IMPROVEMENTS OF SYNTHESIS OF PHOSPHAZENE
TRIMERS AND POLYMERS AND ATTEMPTS TO
MAKE AN IPN OF A PHOSPHAZENE

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IMPROVEMENTS OF SYNTHESIS OF PHOSPHAZENE TRIMERS AND POLYMERS AND ATTEMPTS TO MAKE AN IPN OF A PHOSPHAZENE

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DEDICATION

To my dad, Robert Maresh, for instilling his strength and perseverance in me. For all his sacrifice of time to allow me to focus and accomplish my goal.
    I appreciate and love you very much.

To my children,
    David Frame and Morgan Murray for their unconditional love and understanding the importance of having an aspiration.
    I appreciate and love you both very much.

And to Donna Ross and Lisa Zickefoose
    for their generosity and encouragement.
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CHAPTER I

INTRODUCTION

I. Phosphazenes

Cyclophosphazenes and polyphosphazenes are of great interest. Phosphazenes have alternating phosphorus and nitrogen atoms in the backbone of their structure. In the polymer, the backbone contains subunits of (-P(R)₂=N-)ₙ all through the polymer. Phosphazenes can vary in size from oligomers to very large polymers. In 1895, Stokes was the first to suggest that [PCl₂N]₃ was cyclic.¹ [PCl₂N]₃ is used to generate [P(OPh)₂N]₃ and [P(OCH₂CF₃)₂]₃, which is produced by nucleophilic substitution. [PCl₂N]₃ can undergo a ring opening polymerization by heating it in the range of 210°C to 250°C and [PCl₂N]ₙ is formed.² In the figure below (Figure 1) [PCl₂N]₃ and [PCl₂N]ₙ are shown. [PCl₂N]ₙ contains trivalent, dicoordinate nitrogen and the phosphorus atom is pentavalent and tetracoordinate. The nitrogen atoms don’t have any substituents, whereas the phosphorus contains two. The two chlorine atoms attached to each phosphorus atom can be replaced by nucleophilic substitution. These substituents can be another halogen, aryl, alkyl, alcohol, and an amine groups.
Phosphazenes have a variety of important applications. The presence of phosphorus and nitrogen in the backbone of phosphazenes is what enables flame retardant properties. The nature of the alkyl group that is attached to the phosphorus, and the high oxidation state of the phosphorus provides flame retardant properties. In organic polymers systems the addition of phosphorus compounds is an effective way to decrease the flammability of the system. Phosphazenes are great flame retardant compounds because they can contain halogens, phosphorus and nitrogen which helps to suppress the flame. 

$[\text{P(OCH}_2\text{CF}_3\text{)}\text{N}]_n$ and $[\text{P(OPh)}_2\text{N}]_n$ are now being produced as high performance elastomers. Polyphosphazene elastomers are being used in ground and sea transportation, aerospace applications, and in the field of biomedicine. 

The structures of polyphosphazenes are usually atactic, but can be isotactic or syndiotactic. These sequences favor efficient intermolecular chain packing and microcrystalite formation. The random distribution of two or more different side groups will discourage crystallization and favor elastomeric characterization. Most are synthesized by macromolecular substitution, but there are limitations to this mechanism. The distribution of side groups depends on the steric and electron direction characteristics.
of incoming groups and side groups already present. All nucleophiles will not work. If
there is steric hindrance, only a partial replacement of the chlorine will occur, while
others will be less hindered substituents. 7

Nucleophilic substitution, appears to proceed by a $S_N2$ mechanism (Bimolecular
associative pathway) is the best way to define both cyclic mechanisms. 7 There are two
possible transitional states involved. The first state is a formation of a neutral five-
coordinate phosphorus intermediate proceeded by expulsion of the leaving group. The
second is a concerted $S_N2$ mechanism involving a polar transition state similar to that
found in carbon systems. In both pathways, four coordinate phosphorus is transformed to
a five coordinate state before reverting back to the four coordinate state. 7

Allcock began his studies with a ring opening polymerization (ROP) of $[\text{NPCl}_2]_3$
at 250°C in a vacuum. 2 This was conducted only to a 70% completion otherwise the
polymer would cross-link and become an insoluble rubber. The ionic conductivity of the
molten $[\text{NPCl}_2]_3$ rises suddenly, simultaneously with the initiation of the polymerization.
It has been postulated that the initiation occurs by a heterolytic cleavage of the P-Cl bond
to generate a phophazenium ion. The high electrophilicity of the phosphazenium ion
results in the propagation of the reaction to obtain the polymer. The molten state favors
intermolecular reactions to yield the polymer. The phosphazenium ion can now attack a
skeletal nitrogen atom of another $\text{N}_3\text{P}_3\text{Cl}_6$ causing ring opening and chain growth. This is
where a nucleophile such as water or a Lewis acids is helpful to catalyze the reaction. 7
The problems with this approach include undesirable waste products, tedious synthesis
extensive purification of the starting material, long reaction times branching, product
polydispersity and bimodal molecular weight distributions. This is why a need for better
synthesis has been investigated.

II. Interpenetrating Polymer Networks (IPNs)

IPNs consist of a mixture of two interpenetrating polymers that are cross-linked to some degree. There are three types of IPNs. If both polymers are covalently cross-linked within the matrix, a full IPN is formed. If only one polymer is covalently cross-linked, it is called a partial or semi IPN. If the cross-links of a semi IPN are due to vanderWaals interactions rather than covalent bonds, an apparent IPN results. In all IPNs the cross-linked structure prevents the separation of the two different polymers and prevents domain formation. In a semi or apparent IPN the segregation process of the polymers is retarded because one polymer is intertwined and trapped within the matrix of the first. In an IPN, the property of one polymer is to enhance properties of the other. The type of IPN that was examined in this thesis is a semi- or apparent IPN.

The first step in the synthesis of known phosphazene apparent-IPNs usually involves taking a phosphazene polymer and adding the monomer of an organic polymer. The organic monomer is then polymerized to give the apparent-IPN.

III $^{31}$P NMR and other NMR characterization

Factors that will influence $^{31}$P are the coordination number of phosphorus, the electronegativity of the substituents bonded to the phosphorus and the bonding between phosphorus and its substituents. The more electronegative the substituent attached to phosphorus most of the time the more downfield the chemical shift. This is due to the deshielding of the nuclei. The electronegativity of substituents is related also to the coupling. The less electronegative the lower the $^2J(P-P)$. The J couplings for
phosphazenes are related to the oxidation state of phosphorus. These factors include the geometrical disposition of substituents attached to phosphorus and the nature of the substituents on the third phosphorus atom not involved in the coupling. The latter does not need to be considered further because all substituents are the same in the phosphazenes described herein.

\(^{13}\)C NMR has particular factors including the relationship between polarizability and magnetic susceptibility. The charge on the carbon atom also has influence on the spectra. There is no direct correlation, but it needs to be considered.

IV Thesis work

The cyclic compounds, \([\text{P(OPh}_2\text{)}_2\text{N}]_3\) and \([\text{P(OCH}_2\text{CF}_3\text{)}_2\text{]}_3\), were studied before the polymers to use as models to understand and implement the polymeric system. These compounds were synthesized and completely characterized. On the other hand the polymers were more complicated and not completely understood. The creation of a new IPN system involving the \([\text{PCl}_2\text{N}]_3\) to open up into the polymer and intermix with polypropylene was also investigated.
CHAPTER II

EXPERIMENTAL

General Considerations

Unless otherwise stated, all preparations and reactions were performed using standard anaerobic techniques.\(^4\) All were in an inert atmosphere of nitrogen gas utilizing a polyethylene glove bag, glove-box or a Schlenk line.\(^5\) All chemicals used were reagent grade. Benzene and tetrahydrofuran were distilled under nitrogen from sodium benzophenone ketyl. \([\text{PCl}_2\text{N}]_3\) was obtained from ICN Biomedical Inc. and was sublimed before use. Trifluoroethanol was dried with calcium sulfate and sodium bicarbonate. Hexane, toluene, HCl and phenol were all used as received. All glassware was dried in an oven overnight. Fast atom bombardment (FAB) mass spectra were acquired from a modified Micromass AutoSpec mass spectrometer. Data for \(^1\)H and \(^{13}\)C spectra were referenced to residual protons and \(^{13}\)C nuclei of the solvent. \(^{31}\)P NMR spectra were referenced to external 85% \(\text{H}_3\text{PO}_4\) solution and \(^{19}\)F NMR spectra was referenced to external trifluoroacetic acid. All spectra were obtained on a Gemini 300 MHz instrument. All the equipment used in the compounding and flame retardant
evaluations portion were supplied by A. Schulman Inc. This equipment includes C W Brabender, Atlas HVUL Chamber (UL-94), Perkin Elmer UV, DSC, FTIR, and DMA. Solvay polymers supplied the isotactic polypropylene.

**Synthesis of [P(OPh)₂N]₃**

The methodology used to produce [P(OPh)₂N]₃ was similar to the procedure reported by H. R. Allcock.¹⁶ A polyethylene glovebag was prepared with a nitrogen atmosphere. THF (30 mL) was distilled into a 100 mL Schlenk flask. Phenol, [PCl₂N]₃, sodium metal, hexane and glassware, stirbars and pipettes were all taken into the glove bag. Hexane was used to wash away the oil on the sodium. Sodium (0.40 g, 1.73 mmol) was placed into the flask containing the THF. Phenol (1.62 g, 17.21 mmol) was placed into another Schlenk flask. [PCl₂N]₃ (1.00 g, 2.88 mmol) was placed into the third flask and THF (20 mL) was added via canula. The THF/phenol solution was added via canula to the flask that contained the Na and THF. Once the phenol had stopped reacting, as indicated by the evolution of H₂ gas, the solution of [NPCl₂₃] was added via canula into the sodium phenoxide. The mixture was refluxed for 8 hours and stirred at 25°C for 56 hours. The rest of the synthesis was conducted in air. The solution was filtered and the solid was discarded. To the filtrate, Celite filtering aid was used to remove the last traces of the precipitate. The volatile components were removed using a rotary evaporator. To the remaining product was added 10-15 mL of acetone to dissolve it. Water was added to precipitate the product. The product was filtered and had an initial mp of 102°C. The solid was recrystallized with a 1:1 hexane-toluene mixture, the flask being cooled in ice to obtain the maximum amount of crystals. The crystals were filtered and the mp was
110°C. The second recrystallization was identical to the first except no ice was used; a paper towel was wrapped around the flask to slow the crystallization. The melting point was 111-112°C with a yield a 0.51 g (26%). $^{31}$P NMR (CDCl$_3$): +9.0 ppm. IR: 1250 to 1280 cm$^{-1}$. 

Synthesis of [P(OCH$_2$CF$_3$)$_2$N]$_3$

The methodology used to produce [P(OCH$_2$CF$_3$)$_2$N]$_3$ was similar to the procedure reported by J.L. Schmultz.$^{19}$ 2,2,2,-Trifluoroethanol was dried overnight using CaSO$_4$ and a little NaHCO$_3$. A Schlenk flask with sodium (0.80 g, 34.8 mmol) was combined with freshly distilled THF (24.78 mL). The flask with the [PCl$_2$N]$_3$ (2.00 g, 5.75 mmol) was attached to the line and pump-filled 3 times. Using a gas-tight syringe the trifluoroethanol was slowly added to the Na/THF mixture. The solution of sodium trifluoroethoxide was transferred via canula into the flask with the [PCl$_2$N]$_3$. This mixture was stirred for 48 h. The rest of the synthesis was conducted in air. The product was filtered to remove the insoluble compounds. The filtrate was placed on the rotary evaporator to remove the volatile components. Crystals formed immediately after being taken off of the rotary evaporator. To the crystals acetone (10-15 mL) and 20 mL of water were added. Two layers formed and the immiscible layer at the bottom of the flask was pipetted out. The remaining layer is put on the rotary evaporator and when the volatiles were removed clearer colorless crystals formed. The melting point was 49.5°C. The product was recrystallized once from hot hexane (30 mL). Crystals appeared after one hour. The crystals were sublimed twice under vacuum at 53°C to give a purer product.$^1$ The melting point was 46-47°C which suggested there was some water within the crystals. The crystals were left to dry overnight and in the morning the melting point
was 48-49°C with a yield of 1.53 g (37%). $^{31}$P NMR (CDCl$_3$) +16.21 ppm. $^{13}$C NMR (CDCl$_3$): 123.4 ($^3J_{C-F} = 277$ Hz, CF$_3$) ppm, 63.1 ($^3J = 38$ Hz, CH$_2$) ppm.$^{13,20}$ F NMR (CDCl$_3$): 0.029 ($^3J_{F-H} = 7.5$ Hz, HF$_3$) ppm.$^{21}$ $^1$H NMR (CDCl$_3$): 3.89 ($^3J_{H-F} = 2$ Hz, HF$_3$) ppm.$^{17}$ MS (FAB, m/z): 730 ([P(OCH$_2$CF$_3$)$_2$)$_3$H$^+$), 752 ([P(OCH$_2$CF$_3$)$_2$)$_3$Na$^+$). IR: 1237, 1283 (cm$^{-1}$).$^{22}$

**Synthesis of Partially Cross-linked Poly(dichlorophosphazene)**

The methodology used to produce [PCl$_2$N]$_n$ was similar to the procedure reported by C.W. Allen.$^{23}$ In a polyethylene glove bag with a nitrogen atmosphere the reactants, PCl$_5$ (100.0 g, 0.48 mol), NH$_4$SO$_4$ (42.12 g, 0.107 mol) were placed into a one liter round bottom flask equipped with two 24/40 joints. The flask was equipped with a stirbar and a gas inlet. The apparatus was brought out of the bag and attached to the line. While N$_2$ was flowing through the round bottom flask the cap was taken off and the condenser was added. Tygon tubing was secured to the glass adapter and immersed into a water bubbler. A large diameter adapter was used to prevent sudden detachment because of extreme gas evolution. The water was turned on for the condenser and the flask was submerged at least half way into a 165°C preheated silicone oil bath. A variac was used to keep the temperature constant because of the sensitivity of the reaction. As the reactants began to melt the nitrogen flow was turned off. A great amount of gas evolution occurred and a light yellowish liquid formed. In about 30 minutes the gas evolution stopped. The nitrogen gas flow was turned on. The condenser was replaced by a simple distillation column equipped with a 100 mL collecting flask in a dry ice bath. The temperature of the reaction was increased slowly and a yellowish liquid began to
distill at 185°C. As the temperature was increased 190°C, the liquid turned a golden brown and later at ~220°C the residue turned a brownish color. The yield was 10.4 g (42% theoretical). $^{31}$P NMR (Benzene): -17.40 ppm.$^{17}$

This reaction was carried out another time and a mixture of linear and cross-linked gave a $[\text{PCl}_2\text{N}]_n$ was obtained. The cross-linked polymer was not characterized by NMR because of its insolvability. It will be discussed later on. This mixture of a linear and cross-linked $[\text{PCl}_2\text{N}]_n$ was used as a reagent in the synthesis of the $[\text{P(OPh)}_2\text{N}]_n$ polymer.

**Synthesis of Poly(diphenozyphosphazene)**

The methodology used to produce $[\text{P(OPh)}_2\text{N}]_n$ was similar to the procedure reported by H. R. Allcock.$^{17}$ In a nitrogen atmosphere, 40.0 mL of THF was added into a flask from the stills. Phenol (6.8 g, 72.89 mmol) was added to the flask with the THF. Metallic sodium (1.71 g, 74.38 mmol) was cut and placed into another flask. The phenol/THF solution was slowly transferred via canula into the flask with the sodium. This reaction is very exothermic. After 2.5 h there were still bubbles coming from the mixture; therefore, the reaction was stirred overnight. The sodium phenoxide was transferred via canula into the flask containing $[\text{PCl}_2\text{N}]_n$ (4.2 g). This was also an exothermic reaction; therefore the $\text{N}_2$ was turned on to relieve the pressure. The reaction mixture turned yellow, light pink, to orange-peach and back to a milky white color. The mixture was refluxed and stirred at 74°C overnight. A $^{31}$P NMR was taken and showed resonance at -16.0 ppm (CDCl$_3$). Benzene was added to dissolve the polymer and concentrated HCl was added. The suspension was precipitated with hexane and an
attempt was made to filter by vacuum. The polymer was sticky, with glue like consistency, so the suspension did not filter. The suspension was left to evaporate overnight. The suspension was washed with acetone to remove the color and placed on a rotary evaporator to remove all volatiles. The polymer is now light pink and sticky. Chloroform (25 mL) was added along with large amounts of water to remove the suspected NaCl. This was placed into a large separatory funnel and the washing with water was repeated three times. An emulsion was formed and it was allowed to sit over the weekend. Water was added and a little NaCl to break up the emulsion. The bottom pinkish chloroform layer was separated from which looked white and cloudy. The volatile components were removed from the bottom chloroform layer using the rotary evaporator. To the top aqueous layer, benzene was added to form an azeotrope. A simple distillation apparatus was added to distill the azeotrope mixture. After 2.5 h and 65°C the distillation was complete and the residue is darker pink. The residue was dissolved with hot toluene and precipitated into n-hexane and reprecipitated from hot dioxane into water. The polymer was again reprecipitated into toluene and excess hexane with cooling of the final mixture with ice to increase the yield of the polymer. A mixture of and finally reprecipitated from hot dioxane and water. The residue was placed on the rotary evaporator to remove the volatile components leaving the [P(OPh)_2N]_n polymer as the product. $^{31}$P NMR (CDCl$_3$) -17.12 ppm.$^{17}$

**Attempted synthesis of an IPN from [PCl$_2$N]$_3$ and Polypropylene using a Brabender**

The Brabender mixer was surrounded with a glove bag and purged with an analytical grade argon. At 165°C 50.14 g of polypropylene was mixed for 90 seconds
with a 90 rpm set point. A 1.05 g sample of polypropylene was taken as a reference for the later analysis (I). [PCl₂N]₃ (4.87 g) was added and mixed at 165°C for 210 seconds and a 1.16 g sample was taken (II). The temperature was raised to 200°C and mixed for 210 seconds, and a third sample (1.01 g) was taken (III). The temperature was raised to 210°C and sampled (1.01 g) after 210 seconds (IV). The temperature was raised to 220°C and sampled (1.20 g) after 210 seconds (V). Finally the last temperature increase to 230°C was sampled (1.08 g) at 210 seconds (VI). The last sample (1.10 g) was allowed to mix for 900 seconds before being sampled. The remainder of the sample was removed and sealed. All samples were processed for analytical analysis.
CHAPTER III

RESULTS AND DISCUSSION

Synthesis of [NP(OPh₂)]₃

(Eq. 1)

\[ \text{[P(OPh)₂N]}_3 \] was synthesized by the reaction of \([\text{PCl}_2\text{N}]_3\) and NaOPh in a 1:6 molar ratio in THF (Eq1). The white solid, which was filtered out using Celite, is NaCl. This formula also needs two recrystallizations. The second recrystallization was performed without the use of an ice bath. It was proven that when cooled down to insulate so it cools more slowly the crystals were greater and of more clarity. It is clear that the spectra, the melting point and the clarity of the crystals are all consistent with the properties of \([\text{P(Ph)₂N}]_3\). Careful control of stoichiometry 6:6:1 allows the sequential replacement of chlorine atoms using a nucleophilic reagent.

The melting point of \([\text{P(Ph)₂N}]_3\) proved to need two recrystallizations in order to be raised from 102°C to 112°C. This also improved the clarity of the crystals. The yield
(26%) was of average and could be improved by a slower transition in temperature.

\([\text{P(OPh)}_2\text{N}]_3\) was soluble in acetone, hexane and \(\text{CDCl}_3\).

\(^{31}\text{P}\) NMR spectral analysis (9.90 ppm) as compared to the literature value of (9.00 ppm) is in the range.\(^{17}\) There is only one resonance which makes it apparent that all substituents were successfully substituted. The cyclic compounds will have more of a downfield shift and sharper peaks as compared to the polymers.\(^{24}\) The IR data was ~1250-1280 (cm\(^{-1}\)) which corresponds to the literature value.\(^{18}\)
Figure 2. $^{31}$P NMR Spectrum of $[\text{P(OPh)}_2\text{N}]_3$ in CDCl$_3$
Synthesis of [NP(OCH₂CF₃)₂]₃

\[ \text{[P(OCH₂CF₃)₂]₃} \]

(Eq. 2)

[P(OCH₂CF₃)₂]₃ was synthesized by the reaction of [PCl₂N]₃ and NaOCH₂CF₃ in a 1:6 molar ratio in THF (Eq2). As seen in [P(OPh)₂N]₃, the white solid filtrate is NaCl, but was never tested. To purify the product, recrystallization was not efficient. In contrast, two sublimations under vacuum at 53°C were useful for purifying [P(OCH₂OCF₃)₂N]₃. The crystals were very dense and colorless.

\(^{13}\)C NMR spectral analysis was as defined in the literature. The 116.97 ppm resonance correlates to the CHF₃ as stated in the literature.\(^{13}\) The quartet of 63.10 ppm is due to the C-F coupling.\(^{20}\) The n+1 rule applies and this explains the above quartet. \(^{19}\)F NMR spectral analysis (0.029 ppm) with a \(^{3}\)J₉-H = 7.5 Hz proves all substituents were successfully substituted.\(^{21}\) There is only one fluorine atom; therefore, only one resonance split into three would appear. \(^1\)H NMR spectra (3.88 ppm) is being split by the fluorine atom and this is why a quartet is observed.

The FAB MS of [P(OCH₂CF₃)₂]₃ was obtained using a 3-nitrobenzyl alcohol matrix (NBA). The mass spectra showed regular peak-repetition patterns that are
characteristic of the \( [P(OCH_2CF_3)_2N]_3 \). It confirmed that all 6 substituents were successfully added. Masses 730 are \( [P(OCH_2CF_3)_2N]_3H^+ \) and 752 are \( [P(OCH_2CF_3)_2N]_3Na^+ \). The \(^{13}\)C NMR, \(^{19}\)F NMR, \(^1\)H NMR, and mass spectra conclusively show the successful attachment of all six substituents to the ring.
Figure 3. $^{13}$C NMR Spectrum of [P(OCH$_2$CF$_3$)$_2$N]$_3$ in CDCl$_3$
Figure 4. Mass Spectrum (FAB) of [P(OCH₂CF₂)₂N]₃
Synthesis of $[\text{PCl}_2\text{N}]_n$ by a condensation route

As mentioned in the introduction, there is a need for improved synthesis of $[\text{PCl}_2\text{N}]_n$. A second commercially viable method to prepare $[\text{PCl}_2\text{N}]_n$ is a condensation polymerization and this was the method used. The advantages of this route over the ring opening polymerization described in the introduction are greater molecular weight and control of polydispersity. Also a lower cost than ROP, elimination of complicated equipment and environmentally harmful halogenated hydrocarbon solvents. This is the first synthesis attempt. Phase I (Scheme 1.) refers to the combining of the raw materials in the solid state and heating to form the liquid monomer. This is done in a one pot synthesis. Phase II involves the bulk polymerization of the liquid monomer, $\text{Cl}_3\text{P} = \text{NP(O)Cl}_2$, the by-product $\text{O=PCl}_3$ was distilled off under an inert nitrogen atmosphere. This proposed mechanism of polymerization involves an initiation reaction of a nucleophilic attack by the nitrogen atom of one monomer molecule on the phosphorus center of another monomer. This leads to the formation of oligomers by the elimination of $\text{POCl}_3$. The viscosity of the reaction mixture increases after a certain level of conversion. This mechanism allows for a more efficient and less time consuming preparation.

As stated earlier, the synthesis of $[\text{PCl}_2\text{N}]_n$ was conducted more than once and each time a somewhat different product was obtained. The product of the second synthesis was cross-linked, because it was insoluble in organic solvents. The insolubility was why the cross-linked polymer could not be characterized by solution NMR.
Phase I

\[ 9\text{PCl}_5 + 2\text{(NH}_4\text{)}_2\text{SO}_4 \rightarrow 2\text{Cl}_3\text{P=NP(O)Cl}_2 + \text{oligomers} + \text{gases} + \text{POCl}_3 \]

Phase II

\[ \text{Cl}_3\text{P=NP(O)Cl}_2 \rightarrow [-\text{Cl}_2\text{P=N-}]_n + \text{O=PCl}_3 \]

Scheme 1 Two step condensation synthesis of \([\text{PCl}_2\text{N}]_n\) from \text{PCl}_5 and (\text{NH}_4\text{)}_2\text{SO}_4

The \(^{31}\text{P}\) NMR spectrum of the first synthesis of \([\text{PCl}_2\text{N}]_n\) in benzene showed a resonance at \(-17.40\) ppm and two minor resonances at \(-12.02\) ppm and \(-2.10\) ppm. The literature confirms that the resonance at \(-17.40\) ppm is that of \([\text{PCl}_2\text{N}]_n\). The resonance at \(-12.02\) ppm is the POCl₂ end of the monomer Cl₃P=N-P(O)Cl₂. The resonance at \(-2.10\) ppm is assigned to PCl₃ end.\(^7\) This NMR data proves that the polymer was made.
Figure 5. $^{31}$P NMR Spectrum of $[\text{PCl}_2\text{N}]_n$ in (Benzene)
Synthesis of \([\text{P(OPh)}_2\text{N}]_n\)

\[
\begin{align*}
\text{[} & \begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array} \\
\text{N}
\end{array} \text{]}_n + \text{Oligomers} & \xrightarrow{\text{NaOPh}} \begin{array}{c}
\text{OPh} \\
\text{OPh}
\end{array} \\
\text{[} & \begin{array}{c}
\text{P} \\
\text{N}
\end{array} \text{]}_n
\end{align*}
\]

(Eq. 3)

\([\text{P(OPh)}_2\text{N}]_n\) was synthesized by the reaction of a mixture of oligomeric and polymeric \([\text{PCl}_2\text{N}]_n\) (cross-linked) with NaOPh in a 1:6 molar ratio in THF (Eq3).

\([\text{P(OPh)}_2\text{N}]_n\) created and enormous emulsion and was very difficult to purify. This thick sticky consistency needed NaCl to be added to break up the emulsion 3 times.

\([\text{P(OPh)}_2\text{N}]_n\) was a silly putty consistency; therefore, vacuum filtration was not used. Instead washing and precipitating the residue was efficient to remove the impurities.

After all of the workup the polymer at the end was not as the same consistency.

The \(^{31}\text{P}\) NMR spectrum of \([\text{P(OPh)}_2\text{N}]_n\) showed a resonance at \(-16.60\) ppm. After all of the purification the NMR was \(-17.12\) ppm. This is slightly downfield from the literature \(-18.7\) ppm.\(^{17}\) The presence of a single resonance indicates complete nucleophilic substitution and the solubility suggests no cross-linking of the polymer. The literature indicates that substitution of the cross-linked polymer is difficult to accomplish. Macromolecular substitution did occur, even though the starting polymer was cross-linked. The solubility of \([\text{P(OPh)}_2\text{N}]_n\) also suggests that the organic nucleophile cleaved the cross-linked polymer at the point of the cross-linkage during the substitution. The organophosphazenes are much more hydrolytically stable than the parent polymer.
Figure 6. $^{31}$P NMR Spectrum of $[P(\text{OPh})_2\text{N}]_n$ in (CDCl$_3$)
Attempted Synthesis of an IPN of \([\text{PNCl}_2]_n\) and Polypropylene Using a Brabender

An attempt was made to prepare and IPN of \([\text{PCl}_2\text{N}]_n\) and an organic polymer. As mentioned in the introduction, phosphazenes are known to be fire resistant, strong and depending on substituents, bioerodible. The goal of the attempted IPN synthesis was to add fire retardancy, impart impact resistance and, possibly, bioerodibility to the less expensive organic polymer by adding a small amount of the more expensive inorganic phosphazene polymer. Additional fire retardant properties could be conferred by adding a compound like \(\text{Sb}_2\text{O}_3\) to the IPN. This would create a more stable, practical and useful form of an already known organic polymer.

The planned IPN utilizes polypropylene as the organic polymer, which is hydrolytically stable and commercially available. The IPN synthesis was going to be accomplished by heating a mixture of the monomer \([\text{PCl}_2\text{N}]_3\) and polypropylene in phases to temperatures that were high enough to effect the ring-opening polymerization to give the polymer \([\text{PCl}_2\text{N}]_n\). Air sensitive techniques were to be used during the process. It was hoped that the encapsulated \([\text{PCl}_2\text{N}]_3\) and/or \([\text{PCl}_2\text{N}]_n\) would be protected enough so that the IPN would be air-stable. An IPN retards the segregation process of the polymers because one polymer component is cross-linked while the other is trapped within the matrix of the first.

This synthesis of an IPN was a collaboration with Steve Paolucci and done at A. Schulman Inc. \([\text{PCl}_2\text{N}]_3\) was mixed with polypropylene in a Brabender mixer at 165°C. The temperature was raised to 200°C and a sample was taken (I). The temperature was now raised in ten degree increments up to 230°C and at each temperature; ~1 g sample was removed for later analysis (III-VI).
Melting point (Table 1) and Tg data (Table 2) suggests a semi IPN was not formed from polypropylene and [PCl$_2$N]$_n$ at high temperature because [PCl$_2$N]$_3$ did not ring open. On the other hand, a partial IPN between propylene and the rings [PCl$_2$N]$_n$ ($n = 4, 5, 6 ...$) may have been formed. It is known that heating [PCl$_2$N]$_3$ can give mixtures of the larger rings [PCl$_2$N]$_n$ and, during this process, the polypropylene chains could have become intertwined within the newly formed rings. The data suggest the [PCl$_2$N]$_3$ and/or [PCl$_2$N]$_n$ acts as a plasticizer for polypropylene. The mp of polypropylene is 161°C and the [PCl$_2$N]$_3$ is 114°C. When [PCl$_2$N]$_3$ was added to polypropylene at all different temperatures the melting point was only slightly depressed (Table 1). This is suggestive of a small amount of [PCl$_2$N]$_3$ penetrating the polypropylene, but not opening up into [PCl$_2$N]$_n$. The Tg of polypropylene is at 0 to –20°C and that of [PCl$_2$N]$_n$ is –66°C. When the [PCl$_2$N]$_3$ was added at all different temperatures, the Tg did not go below -20°C (Table 2). This suggests that no [PCl$_2$N]$_n$ was present in the mixture and is consistent with a less flexible backbone for the polypropylene. The entrapment of
polypropylene within the larger rings $[\text{PCl}_2\text{N}]_n$ may account for the reduced flexibility. Therefore, a partial IPN appears to have been formed.

IR analysis of sample (I) and sample (II) are in Table 3. The results show some inter mixing of the polypropylene and $[\text{PCl}_2\text{N}]_3$ but the total degree is not known. This concurs with the above results of a partial IPN being formed.
Table 1. Melting Point Data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point (°C)</th>
<th>Reference (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PNCI₂)₂₃</td>
<td>114 &amp; 151</td>
<td>114: 151=impurity</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>161</td>
<td>165</td>
</tr>
<tr>
<td>(PN(OCH₂CF₃)₂)₃</td>
<td>49 &amp; 114</td>
<td>49-50</td>
</tr>
<tr>
<td>(PN(OPh)₂)₃</td>
<td>119 &amp; 114</td>
<td>115-115.5: 114=unreacted</td>
</tr>
<tr>
<td>Polypropylene + Trimer (Sample II)</td>
<td>159</td>
<td>Experimental: no Ref Melting Point Depression</td>
</tr>
<tr>
<td>Polypropylene + Trimer (Sample III)</td>
<td>156</td>
<td>Experimental: no Ref Melting Point Depression</td>
</tr>
<tr>
<td>Polypropylene + Trimer (Sample IV)</td>
<td>156</td>
<td>Experimental: no Ref Melting Point Depression</td>
</tr>
<tr>
<td>Polypropylene + Trimer (Sample V)</td>
<td>154</td>
<td>Experimental: no Ref Melting Point Depression</td>
</tr>
<tr>
<td>Polypropylene + Trimer (Sample VI)</td>
<td>155</td>
<td>Experimental: no Ref Melting Point Depression</td>
</tr>
<tr>
<td>Polypropylene + Trimer (Sample VII)</td>
<td>154</td>
<td>Experimental: no Ref Melting Point Depression</td>
</tr>
</tbody>
</table>

Table 2. DMA Tₙ Results

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tₙ (°C)</th>
<th>Reference (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample (I)</td>
<td>0</td>
<td>0 to -20</td>
</tr>
<tr>
<td>Sample (II)</td>
<td>-11</td>
<td>Experimental: no Ref</td>
</tr>
<tr>
<td>Sample (III)</td>
<td>-15</td>
<td>Experimental: no Ref</td>
</tr>
<tr>
<td>Sample (IV)</td>
<td>-15</td>
<td>Experimental: no Ref</td>
</tr>
<tr>
<td>Sample (V)</td>
<td>-11</td>
<td>Experimental: no Ref</td>
</tr>
<tr>
<td>Sample (VI)</td>
<td>-10</td>
<td>Experimental: no Ref</td>
</tr>
<tr>
<td>Sample (VII)</td>
<td>-10</td>
<td>Experimental: no Ref</td>
</tr>
</tbody>
</table>
Table 3. Characteristic P-N Stretching Vibrations for Cyclo- and Polyphosphazenes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(cm$^{-1}$)</th>
<th>Reference (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PNCl$_2$)$_3$</td>
<td>~1200 peaks not labeled</td>
<td>1218</td>
</tr>
<tr>
<td>Polypropylene (Sample I)</td>
<td>2900, 1470, &amp; 1370</td>
<td>2900 C-H stretch</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1470 CH$_2$ deformation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1370 symmetric CH$_3$ deformation</td>
</tr>
<tr>
<td>(PN(OCH$_2$CF$_3$)$_2$)$_3$</td>
<td>1238, 1284</td>
<td>1240, 1280</td>
</tr>
<tr>
<td>(PN(OPh)$_2$)$_3$</td>
<td>~1250-1280 peaks not labeled</td>
<td>1250, 1280</td>
</tr>
<tr>
<td>Polypropylene (Sample II)</td>
<td>2900, 1470, 1370, &amp; 1218</td>
<td></td>
</tr>
</tbody>
</table>
In this work a number of phosphazene trimers, polymers and an IPN were synthesized and characterized. It is very helpful to investigate the synthesis of the trimeric phosphazenes before the polymers to learn the chemistry and behavior of phosphazenes. The data showed that all trimers and phosphazene polymers were successfully synthesized.

Several improvements and modifications were made. The synthesis of \([P(O\text{P}h_2)N]_3\) proved to have a higher yield which is attributed to the technique of slowing the crystallization process down, which may have allowed more crystals to come out of solution. Several modifications of the condensation synthesis of \([PCl_2N]_n\) were investigated. It proved to be more efficient than the ring opening polymerization technique. The macromolecular substitution of \([P(O\text{P}h_2N)]_n\) proved to be successful, even when a cross-linked \([PCl_2N]_n\) was used as a reagent.

The data was inconclusive to the synthesis of an IPN involving polypropylene and \([PCl_2N]_n\). The melting point and the Tg data suggest there is some intermixing and a semi or apparent IPN may have formed, but the degree of mixing is unknown. A solid state NMR may be useful to obtain the degree of mixing and to determine the form of the phosphazene in the mixture. In the future, the stoichiometry of the reaction needs to be
examined more carefully. The ratio of \([\text{PCl}_2\text{N}]_3\) to polypropylene should be varied to see if more significant changes to the Tg can be obtained. Functional polyphosphazenes are expected to play a major role in the future development of new polymer IPN’s.
REFERENCES


