
| **B.A.** | Chemistry, Virginia Polytechnic Institute and State University | 1996 |

## MAJOR PROJECTS

**Green Polymerization Systems for IIR Manufacture:** Developed (under contract) 3 general classes of new polymerization systems for the manufacture of IIR (butyl rubber) at elevated reaction temperatures and under neat conditions. This system provides energy savings in both polymerization and post polymerization purification steps in addition to eliminating the need for polluting solvents. Project is ongoing and a patent application is in progress.

**Development of Catalysts to Improve Synthesis of Monomers:** Conducted contract R&D for the Hanson Group LLC to improve the synthesis of monomers used in the polyurethane industry that led to new, 1st generation catalysts that enable monomer production under less demanding operating conditions.

**Manufacture of Specialty Lewis Acids:** Developed new routes to perfluoroarylated Lewis acids typically used in conjunction with metallocenes for olefin polymerization and invented new compounds in this class (patent pending).

**Solution and Aqueous Suspension/Emulsion Polymerization of Isobutylene Coinitiated by 1,2-$C_6F_4[B(C_6F_5)_2]_2$:** Greatly improved the synthesis of $C_6F_4$-1,2-$[B(C_6F_5)_2]_2$ and invented new surfactants. Modified the complex counteranion theory (a long standing theory in the cationic polymerization field). Demonstrated proton trap (2,6-di-*t*-butyl-4-methylpyridine) is not benign towards carbocations paired with weakly coordinating anions. Conducted the first quantitative polymerizations of isobutylene in the absence of chlorinated solvents and invented the only aqueous emulsion & suspension polymerizations of isobutylene (the only green production method for polyisobutylene and butyl rubber).

**I. Zeolitic and Mesoporous Sieve Catalyzed Transesterification of Dimethylterephthalate and Ethylene Glycol II. Synthesis of Polycarbonate Layered Silicate Nanocomposites:** Investigated the transesterification of dimethylterephthalate with ethylene glycol using zeolites and mesoporous sieves as shape-selective catalysts for cyclic-ester production. Worked jointly with another student and an USAF officer on polycarbonate nanocomposites.

## INSTRUMENTATION

The applicant is well versed in a multitude of analytical techniques including: high precision liquid chromatography (HPLC), gas chromatography (GC), gas chromatography coupled mass spectroscopy (GC-MS), Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), gel permeation chromatography (GPC), and ultraviolet spectroscopy (UV).

**PUBLICATIONS/PATENTS**

Jianfang, C.; **Lewis, S. P.**; Collins, S.; Sciarone, T. J. J.; Henderson, L. D.; Chase, P. A.; Irvine, G. J.; Piers, W. E.; Elsegood, M. R. J.; Clegg, W. *Organometallics*, **2007**, *26*, 5667-5679.

Jianfang, C.; **Lewis, S. P.**; Kennedy, J. P.; Collins, S. *Macromolecules*, **2007**, *40*(21), 7421-7423.

**Lewis, S. P.** US Patent Application *in progress* covering green IIR polymerizations (2008).

**Lewis, S. P.** US Patent Pending covering PFLAs (2008).

**Lewis, S. P.**; Kennedy, J. P.; Collins, S. US Patent 7,202,317 (2007).

**Lewis, S. P.**; Piers, W. E.; Collins, S. US Patent 7,196,149 (2007).

Vommerhaus, R.; Tomasszewski, R.; Pengcheng, S.; Nicholas, T. J.; Wiacek, K.J.; **Lewis, S. P.**; Al Humydi, A.; Collins, S. *Organometallics* **2005**, *24*(4), 494-507.

**Lewis, S. P.**; Henderson, L.; Parvez, M. R.; Piers, W. E.; Collins, S. *J. Am. Chem. Soc.* **2005**, *127*, 46-47.

**Lewis, S. P.**; Piers, W. E.; Taylor, N.; Collins, S. *J. Am.Chem. Soc.* **2003**, *125*(48), 14686-14687.

Huang, X.; **Lewis, S.**; Brittain, W. J.; Vaia, R. A. *Polym. Prepr.* **2000**, *41*(1), 589-590.

Huang, X.; **Lewis, S.**; Brittain, W. J.; Vaia, R. A. *Macromolecules* **2000**, *33*(6), 2000-2004.

***Robert T. Mathers*, Ph.D.**

Assistant Professor of Chemistry
Pennsylvania State University
New Kensington, PA 15068
rtm11@psu.edu
724-334-6741

Professor Mathers' areas of interest include integration of renewable resources and catalysis for the synthesis of polyesters and polyolefins. Dr. Mathers has conducted projects involving the replacement of petroleum solvents with renewable monoterpenes (*e.g.* limonene). His interest in green chemistry combined with his synthetic laboratory skills makes him a valuable asset in the completion of this project.

**PROFESSIONAL EXPERIENCE**

Assistant Professor of Chemistry, Penn State New Kensington, August 2004-present

Postdoctoral Research Associate, Cornell University, May 2002-May 2004
Department of Chemistry and Chemical Biology- Advisor: Professor G. W. Coates

**EDUCATIONAL BACKGROUND**

Ph.D., The University of Akron, May 2002
Department of Polymer Science- Advisor: Professor R. P. Quirk

B.S., North Carolina State University, May 1996
Department of Chemistry (Honors)

**SELECT PUBLICATIONS**

Mathers, R. T. Damodaran, K. Renewable chain transfer agents for metallocene polymerizations: The effects of chiral monoterpenes on the polyolefin molecular weight and isotacticity. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, in press.

Mathers, R. T.; McMahon, K. C.; Damodaran, K.; Retarides, C. J.; Kelley, D. J. Ring opening metathesis polymerizations in d-limonene: A renewable polymerization solvent and chain transfer agent for the synthesis of alkene macromonomers. *Macromolecules* **2006**, *39*, 8982 - 8986.

Mathers, R. T.; Coates, G. W. An efficient cross-metathesis functionalization of polyolefins. *Chem. Commun.* **2004**, 422-423.

Quirk, R. P.; Mathers, R. T.; Cregger, T.; Foster, M. D. Anionic synthesis of block copolymer brushes grafted from a 1,1-diphenylethylene monolayer. *Macromolecules* **2002**, *35*, 9964-9974.

**PATENTS**

Quirk, R. P.; Mathers, R. T. Polymerization of oxiranes with a lithium-containing initiator. U.S. Pat. Appl. Publ. 2005038227, 2005.

**SELECT CONFERENCE PROCEEDING**

Mathers, R. T.; McMahon, K. C.; Baker, J. R. Utilizing d-limonene as a polymerization solvent and chain transfer agent for ring opening metathesis polymerizations. *Polym. Mater. Sci. Eng.* **2007**, *96*, 842.

**SELECT PRESENTATIONS**

Spring 2007, ACS National Meeting, Chicago (Oral presentation)
October 2006, ACS Pittsburgh Polymer Group, Pittsburgh, PA (Invited talk)
November 2005, Ohio Inorganic Chemistry Meeting, Kenyon College, OH (Poster)
June 2005, Polymers (East) Gordon Research Conference, Holyoke, MA (Poster)

**SELECT GRANTS AND AWARDS**

ACS Petroleum Research Fund Starter Grant, 2005-2007
College Equipment Grant, Spectroscopy Society of Pittsburgh, 2005
ICI Student Award Symposium, ACS National Meeting, Chicago, Fall 2001
Hoffmann LaRoche Undergraduate Research Award, 1995

**PROFESSIONAL AFFLIATIONS**

American Chemical Society - Polymer Division
Spectroscopy Society of Pittsburgh
Society of Analytical Chemists of Pittsburgh

***Paul A. Deck*, Ph.D.**

Associate Professor of Chemistry
Virginia Polytechnic Institute and State University (Virginia Tech)
107 Davidson Hall, Mail Code 0212
Blacksburg, Virginia 24061
pdeck@vt.edu
540-231-3493

Professor Deck's research is divided into two areas. Since 1995, he has studied organometallic complexes (including metallocene olefin polymerization catalysts) that have cyclopentadienyl ($C_5H_5$ or Cp) ligands substituted with perfluorinated aromatic substituents. Since 2004, his group has undertaken a new program in fluoropolymers. All of his work involves fluoroaromatic chemistry and makes extensive use of NMR spectroscopy and inert-atmosphere synthetic techniques. Prof. Deck studied organic chemistry at University of Minnesota with Paul G. Gassman, organometallic chemistry at Northwestern University with Tobin J. Marks, and more recently, polymer chemistry with Klaus Muellen at the Max

Planck Institute for Polymer Research. His breadth of knowledge and depth of synthetic and spectroscopic expertise are invaluable to the proposed projects.

**PROFESSIONAL EXPERIENCE**
Director of Graduate Studies, Virginia Tech Chemistry Department, from July 2007.
Sabbatical, Max Planck Institute for Polymer Research (Mainz), January-May 2005.
Associate Professor of Chemistry, Virginia Tech, June 2002 to present.
Assistant Professor of Chemistry, Virginia Tech, July 1995 to May 2002.
NSF Postdoctoral Research Fellow, Northwestern University, July 1993 to June 1995.
Dow Postdoctoral Research Fellow, Northwestern Univ., December 2002 to June 1993.

**EDUCATIONAL BACKGROUND**
Ph.D. in Chemistry, University of Minnesota, June 2003. Advisor: P. G. Gassman.
B.S., *Summa Cum Laude* and First in Class, Hope College, Holland, Michigan, 1987.

**SELECT PUBLICATIONS**
"Perfluoroaryl-substituted cyclopentadienyl complexes of transition metals." P. A. Deck. *Coord. Chem. Rev*. **2006**, *250*, 1032-1055.

"Transition metal cyclopentadienyl complexes bearing perfluoro-4-tolyl substituents." P. A. Deck, B. D. McCauley, and C. Slebodnick. *J. Organomet. Chem*. **2006**, *691*, 1973-83.

"Synthesis, Structure, and Olefin Polymerization Catalytic Behavior of Aryl-Substituted Zirconocene Dichlorides." M. P. Thornberry, N. T. Reynolds, P. A. Deck, Frank R. Fronczek, A. L. Rheingold, and L. M. Liable-Sands. *Organometallics* **2004**, *23*, 1333-1339.

"Analysis of Metallocene-Methylalumoxane Methide Transfer Processes in Solution Using a $^{19}$F NMR Spectroscopic Probe." E. J. Hawrelak and P. A. Deck. *Organometallics* **2003**, *22*, 3558-3565.

"Highly Electrophilic Olefin Polymerization Catalysts. Quantitative Reaction Coordinates for Fluoroarylborane/Alumoxane Methide Abstraction and Ion Pair Reorganization in Group 4 Metallocene and 'Constrained-Geometry' Catalysts." P. A. Deck, C. L. Beswick, and T. J. Marks. *Journal of the American Chemical Society* **1998**, *120*, 1772.

**SELECT INVITED PRESENTATIONS**

"A Diels-Alder Platform for Highly Fluorinated Polyphenylenes." ACS Polymer Division Workshop Fluoropolymer 2006, Charleston, South Carolina, October 15-18, 2006.

"Aromatic C-F activation reactions using transition metal reagents." Pacifichem **2005**, Honolulu, Hawaii, December 15-20, 2005. Abstract 4144.

"Synthesis, structure and reactivity of perfluorinated tetracyclones." Pacifichem **2005**, Honolulu, Hawaii, December 15-20, 2005. Abstract 4351.

**SELECT FUNDED GRANTS AND CONTRACTS**
Sandia National Laboratories (Fluoropolymers), 2005-2006.
ACS Fluorine Division (Fluoropolymers), 2006.
ACS Petroleum Research Fund Type AC Grant (Fluoropolymers), 2006-2008
NSF Grant (Metallocene Catalysts), 1998-2003.
Research Corporation Grant (Metallocene Catalysts), 1998-2002.

**SELECTED AWARDS**
Alan F. Clifford Faculty Service Award, Virginia Tech Chemistry Department, 2007.
ACS Fluorine Division Henri Moisson Fellowship, 2006.

National Science Foundation Faculty Early Career Development Award, 1998.
Research Corporation Cottrell Scholarship, 1998.
National Science Foundation Postdoctoral Research Fellowship, 1993 - 1995.
National Science Foundation Graduate Fellowship, 1987 - 1990.
Almon T. Godfrey Senior Chemistry Award, Hope College, 1987.

**PROFESSIONAL AFFLIATIONS**
American Chemical Society – Organic, Inorganic, and Polymer Divisions

***Hiram Allen*, *Matrix Scientific***

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Matrix Scientific manufactures and supplies research and building block chemicals. The company was founded in 1999 by Hiram Allen as an outgrowth of other businesses Mr. Allen had been engaged in since 1965 with its main headquarters being located in Columbia, South Carolina. Since that time Matrix Scientific has become a dominate manufacturer/supplier of fine chemicals and currently offers more than 17,000 products. Many of these products are unique to Matrix Scientific alone. Due to their experience in the chemical industry, Matrix Scientific has the capability to supply materials in quantities ranging from grams to tons. Through the course of its business over the years Matrix Scientific has built up an extensive network of valuable contacts in both academia and industry. Matrix Scientific will play an integral role in the commercialization of the technology developed from this research effort.

## 6. Relationship with Future Research or Research and Development

Minor improvements to the synthesis of PFLAs can have a dramatic impact on the production of polyolefins. The current impediment to mass use of SSCs is the high cost of the activator.[7] Lower cost PFLAs will allow for SSCs to compete with and displace ZNCs. This translates into better quality polyolefins with a concomitant reduction in the environmental impact that production of these materials has. Current methods for production of PFLAs are energy intensive, polluting, and costly.

## 7. Facilities

ST has 625 square feet of space of dedicated laboratory facilities. The laboratory facilities contain 2 chemical fume hoods, a glove box, a solvent storage cabinet, an acid storage cabinet, multiple sinks, and ample benchtop and storage space. ST has an inventory of glassware exceeding $10,000 encompassing general use items (*i.e.* Erlenmeyer flasks) as well as specialized equipment (*e.g.* Schlenk ware). ST also owns a myriad of other laboratory items (including but not limited to) magnetic stirrers, rotary vacuum pumps, gas regulators, and balances. ST has walkup access to a number of state of the art analytical instruments at VT (5 miles from ST) required for successful completion of the project. A partial list of instrumentation includes: high precision liquid chromatography (HPLC), GC, GC-MS, FTIR, NMR. Dr. Lewis is trained and checked out in the use of most of these instruments.

Dr. Mathers has 1520 square feet of newly renovated laboratory space encompassing two rooms at Penn State, New Kensington. These laboratories contain a total of eight fume hoods each equipped with nitrogen, water, and vacuum inlets in addition to solvent storage base cabinetry. The laboratory facilities contain a wide variety of glassware and equipment required for organic, organometallic, and polymer synthesis. Additional specialized equipment includes vacuum manifolds fitted with mechanical and diffusion pumps, a glove box, and pressure reactors all of which are useful for air-sensitive chemistry. The laboratory also has a number of analytical instruments useful in characterization of small molecules and polymers including FTIR,UV/Vis, HPLC and GC.

## 8. Consultants

Professors Deck is a consultant for this project and his involvement is discussed throughout this proposal. Professor Mathers will serve as a subcontractor for part of the synthetic work involved in this project as outlined previously. Their participation although vital is limited to the consultancy/subcontractor role(s) due to restrictions placed on the number of hours they can work outside of their academic positions and also so that ST can retain full rights to the developed IP.

## 9. Commercialization Plan

Stewart's Technologies[12] is a privately owned company with its principal place of business at 3154 State St., STE 2300, Blacksburg, VA 24060. Its main concern is small scale-production (gram quantities) of PFLAs. These materials are offered for research and development purposes to both academic and industrial entities. Despite its size, ST offers the largest range of commercially available PFLAs. ST has provided materials to a number of renowned academic researchers and companies including.

1. Dr. Hans-Michael Walter, BASF Aktiengesellschaft
2. Dr. John Severn, Borealis Polymers Oy
3. Professor Maurice Brookhart, University of North Carolina
4. Professor Richard F. Jordan, The University of Chicago
5. Professor Geoffrey W. Coates, Cornell University

As a result of its activities, ST has attracted the attention of a number of chemical distributors. The most significant of these is Matrix Scientific, a leading supplier of fluorinated precursors used in the production of PFLAs. Due to extensive business dealings between the two companies Matrix Scientific has offered to market PFLAs produced by ST. Matrix Scientific has also agreed to supply fluorinated precursors at competitive prices in the industrial sized quantities required for full scale implementation of the developed IP. Matrix Scientific has also expressed interest in becoming intimately involved in future PFLA manufacture.

The commercial implications of the intellectual property developed from this research effort are far reaching. Polyolefins are the largest segment of the polymer industry[2,3] ($148 billion per year globally[4]) and global demand is projected to grow at > 5% per year. The polyolefin catalyst market in the U.S. alone is valued at > $2.8 billion with growth rate of 4-5% per year.[7c] Although SSCs make up only about 5% of this figure they are growing by 15-20% per year.[7b,c] A conservative estimate is that by 2009, 9% of all polyolefins will be produced using SSCs. [7b,c] Wide-scale implementation of SSCs has been prevented due to high activator costs[7] even though they produce superior quality polyolefins in a more efficient manner.[6] The chemistry developed from this research will lower activator cost by allowing the use of cheaper precursors in addition to reducing the overall environmental impact that such chemistry has on the environment. This will allow SSCs to effectively compete with ZN catalysts in such a cost sensitive market. Not only will this result in better grades of polyolefins at lower prices but it will reduce the strain that such activities have on limited petro-feedstocks through increased polymerization efficiency. The economic potential of SSCs is so great that > $4 billion[5a,b] has been spent on their research and development.

It should be recognized that even incremental improvements in the synthesis of PFLAs are of great value. With this in mind, ST will protect any developed IP with a patent filing. ST recently applied for its first patent filing on PFLA related chemistry in January 2007.[12b] This filing covers improved methods for making existing PFLAs and details new types of PFLAs (compositions of matter). This patent filing allows ST to offer a broader range of PFLAs than currently available at reduced cost giving it a competitive advantage. It should be mentioned in passing that licensing of patents covering SSC related technologies is becoming commonplace with license agreements running in the tens of millions of dollars.[6g] Due to the large size of the polyolefin market ST intends to make licenses of the developed IP available to interested entities to fully capitalize on it. A short list of potential licensees ranging from PFLA manufacturers to polyolefin producers are as follows.

1. ExxonMobil
2. Dow Chemical

3. DSM
4. Akzo Nobel
5. Albemarle
6. ChevronPhillips

ST has already conducted a thorough review of the scientific and patent literatures covering PFLAs to ensure that the proposed methodologies to be studied in Phase I have not already been disclosed publicly. It is estimated that the IP stemming from this research has the potential to cut current PFLA production costs by as much as 50%. Once a patent filing has been secured (possibly prior to securing Phase II funding) ST will begin to offer gram sized quantities (marketed through Matrix Scientific) of PFLAs for sale to both academic an industrial research communities. Within 5 years following the initial patent filing it is estimated that ST could capture a minimum of 40% of all R&D related sales of PFLAs. Following the initial patent filing ST will approach potential licensees (under the additional protection of a confidentiality agreement) and provide them with gram quantity samples of PFLAs. Depending on the level of interest ST will then enter preliminary talks with interested companies. If Phase II funding is awarded ST will begin production of PFLAs on a pilot plant scale using the developed IP. These materials will be marketed through Matrix Scientific for both research and commercial applications.

## 10. Cost Breakdown/Proposed Budget

### Proposal Summary Budget

**Organization and Address:** Stewart's Technologies, LLC
3154 State Street - Suite 2300
Blacksburg, VA 24060

**A. DIRECT LABOR (PI and other staff, list separately) Hours/Est. Rate:** $ 50,000
Stewart P. Lewis Principle Investigator 1000 hrs @ $50/hr

**B. OVERHEAD:** $ 20,000
Rate = 40% of direct labor.

**C. OTHER DIRECT COSTS: (list separately)** $ 15,000
Chemicals $10,000
Analytical Instrumentation $5,000

**D. TRAVEL: List purpose and individuals and or title** $ 0

**E. CONSULTANTS: (List Est. Rate and Hours)** $ 30,200
Paul A. Deck certification of analytical data 52 hrs @ $100/hr
Robert T. Mathers subcontract of synthesis work 500 hrs @ $50/hr

**F. GENERAL AND ADMINISTRATIVE:** $ 8,160
Administrative 72 hrs @ $30/hr
General $6,000

**TOTAL COSTS (Total of A thru F above)** **$ 123,360**

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## 11. Phase I Quality Assurance Statement (QAS)

Dr. Deck's primary functions are to provide expert consulting services to the Phase I effort. His expertise will be directed toward synthetic experimental design and troubleshooting, as well as assistance with the interpretation of analytical data. As such, his involvement fulfills a critical Quality Assurance role. The selected published articles listed in a previous section demonstrate his authority in the areas of perfluoroaromatic chemistry, especially as it applies to organometallic chemistry and catalysts. The close proximity of Virginia Tech to ST (five minutes by car) and Dr. Deck's availability and willingness to assist the proposed research program in an ongoing, consulting capacity should be construed as a unique coincidence that stands squarely in our favor.

Dr. Deck will play an integral part in leading the research to its ultimate objectives as summarized in the Phase I Objective section. In fact, he has already reviewed the proposed chemistry and helped us establish our initial research priorities. During the Phase I effort he will review all laboratory procedures prior to help us exclude potential safety hazards while optimizing the efficiency of the overall research effort. It is anticipated that he will consult to the project on a weekly basis and make recommendations on the basis of empirical findings and especially analytical (spectroscopic) data. Dr. Deck will evaluate the quality of work using existing data as summarized in the chemical literature in conjunction with his chemical expertise.

ST uses a stepwise approach for conducting quality research as follows. By following these guidelines in conjunction with Dr. Deck's expertise in spectroscopic analyses and troubleshooting of organometallic chemistry the ultimate goals of this project will be obtained.

1. Specific problems within large-scale petrochemical processes are identified and matched to ST's unique skill set. Problems may involve decreasing the environmental footprint of a process, increasing materials or cost efficiency, or establishing new, protectable intellectual property.
2. ST conceives novel materials and processes, which are duly recorded, witnessed, expertly reviewed, and secured in accord with best practices.
3. All research problems and novel conceptions are framed in a proper context of existing art by utilizing search engines provided by Chemical Abstracts Service, USPTO, and international patent and trademark organizations, in addition to publicly accessible library holdings at Virginia Tech (books, current journals).
4. When ST identifies a good match between an existing industrial problem and ST's unique skills and ideas, a research program is devised to apply ST expertise to solve that problem in the most efficient manner possible. ST's willingness to utilize external consultants in this process should be construed as a strength.
5. The research is carried out using standard best laboratory practices for safety, chemical hygiene, and notekeeping, including organization of analytical data.
6. Research progress is evaluated in an objective manner by comparison to reasonable benchmarks and by utilizing external consultants.
7. When a problem has been solved, the solution (IP) is either retained as a trade secret or is used to serve as the basis for a patent filing.

## 12. References

1. (a) Andrews, G. D.; Dawson, R. L. in *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G.; Kroschwitz, J. I. Eds.; Wiley: New York, 1985; Vol. 6, p 383-522. (b) Lieberman, R. B.; Barbe, P. C. in *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G.; Kroschwitz, J. I. Eds.; Wiley: New York, 1985; Vol. 13, p 464-531. (c) Strate, G. V. in *Encyclopedia of Polymer Science and*

*Engineering*, 2nd ed.; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G.; Kroschwitz, J. I. Eds.; Wiley: New York, 1985; Vol. 6, p 522-564.

2. (a) Galli, P.; Vecellio, G. J. *J. Polym. Sci., Polym. Chem.* **2004**, *42*, 396. (b) *2000 World Polyolefins Analysis*, CMAI: 2000.

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