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A STUDY OF THE SYNTHESIS AND REACTIVITY OF FLUORINATED
PHOSPHAZENES

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ABSTRACT

Polyphosphazenes have been studied extensively due to their wide range of unique properties. These polymers consist of an alternating phosphorous-nitrogen backbone and have been modified by a wide range of side groups to be useful in biomedical, electronic, and elastomeric applications, as well as others. The vast majority of these syntheses have relied upon poly(dichlorophosphazene) ($[\text{NPCl}_2]_n$) as the reactive intermediate to allow for the addition of the various substituents. These reactions are extremely complex, and it has become common practice to utilize hexachlorocyclotriphosphazene ($[\text{NPCl}_2]_3$), as a small molecule model for the high polymer reactions. However, these compounds have limitations, especially regarding substitutions with organometallic reagents. To overcome these limitations, it was hypothesized that a fluorinated version of these compounds might affect the reactivity in a way that would allow for substitution to occur with organometallic reagents. The fluorinated phosphazene compounds $[\text{NPF}_2]_3$ and $[\text{NPF}_2]_n$ were successfully synthesized and used as reactive intermediates in substitution reactions with trifluoroethanol (TFE), resulting in $[\text{NP}(\text{OTFE})_2]_3$ and $[\text{NP}(\text{OTFE})_2]_n$, respectively. These products were analyzed and confirmed by ^{31}P NMR. However, insolubility of the fluoropolymer in THF was still encountered at high molecular weights and only very low molecular weights of $[\text{NP}(\text{OTFE})_2]_n$ were recovered. Overall, the experiments performed and described in this thesis work provided important information about fluorinated phosphazenes, but there is still a lot of research to be done in order to take advantage of organometallic reagents and the unique properties they may bring to phosphazene materials.

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Chapter 1

Background

The field of phosphazene chemistry originated in the 1800s and since that time has provided unique solutions to scientific and technological problems by bridging organic and inorganic chemistry.¹ The earliest compounds were small, cyclic molecules of alternating phosphorus and nitrogen atoms. Larger rings and linear chains of various lengths have been discovered and utilized. In addition to having a common backbone, the compounds have two side groups on each phosphorus that can easily be varied.² This variation is the main contributor to the wide range of applications that have been discovered. Early research focused on the synthesis of halogenophosphazenes. This research was followed by a period that focused on the substitution of the halogens by organic groups (alkoxides, aryloxides, amines), generally through an S_N1 or S_N2 mechanism. Since the 1960s, the focus of phosphazene chemistry has shifted to the reactions and syntheses of the high molecular weight polymeric phosphazenes and their applications.³ Past research has focused mainly on the use of hexachlorocyclotriphosphazene ([NPCl₂]₃) and poly(dichlorophosphazene) ([NPCl₂]_n) as reactive intermediates. This has resulted in hundreds of unique compounds but some limitations have been reached, especially regarding the use of organometallic reagents. The experiments described in this thesis explore the feasibility of hexafluorocyclotriphosphazene ([NPF₂]₃) and poly(difluorophosphazene) ([NPF₂]_n) as alternative reactive intermediates.

Hexachlorocyclotriphosphazene

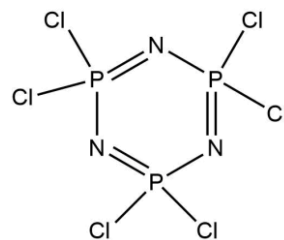


Figure 1: Hexachlorocyclotriphosphazene

Hexachlorocyclotriphosphazene (Figure 1) was one of the first phosphazene compounds to be discovered and has continued to be one of the most widely utilized small-molecule compounds in phosphazene research.² While commercially available as a crystalline solid, hexachlorocyclotriphosphazene ($[\text{NPCl}_2]_3$) is rarely used outside the role of a reagent in an organic substitution due to its hydrolytic instability.⁴ $[\text{NPCl}_2]_3$ is soluble in tetrahydrofuran (THF), as are many organic side groups. Therefore, solvent based substitutions are highly utilized preparation methods. The compound is useful in heat-induced ring-opening polymerization which results in the high molecular weight polymer.⁵ The cyclic trimers were instrumental in proving that the phosphorus-nitrogen backbone was robust enough to withstand substitution reactions without cleaving.⁴ There are some uses for the substituted small-molecule phosphazenes⁶⁻⁹ that result from reactions with $[\text{NPCl}_2]_3$, but they are largely used to model reactions that will be attempted on $[\text{NPCl}_2]_n$ if successful. While the reactivities of the small molecules and high polymers do not always align due to the differences in structural geometry, small molecules tend to be accurate in predictions involving relative rate, degree, and pattern of substitution.⁴

Poly(dichlorophosphazene)

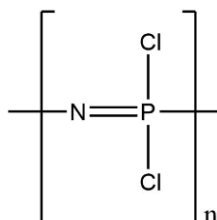


Figure 2: Poly(dichlorophosphazene)

Cyclic molecules are crucial to understanding the fundamental science of phosphazene chemistry, but the technological applications generally result from organic substitutions onto poly(dichlorophosphazene). (Figure 2) These substitutions have resulted in polymers with a wide variety of properties, finding applications in the fields of energy, biomedicine, and photonic materials. The phosphorus-nitrogen backbone provides flame resistance, making polyphosphazenes more suitable for fuel cells than the flammable organic electrolytes.¹⁰ Bio-erodible phosphazenes can be used for tissue engineering¹¹ or drug delivery¹² while bio-stable phosphazenes can be used as detection devices¹³ or cardiovascular materials.¹⁴ The range of substituents that can be bonded to the phosphorus of the backbone allows for the tuning of the refractive index of the materials¹⁵ and the creation of electroluminescent polymers.¹⁶ While these chemical properties are generally determined by the specific organic side group being used, polymers with a mixture of side groups can also be synthesized. In these cases, the ratio of the side groups can be used to control the mechanical properties of the polymers by adjusting the number of cross-linking side groups that are present.¹⁷ Organic-substituted polyphosphazenes have proven to be extremely diverse and useful, but there are still more possibilities to explore.

Fluorinated Phosphazenes

The surface has barely been scratched when it comes to studying organometallic reagents and phosphazenes. This is largely due to the significant chain cleavage that occurs during substitutions utilizing $[\text{NPCl}_2]_3$ and $[\text{NPCl}_2]_n$, breaking the bond between the nitrogen and phosphorus atoms. This leads to an undesirable final product and has deterred further research in the area. In order to avoid chain cleavage, some attempts have been made to use fluorinated phosphazenes with varying degrees of success. The chain cleavage is thought to be caused by a side group attacking the nitrogen as opposed to the phosphorus. Since fluorine is electron withdrawing, bonding it to phosphorus could make the phosphorus the more reactive center. There are a number of experiments that show successful substitution with $[\text{NPF}_2]_3$ ¹⁸⁻²⁵ (Figure 3) or slightly larger cyclic phosphazenes.²⁶⁻²⁸ However, many of these compounds are not fully substituted²⁹⁻³² and the remaining fluorine atoms will make them vulnerable to decomposition by hydrolysis. While these experiments can be used as a starting point, this complication still requires a solution to create a useful product. There have been a small number of attempts to react organometallics with $[\text{NPF}_2]_n$. (Figure 3) These were hindered by solubility issues with the fluoropolymer as it was only soluble in fluorinated solvents.³³ The synthesis method was extremely susceptible to cross-linking, rendering the fluoropolymer useless and insoluble, and had rather low yield if cross-linking was avoided. The low solubility of $[\text{NPF}_2]_n$ made creating a homogeneous reaction solution difficult, resulting in inefficient substitution. When substitution was successful, some differences in reactivity compared to the chloropolymer could be observed, but the conclusion was that the chloropolymer remained the superior reactive intermediate.³⁴

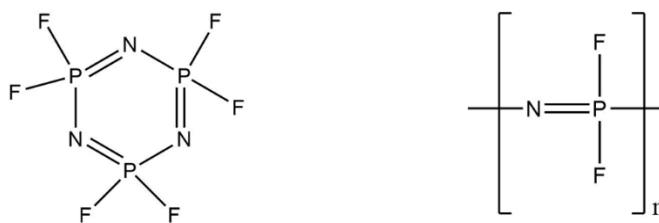


Figure 3: Hexafluorocyclotriphosphazene and Poly(difluorophosphazene)

The series of experiments described in this thesis pick up where the previously mentioned experiments left off. There is enough evidence in prior research to indicate the organometallic substitution with fluorinated polyphosphazenes might be successful. If this substitution can be completed, a whole new field of phosphazene chemistry could open with the potential to create materials with unique properties. Starting with the small molecules, these experiments were designed to study the difference in reactivity between the chlorinated and fluorinated phosphazenes. The ultimate goal of these experiments is to discover a method that would allow for organometallic side groups to be used with polyphosphazenes without chain cleavage. It was determined that a soluble version of $[\text{NPF}_2]_n$ was an imperative building block of the organometallic-phosphazene materials and the information regarding relative reactivities was gathered with that goal in mind. The following chapters describe the experiments that were performed and the results thereof.

Chapter 2

Hexafluorocyclotriphosphazene

Introduction

For years, hexachlorocyclotriphosphazene ($[\text{NPCl}_2]_3$) has been an important component of phosphazene research in that it is a useful reactive intermediate for substitution reactions that result in a multitude of different cyclotrimeric phosphazenes and is commercially available. It is also the precursor to poly(dichlorophosphazene) ($[\text{NPCl}_2]_n$), as it is able to undergo ring-opening polymerization to create high molecular weight compounds.³ Due to the chlorotrimer's importance in past phosphazene reactions, finding a synthetic route that consistently produced hexafluorocyclotriphosphazene ($[\text{NPF}_2]_3$) at a high purity was extremely important. A number of pathways were reported in the literature with various fluorinating agents^{35,36} or catalysts,³⁷ but the one explored in this experiment was originally reported by Seel and Langer in 1958.³⁸ This procedure was selected as it involved only two reactants, $[\text{NPCl}_2]_3$ and NaF, meaning it would likely be the simplest way to get the high purity product that was desired.

Experimental

Hexafluorocyclotriphosphazene. Hexachlorocyclotriphosphazene (28 g, 0.803 mol) was dissolved in dry acetonitrile (100 mL) under argon with gentle heating and stirring. 8 equivalents of sodium fluoride (27 g, 0.643 mol) were added to the mixture and gently refluxed ($\sim 80^\circ\text{C}$) for 24 hours while stirring. This resulted in a clear liquid with a white solid and a ^{31}P NMR was taken, confirming the presence of hexafluorocyclotriphosphazene. The mixture was purified by fractional

distillation under argon and the clear liquid product was collected at 45 °C. Slow cooling to room temperature resulted in clear, hexagonal crystals in liquid. Further crystallization was induced by slow cooling to 4 °C. Some liquid remained along with the crystals, so a cold vacuum filtration was used to remove excess solvent. The product (11 g, 55% yield) was sealed in an air-tight container and stored at -3 °C.

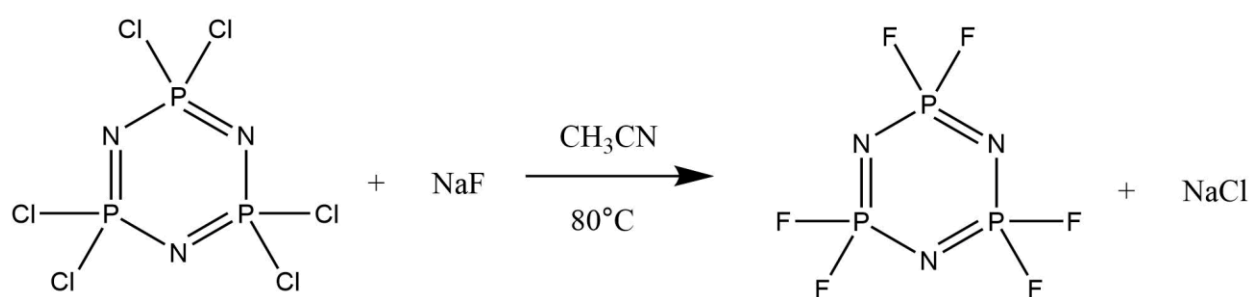


Figure 4: Hexafluorocyclotriphosphazene Synthesis

Results and Discussion

Although this synthesis route was taken directly from the literature,³⁸ it was important to confirm that it could be duplicated. A relatively small-scale reaction was run at first with a predicted yield of 20 g $[\text{NPF}_2]_3$. Due to the known sensitivity of $[\text{NPCl}_2]_3$ to moisture, the reaction was run under argon and a dry solvent was used to prevent decomposition that could lead to unwanted by-products. The $[\text{NPCl}_2]_3$ had a low solubility in the acetonitrile (CH_3CN), so a small amount of heat was required to fully dissolve the starting material. The sodium fluoride (NaF) was dried under vacuum prior to addition as the compound tends to be hygroscopic. Upon addition, sodium chloride (NaCl) precipitated quickly and settled to the bottom of the flask as a fine white powder. A ^{31}P NMR was taken at 162 MHz after about 24 hours of stirring at a gentle reflux

condition. (NMR 1, Appendix) This spectrum was dominated by a very distinctive splitting pattern of a triplet peak centered at about 11.08 ppm with multiplets due to long-range coupling. This was nearly identical to the splitting pattern of the known literature spectrum for $[\text{NPF}_2]_3$, although the literature had the peak centered at about 10.2 ppm.³⁹ Since the splitting aligned almost perfectly with the expected result due to fluorine coupling, this peak was determined to be the desired product. The difference in ppm shift could potentially be attributed to the calibration of the NMR. There were a few smaller singlet peaks in the negative ppm region that indicated a small amount of impurities, but the vast majority of phosphorus containing compounds in the reaction mixture were $[\text{NPF}_2]_3$.

Fractional distillation was selected as the purification method, as the melting point and boiling point of $[\text{NPF}_2]_3$ were reported to be about 30°C and 50°C, respectively.³⁶ A clear liquid began to condense at about 45°C which was lower than expected. This temperature held constant for a few hours before continuing to increase, at which point the distillation was ended. ³¹P NMR again confirmed the presence of $[\text{NPF}_2]_3$, so the boiling point depression was likely due to the simultaneous extraction of some CH_3CN . There was a high solvent concentration relative to the product and a small separation of boiling points (CH_3CN boils at 80°C), making full separation from a single distillation difficult. As the sample cooled to room temperature large, clear, hexagonal crystals began to form in the flask. To induce further crystallization and increase yield, the flask was put in the refrigerator to cool further. This process resulted in the formation of even more crystals so that the flask contained nearly pure solid. There was, however, a small amount of liquid remaining. The contents of the flask were vacuum filtered and briefly air dried to remove the remaining liquid, presumably CH_3CN . This process had to be performed quickly to minimize product loss, as it was observed that small crystals that remained stuck to the flask sublimed after

only a few minutes. The product was weighed, sealed, and stored in the freezer after confirming by ^{31}P and ^1H NMR that the product was pure $[\text{NPF}_2]_3$. Approximately 11 g of crystals were recovered, giving a percent yield of about 55%. Higher yields have been reported,³⁶ but the focus at the time was on successful synthesis of a highly pure product.

Since purity was the main goal and solvent came out with the product during distillation, other solvents were explored with the idea that a solvent with a higher boiling point could be found that would still facilitate the reaction. The higher boiling point of the solvent would allow for greater separation during distillation, eliminating unwanted liquid from the collection. Both dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were attempted as they have significantly higher boiling points than CH_3CN , but both reacted with the $[\text{NPCl}_2]_3$. The DMF quickly dissolved the $[\text{NPCl}_2]_3$ without heating, but the solution started turning yellow immediately and was a deep red color after only 15 minutes of stirring. The DMSO reacted even more quickly, having an exothermic reaction that resulted in a malodorous gas and a charred solid. These reactions clearly indicated that the tested solvents were not suitable for use in the synthesis of $[\text{NPF}_2]_3$ and CH_3CN remained the preferred solvent.

Conclusions

This experiment showed that the synthesis route proposed by Seel and Langer³⁸ for converting $[\text{NPCl}_2]_3$ into $[\text{NPF}_2]_3$ using NaF in CH_3CN is viable and that a high purity of product can be achieved. While the process proposed by Seel and Langer works well, there are still improvements that could be made before increasing the scale of the reaction. The largest area for improvement would be to find a solvent with a higher boiling point than CH_3CN so that greater separation of solvent and product can occur during distillation. DMF and DMSO were unsuccessful, but another solvent that could be tried would be propionitrile ($\text{CH}_3\text{CH}_2\text{CN}$) due to its similarity to acetonitrile. Until more solvents are tested and a better option is discovered, the synthesis route involving CH_3CN is the best option to produce $[\text{NPF}_2]_3$ for future reactions.

Chapter 3

Poly(difluorophosphazene)

Introduction

Nearly all of the past work involving polyphosphazenes relied on poly(dichlorophosphazene) as the reactive intermediate, but a brief attempt had been made to work with poly(difluorophosphazene).^{33,34,40} The synthesis of the material was modeled after the chlorinated polymer and therefore used ring-opening polymerization. However, this resulted in solubility issues, preventing the fluorinated polymer from being an effective intermediate. In order to create a soluble version of the polymer, a different approach was taken. Instead of trying to use ring-opening polymerization to increase the molecular weight, the fluorine was substituted directly onto poly(dichlorophosphazene). In this way, the fluorine was treated more like a side group and mirrored the synthetic procedure of the fluorotrimer as opposed to trying to mirror the polymerization technique.

Experimental

Poly(difluorophosphazene). Poly(dichlorophosphazene) was prepared by the thermal ring-opening polymerization of recrystallized and sublimed hexachlorocyclotriphosphazene in evacuated Pyrex tubes at 250 °C.⁵ Then poly(dichlorophosphazene) (1.0 g, 8.6 mmol) was dissolved in dry THF (75 mL) while stirring under argon. Once fully dissolved, 2.5 equivalents of

potassium fluoride (1.25 g, 21.5 mmol) were added and stirred under argon for 7 days, at which time the product was confirmed by ^{31}P NMR.

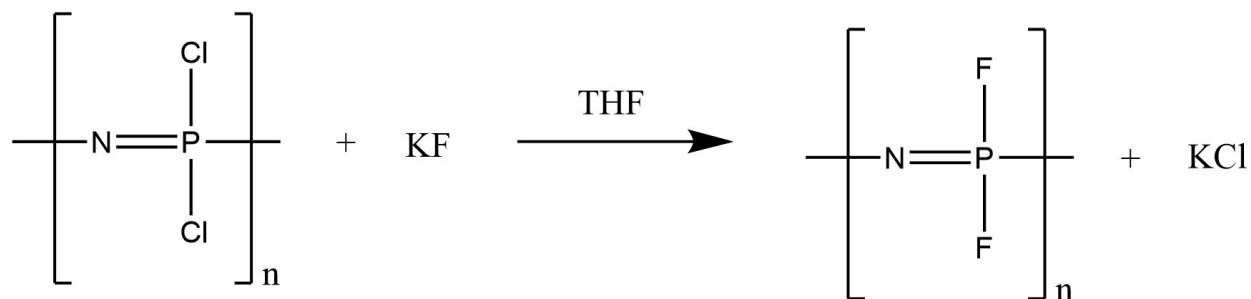


Figure 5: Poly(difluorophosphazene) Synthesis

Results and Discussion

Many phosphazene polymers are synthesized via thermal ring-opening polymerization from the cyclic trimer. However, when this method is used for fluorinated phosphazenes such as the ones in these experiments, the obtainable molecular weight is limited by cross-linking. If the polymer is heated for too long, it becomes insoluble in nearly all organic solvents, making it difficult to use as a reactive intermediate for further substitutions.³³ In order to make a useful version of poly(difluorophosphazene) ($[\text{NPF}_2]_n$) the polymer had to be soluble, so a different approach to the synthesis was taken. By starting with an uncross-linked chloropolymer, a method of substitution similar to that used in the synthesis of $[\text{NPF}_2]_3$ was used to create the soluble fluoropolymer. The route that was initially attempted directly mirrored the fluorotrimer synthesis, using CH_3CN and NaF . However, $[\text{NPCl}_2]_n$ is not soluble in acetonitrile or mixtures of acetonitrile and THF, so pure THF was used as the solvent to make sure the polymer was fully in solution. There were also some issues with using NaF as the source of fluorine atoms for the substitution.

The reaction with NaF took multiple days to run to completion and required constant heating to drive the substitution. The ^{31}P NMR spectra consistently showed unidentified impurities. In order to avoid these complications, potassium fluoride (KF) was used as the alkali halide. KF had greater solubility in THF due to the larger cation which reduced the impurities and eliminated the need for heat. If the reaction with KF was heated, the reaction time was also reduced, but it often resulted in rapid degradation of the polymer. Four equivalents of alkali halide were used initially but reducing the amount to 2.5 equivalents of KF still resulted in the fully substituted product, as confirmed by ^{31}P NMR. (NMR 2, Appendix) Therefore, using KF made the synthesis of poly(difluorophosphazene) more efficient.

While a soluble version of the fluoropolymer was synthesized, it could not be isolated. The potassium chloride precipitate formed a fine powder that could not be removed using standard filtration methods. This meant the product could not be removed from the solvent without being contaminated by other solid impurities. It was also noted that the fluoropolymer did not have a long shelf-life even in THF under argon, so it would likely degrade even more quickly once removed from the solvent. Being able to remove all impurities from the reactive intermediate would likely be helpful in having cleaner substitutions on the polymer and is something that should get attention in the future.

To learn more about the details of this reaction mechanism, the equivalents of KF were reduced further to 1 equivalent KF, which would theoretically result in a polymer that contained 50% fluorine and 50% chlorine bonded to the phosphorus. This reaction was run for 5 days without heat and progressed extremely slowly. At the end of the 5 days, the ^{31}P NMR still showed mostly the chloropolymer singlet with just a small peak of fluoropolymer triplets. (NMR 3, Appendix A) The spectrum was integrated which determined that not all of the KF had reacted since the

fluoropolymer peaks constituted less than half the total area under the polymer peaks. Another determination from this spectrum was that the fluorine substitutes onto the polymer in a geminal fashion. This conclusion was made because only one set of clear fluoropolymer triplets appeared in the spectrum instead of multiple broad sets. This indicates that there are sections of the polymer that are entirely fluorinated while others are entirely chlorinated instead of the halides being intermingled. This could have important implications down the road as this type of substitution may allow for selective substitution to create block copolymers.

Conclusions

Taking a new approach to the synthesis of halogenated polyphosphazenes resulted in the successful synthesis of a soluble version of poly(difluorophosphazene). Substituting directly onto the polymer and avoiding the use of heat appeared to play a major role in eliminating the cross-linking and degradation that had been seen in other methods. While CH_3CN and NaF were the best combination for the fluorotrimer synthesis, using THF and KF worked much better for the polymer. While the product could not be fully isolated, a soluble version was still created that can be used as an intermediate for further substitution reactions. It was also determined that fluorine substitutes onto $[\text{NPCI}_2]_n$ in a geminal fashion, which creates block polymers that could allow selective substitution, but that 1 equivalent of KF will not create a 1:1 ratio of fluorine to chlorine atoms in the polymer. All of this information will be helpful in continuing to explore the possibilities of $[\text{NPF}_2]_n$ as an intermediate.

Chapter 4

Trimer Reactions

Introduction

The aim of these experiments is to advance our understanding of phosphazene reactivity in order to create new phosphazene compounds with unique properties. While the polymeric phosphazenes will likely have the most impact, a lot can be learned from studying the reactions of small-molecule phosphazenes. In our lab, it has become established practice to preview reactions on the cyclic trimer before attempting the substitution on the polymer. While many aspects of the two reactions are the same, the substitution on the trimer tends to be more facile. The trimer has greater solubility due to its smaller size, and the size and orientation of the phosphorus atoms reduce steric hindrance among side groups. This means that if the substitution is not successful with the trimer, it will be nearly impossible to have a successful substitution on the polymer. The reaction with the trimer is also useful in determining the degree of substitution that can be achieved, although it may not translate exactly to the polymer.⁴ Performing initial experiments on hexachlorocyclotriphosphazene is a cornerstone of our lab's methodology, so it is important to explore if a similar procedure will work with hexafluorocyclotriphosphazene. This was determined using a comparison of trifluoroethoxide substitutions onto the chlorotrimer and fluorotrimer.

Experimental

Hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene. A powder of 60% sodium hydride in mineral oil (0.90 g, 22.5 mmol) was combined with dry THF (20 mL) by stirring under argon. While still stirring and in a water bath, 2,2,2-trifluoroethanol (2.25 g, 22.5 mmol) was added dropwise and allowed to react until the foaming stopped and a yellow-tinted translucent solution formed. In the meantime, hexafluorocyclotriphosphazene (0.75 g, 3 mmol) was dissolved in dry THF (20 mL) under argon. Once reacted, the 7.5 equivalents of sodium trifluoroethoxide was added to the fluorotrimer solution and stirred under argon. This resulted in an oily yellow precipitate, but the product was confirmed to be present in solution by ^{31}P NMR.

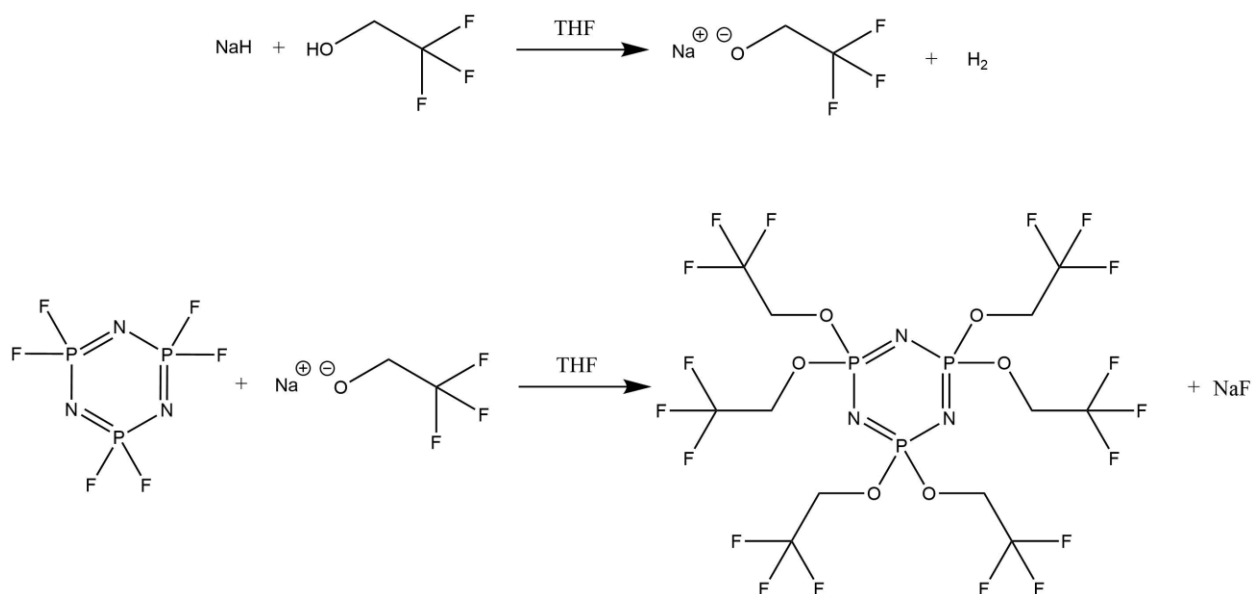


Figure 6: Fluorotrimer Reaction with NaOTFE

Results and Discussion

Trifluoroethoxy substituted phosphazenes are some of the most common phosphazene materials⁴¹ and trifluoroethoxide is one of the easiest groups to react with the chlorotrimer, so it was logical to attempt the substitution on the fluorotrimer. The comparison of reactions would determine if substitutions involving the fluorotrimer were feasible. The same reaction procedures that had been established for the chlorotrimer were followed, except the purified fluorotrimer crystals were used in place of the chlorotrimer. The two reactions were run side by side so that comparisons could be made and differences could be observed immediately. When adding the NaOTFE solution to the chlorotrimer, a white precipitate immediately formed in the reaction vessel. In the fluorotrimer reaction it took a few minutes for any sort of change to be visible, and when a change did occur, it was not a white powder. Instead, the precipitate took the form of an oily yellow substance. The precipitate of the chlorotrimer reaction was NaCl, which accounts for the white powder, and since the by-product of the fluorotrimer reaction is NaF, it is no surprise there are some differences. While pure, solid NaF is a white powder similar to NaCl, NaF has a slightly higher solubility in THF, which could give rise to the oily nature of the precipitate. The difference between being fluid and solid could also be the cause of the different colors that were observed.

The other major difference between the reactions was also observed almost immediately in association with the addition of NaOTFE solution. Both reactions are slightly exothermic, but the heat produced by the two reactions was slightly different. The chlorotrimer reaction seemed to produce the heat more quickly and to a higher degree, but it also subsided about as fast as it built up. The fluorotrimer reaction, on the other hand, heated up a bit more slowly and stayed warm for a longer period of time, never quite reaching the same maximum as the chlorotrimer reaction.

These are simply qualitative observations, as no temperature data was recorded during the experiment, but the fact that the experiments were side by side allows for a relatively accurate comparison. These observations of heat in conjunction with the difference in precipitation rates serve as an indication as to the relative rates of reaction. The precipitation may also be contributing to the rate, as the greater insolubility of NaCl may drive the reaction forward through Le Chatelier's principle. It seems that NaOTFE substitutes more quickly onto the chlorotrimer than it does the fluorotrimer. Despite these early differences, the ^{31}P NMR spectra produced by the products after a day of stirring under argon were identical, showing singlet peaks at 17.2 ppm. (NMR 4, Appendix). This is the expected shift and splitting for hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene,⁴² so TFE was successfully substituted on both the chlorotrimer and fluorotrimer.

Conclusions

While the reactions did not proceed in an entirely identical manner, the same product was achieved when either $[\text{NPCl}_2]_3$ or $[\text{NPF}_2]_3$ was used as the reactive intermediate. Some differences are to be expected when using fluorine instead of chlorine due to the change of size and electronegativity. Those differences were observed in rate of reaction and by-product formation. The fact that TFE substitution using the fluorotrimer as a reactive intermediate was successful is a promising indicator that other substitutions will also work. This reaction may also be particularly helpful in replacing any remaining fluorine atoms if the substitution is not complete, which will allow for the stabilization of more phosphazene compounds. The successful synthesis of hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene from $[\text{NPF}_2]_3$ is an important step towards creating novel phosphazene materials.

Chapter 5

Polymer Reactions

Introduction

Once the reactivity of the fluorotrimer had been established, the next step was to determine if the fluoropolymer behaved in a similar fashion. The successful substitution of fluorine with trifluoroethoxide would be an important step toward creating novel polyphosphazenes from poly(difluorophosphazene). The halogenated phosphazenes tend to be unstable and decompose when exposed to moisture.³ Replacing fluorine with trifluoroethoxide would stabilize the material, and if full substitution with TFE is possible, it could be used to stabilize polymers with organometallic side groups that did not fully substitute. Due to the instability of poly(difluorophosphazene), it is helpful to synthesize poly[bis(trifluoroethoxide)phosphazene] in order to determine the molecular weight of the polymer. The reaction of sodium trifluoroethoxide with poly(dichlorophosphazene) is fairly common,⁴¹ so the substitution with poly(difluorophosphazene) provides another important comparison of the reactivities.

Experimental

Poly[bis(trifluoroethoxy)phosphazene]. Poly(difluorophosphazene) (0.713 g, 8.6 mmol) was synthesized via the route described in the previous pages. As soon as full substitution was confirmed by ³¹P NMR, trifluoroethanol (2.15 g, 21.5 mmol) was slowly added to a solution of

dry THF (20 mL) and 60% sodium hydride in mineral oil (0.860 g, 21.5 mmol). This mixture was stirred under argon until the solution turned clear, indicating a completed reaction. This solution of 2.5 equivalents of sodium trifluoroethoxide was then added dropwise to the polymer reaction vessel and stirred under argon overnight. The ^{31}P NMR spectrum indicated full substitution onto the polymer. To isolate and purify the poly[bis(trifluoroethoxy)phosphazene] product, the solution was diluted with THF and filtered through 315 paper to remove the solids that had precipitated. The volume of the mixture was reduced by rotary evaporator until a small amount of viscous solution remained. This solution was slowly precipitated into water to extract the polymer, which was then left to dry. The final result was 0.31 g (17% yield) of a yellowish polymer.

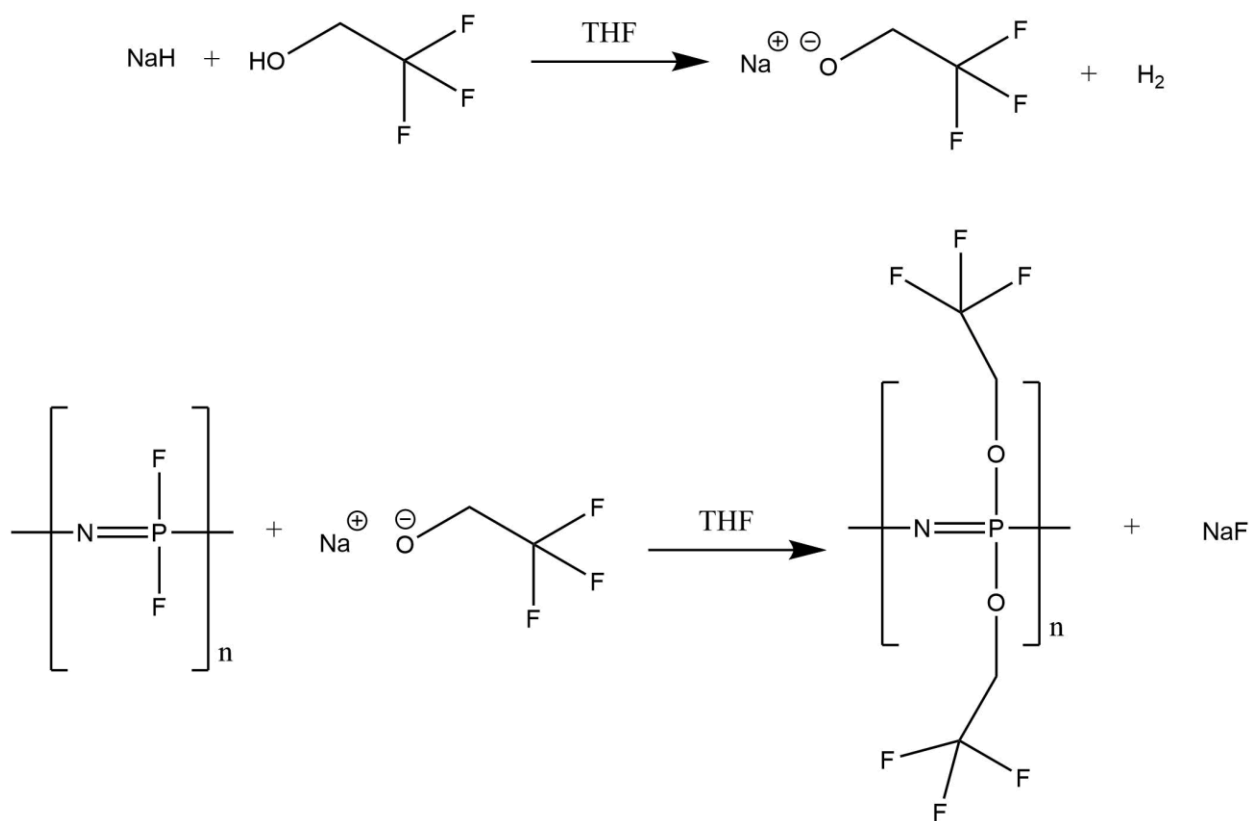


Figure 7: Fluoropolymer Reaction with NaOTFE

Results and Discussion

It proved to be rather difficult to get a reasonable yield from this reaction as many adjustments had to be made between attempts. The first attempt tried to use fluoropolymer synthesized via NaF, which had too many impurities in the intermediate solution to have a clean reaction. After optimizing the fluoropolymer synthesis with KF to have no phosphorus impurities, the substitution was attempted again, this time reaching the work up procedure. However, when this polymer was precipitated in water, only fine powder came out, indicating that only an undesirable, low molecular weight had been recovered. A number of problem areas were identified, including old chloropolymer, waiting too long between fluoropolymer synthesis and the addition of TFE, potential exposure to excess moisture, and impurities in the KF. Any combination of these issues could have led to the chain cleavage that was observed, and all of them were remedied in the next attempt. A fresh batch of chloropolymer was used for fluoropolymer synthesis, as well as a new source of KF that had been dried thoroughly under vacuum and heat. The TFE solution was added as soon as the entire chloropolymer peak had disappeared from the NMR to prevent any possible decomposition. The ^{31}P NMR indicated complete substitution of TFE (NMR 5, Appendix), but there were some impurities and the recovered polymer was still very low molecular weight.

During the work up process, small strands of polymer precipitated into the water, but only enough to provide 17% of the theoretical yield by mass. The polymer was very sticky, indicating the molecular weight was still relatively low, and the water solution was cloudy, meaning some even smaller molecular weight product was dispersed in the water and could not be recovered. In an attempt to determine where the remainder of the polymer mass went, the solid that had dried on the filter paper was dissolved in THF. The ^{31}P NMR indicated significant amounts of the TFE

polymer were stuck on the filter paper. However, when the filtered solids were dissolved in THF and precipitated into water, the only solid recovered from the water was pulp from filter paper that had stuck to the solids.

Another experiment was set up following the same conditions in order to attempt a new method of purification and extraction that didn't involve filtration. The salt impurities should be soluble in water, so they should dissolve as the polymer precipitates. However, the TFE was never added to the reaction mixture due to complications with the synthesis of the fluoropolymer. During this attempt at the reaction, the fluoropolymer peak never appeared in the NMR, even after heating. The reaction mixture continued to get more viscous until a solid starting to coagulate, which is theorized to be the fluoropolymer. The molecular weight of the polymer used in this last attempt was higher than the previous batches since less catalyst was used during the polymerization process. The insolubility of products from high molecular weight reactants indicates that the molecular weight of the poly(difluorophosphazene) is the limiting factor in solubility. This is in contrast to earlier conclusions that cross-linking or method of preparation was the cause of fluoropolymer insolubility.

Conclusions

While the desired poly[bis(trifluoroethoxide)phosphazene] was successfully synthesized and recovered to a degree, a number of significant complications in the process indicate that there is more work to be done. Impurities, chain cleavage, and low yield make this an inefficient synthesis route for a product that already has a well-established mechanism through $[\text{NPCI}_2]_3$. However, this substitution experiment pointed out flaws in earlier steps that still need to be reconciled. The challenge of synthesizing and dissolving a high molecular weight $[\text{NPF}_2]_n$ remains, but once this hurdle is cleared, TFE substitution may still be possible.

Chapter 6

Conclusions and Further Research

Final Conclusions

While the ultimate goal of organometallic substitution onto a polyphosphazene was not achieved, many important foundational experiments were performed that resulted in important insights towards that goal. A relatively simple synthesis and purification of $[\text{NPF}_2]_3$ was developed. This resulted in a number of observations regarding the product, most notably its tendency to sublime at room temperature. Reactions involving the fluorotrimer provided information about the relative reactivity of the chlorinated and fluorinated small-molecule phosphazenes. While the fluorotrimer may be slightly less efficient than the chlorotrimer, the substitution reaction with TFE will still result in the desired product.

The experiments resulted in important developments towards creating a soluble version of poly(difluorophosphazene). At low molecular weights, this synthesis was successful, but as the molecular weight of the $[\text{NPCl}_2]_n$ increased, the solubility of the synthesized $[\text{NPF}_2]_n$ in THF decreased. This solubility trend is similar to the fluoropolymer previously synthesized by heat-induced ring-opening polymerization. However, the results indicated that molecular weight is the greatest predictor of insolubility as opposed to degree of cross-linking, as previously thought. The substitution experiments with the fluoropolymer showed that the synthesis of poly[bis(trifluoroethoxide)phosphazene] from $[\text{NPF}_2]_n$ is possible when the fluoropolymer is

soluble, but there is still work to be done to perfect the extraction and purification process. The molecular weight needs to be increased for a useful product to form, which can be improved by continued work on the initial fluoropolymer synthesis. With further research and experimentation, it seems plausible that organometallic reagents could be used in combination with phosphazenes to create new materials.

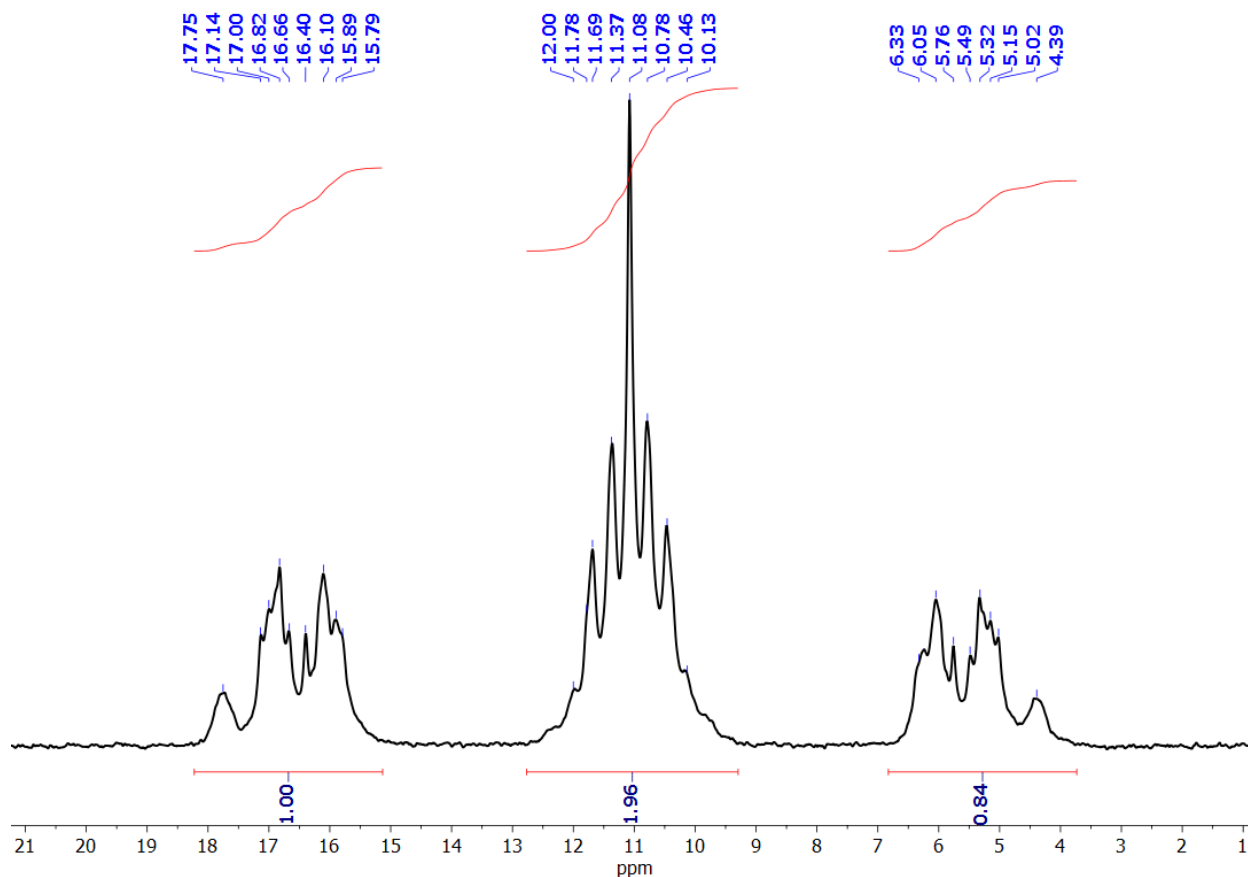
Suggestions for Future Work

There are still a lot of improvements that can be made to the synthesis procedure and a number of different options to explore before organometallic phosphazene materials can be produced. Fluorotrimer reactions with organometallics such as organolithiums and Grignard reagents are an important next step. In order to truly integrate organometallic reagents into phosphazene materials, it is imperative to synthesize a soluble version of the fluoropolymer. It was already shown that increasing the size of the ion in the fluorinating agent can result in cleaner substitution by comparing results from NaF and KF experiments. This means that cesium fluoride has the potential to continue that trend and may result in an even better product. The solution to the solubility conundrum could lie in the solvent as opposed to the product. It has already been shown that select fluorinated solvents can dissolve the fluoropolymer, so a further exploration of solvents could be performed. Another possibility is that the siliconized coating on the glassware is reacting with the polymer, either directly or via hydroxy groups. This would degrade the polymer and result in unsuitable products. To avoid this, specialized reaction vessels coated in Teflon or other fluorinated compounds could be helpful.

There are other methods of polymer synthesis that could potentially be exploited. While heat-induced polymerization has already been attempted on $[\text{NPF}_2]_3$, new polymerization methods using high pressure could be viable options.⁴³ As long as the reaction chamber can be kept sufficiently cold the low melting point of the fluorotrimer should not be an issue. There have already been a number of successful organometallic substitutions with the $[\text{NPF}_2]_3$,²⁶⁻²⁸ so it may also be possible to synthesize the small molecules and then perform the heat-induced ring-opening polymerization. However, the specific side group being used could easily cause unforeseen complications in this process. There are many other possibilities to explore that may yet result in polyphosphazenes with organometallic side groups.

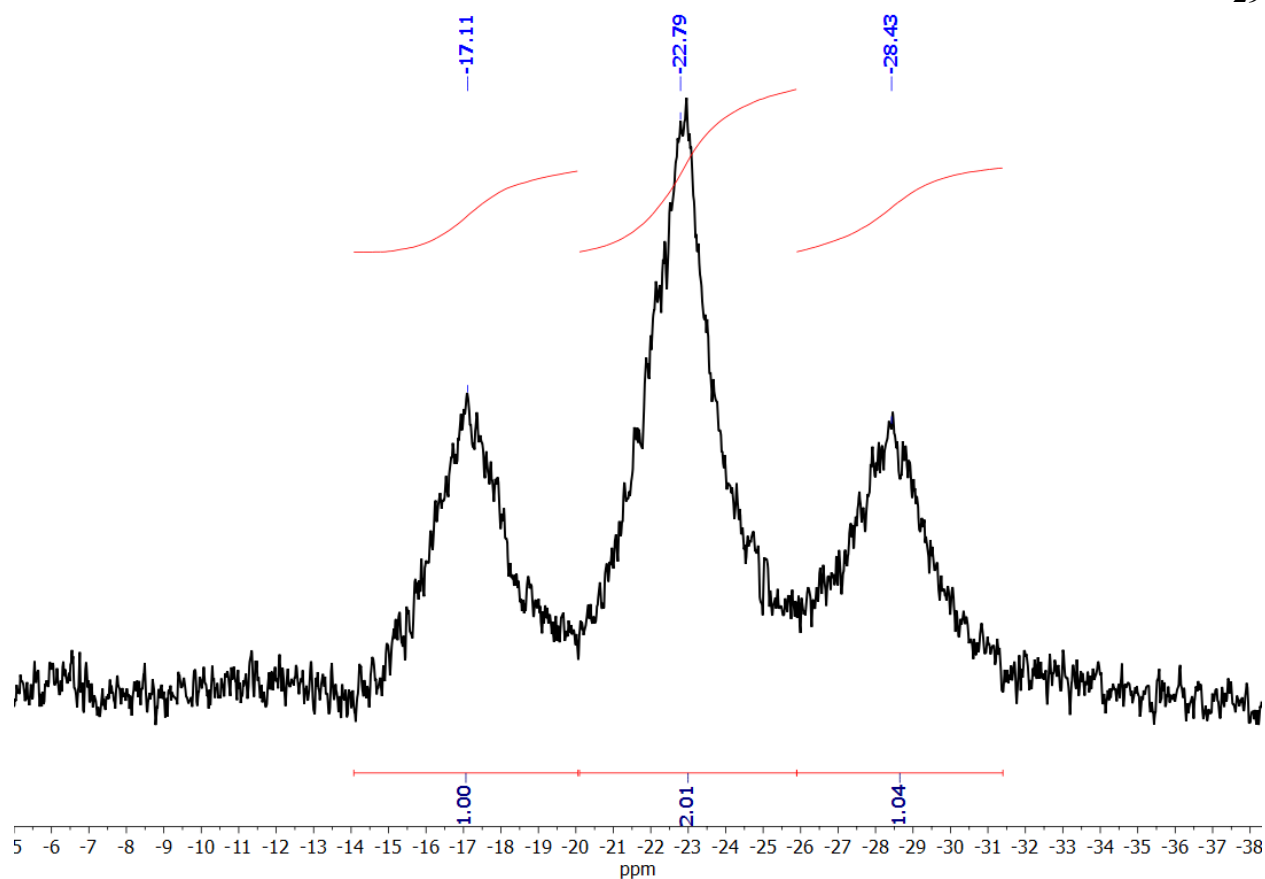
Appendix

Nuclear Magnetic Resonance (NMR) Spectra



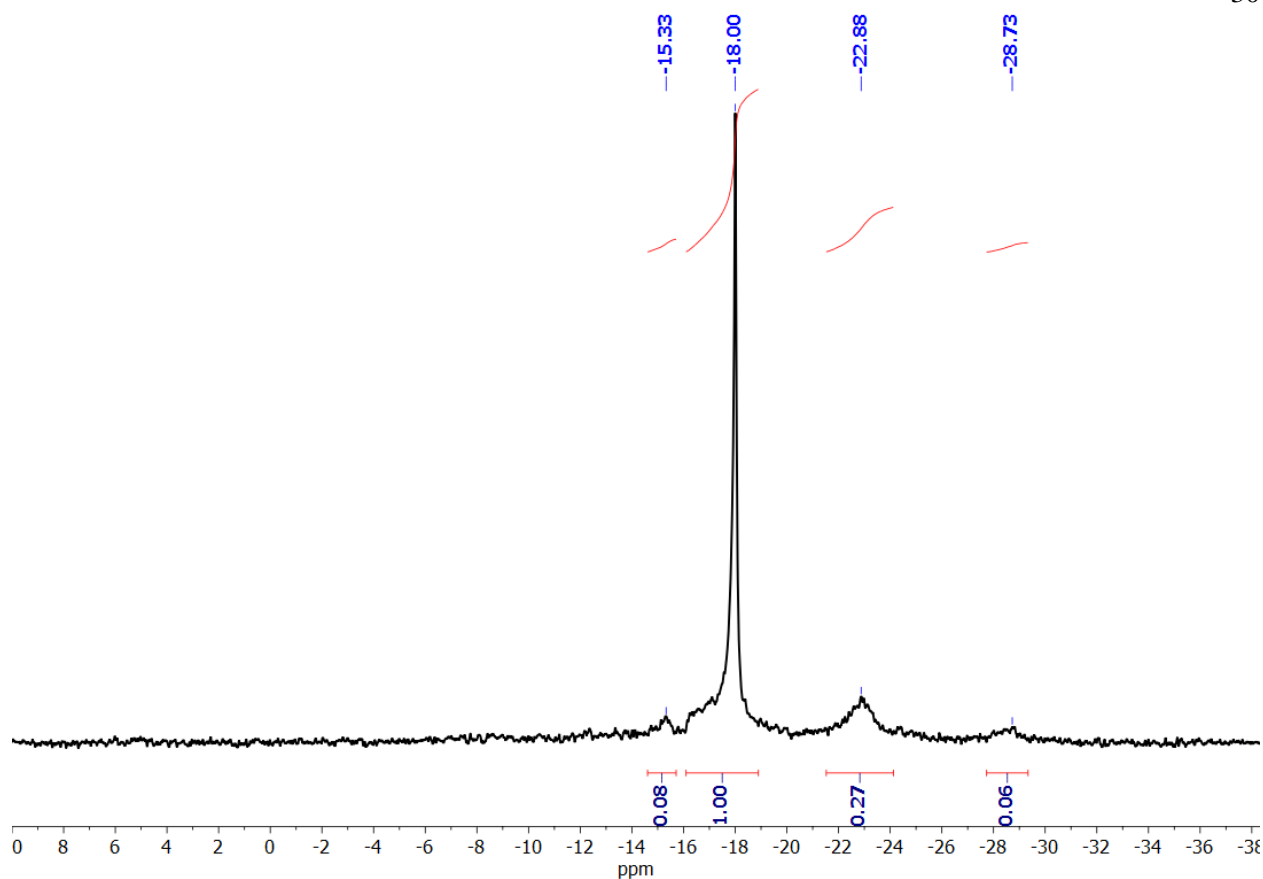
NMR 1: Hexafluorocyclotriphosphazene (31P)

This is the spectrum obtained from the crude reaction mixture showing the product of $[\text{NPF}_2]_3$. The distinguishing feature is the triplet of multiplets centered at 11.08 ppm with a J value of about 5.5 ppm and a 1:2:1 integration pattern. This indicates strong coupling from two fluorine atoms adjacent to a phosphorus atom. The multiplets likely come from long-range coupling due to the cyclic nature of the compound. This closely agrees with the spectra from previous literature.³⁹



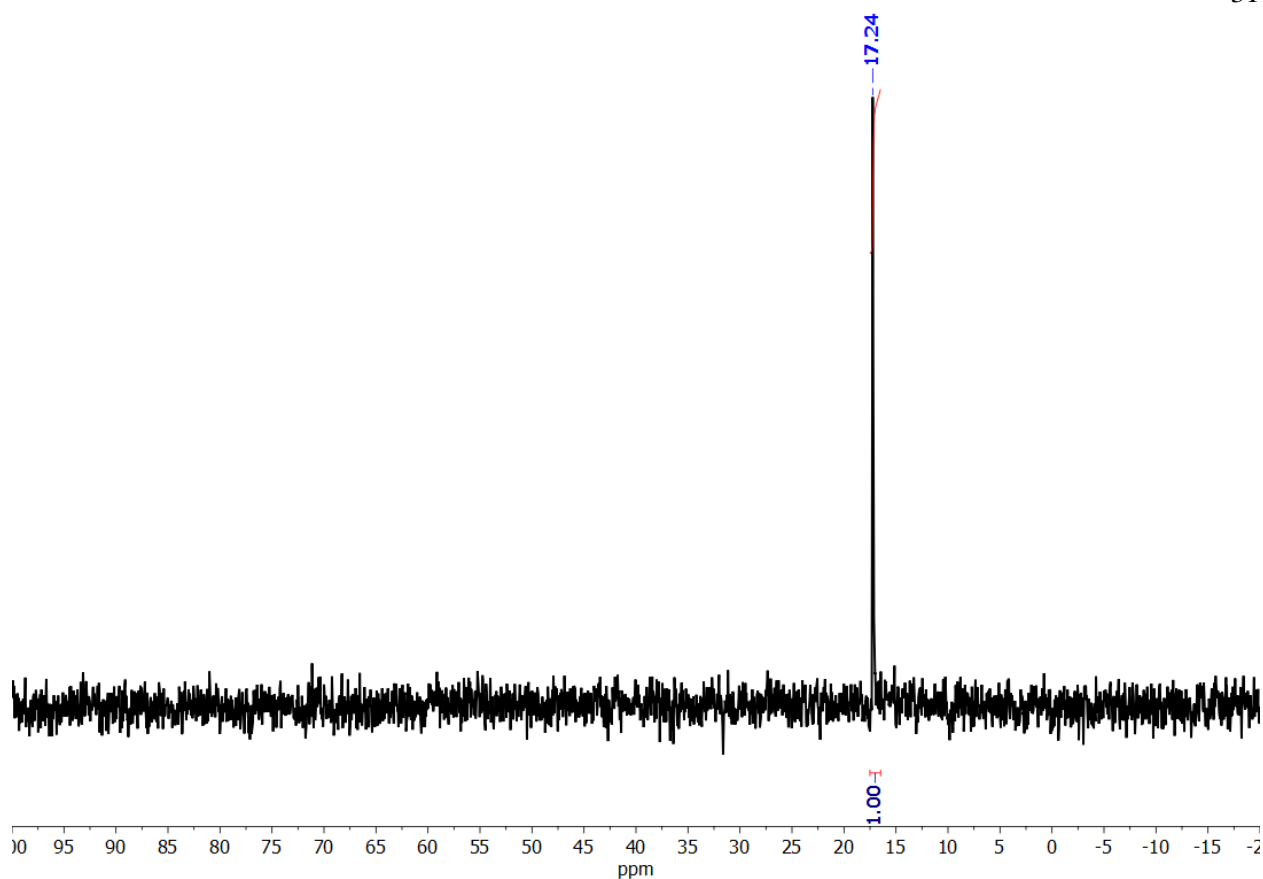
NMR 2: Poly(difluorophosphazene) (31P)

This spectrum shows the $[\text{NPF}_2]_n$ product. The characteristic triplet of multiplets in a 1:2:1 integration ratio remains, but has shifted upfield due to greater shielding. This is a similar shift as that observed between $[\text{NPCl}_2]_3$ and $[\text{NPCl}_2]_n$ and the center peak appearing at about -23 ppm is shown in prior literature.³³ The polymeric nature makes the difference between phosphorus atoms less distinct and has room for greater natural variation in the product, which leads to the broadening of peaks and decrease of separation in long-term coupling peaks.



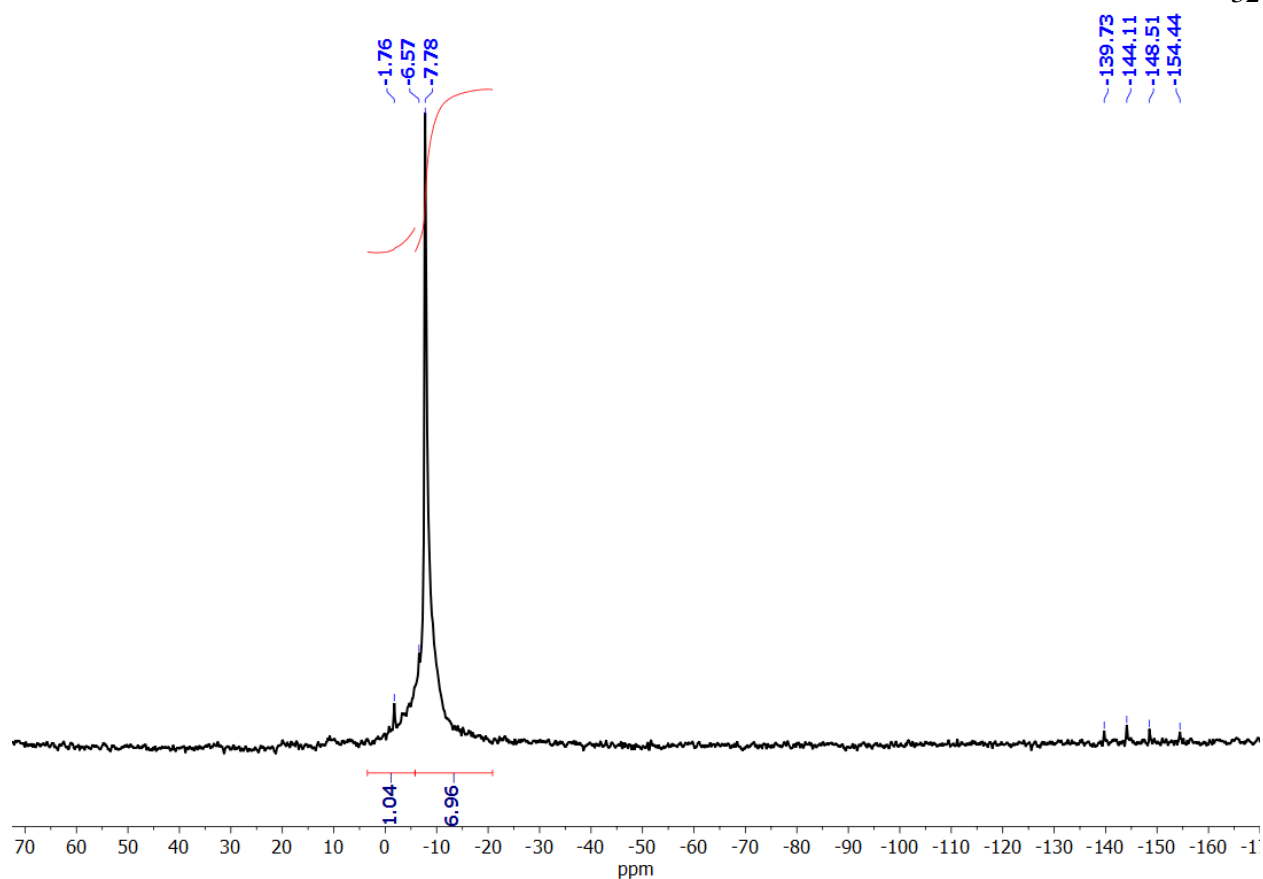
NMR 3: Partially Fluorinated Chloropolymer (31P)

This spectrum shows distinct patterns that relate to both $[\text{NPCl}_2]_n$ and $[\text{NPF}_2]_n$ with peaks at -18 ppm and -22 ppm, respectively. The product being tested was from a reaction that only utilized 1 KF molecule for every chlorine atom present on the polymer, meaning the integration ratio of $[\text{NPCl}_2]_n$ to $[\text{NPF}_2]_n$ was expected to be 1:1. However, the ratio is closer to 2:1, which means there is a significant amount of KF that is not reacting with the chloropolymer.



NMR 4: Hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (31P)

This spectrum shows the expected singlet for $[\text{NP}(\text{OTFE})_2]_3$ at 17.2 ppm.⁴² The result was independent of starting material as the spectra were identical for the products starting from $[\text{NPCl}_2]_3$ and $[\text{NPF}_2]_3$.



NMR 5: Poly[bis(trifluoroethoxide)phosphazene] (31P)

This spectrum shows the expected singlet for the TFE polymer at -7.5 ppm, with slight impurity peaks at -1.8 ppm and -146 ppm. These impurity peaks were not present after filtration and precipitation of the polymer. Again, note that the polymer signal is wider than the signal from the equivalent trimer.

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