Abstract

New $P$-Mes (Mes = 2,4,6-trimethylphenyl) phosphaalkenes bearing conjugated C-substituents have been prepared: MesP=C(Naph)(Ph) (Naph = 1-naphthyl) (1a), MesP=C(Phen)(Ph) (Phen = 9-phenanthrenyl) (1b), and MesP=C(C$_4$H$_3$S)(Ph) (C$_4$H$_3$S = 2-thienyl) (1c). Compounds 1a and 1c were prepared by the base-catalyzed phospha-Peterson reaction, whereas 1b was prepared via the standard phospha-Peterson route. Anionic polymerization of 1a and 1b afforded [MesP–C(Naph)(Ph)]$_n$ (2a) and [MesP–C(Phen)(Ph)]$_n$ (2b), respectively. The anionic polymerization of 1c was attempted, but there was no polymer formation.

Poly(methylene phosphine)s 2a and 2b were chemically functionalized at the phosphorus centres by oxidation and coordination to BH$_3$ moieties. The electronic properties of 1a, 1b, 2a, 2b, and the functionalized polymers were investigated by UV/Vis and fluorescence spectroscopy. The results showed that naphthyl-derivatized phosphaalkene 1a and poly(methylene phosphine) 2a were non-emissive, whereas the functionalized naphthyl-derivatized polymers emitted in the UV region when excited at 288 nm. Similarly, for the phenanthrenyl-derivatized species, phosphaalkene 1b and phosphine polymer 2b were observed to be weakly fluorescent in comparison to the more emissive functionalized polymers. These results are consistent with the sensory behavior exhibited by “turn-on” chemical sensors.

The phosphaalkene monomer, MesP=CPH$_2$ (3) was copolymerized with styrene (Sty) using radical initiator 1,1’-azobis(cyclohexanecarbonitrile) over a range of monomer feed ratios to afford poly(methylene phosphine)-co-polystyrene (PMP-co-PS) copolymers. The compositions of these copolymers were evaluated using inverse gated proton decoupled $^{13}$C NMR spectroscopy. An adaptation of the Tidwell-Mortimer experimental approach was
employed to calculate reactivity ratios for the PMP-co-PS system. The first step of the approach involved a preliminary estimation of the reactivity ratios by the Fineman-Ross linearization and the Mayo-Lewis intersection method. Using the preliminary estimates, the Tidwell-Mortimer heuristic rules were applied to determine optimal feed compositions for further experimentation. Lastly, a nonlinear least squares regression was performed to provide the best estimates of the reactivity ratios \( r_{PA} = 0.11 \) and \( r_{Sy} = 0.24 \). Based on these \( r \) values, \( Q-e \) reactivity parameters of phosphaalkene 3 were computed and the microstructure of PMP-co-PS was examined which revealed an alternating pattern of phosphaalkene and styrene units in the copolymer backbone.
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<th>Full Form</th>
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<tr>
<td>Anal.</td>
<td>analysis</td>
</tr>
<tr>
<td>aq.</td>
<td>aqueous</td>
</tr>
<tr>
<td>Ar</td>
<td>aryl</td>
</tr>
<tr>
<td>a.u.</td>
<td>arbitrary units</td>
</tr>
<tr>
<td>$AW_p$</td>
<td>atomic mass of phosphorus</td>
</tr>
<tr>
<td>br</td>
<td>broad (spectra)</td>
</tr>
<tr>
<td>Bu</td>
<td>butyl</td>
</tr>
<tr>
<td>$n$-Bu</td>
<td>$n$-butyl</td>
</tr>
<tr>
<td>$i$-Bu</td>
<td>$iso$-butyl</td>
</tr>
<tr>
<td>$sec$-Bu</td>
<td>$sec$-butyl</td>
</tr>
<tr>
<td>C</td>
<td>Celsius</td>
</tr>
<tr>
<td>ca.</td>
<td>circa</td>
</tr>
<tr>
<td>Calcd</td>
<td>calculated</td>
</tr>
<tr>
<td>$C_{Ar}$</td>
<td>integration: value of the chemical shift assigned to aryl carbons</td>
</tr>
<tr>
<td>cat.</td>
<td>catalytic</td>
</tr>
<tr>
<td>CD</td>
<td>circular dichroism</td>
</tr>
<tr>
<td>$C_{Me}$</td>
<td>integration: value of the chemical shift assigned to methyl carbons</td>
</tr>
<tr>
<td>COD</td>
<td>1,5-cyclooctadiene</td>
</tr>
<tr>
<td>Cp</td>
<td>cyclopentadienyl</td>
</tr>
<tr>
<td>d</td>
<td>day</td>
</tr>
<tr>
<td>dba</td>
<td>dibenzylideneacetone</td>
</tr>
</tbody>
</table>
\( \frac{dn}{dc} \) refractive index increment

DP degree of polymerization

DSC differential scanning calorimetry

DVDS divinyltetramethyldisiloxane

e polarity parameter according to Alfrey-Price \( Q-e \) scheme

E electrophile

energy

\( E \) entgegen (configuration)

EA elemental analysis

e.g. for example

EI electron impact

\( e_{PA} \) polarity parameter of mesityldiphenylphosphaalkene according to Alfrey-Price \( Q-e \) scheme

eq equation

equiv equivalent(s)

\( e_{Sty} \) polarity parameter of styrene according to Alfrey-Price \( Q-e \) scheme

Et ethyl

et al. and others

exp exponential function

FW formula weight

\( FW_{PA} \) formula weight (or molar mass) of phosphaalkene

\( FW_{Sty} \) formula weight (or molar mass) of styrene

GOF goodness of fit (crystallography)
GPC | gel permeation chromatography
---|---
h | hour
HOMO | highest occupied molecular orbital
HPLC | high-performance liquid chromatography
i | ipso
i.e. | that is
$I_{PL}$ | intensity of photoluminescence
IR | infrared
$k$ | rate constant
K | kelvin
$\lambda$ | wavelength
$\Delta\lambda$ | red shift
$\lambda_{em}$ | wavelength of emission
$\lambda_{ex}$ | wavelength of excitation
$\lambda_{max}$ | absorption maximum
$I_{PA}$ | average sequence length of consecutive phosphaalkene units
$I_{Sty}$ | average sequence length of consecutive styrene units
LLS | laser light scattering
LUMO | lowest unoccupied molecular orbital
m | multiplet (spectra)
$M^+$ | molecular ion
Me | methyl
Mes | mesityl; 2,4,6-trimethylphenyl
MHz  megahertz
min  minute
$M_n$  number average molecular weight
mol  mole
$m_{PA}$  mole fraction of phosphaalkene in the copolymer composition
$M_{PA}$  mole fraction of phosphaalkene in the monomer feed
MS  mass spectrometry
$m_{Sy}$  mole fraction of styrene in the copolymer composition
$M_{Sy}$  mole fraction of styrene in the monomer feed
$M_w$  weight average molecular weight
m/z  mass-to-charge ratio
Naph  1-naphthyl
NMR  nuclear magnetic resonance
$o$  ortho
OTf  trifluoromethanesulfonate; $\text{CF}_3\text{SO}_3^-$
OLED  organic light emitting diode
$\phi_{PL}$  quantum yield of photoluminescence
$p$  para
PA  mesityldiphenylphosphaalkene
PDI  polydispersity index
$\%P_{EA}$  percent of phosphorus detected by elemental analysis
Ph  phenyl
Phen  9-phenanthrenyl
PLED  polymer-based light emitting diode
PMP  poly(methylene phosphine)
PMP-co-PS  poly(methylene phosphine)-co-polystyrene
ppm  parts per million
PPV  poly(p-phenylene vinylene)
PS  polystyrene
$Q$  reactivity parameter from Alfrey-Price $Q$-e scheme
$Q_{PA}$  reactivity parameter of mesityldiphenylphosphaalkene from Alfrey-Price $Q$-e scheme
$Q_{Sty}$  reactivity parameter of styrene from Alfrey-Price $Q$-e scheme
$r$  reactivity ratio
$R$  average number of sequences per 100 units, also known as run number
R or R'  side group
ref.  reference
RMSE  root mean squared error
ROP  ring-opening polymerization
$r_{PA}$  monomer reactivity ratio of mesityldiphenylphosphaalkene
$r_{Sty}$  monomer reactivity ratio of styrene
RT  room temperature
s  second
sh  shoulder
Sty  styrene
t \quad \text{time}

T_1 \quad \text{spin lattice relaxation}

Temp \quad \text{temperature}

T_g \quad \text{glass transition}

THF \quad \text{tetrahydrofuran}

TMEDA \quad N,N,N',N'-tetramethylethylenediamine

UV \quad \text{ultraviolet}

UV/Vis \quad \text{ultraviolet/visible}

VAZO 88 \quad 1,1'-azobis(cyclohexancarbonitrile)

vs. \quad \text{versus}

X \quad \text{monomer conversion}

X_{PA} \quad \text{monomer conversion of mesityldiphenylphosphaalkene}

X_{Sy} \quad \text{monomer conversion of styrene}

Z \quad \text{zusammen (configuration)}
Acknowledgements

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For fun times, yummy food, tvb soaps, and for passing the mic

Mommy, Dad, 婆婆, and 公公

For unconditional love and support

Michael, Lily, Andrew, and Sarah

For being a good brother/sister

Neal Yonson

For assistance, support, encouragement, patience, and love
Dedication

To my mother
Statement of Co-authorship

The results presented in Chapters 2 and 3 will be submitted for publication in due course. A version of Chapter 4 has been prepared as a manuscript to be submitted for publication shortly. A detailed account of contributions by other researchers is stated below and included in Section 1.4 (Page 23).

Some of the work in this thesis was achieved in collaboration with other researchers. For Chapter 2, all of the synthetic work was done by myself with the exception of the synthesis and recrystallization of MesP=C(C₄H₃S)(Ph) (C₄H₃S = 2-thienyl), which was a collaborative effort between myself and Fergus Chung. Fergus was an undergraduate researcher under my supervision. All crystallographic data were obtained primarily by Josh Bates with some assistance from Paul Siu using the departmental X-ray diffractometer. The solution and refinement of the molecular structures of MesP=C(Naph)(Ph) (Naph = 1-naphthyl) and MesP=C(C₄H₃S)(Ph) were completed by Josh. The solution and refinement of the molecular structure of MesP=C(Phen)(Ph) (Phen = 9-phenanthrenyl) were performed by Paul. All of the work presented in Chapters 3 and 4 was completed by myself.
Chapter One

Introduction

1.1 Phosphorus-Containing Polymers

Since the discovery of “inorganic rubber” by Stokes in the 1890s, history has witnessed an exciting evolution of inorganic polymers with phosphorus atoms in the main chain.5-9 “Inorganic rubber”, which is actually a crosslinked form of poly(dichlorophosphazene), was first prepared by the thermal ring-opening polymerization (ROP) of hexachlorocyclotriphosphazene (Scheme 1.1, Route A). The resulting material was insoluble and hydrolytically unstable. Due to its intractability, “inorganic rubber” remained a chemical curiosity until the 1960s. That was when Allcock and Kugel showed that the carefully controlled ROP of sublimed hexachlorocyclotriphosphazene afforded uncrosslinked poly(dichlorophosphazene) (1.1a) which was soluble in organic solvents (Scheme 1.1, Route B).10 Nearly half a century after this discovery, research on polyphosphazene-based materials continues to grow.11,12

Scheme 1.1

The discovery of polyphosphazenes has also inspired the development of other polymers with phosphorus atoms in the main chain.5-9,11 The synthesis of phosphorus-containing polymers, like that of other inorganic macromolecules, is challenging but offers the potential of accessing new materials with useful and interesting properties.13 This introduction will feature some

References begin on page 24
examples of phosphorus-containing polymers to demonstrate their uniqueness and highlight the strategies employed to overcome synthetic obstacles.

1.1.1 Polyphosphazenes and Derivatives

Polyphosphazenes comprise the most heavily studied class of main group polymers.\textsuperscript{11,12} As mentioned in the introduction, the preparation of poly(dichlorophosphazene) (1.1a) via thermal ROP of pure hexachlorocyclotriphosphazene affords a material that is soluble in organic solvents. However, 1.1a is unstable due to its hydrolytically sensitive P–Cl bonds. This reactive polymeric species can be treated with nucleophiles in a macromolecular substitution approach, allowing replacement of the chlorine groups by alkoxide, aryloxide, or amino groups to afford a wide range of hydrolytically stable polyphosphazenes (1.1b) (Scheme 1.2).\textsuperscript{10,11,14}

![Scheme 1.2](image)

There are other methods to prepare polyphosphazenes. A polycondensation method was developed in the mid-1980s by Neilson and Wisian-Neilson and their co-workers to afford 1.1c, which has alkyl or aryl side groups (Scheme 1.2).\textsuperscript{15,16} The number average molecular weight ($M_n$) of these polymers ranged between 29,000 g mol$^{-1}$ and 94,500 g mol$^{-1}$, and the polydispersity index (PDI) of 1.1c ranged between 1.7 and 2.2.

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In 1995, Honeyman et al. reported an ambient temperature route using PCl$_5$ (Scheme 1.3), affording poly(dichlorophosphazene) 1.1a of controllable molecular weights and low polydispersity (PDI = 1.04), a feat that was unprecedented for polyphosphazenes. While the original polymer prepared by Allcock and Kugel contained about 370 PN units in the backbone, the average number of PN units in the poly(dichlorophosphazene) prepared by Honeyman et al. was 55 units. There are many other methods reported for the preparation of polyphosphazenes, however it is beyond the scope of this introduction to describe each one.

\[
\text{Cl}_3\text{P} = \text{NSiMe}_3 \xrightarrow{\text{PCl}_5} \begin{bmatrix} \text{Cl} \\ \text{P} = \text{N} \\ \text{Cl} \end{bmatrix}_n 
\]

\text{Scheme 1.3}

With over 300 known examples, the wide structural diversity of polyphosphazenes gives rise to materials with unique properties including: flame-resistance, hydrophilicity or hydrophobicity, amorphous or microcrystalline structure, or with nonlinear optical, liquid crystalline or photochromic properties. Important applications of polyphosphazenes include dental liners, fuel liners, and flame-retardant materials.

Similar to polyphosphazenes are poly(thionylphosphazene)s (1.2), which have phosphorus, nitrogen and sulfur atoms in the backbone. Polymers of 1.2 containing hydrolytically sensitive sulfur(IV)–nitrogen bonds were first reported by Allcock and co-workers in 1990. In 1991, Liang and Manners reported the preparation of the more stable sulfur(VI) analogue by ROP of a cyclic thionylphosphazene at 165 °C. Both groups had prepared 1.2

References begin on page 24
bearing chlorine substituents (i.e. \( R = R' = \text{Cl} \)), which could be replaced by aryloxy or amino groups via macromolecular substitution. Turner and co-workers extended the work on poly(thionylphosphazene)s by synthesizing polymers in which the substituents are alkyl groups.\(^{20}\)

Remarkable properties of poly(aminothionylphosphazene)s, derivatives of \( R = R' = \) amino groups), include high free volume in the material, as demonstrated by studies of gas permeability, high solubility and processability.\(^{22}\) Some of these polymers have glass transitions, \( T_g \)‘s, below \(-10 \, ^\circ \text{C}\), an important characteristic that allows for large-scale conformational motions for effective gas diffusion.\(^{23,24}\) Block copolymers, poly(aminothionylphosphazene)-b-poly(tetrahydrofuran) have found application as matrices for fluorescent dyes which are very effective as photoluminescent oxygen sensors for pressure-sensing composite technology.\(^{22,25,26}\)

1.1.2 Polymers with Phosphorus and Other Inorganic Elements in the Backbone

A rare example of a phosphorus-containing polymer is poly(ferrocenylphosphine) (1.3) because the backbone includes not only phosphorus atoms but also the transition metal iron.\(^{27-29}\) These polymers were first prepared by Seyferth and co-workers in 1982 by a condensation polymerization involving dilithioferrocene, \( N,N,N',N'\)-tetramethylethylenediamine (TMEDA) and PhPCl\(_2\) (Scheme 1.4, Route A).\(^{27}\) In 1996, Manners and co-workers discovered that phosphorus-bridged ferrocenophanes could undergo thermal ROP to afford 1.3.\(^{28}\) Shortly thereafter, they reported that the ROP could also proceed in a living fashion by an anionic method at room temperature provided that the starting monomers were of high purity (Scheme 1.4, Route B).\(^{29}\)
The living route allowed access to well-defined architectures such as block copolymers of poly(ferrocenylphenylphosphine)-b-poly(dimethyldimethylsiloxane) and poly(ferrocenylphenylphosphine)-b-poly(ferrocenyldimethylsilane). In addition to opening the door to the construction of specially designed macromolecular architectures, living polymerization in general allows one to access polymers of narrow polydispersities and to control their molecular weights by varying the monomer:initiator ratio.

Another interesting class of phosphorus-containing polymers is polyphosphinoboranes (I.4), which are composed alternating four-coordinate boron and phosphorus atoms in the skeleton chain. Cyclic phosphinoboraneshave been known since the 1950s. There is limited documentation of polyphosphinoboranes from that time, and product characterization was only partially reported or not reported at all. In 2000, the preparation of polyphosphinoboranes I.4 was reported by Manners and co-workers which involved a rhodium-catalyzed dehydrocoupling of RPH₂BH₃ (Scheme 1.5). Interestingly, I.4 is air and water stable in the solid state, but has low thermal stability.

\[
\text{RPH}_2\text{BH}_3 \xrightarrow{[\text{Rh}]} \text{H}_2 \xrightarrow{100 - 120 \degree C} \text{R} \begin{bmatrix} P - \text{BH}_2 \end{bmatrix}_n
\]

\[ R = \text{Ph, i-Bu, p-n-BuC}_6\text{H}_4, \text{or p-dodecylC}_6\text{H}_4 \]

Scheme 1.5

References begin on page 24
1.1.3 $\pi$-Conjugated Polymers containing Phosphorus in the Main Chain

1.1.3.1 Phosphole-Based $\pi$-Conjugated Polymers

Inorganic materials based on polypyrrole and polythiophene architectures are widely known and have been extensively studied with regard to their synthesis, conductivity, and photochemical properties. Phosphole, the phosphorus analogue of pyrrole and thiophene, has also recently been investigated for incorporation into extended $\pi$-conjugated structures.\(^6\)\(^8\)\(^35\) Phosphole-containing $\pi$-conjugated polymers are interesting candidates for applications involving organic or polymer-based light emitting diodes (OLEDs/PLEDs) and chemical sensors.\(^36\)\(^38\) Due to the versatile reactivity of trivalent three-coordinate phosphorus (i.e. complexation to Lewis acids or transition metals, oxidation),\(^39\)\(^40\) electronic tuning of phosphole-containing $\pi$-conjugated materials should be feasible, giving a diversity of properties and functions.\(^6\)\(^7\)\(^35\)\(^41\) Table 1.1 summarizes the key physical and electronic properties of the phosphole-based polymers which will be discussed in this section.

The first report of phospholes being integrated into $\pi$-conjugated systems occurred in 1990 when Mathey and co-workers reported their work on oligomers containing two phosphole and four thiophene units.\(^42\) In 1997, Mao and Tilley synthesized the first $\pi$-conjugated polymer containing phosphole moieties in the backbone.\(^43\) The synthesis of the biphenyl-bridged phosphole polymer (1.5) was achieved using a zirconocene-coupling method (Scheme 1.6). The different regiochemistry in 1.5 originated from its precursor and was confirmed by $^1\text{H}$, $^{13}\text{C}$, and $^{31}\text{P}$ NMR spectroscopy. Interestingly, 1.5 exhibited photoluminescence in the visible blue-green region ($\lambda_{\text{em}} = 470$ nm). Its Stokes shift of 157 nm is large in comparison to the range of Stokes shifts reported for other phosphole-containing $\pi$-conjugated polymers (Table 1.1). Analysis of 1.5 by gel permeation chromatography (GPC) suggested that it exhibited an $M_n$ value of 6,200 g
### Table 1.1 Summary of selected characterization data for 1.5, 1.7a-c, 1.10 – 1.13.

<table>
<thead>
<tr>
<th>polymer</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\Delta \lambda^a$ (nm)</th>
<th>$\lambda_{\text{em}}$ / $\lambda_{\text{ex}}$ (nm)</th>
<th>Stokes shift (nm)</th>
<th>$\Phi_{\text{PL}}$</th>
<th>$M_n$ (g mol$^{-1}$) / [DP]</th>
<th>PDI</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>308</td>
<td>62</td>
<td>470 / [313]</td>
<td>157</td>
<td>0.092</td>
<td>6,200 / [17]</td>
<td>2.58</td>
<td>43</td>
</tr>
<tr>
<td>1.7a</td>
<td>410</td>
<td>56</td>
<td>490 / [410]</td>
<td>80</td>
<td>0.09</td>
<td>10,200 / [15]</td>
<td>1.5</td>
<td>45</td>
</tr>
<tr>
<td>1.7b</td>
<td>414</td>
<td>60</td>
<td>487 / [410]</td>
<td>77</td>
<td>0.14</td>
<td>10,000 / [12]</td>
<td>1.4</td>
<td>45</td>
</tr>
<tr>
<td>1.7c</td>
<td>382</td>
<td>28</td>
<td>435 / [390]</td>
<td>45</td>
<td>0.08</td>
<td>6,800 / [7]</td>
<td>1.3</td>
<td>45</td>
</tr>
<tr>
<td>1.10</td>
<td>378</td>
<td>21</td>
<td>460 / [378]</td>
<td>82</td>
<td>0.562</td>
<td>8,000 / [15]</td>
<td>3.1</td>
<td>46</td>
</tr>
<tr>
<td>1.11</td>
<td>353 (sh), 393</td>
<td>10</td>
<td>459 / [393]</td>
<td>66</td>
<td>0.566</td>
<td>10,000 / [20]</td>
<td>3.2</td>
<td>46</td>
</tr>
<tr>
<td>1.12</td>
<td>456 (sh), 502</td>
<td>123</td>
<td>555 / [502]</td>
<td>53</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>37</td>
</tr>
<tr>
<td>1.13</td>
<td>345, 485</td>
<td>109</td>
<td>509, 540 / [485]</td>
<td>24</td>
<td>0.47</td>
<td>5,800 / [9]</td>
<td>1.7</td>
<td>47</td>
</tr>
</tbody>
</table>

$^a$ $\lambda_{\text{max}}$ of polymer compared to the $\lambda_{\text{max}}$ of model compounds (i.e. red shift).

$^b$ $\Phi_{\text{PL}}$ = quantum yield of photoluminescence.

---

![Scheme 1.6](image)

**Scheme 1.6**

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mol\(^{-1}\), which translates to approximately 17 repeat units. While this number of repeat units seems rather low, it is similar to the degree of polymerization (DP) for other phosphole-based polymers listed in Table 1.1. A common synthetic challenge shared by researchers in this field is increasing the DP values.

Another convenient method to access phosphole-containing π-conjugated polymers was reported by the Réau group which involved the electropolymerization of a protected 2,5-bis(2-thienyl)phosphole followed by deprotection (Scheme 1.7).\(^ {38,44} \) This resulted in a material that was insoluble in common organic solvents, and thus no GPC data were reported. Remarkably, the phosphorus centres in 1.6 were strongly coupled to the conjugated system along the backbone, and could act as receptor sites for elemental chalcogenides in chemical sensing experiments.\(^ {38} \) The sensor properties were evaluated by using optical and electrochemical responses measured by UV/Vis spectroscopy and cyclic voltammetry. In the presence of S\(_8\) or Se, bathochromic shifts were observed in the UV/Vis spectra and positive shifts of the oxidation current offset were observed in the cyclic voltammograms.

![Scheme 1.7](image)

More phosphole-containing π-conjugated polymers (1.7a-c) were prepared by Chujo and co-workers via the Heck-Sonogashira reaction.\(^ {45} \) The palladium-catalyzed coupling of bis(p-bromophenyl)phosphole with diethynylarenes (Scheme 1.8) afforded 1.7a-c, which have extended π-conjugation. The extension of the π-conjugation was supported by UV/Vis data: the absorption bands of the polymers were red-shifted compared to the absorption band of the
Heck-Sonagashira coupling

Scheme 1.8

phosphole compound, 1.8. Interestingly, 1.7a (M$_n$ = 10,200 g mol$^{-1}$; PDI = 1.5) and 1.7b (M$_n$ = 10,000 g mol$^{-1}$; PDI = 1.4) were green emitters when irradiated at 410 nm, and 1.7c (M$_n$ = 6,800 g mol$^{-1}$; PDI = 1.3) emitted blue light when excited at 390 nm (see Table 1.1). In this sense, electronic properties of 1.7 can be tuned by varying the conjugated spacer in the main chain.

There are also polymers based on dithienophosphole (1.9), originating from the research group of Baumgartner.$^{37,46,47}$ The advantage offered by the annelated ring system is maximization of the π-overlap by forcing a coplanar geometry.
Using PtDVDS (DVDS = divinyltetramethyl disiloxane), Baumgartner and co-worker synthesized polymers 1.10 and 1.11 (Scheme 1.9) with $M_n$ values up to 8000 g mol$^{-1}$ and 10,000 g mol$^{-1}$, respectively.$^{46}$ Compared to other phosphole-containing polymers, 1.10 and 1.11 have relatively high PDI values (Table 1.1). The absorption and emission properties of 1.10 and 1.11 are very similar to those of their respective model compounds, suggesting a nearly localized $\pi$-system. This is not surprising since it is expected that the $-\text{SiMe}_2-$ moieties would inhibit $\pi$-delocalization from one dithienophosphole unit to the next.

Scheme 1.9

Dithienophosphole-based $\pi$-conjugated polymers, 1.12 and 1.13, were obtained via a Stille coupling and Suzuki-Miyaura coupling, respectively (Scheme 1.10).$^{37,47}$ The absorption and emission properties of 1.12 and 1.13 were strongly red-shifted compared to those of the corresponding monomers ($\Delta \lambda_{1,12} = 123 \text{ nm}; \Delta \lambda_{1,13} = 109 \text{ nm};$ see Table 1.1). These data suggest significant $\pi$-delocalization along the conjugated backbone. Both polymers fluoresce in the yellow-green region of the visible spectrum. Despite having long alkoxy chains, 1.12 exhibits poor solubility in THF, and thus the investigators have been unable to analyze 1.12 by GPC. The Stokes shift reported for 1.13 is small compared to those of other phosphole-based polymers (see...
Table 1.1), which was attributed to rigidity in the main chain. In addition to the extended π-conjugation, the ionic nature of 1.13 makes this material a promising candidate for conjugated polyelectrolyte applications.47

1.1.3.2 Poly(arylphosphine)s

Poly(arylphosphine)s (1.14) comprise a class of polymers developed by Lucht and co-workers.48-50 In 2000, Lucht and St. Onge reported the synthesis of poly(p-phenylenephosphine)s (1.14a) by a palladium-catalyzed carbon-phosphorus bond formation (Scheme 1.11).48 The $M_n$ of 1.14a varied between 1,300 g mol$^{-1}$ and 3,100 g mol$^{-1}$, depending on the R substituent (isobutyl, phenyl or 2,4,4-trimethylpentyl) on the phosphorus centre. The number of repeat units ranged between 7 to 14 units. The intriguing feature of 1.14a was the spectroscopic evidence for electronic delocalization along the backbone which must formally pass through the phosphorus atoms. The extended π-conjugation was supported by red shifted optical absorptions ($\Delta \lambda = 30$ nm for 1.14a R = Ph) and lower oxidation potentials of the polymers compared to model
compounds. These results are puzzling because the type and degree of overlap between the lone pair on phosphorus and the adjacent aromatic groups are unclear.

\[
\begin{align*}
&\text{I–Ar–I} + \text{RPH}_2 \xrightarrow{\text{Pd(PPh}_3)_4} \left[ \text{Ar–P–Ar} \right]_n \xrightarrow{\text{Ni(COD)}_2} \text{Br–\(\begin{array}{c}
P \\
\end{array}\)–Ar–Br} \\
\text{a:} &\quad \text{Ar–} = \begin{array}{c} \text{O} \\
\end{array} \text{, R = } \text{t-Bu, Ph, or } 2,4,4\text{-trimethylpentyl} \\
\text{b:} &\quad \text{Ar–} = \begin{array}{c} \text{O} \\
\end{array} \text{, R = } 2,4,4\text{-trimethylpentyl}
\end{align*}
\]

\[
\text{Scheme 1.11}
\]

In 2002, Lucht and Jin reported an extension of their work that employed palladium and nickel mediated coupling, as shown in Scheme 1.11, to prepare poly(arylphosphine)s in which the aryl group was biphenyl. The \(M_n\) value of 1.14b was 3,100 g mol\(^{-1}\), which suggested approximately 10 repeat units. The low molecular weights and low number of repeat units in 1.14a and 1.14b were attributed to poor solubility, consequently precipitating out of the reaction mixture before higher molecular weight polymers could be attained.

In 2005, Lucht and Jin prepared poly(p-phenylenephosphine)-co-polyaniline. Like 1.14a, characterization of the copolymer obtained by UV/Vis spectroscopy and cyclic voltammetry provided the spectroscopic evidence for extended \(\pi\)-conjugation through the copolymer backbone, which must formally pass through the trivalent phosphorus centres. More interestingly, oxidation of the phosphorus centres to phosphine oxides inhibited the electronic delocalization, suggesting participation from the phosphorus lone pair in the conjugated system when phosphorus was in the trivalent state.

1.1.3.3. Phosphorus Analogues of PPV

Poly(p-phenylenephosphaalkene)s\(^{51-55}\) comprise a very interesting class of conjugated

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phosphorus-containing polymers because they represent the phosphorus analogues of poly($p$-phenylenevinylene) (PPV), a luminescent organic macromolecule. The first example, 1.15a, was reported in 2002 by Wright and Gates and was achieved by thermolysis of tetramethyletherththaloyl chloride and (SiMe$_3$)$_2$P-C$_6$H$_4$-P(SiMe$_3$)$_2$, eliminating SiMe$_3$Cl (Scheme 1.12).\(^{51}\)

![Scheme 1.12](image)

$\text{^{31}P NMR spectroscopic analysis of 1.15a suggested that the polymer was comprised of E- and Z-$P=C$ units (i.e. a mixture of cis and trans arylene moieties). The } M_n \text{ value of 1.15a was estimated to be 10,500 g mol}^{-1} \text{ using end group analysis, while a degree of polymerization equal to 21 was considered to be moderate and not unusual for a step-growth reaction. Polymer 1.15a was studied by UV/Vis spectroscopy, which showed a broad absorption ($\lambda_{\text{max}} = 338$ nm) slightly red shifted compared to the absorption band of the model compound for 1.15a. The red shift is small (ca. 28 nm) in comparison to the red shift exhibited by organic counterparts (ca. 125 nm for trans-PPV vs. trans-stilbene), and is possibly due to the mixture of isomers present (E and Z) in 1.15a.}

References begin on page 24
A very similar derivative, **1.15b**, was reported in 2006 (Scheme 1.12).\(^5^2\) In contrast to the mixture of E- and Z-P=C units along the backbone of **1.15a**, the main chain of **1.15b** consisted of solely Z-P=C moieties (i.e. trans arylene moieties). This polymer was isolated as a brittle solid that was insoluble in common organic solvents, thus the molecular weight of **1.15b** could not be obtained. The absorption maximum exhibited by **1.15b** (\(\lambda_{\text{max}} = 338\) nm) is red shifted compared to that of a mono(phosphaalkene) model compound (\(\Delta\lambda = 70\) nm), giving strong evidence of \(\pi\)-conjugation along the main chain.

The Protasiewicz group found that poly(p-phenylenephosphaalkene)s could also be prepared by a phospha-Wittig reaction provided that substituents were bulky enough to protect the P=C bond (Scheme 1.13).\(^5^3\)\(^5^4\) Using the phospha-Wittig methodology, they obtained (E)-poly(p-phenylenephosphaalkene)s (1.16a-d). Polymer **1.16a** was moderately fluorescent, with fluorescence intensity per P=C unit measured to be about 8% that of E-stilbene.\(^5^3\) On the other hand, fluorescence intensities of **1.16b-d** were approximately equal to that of E-stilbene (see Table 1.2).\(^5^4\) The molecular weights (\(M_n\)) of **1.16a-d** ranged between 5,000 g mol\(^{-1}\) to 7,300 g mol\(^{-1}\), and each polymer chain consisted of approximately 4 to 6 repeat units. Although these numbers seem low, the total number of aromatic units in the chains ranges from 18 to 26 units, resulting in an extended \(\pi\)-delocalized system.

**Table 1.2** Summary of selected characterization data for **1.16a-d** and **1.17**.

<table>
<thead>
<tr>
<th>polymer</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>(\lambda_{\text{em}}) (nm)</th>
<th>(I_{\text{PL}}) (%)(^a)</th>
<th>(M_n) (g mol(^{-1})) / [DP]</th>
<th>PDI</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1.16a</strong></td>
<td>445</td>
<td>545</td>
<td>8</td>
<td>6,500 / [6]</td>
<td>N/A</td>
<td>53</td>
</tr>
<tr>
<td><strong>1.16b</strong></td>
<td>435</td>
<td>481</td>
<td>80</td>
<td>5,000 / [4]</td>
<td>2.3</td>
<td>54</td>
</tr>
<tr>
<td><strong>1.16c</strong></td>
<td>427</td>
<td>486</td>
<td>130</td>
<td>7,200 / [6]</td>
<td>2.2</td>
<td>54</td>
</tr>
<tr>
<td><strong>1.16d</strong></td>
<td>416, 473 (sh)</td>
<td>481</td>
<td>110</td>
<td>7,300 / [6]</td>
<td>1.9</td>
<td>54</td>
</tr>
<tr>
<td><strong>1.17</strong></td>
<td>435, 481</td>
<td>none</td>
<td>0</td>
<td>5,900 / [6]</td>
<td>2.1</td>
<td>54</td>
</tr>
</tbody>
</table>

\(^a\) \(I_{PL}\) = intensity of photoluminescence compared to E-stilbene

References begin on page 24
The Protasiewicz group also synthesized a diphosphene analogue of P3V.\textsuperscript{54} Polymer 1.17 was prepared by thermolysis or photolysis of $\text{Me}_3\text{P}=\text{P}−\text{Ar}−\text{P}=\text{PMe}_3$, eliminating two equivalents of $\text{PMe}_3$ (Scheme 1.14). Remarkably, 1.17 ($M_n = 5,900$ g mol$^{-1}$; DP = 6; PDI = 2.1) is the first polymer with multiple bonds between two heavier main group elements in the main chain. Although structurally interesting, 1.17 does not exhibit fluorescence, which may be due to quenching by the phosphorus lone pairs.
A common strategy used by the research groups of Gates and Protasiewicz is the employment of bulky groups to protect the heavy-element multiple bond (i.e. P=C or P=P) and prevent dimerization and/or cyclooligomerization. This strategy is in fact commonly used to stabilize exotic multiply bonded inorganic molecules and monomers for polymerization.13,56-59

### 1.1.4 Unconjugated Phosphorus-Carbon Polymers

Recently, a new class of phosphorus-containing polymers was developed by Vanderark et al. via the anionic ring-opening polymerization of a strained phosphirene (Scheme 1.15).60 This synthetic route led to polyvinylene phosphine (1.18). High molecular weight 1.18 ($M_n = 18,000$ g mol$^{-1}$; DP = 111; PDI = 1.23) was obtained. However, properties and potential applications of 1.18 have not been reported.

![Scheme 1.15](image)

In 2007, Chujo and co-workers reported the synthesis of polymers containing chiral phosphorus atoms in the backbone (1.19).61 This was achieved by using chiral biphosphineborane adducts and $\alpha,\alpha'$-dibromoxylene as building blocks (Scheme 1.16). Polymers 1.19 were studied by circular dichroism (CD) spectroscopy and differential scanning calorimetry (DSC) experiments. The results from CD spectroscopy suggested that the polymers derived from meta-xylene and para-xylene exhibited optically active higher-ordered structures, such as helical

References begin on page 24
chains. On the other hand, the polymer derived from ortho-xylene displayed an unresponsive CD spectrum, suggesting the absence of a higher-ordered structure. Potential applications for 1.19 include heavy-metal sensors and transition-metal catalysts for asymmetric reactions, however no studies have been reported thus far to demonstrate this possibility.

\[
\begin{align*}
1) & \; 2 \text{ equiv sec-BuLi, } (-)-\text{sparteine} \\
2) & \; \text{BrJ} / \text{Br}
\end{align*}
\]

**Scheme 1.16**

Poly(methylenephosphine)s are polymers composed of alternating phosphorus and carbon atoms in the main chain. Since the work on these polymers was conducted by the Gates group and builds the foundation for virtually all of the work presented in this thesis, a brief history of poly(methylenephosphine)s demands a section of its own.

### 1.2 Brief History of Poly(methylenephosphine)s

In 2003, Chi-Wing Tsang and Mandy Yam of the Gates group discovered the first addition polymerization of a phosphaalkene (1.20) to afford poly(methylenephosphine) (1.21). The discovery of 1.21 occurred after the purification of 1.20 by vacuum distillation at 150 °C. Through GPC and NMR spectroscopic analysis, Tsang and Yam showed that the gummy, pale-brown residue that remained after distillation contained poly(methylenephosphine) \((M_n = 11,500 \text{ g mol}^{-1}; \text{DP} = 36; \text{PDI} = 1.25)\). It was slightly surprising that the polymerization occurred so readily with just heat alone. Subsequently, it was shown that the polymerization could be achieved using a radical initiator such as 1,1′-azobis(cyclohexanecarbonitrile) (VAZO 88), or

*References begin on page 24*
using an anionic initiator such as MeLi or $n$-BuLi (Scheme 1.17). These methods afforded 1.21 with $M_n$ values ranging between 5,400 g mol$^{-1}$ and 6,600 g mol$^{-1}$ (DP = 17 to 21) and PDI values between 1.10 and 1.55.$^6$2

\[
\begin{align*}
\text{Scheme 1.17} \\
\text{The development by Tsang and Yam is an incredible feat for two reasons. Firstly, their} \\
development introduced a new method to access inorganic polymers. Although addition 
polymerization is well-established for olefins,$^{63}$ prior to Tsang and Yam's development addition 
polymerization had not been generalized to heavy-element multiple bonds. Most synthetic 
methods to access inorganic polymers involve a ROP process, polycondensation or a coupling 
strategy, all of which were shown as examples in section 1.1. Secondly, it has been observed that 
phosphaalkenes share some of the same reactivities as olefins, such as 1,2-addition of polar 
molecules (i.e. HX), the Diels-Alder reaction, epoxidation, metal complexation and 
hydrogenation (Scheme 1.18).$^{39,56,64,65}$ Tsang and Yam's development is significant because it 
expands the analogy between P=C and C=C bonds to polymer science.$^{55}$
\end{align*}
\]
In 2004, the Gates group reported their work on the radical copolymerization of phosphaalkene \( \text{1.20} \) and styrene to afford random copolymers \( \text{(1.22)} \) (Scheme 1.19).\(^{66}\)

\[
\begin{align*}
\text{Mes} & \begin{array}{c}
\text{P} = \text{C} \\
\text{Ph}
\end{array} & + & \begin{array}{c}
\text{H} = \text{C} = \text{H} \\
\text{H} \quad \text{Ph}
\end{array} & \xrightarrow{1\% \text{ VAZO}} & \text{100°C} & \left[ \begin{array}{c}
\left\{ \begin{array}{c}
\text{Mes} \\
\text{P} = \text{C} \\
\text{Ph}
\end{array} \right\} \right]_x \left\{ \begin{array}{c}
\text{H} \\
\text{C} = \text{C} \\
\text{H} \quad \text{Ph}
\end{array} \right\} y \\
\text{1.22}
\end{align*}
\]

The new hybrid inorganic-organic macromolecule, \( \text{1.22} \), was tested as a ligand for the Suzuki cross-coupling of bromobenzene and phenylboronic acid to form biphenyl. Results showed that in the presence \([\text{Pd}_2(\text{dba})_3]\) (\(\text{dba} = \text{dibenzylideneacetone}\)), \(\text{CsF}\), and copolymer \(\text{1.22}\), the cross-coupling proceeded and biphenyl was isolated in 90% yield. However, when the cross-coupling reaction was attempted using \([\text{Pd}_2(\text{dba})_3]\), \(\text{CsF}\) and homopolymer \(\text{1.21}\), the yield was
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the same as that in the absence of any ligand (yield = 25%). Thus, the study provided evidence for the potential of copolymer 1.22 for use in polymer-supported catalysis.

In 2006, Kevin Noonan of the Gates group showed that the anionic polymerization of phosphaalkene 1.20 could proceed at ambient temperature and in a living fashion using substoichiometric quantities of n-BuLi.\textsuperscript{67} This allowed for control over the molecular weight of the poly(methylenephosphine) with $M_n$ values up to 29,600 g mol\textsuperscript{-1} (DP = 94) and polymers of low polydispersities (PDI = 1.0 – 1.1). Furthermore, the living polymerization of 1.20 permitted the preparation of block copolymers, such as polystyrene-\textit{b}-poly(methylenephosphine) (1.23) (Scheme 1.20).\textsuperscript{67}

```
1) 1 mol% n-BuLi, toluene
2) m 1.20, glyme
3) MeOH

\begin{align*}
\text{1.23}
\end{align*}
```

Scheme 1.20

The chemical functionality of poly(methylenephosphine) 1.21 has also been investigated. Like most three-coordinate trivalent phosphines, the phosphine moieties in 1.21 can be oxidized using $O_2$, $H_2O_2$ or $S_8$ (Scheme 1.21).\textsuperscript{62} Similar to phosphine ligands, the phosphine moieties can also be coordinated to transition metals.\textsuperscript{68} Additionally, 1.21 can be chemically modified by coordinating the phosphorus atoms to BH\textsubscript{3} moieties to form phosphine-borane adducts along the backbone, or by reacting with MeOTf to afford methylphosphonium ionomers.\textsuperscript{69}

References begin on page 24
Although there have been more studies on poly(methylenephosphine) 1.21 and derivatives thereof, brevity limits me and I have discussed the founding developments that lead to my research objectives.

1.3 Research Objectives

It is clear that the polymerization of phosphaalkenes is a convenient method to prepare polymers with alternating phosphorus and carbon atoms in the main chain.\textsuperscript{62,67} It has also been shown by previous members in the Gates group that the chemical functionalization of phosphorus centres in poly(methylenephosphine) 1.21 can be easily achieved via oxidation reactions, or complexation to transition metals or Lewis acids.\textsuperscript{62,68,69} When I joined the Gates group, my first goal was to prepare poly(methylenephosphine)s bearing fluorescent side groups, and my second objective was to study the changes in electronic properties upon chemical
modification. The synthetic work will be discussed in Chapter 2, whereas the chemical functionalization of the new polymers and the concomitant changes in electronic properties will be covered in Chapter 3. The long-term goal behind the work presented in Chapters 2 and 3 is to develop a chemical sensor based on poly(methylenephosphine). This would require further studies, such as experiments examining their selectivity and sensitivity, which have not been conducted to this date. Thus, the results included in Chapters 2 and 3 represent the groundwork towards the long-term goal of poly(methylenephosphine)-based chemosensors.

While Chapters 2 and 3 focus on homopolymers, sensory behaviors may also be realized by random copolymers derived from phosphaalkenes since it may not be necessary to have phosphorus at every other atomic site in the backbone. As mentioned in section 1.2, some promising work had been achieved on the radical copolymerization of phosphaalkene 1.20 and styrene, affording poly(methylenephosphine)-co-polystyrene 1.22. However, little information was known about the microstructure of 1.22, such as the monomer distribution along the copolymer chain. To model the microstructure of a random copolymer formed by radical copolymerization, one would need to calculate the associated reactivity ratios. In addition to modeling the microstructure of 1.22, the reactivity ratios of phosphaalkene 1.20 and styrene would also be key synthetic parameters for future designs of tailored copolymers using phosphaalkenes and other monomers, such as copolymers for chemical sensory applications. Thus my third goal was to calculate the reactivity ratios of phosphaalkene 1.20 and styrene. More information about reactivity ratios and the experiments conducted to achieve my third goal will be included in Chapter 4. Lastly, Chapter 5 summarizes the findings of this thesis and proposes some future directions for this work. This thesis has been written following the style of

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Chapter One

a manuscript-based thesis. Each chapter is essentially self-contained with its own introduction, results and discussion, summary, experimental section and references.

1.4 Contributions by Other Researchers to This Work

Some of the work in this thesis was achieved in collaboration with other researchers. For Chapter 2, all of the synthetic work was done by myself with the exception of the synthesis and recrystallization of \( \text{MesP} = \text{C} \left( \text{C}_4 \text{H}_3 \text{S} \right) \left( \text{Ph} \right) \left( \text{C}_4 \text{H}_3 \text{S} = 2 \text{-thienyl} \right) \), which was a collaborative effort between myself and Fergus Chung. Fergus was an undergraduate researcher under my supervision. All crystallographic data were obtained primarily by Josh Bates with some assistance from Paul Siu using the departmental X-ray diffractometer. The solution and refinement of the molecular structures of \( \text{MesP} = \text{C} \left( \text{Naph} \right) \left( \text{Ph} \right) \left( \text{Naph} = 1 \text{-naphthyl} \right) \) and \( \text{MesP} = \text{C} \left( \text{C}_4 \text{H}_3 \text{S} \right) \left( \text{Ph} \right) \) were completed by Josh. The solution and refinement of the molecular structure of \( \text{MesP} = \text{C} \left( \text{Phen} \right) \left( \text{Phen} = 9 \text{-phenanthrenyl} \right) \) were performed by Paul. All of the work presented in Chapters 3 and 4 was completed by myself.

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1.5 References


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Chapter Two

Synthesis and Polymerization Studies of New Phosphaalkenes Bearing Conjugated Substituents*

2.1 Introduction

As mentioned in Chapter 1, the first goal of this thesis work is to synthesize poly(methyleneophosphine)s bearing conjugated substituents. The motivation behind this work is to develop poly(methyleneophosphine)-based chemical sensors. Thus far, the field of phosphorus-containing macromolecular chemosensors is dominated by phosphole-based polymers. The changes in electronic properties upon chemical modification of poly(methyleneophosphine)s with conjugated substituents are of interest and expected to give a sensor-like behavior. Chemical modification of these new polymers should be feasible given the demonstrated functionalization of phosphorus centres in [MesP–CPh2]n by oxidation and coordination to electrophiles (e.g. transition metals and boranes). The purpose of the conjugated groups is to facilitate the detection of changes in electronic responses upon functionalization at phosphorus. Although the long-term goal of this project is to develop a polymeric chemosensor, this thesis discusses only the synthesis and functionalization of these polymers and the concomitant changes in their electronic properties.

This chapter relates to the synthetic work involved in preparing the new poly(methyleneophosphine)s for the project described above. To access these polymers, it is necessary to first synthesize phosphaalkene monomers 2.1 – 2.3 (Scheme 2.1).

*A version of this chapter will be submitted for publication.
Chapter Two

A convenient method that has been commonly used to prepare $P$-mesityl phosphaalkenes is the phospha-Peterson reaction,\textsuperscript{10-18} a phosphorus analogue of the Peterson olefination reaction.\textsuperscript{19} This synthetic route involves the reaction between a silyl phosphide and a ketone or an aldehyde to yield a phosphaalkene provided that sufficiently bulky substituents are employed to protect the $P=C$ bond (Scheme 2.2).

\[
\begin{align*}
\text{Scheme 2.1} \\
&
\end{align*}
\]

Similar to the phospha-Peterson reaction is the base-catalyzed phospha-Peterson reaction.\textsuperscript{20,21} In this analogous reaction, a bis(trimethylsilyl)phosphine is mixed with one equivalent of a ketone and a catalytic amount (0.5 mol%) of anhydrous base (i.e. KOH or NaOH) to afford $P$-mesityl phosphaalkenes with a variety of aromatic C-substituents (Scheme 2.3).\textsuperscript{22}

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Presumably, a catalytic amount of base facilitates the in situ generation of the \([\text{MesP(SiMe}_3)]^-\) anion. The byproduct, hexamethyldisiloxane, is a volatile nonpolar liquid that can be easily removed in vacuo. In short, the base-catalyzed phospha-Peterson reaction is attractive because it is a simple one-step method to access \(P\)-mesityl phosphaalkenes bearing aromatic \(C\)-substituents. Both the standard phospha-Peterson reaction and the base-catalyzed phospha-Peterson approach were employed to prepare the target phosphaalkenes 2.1 – 2.3.

\[
\begin{align*}
\text{Mes-P} & \quad \text{SiMe}_3 \quad + \quad \text{O-C} & \quad \text{R} \\
\text{SiMe}_3 & \quad \text{R'} \quad \text{KOH or NaOH (cat.)} & \quad \text{- (SiMe}_3)_2\text{O} \\
& \quad \text{Mes-P} = \quad \text{C} & \quad \text{R} \\
& \quad \text{R'} & \quad \text{R'} \\
\end{align*}
\]

**Scheme 2.3**

As discussed in Chapter 1, the polymerization of phosphaalkenes can be achieved using a radical initiator such as 1,1'-azobis(cyclohexanecarbonitrile) (VAZO 88)\(^7\) or using an anionic initiator such as \(n\)-BuLi.\(^7,23\) The anionic method was chosen for the work presented in this chapter as it is less laborious. Herein, the syntheses and structures of phosphaalkenes 2.1 – 2.3 are reported, followed by a discussion on the polymerization studies of these phosphaalkene monomers.

### 2.2 Results and Discussion

#### 2.2.1 Synthesis of Phosphaalkene 2.1

Given the simplicity of the base-catalyzed phospha-Peterson reaction,\(^20,21\) this method was employed to prepare Mes\(P=\text{C}(\text{Naph})(\text{Ph})\) (2.1) (Naph = 1-naphthyl). The precursors to 2.1, Mes\(\text{P(SiMe}_3)_2\)\(^20\) and 1-benzoynaphthalene,\(^24\) were prepared following modified literature procedures. To prepare compound 2.1, Mes\(\text{P(SiMe}_3)_2\) was mixed with one equivalent of 1-benzoynaphthalene in the presence of a catalytic quantity of KOH (Scheme 2.4). The reaction mixture turned yellow within five minutes of being stirred.

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Scheme 2.4

The reaction progress was rather slow and was monitored over 2 weeks by $^{31}$P NMR spectroscopy (Figure 2.1). The spectra revealed that the signal assigned to MesP(SiMe$_3$)$_2$ ($\delta_{31P} = -161$; Figure 2.1a) was gradually depleted and replaced by signals assigned to phosphaalkene 2.1 ($\delta_{31P} = 251$ and 239, E/Z mixture; Figure 2.1b). There were two unidentifiable impurities in the reaction mixture, labeled A and B on the $^{31}$P NMR spectrum in Figure 2.1b. The minor impurity labeled C is MesPH$_2$, and the signal labeled D is residual MesP(SiMe$_3$)$_2$.

Figure 2.1. $^{31}$P NMR spectra (THF, 122 MHz) of (a) MesP(SiMe$_3$)$_2$ and (b) 2.1 (E/Z mixture) formed after 2 weeks. Minor impurities are labeled A – C. The identities of A and B are unknown, and C is MesPH$_2$. The signal labeled D is residual MesP(SiMe$_3$)$_2$.

The product, C-naphthyl-substituted phosphaalkene 2.1, was purified by vacuum distillation followed by multiple recrystallizations from hexanes, and isolated as yellow crystals.
in 25% yield. X-ray diffraction analysis of the yellow crystals showed 2.1 in the E configuration. The $^{31}$P NMR spectrum of the yellow crystals showed one signal at 239 ppm, hence this chemical shift was assigned to E-2.1. However, over time (i.e. 24 h), $^{31}$P NMR spectroscopic analysis of the same sample showed two signals at 251 ppm and 239 ppm, suggesting the occurrence of E/Z isomerization in solution. The isomerization of phosphaalkenes has been studied before.$^{11,12,22,26-28}$ This process can occur in as short as 30 min when irradiated with UV light, 24 h when exposed to sunlight, and 48 h in the absence of light.$^{22}$

The $^1$H NMR spectrum of E-2.1 in CDCl$_3$ (Figure 2.2) exhibits the characteristic upfield signal assigned to the ortho-$CH_3$ that has double the intensity of the signal assigned to the para-

![Figure 2.2](attachment:image.png)

**Figure 2.2.** $^1$H NMR spectrum (CDCl$_3$, 400 MHz) of E-2.1. Residual CHCl$_3$ (*). Silicone grease (†).

*The molecular structure and X-ray crystallographic analysis of E-2.1 will be presented in section 2.2.4.*
$\text{CH}_3$ of the mesityl ring. Integration of the $^1\text{H}$ NMR spectrum accounts for 9 methyl hydrogens ($\delta_{^1\text{H}} = 2.4$ and 2.3 ppm) and 14 aromatic hydrogens ($\delta_{^1\text{H}} = 7.9 - 6.8$ ppm). Compound 2.1 was also characterized by $^{13}\text{C}\{^1\text{H}\}$NMR spectroscopy (see Experimental).

### 2.2.2 Synthesis of Phosphaalkene 2.2

Similar to the preparation of 2.1, the synthesis of Mes$\text{P} = \text{C}(\text{C}_4\text{H}_3\text{S})(\text{Ph})$ (2.2) ($\text{C}_4\text{H}_3\text{S} = 2$-thienyl) was achieved via the base-catalyzed phospha-Peterson route (Scheme 2.5). The ketone precursor to 2.2, 2-benzoylthiophene, was prepared via a Friedel-Crafts acylation following an adapted literature procedure. The reaction between 2-benzoylthiophene and Mes$\text{P}(\text{SiMe}_3)_2$ ($\delta_{^3\text{P}} = -161$) in THF with a catalytic amount of KOH afforded 2.2 as a mixture of $E$- and $Z$-isomers ($\delta_{^3\text{P}} = 227$ and 220) over 5 days (Figure 2.3).

The C-thienyl-substituted phosphaalkene, 2.2, was purified by vacuum distillation, resulting in a yellow viscous oil (yield = 60%). Recrystallization of 2.2 in hexanes afforded bright yellow crystalline needles. The $^{31}\text{P}$ NMR spectrum of the needles showed the same two signals ($\delta_{^3\text{P}} = 227$, 58%; $\delta_{^3\text{P}} = 220$, 42%) as observed during the course of the reaction. The $^1\text{H}$ NMR spectrum of 2.2 dissolved in C$_6$D$_6$ is displayed in Figure 2.4. There are four signals in the upfield region due to the presence of two isomers. Based on integration, the more intense signal of the pair of chemical shifts assigned to the ortho-$\text{CH}_3$ and the more intense signal of chemical shifts assigned to the para-$\text{CH}_3$ were attributed to the same isomer. The remaining two signals

---

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Figure 2.3. $^{31}$P NMR spectra (THF, 122 MHz) of (a) MesP(SiMe$_3$)$_2$ and (b) 2.2 (E/Z mixture) (after 5 d).

were assigned to the other isomer. The ratio of isomers (58:42) based on integration of the $^{31}$P NMR spectrum agrees with that based on integration of the methyl protons in the $^1$H NMR spectrum. Integration of the benzylic region relative to the aromatic region gives 9 methyl hydrogens and 10 aromatic hydrogens. Compound 2.2 was also characterized by $^{13}$C{$^1$H} NMR spectroscopy (see Experimental).

Figure 2.4. $^1$H NMR spectrum (C$_6$D$_6$, 400 MHz) of 2.2 (E/Z mixture). Residual C$_6$D$_5$H (*).
2.2.3 Synthesis of Phosphaalkene 2.3

The synthesis of MesP\(=\text{C(Phen)(Ph)}\) (2.3) (Phen = 9-phenanthrenyl) via the base-catalyzed phospha-Peterson reaction was attempted. The ketone precursor, 9-benzoylphenanthrene, was prepared from benzoyl chloride and 9-bromophenanthrene according to modified literature procedures following a copper(I) coupling and using LiCl as an additive.\(^{24,30}\) Unfortunately, the preparation of 2.3 via the base-catalyzed route required extremely long reaction times (over 1 month), even at elevated temperatures (i.e. 50 °C), and afforded a mixture of products.

For these reasons, the preparation of 2.3 was attempted via the standard phospha-Peterson reaction described in the introduction of this chapter. By this method, one equivalent of a silyl phosphide (prepared in situ, \(\delta_{\text{31P}} = -187\), Figure 2.5a) was treated with 9-benzoylphenanthrene in THF at \(-78 ^{\circ}\) C (Scheme 2.6).

![Scheme 2.6](image)

An aliquot was removed from the dark green reaction mixture and analyzed by \(\text{\text{31P}}\) NMR spectroscopy. As shown in Figure 2.5b, the \(\text{\text{31P}}\) NMR spectroscopic analysis suggested a quantitative conversion of Li[MesP(SiMe\(_3\))] to the desired product 2.3 (\(\delta_{\text{31P}} = 252\) and 238; E/Z mixture). Upon quenching of the presumed byproduct LiOSiMe\(_3\) with Me\(_3\)SiCl, the reaction mixture instantaneously turned red. A red oil remained after the removal of solvent in vacuo, and was admixed with hexanes. Insoluble salts were removed by filtering the mixture through Celite. Phosphaalkene 2.3 was isolated as yellow crystals from recrystallization in hexanes.

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The $^{31}$P NMR spectrum of the yellow crystals dissolved in C$_6$D$_6$ showed one signal at 252 ppm. The X-ray diffraction analysis of the yellow crystals showed 2.3 in the Z stereochemistry, hence the $^{31}$P NMR signal at 252 ppm was assigned to Z-2.3.$^\dagger$

The $^1$H NMR spectrum of 2.3 dissolved in C$_6$D$_6$, shown in Figure 2.6, exhibits broad resonances in the aromatic region ($\delta_{\text{H}} =$ 6.5 and 6.0) and the allylic region ($\delta_{\text{H}} =$ 2.5 and 2.0). The multiple broad signals are likely to be due to restricted rotation of the mesityl ring. As indicated on the $^1$H NMR spectrum in Figure 2.6, the broad resonances at 6.5 ppm and 6.0 ppm are assigned to Mes-$H$, while the broad resonances at 2.5 ppm and 2.0 ppm are assigned to the ortho-$CH_3$. Integration of the spectrum agrees with this assignment and accounts for the remaining hydrogens in the molecule. A variable-temperature NMR experiment showed that the two pairs of broad signals ($\delta_{\text{H}} =$ 6.5 and 6.0; $\delta_{\text{H}} =$ 2.5 and 2.0) eventually coalesced upon heating at 45 °C, giving one broad signal at 6.3 ppm and one broad signal at 2.3 ppm.

$^\dagger$ The molecular structure and X-ray crystallographic analysis of Z-2.3 will be presented in section 2.2.4.
**Figure 2.6.** $^1$H NMR spectrum (C$_6$D$_6$, 400 MHz) of 2.3. The multiple broad signals are likely to be due to restricted rotation of the mesityl ring. Residual C$_6$D$_5$H (*). Silicon grease (†).

2.2.4 X-ray Crystallographic Analysis of Phosphaalkenes 2.1 – 2.3

In all three cases, crystals suitable for X-ray diffraction were successfully grown from concentrated hexanes solutions at room temperature. Under these conditions, 2.1 crystallizes as the $E$ isomer, 2.2 crystallizes as a mixture of $E/Z$ isomers, and 2.3 surprisingly crystallizes as the $Z$-isomer, as opposed to the expected $E$ configuration based on steric factors. This surprising result may be due to a conjugation or crystal packing effect, both discussed towards the end of this section. The molecular structures of $E$-2.1, 2.2, and $Z$-2.3 are displayed in Figures 2.7, 2.8, and 2.9, respectively. The solution and refinement of these molecular structures were completed by Josh Bates and Paul Siu.

*References begin on page 59*
Figure 2.7. Molecular structure $E$-MesP=CNaph(Ph) ($E$-2.1). Ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.8307(16), P(1)–C(10) 1.6876(14), C(10)–C(11) 1.4821(18), C(10)–C(17) 1.4933(19), C(1)–P(1)–C(10) 108.36(7), P(1)–C(10)–C(11) 129.23(10), P(1)–C(10)–C(17) 114.15(10), C(17)–C(10)–C(11) 116.56(12).
Figure 2.8. Molecular structure of MesP=\(\text{C}(\text{C}_4\text{H}_3\text{S})(\text{Ph})\) (2.2). Ellipsoids are drawn at 50% probability, hydrogens are omitted for clarity, and overlapping atoms are omitted in respective isomers. Selected bond lengths (Å) and angles (°): P(1)—C(1) 1.827(3), P(1)–C(10) 1.687(3), C(10)–C(11a) 1.484(10), C(10)–C(15a) 1.458(8), C(10)–C(11b) 1.49(2), C(10)–C(15b) 1.44(2), C(1)–P(1)–C(10) 107.39(12), C(1)–P(1)–C(10)–C(11a) 116.2(4), P(1)–C(10)–C(11a) 116.2(4), P(1)–C(10)–C(15a) 127.5(3), C(11a)–C(10)–C(15a) 116.3(5), P(1)–C(10)–C(15b) 115.2(10), P(1)–C(10)–C(11b) 129.9(9), C(11b)–C(10)–C(15b) 114.8(13).

A summary of cell constants and refinement parameters is displayed in Table 2.1.

Important metrical parameters of phosphaalkenes 2.1 – 2.3 are presented in Table 2.2, and for comparison, metrical parameters of MesP=\(\text{CPh}_2\), reported by the Bickelhaupt and Becker groups independently,\(^{31,32}\) are also included.

Before proceeding to a discussion of the metrical parameters of the new phosphaalkenes, the evident disorder in the refined structure of 2.2 (Figure 2.8) demands an explanation. The elongated and enlarged ellipsoids of a few atoms are attributed to disorder in the \(C\)-substituents. Disorder in the aromatic \(C\)-substituents of asymmetric phosphaalkenes has been observed in previous work in our lab. The solution and refinement process of the molecular structures of 2.2

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Figure 2.9. Molecular structure Z-MesP=C(Phen)(Ph) (Z-2.3). Ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)—C(1) 1.8273(18), P(1)—C(10) 1.6926(16), C(10)—C(11) 1.483(2), C(10)—C(17) 1.483(2), C(1)—P(1)—C(10) 105.76(8), P(1)—C(10)—C(11) 117.74(12), P(1)—C(10)—C(17) 123.89(12), C(17)—C(10)—C(11) 118.14(13).

proved to be challenging due to the overlapping electron densities from both isomers.

Considering the challenge and difficulties in modeling the molecular structure of 2.2, the hard work in accomplishing this task is credited to Josh Bates despite the disorder. To overcome this challenge during the solution and refinement process, the metrical parameters of the phenyl and thienyl rings of the dominant isomer (i.e. E-2.2) were used to give relative positions of atoms in the rings of the other isomer. The reason why there is an elongated ellipsoid for C(20a) is due to the influence of the electron density from the sulfur atom in the other isomer (i.e. S(1b)). Other enlarged or elongated ellipsoids observed in the molecular structure of 2.2 can be similarly explained by the influence of overlapping electron densities. Due to this disorder, only the

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metrical parameters that do not involve the phenyl and thienyl rings in 2.2 can be discussed with confidence, whereas the metrical parameters involving these rings are reported for completion and must be taken with caution.

Table 2.1. X-ray crystallographic data for E-2.1, 2.2 (E/Z mixture), and Z-2.3

<table>
<thead>
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<th>compound</th>
<th>E-2.1</th>
<th>2.2 (E/Z mixture)</th>
<th>Z-2.3</th>
</tr>
</thead>
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<td>Formula</td>
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<td>C₂₀H₁₉PS</td>
<td>C₃₀H₂₅P</td>
</tr>
<tr>
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<td>322.38</td>
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<td>monoclinic</td>
</tr>
<tr>
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<td>P 2₁/c</td>
<td>C 2/c</td>
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<td>yellow</td>
<td>yellow</td>
</tr>
<tr>
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<td>11.4651(14)</td>
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</tr>
<tr>
<td>b (Å)</td>
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<td>6.1645(9)</td>
<td>13.3010(14)</td>
</tr>
<tr>
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<td>24.1496(28)</td>
<td>20.028(2)</td>
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<td>90.0</td>
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</tr>
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References begin on page 59
Table 2.2. Important metrical parameters for E-2.1, E-2.2, Z-2.2, Z-2.3, and MesP=CPh₂.

<table>
<thead>
<tr>
<th>compound</th>
<th>E-2.1</th>
<th>E-2.2</th>
<th>Z-2.2</th>
<th>Z-2.3</th>
<th>MesP=CPh₂</th>
<th>MesP=CPh₂</th>
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<tbody>
<tr>
<td>Bond lengths (Å)</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>P=C</td>
<td>1.6876(14)</td>
<td>1.687(3)</td>
<td>1.687(3)</td>
<td>1.6926(16)</td>
<td>1.692(3)</td>
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<tr>
<td>P–C_Mes</td>
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<td>1.827(3)</td>
<td>1.827(3)</td>
<td>1.8273(18)</td>
<td>1.828(3)</td>
<td>1.830(2)</td>
</tr>
<tr>
<td>C–C_trans</td>
<td>1.4933(19)</td>
<td>1.484(10)</td>
<td>1.44(2)</td>
<td>1.483(2)</td>
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<tr>
<td>C–C_cis</td>
<td>1.4821(18)</td>
<td>1.458(8)</td>
<td>1.49(2)</td>
<td>1.483(2)</td>
<td>1.487(4)</td>
<td>1.489(2)</td>
</tr>
</tbody>
</table>

| Bond Angles (°)   |        |        |        |        |           |           |
| Φ_C_Mes–P=C       | 108.36(7) | 107.39(12)  | 107.39(12) | 105.76(8) | 107.5(2)  | 107.6(2)  |
| Φ_P=C–C_trans     | 114.15(10) | 116.2(4)  | 115.2(10) | 117.74(12) | 116.2(2)  | 118.0(2)  |
| Φ_P=C–C_cis       | 129.23(10) | 127.5(3)  | 129.9(9)  | 123.89(12) | 127.2(2)  | 124.8(2)  |
| Φ_C_trans–C–C_cis | 116.56(12) | 116.3(5)  | 114.8(13) | 118.14(13) | 116.6(2)  | 117.1(3)  |

| Angles between planes (°)  |        |        |        |        |           |           |
| Ar_trans           | 59.3   | 34     | 43     | 20.6   | 36.6      | 21.4      |
| Ar_cis             | 41.8   | 44     | 51     | 63.2   | 42.9      | 59.2      |
| Mes                | 64.8   | 73.7   | 73.7   | 85.3   | 71        | 72.2      |
| Reference          | This work | This work | This work | This work | This work | 31        |

Reference begins on page 59.
bond lengths in $E\cdot 2.1, 2.2$, and $Z\cdot 2.3$ (ca. 1.69 Å) are indicative of phosphorus-carbon double bonds. They are clearly shorter than the typical P–C single bond (1.83 Å – 1.90 Å)$^{33}$ and are in the range of P=C bond lengths of related C-substituted phosphaalkenes (1.61 Å – 1.71 Å).$^{34}$ The P=C bond lengths exhibited by $E\cdot 2.1, 2.2$, and $Z\cdot 2.3$ are in the long end of this range, which is characteristic of P-mesityl phosphaalkenes with aromatic C-substituents, such as MesP=CPh$_{2}$.$^{22,31,32}$ The P–C$_{\text{Mes}}$ bond lengths exhibited by 2.1 – 2.3 (ca. 1.83 Å) are consistent with the average P–C$_{\text{Ar}}$ bond length (1.836 Å).$^{33}$ The C–C$_{\text{trans}}$ and C–C$_{\text{cis}}$ bond lengths in $E\cdot 2.1$ and $Z\cdot 2.3$ (ca. 1.48 Å – 1.49 Å) are shorter than the average C–C single bond length (1.54 Å),$^{33}$ but agree with the typical C$_{sp^{2}}$–C$_{\text{Ar}}$ bond lengths (1.483 Å).$^{33}$ It is noticeable in Table 2.2 that the C–C$_{\text{trans}}$ bond length of $Z\cdot 2.2$ and the C–C$_{\text{cis}}$ bond length of $E\cdot 2.2$ appear to be comparatively short (ca. 1.44 Å – 1.45 Å). These are the bonds between C(10) and the ipso carbon of the thienyl substituent. The molecular structure of 2-benzoylthiophene shows a similar shortening effect of the analogous bond.$^{35}$ The bond length between the carbonyl carbon and the ipso carbon of the thienyl substituent measures 1.459 Å, and the bond length between the carbonyl carbon and the ipso carbon of the phenyl group is 1.482 Å.

The geometry of the carbon atom in the P=C bond is essentially planar (sum of angles ≈ 360°) in 2.1 – 2.3. All of the $\angle P=C–C_{\text{cis}}$ angles in $E\cdot 2.1, E\cdot 2.2, Z\cdot 2.2$, and $Z\cdot 2.3$ are greater than the $\angle P=C–C_{\text{trans}}$ angles ($\sim 123° – 129°$ vs. $\sim 114° – 117°$) implying that the Ar$_{\text{cis}}$ rings are bent further away from the P=C bond than the Ar$_{\text{trans}}$ rings. This is most likely an impact of steric repulsion between the Ar$_{\text{cis}}$ and the mesityl rings. However, it is interesting that the angles $\angle C_{\text{Mes}}–P=C$ and $\angle P=C–C_{\text{cis}}$ in $Z\cdot 2.3$ are smaller than the analogous angles in the other phosphaalkenes reported in Table 2.2, indicating that the mesityl and the phenanthrenyl rings surprisingly bend closer towards each other. This may be an effect of the crystal packing of $Z$-
2.3. As shown in Figure 2.10, the crystal packing of Z-2.3 exhibits \( \pi-\pi \) interactions (3.4 Å) between the carbons along the edges of the phenanthrenyl moieties of adjacent phosphaalkene molecules. These interactions are very similar to the \( \pi-\pi \) interactions in the crystal packing of phenanthrene molecules reported by Professor Trotter of this department in 1963.\(^{36}\) The phenanthrene rings in Trotter's report were oriented in the same fashion, respective to each other, as shown in Figure 2.10. And remarkably, the \( \pi-\pi \) interactions existed between the same carbons of the phenanthrenyl ring.

![Figure 2.10](image-url)  
*Figure 2.10.* The crystal packing of Z-2.3. Green dotted lines represent the \( \pi-\pi \) interactions (3.4 Å).

The angle between the best planes of the P=C bond and the aromatic P- and C-substituents in the phosphaalkenes can indicate the degree of \( \pi \)-conjugation present in the

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molecule. A larger angle would suggest minimal \( \pi \)-conjugation, whereas a smaller angle would suggest a larger degree of \( \pi \)-conjugation between the P=C bond and the respective aromatic moiety. In the molecular structure of Z-2.3, the angle between the best planes of the mesityl ring and the P=C bond is 85.3°, indicating little or no conjugation between these moieties. On the other hand, the angle between the P=C bond and the best plane of the phenyl ring is 20.6°, suggesting that the P=C bond is more likely to be conjugated with the phenyl ring than the mesityl ring. In E-2.1, the angle between planes of the naphthyl ring and the P=C bond is 59.3°, and the angle between planes of the phenyl ring and the P=C bond is 41.8°. The data suggest that the existence of \( \pi \)-conjugation among the naphthyl ring, phenyl ring, and the P=C bond in E-2.1 is unlikely.

2.2.5 Polymerization Studies of Phosphaalkene Monomers 2.1 – 2.3

We aimed to polymerize phosphaalkenes 2.1 – 2.3 by anionic polymerization. The polymerization of 2.1 and 2.3 was successfully achieved by treating a THF solution of the monomer with n-BuLi (2 mol%) at room temperature (Scheme 2.7). The polymerization of 2.2 was attempted, but no evidence of polymer formation was observed. This observation will be discussed later in this section.

![Scheme 2.7](image)

The addition of the anionic initiator n-BuLi (2 mol%) to a yellow solution of 2.1 resulted in an instantaneous color change to dark green. The progress of the anionic polymerization was

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monitored by $^{31}$P NMR spectroscopy. As the polymerization advanced, the $^{31}$P NMR signals of 2.1 ($\delta_{31P} = 251$ and 239, $E/Z$ mixtures) gradually decreased in relative intensity and were replaced by a broad signal ($\delta_{31P} = -9$ ppm). This broad signal was assigned to [MesP–C(Naph)(Ph)]$_n$ 2.4 and is similar to the broad $^{31}$P NMR chemical shift of [MesP–CPh$_2$]$_n$ ($\delta_{31P} = -10$ ppm).$^7$

After 14 days, the color of the reaction mixture was brown-green. Analysis of the $^{31}$P NMR spectrum of an aliquot removed from the reaction mixture suggested very little advancement in the polymerization. Integration of the $^{31}$P NMR spectrum showed 73% conversion of monomer 2.1 to polymer 2.4 (Figure 2.11a). Since there was little advancement in the polymerization thereafter, 2.4 was isolated by addition of methanol to quench any remaining lithiates, followed by repeated precipitations using hexanes (yield = 40%). A $^{31}$P NMR spectrum of the isolated polymer is shown in Figure 2.11b.

![NMR Spectra](image)

Figure 2.11. $^{31}$P NMR spectra (THF, 122 MHz) of (a) an aliquot removed from polymerization of phosphaalkene 2.1 to form polymer 2.4 (after 14 d); (b) isolated polymer 2.4.
Analysis of 2.4 by triple detection gel permeation chromatography (GPC) showed that the polymer had an absolute number average molecular weight ($M_n$) of 40,100 g mol$^{-1}$ and a polydispersity index (PDI) of 1.42. GPC traces of 2.4 from the laser light scattering signal and the refractive index signal are presented in Figure 2.12. The anticipated molecular weight of the polymer based on the monomer feed and initiator feed is 18,300 g mol$^{-1}$. Although the goal of this project was to simply prepare poly(methylenephosphine) bearing the specified substituents, an explanation is required for the difference between the anticipated molecular weight and $M_n$ measured by GPC.

![Figure 2.12. GPC trace of 2.4; $M_n = 40,100$ g mol$^{-1}$, PDI = 1.42. (Red trace – laser light scattering signal, blue trace – refractive index signal.)](image)

The higher than anticipated $M_n$ value is mostly likely due to a fair amount of quenching of reactive chain ends during the polymerization by minor impurities, and there is evidence of impurities in the $^1$H NMR spectrum of 2.1 (Figure 2.2). The quenching would result in shorter chains of the quenched species and higher molecular weights for the remaining polymer chains. Most of the shorter chains were probably removed from the isolated product during the work-up.
explaining why the measured $M_n$ of the isolated polymer was so much higher than the anticipated molecular weight. The polymerization of 2.1 was repeated a number of times and gave similar results.

Similar to the polymerization of 2.1, the same color change from yellow to dark green was observed when a solution of $C$-phenanthrenyl-substituted phosphaalkene 2.3 was treated with $n$-BuLi (2 mol%). As the polymerization moved forward, the conversion of monomer 2.3 ($\delta_{31P} = 252$ and 238, $E/Z$ mixtures) to polymer 2.5 ($\delta_{31P} = -10$, broad) was monitored by $^{31}$P NMR spectroscopy (Figure 2.13a). After 8 days, the conversion of monomer to polymer was 60%, and the reaction mixture was brown-green in color. At this point, there was very little progress in the polymerization, and thus methanol was added to the reaction mixture to quench any remaining lithiates. Polymer 2.5 was isolated in the same manner as described for the isolation of 2.4 with a 32% yield. The $^{31}$P NMR spectrum of 2.5 is shown in Figure 2.13b.

![Figure 2.13. $^{31}$P NMR spectra (THF, 122 MHz) of (a) an aliquot removed from the reaction mixture of the polymerization of phosphaalkene 2.3 to form polymer 2.5 (after 8 d); (b) isolated polymer 2.5.](image-url)
According to the data analysis of 2.5 by triple detection GPC, the polymer had an $M_n$ of 27,100 g mol$^{-1}$ and a PDI of 1.39. The GPC traces of 2.5 are displayed in Figure 2.14. The analyzed $M_n$ is greater than the anticipated molecular weight (20,900 g mol$^{-1}$). This difference alludes to the event of quenching by impurities in solution during the polymerization progress, which was previously discussed. It is puzzling and unclear why the elemental analysis of polymers 2.4 and 2.5 showed a lower carbon content than expected; this may be a sign of inorganic impurities or fragmentation of $-\text{C}(\text{R})(\text{Ph})$ chain ends ($\text{R} = \text{Naph or Phen}$).

![Figure 2.14](image)

**Figure 2.14.** GPC trace of 2.5; $M_n = 27,100$ g mol$^{-1}$, PDI = 1.39. (Red trace – laser light scattering signal, blue trace – refractive index signal.)

As mentioned earlier in this section, the polymerization of C-thienyl-substituted phosphaalkene 2.2 was attempted, but there was no polymer formation. The polymerization was first attempted using 2 mol% $n$-BuLi at room temperature. Upon the addition of the anionic initiator to a THF solution of 2.2, a change of coloration from yellow to dark red was observed. The polymerization was monitored over 7 days by removing aliquots from the reaction mixture, then analyzing the aliquots by $^{31}$P NMR spectroscopy. No change was observed in the $^{31}$P NMR
spectra of the aliquots. More specifically, only signals assigned to phosphaalkene 2.2 ($\delta_{31p} = 227$ and 220, E/Z mixture) were observed and there was no broad signal that would be characteristic of phosphine moieties in poly(methylenephosphine).

The polymerization of 2.2 was further attempted with a higher initiator loading (up to 5 mol%) and at elevated temperatures (45 °C). Again, reactions were monitored by $^{31}$P NMR spectroscopy and there was no evidence of polymer growth. There are several possible reasons to account for the absence of polymerization activity:

1. The initiated species, Li[Mes(n-Bu)P—C(C4H3S)(Ph)], did not form. However, reactivity was observed in an NMR-scale experiment in which 2.2 was treated with one equivalent of MeLi at −78 °C in THF. $^{31}$P NMR analysis of the red reaction mixture showed two signals at −32 ppm and −44 ppm (Figure 2.15a). It was speculated that both signals are representative of the lithiated species, whereby one was assigned to Li[Mes(Me)P—C(C4H3S)(Ph)], and the other signal was assigned to Mes(Me)PCH(Ph)(C4H2SLi) (lithium at the α-position of the thienyl ring). As a reference, Li[Mes(Me)P—CPh2] has a $^{31}$P chemical shift of −42 ppm in THF.37 When the reaction mixture was quenched with MeOH, there was one singlet at −18 ppm in the $^{31}$P NMR spectrum of the quenched reaction mixture, suggesting the formation of Mes(Me)P—CH(C4H3S)(Ph) (Figure 2.15b). For comparison, the phosphine, Mes(Me)P—CHPh2, has a $^{31}$P chemical shift of −24 ppm.37 The species at −18 ppm was not isolated as this was a test reaction at NMR-scale.

2. Assuming that the formation of the initiated species was successful, then it is possible that the initiated species did not attack any monomers in solution to initiate the propagation step for forming a growing chain. The lack of propagation could be due to the stability of the carbanion, thereby not being reactive enough to attack a monomer. In
order for propagation to occur, the carbanion must be relatively unstable thereby giving a driving force for the addition to a monomer.

3. It has been shown the anionic polymerization of phosphaalkenes requires conditions of high purity.\textsuperscript{23} It is possible that the samples of 2.2 used in the polymerization experiments were not pure enough as there is evidence of minor impurities in the $^1$H NMR spectrum of 2.2 (Figure 2.4). Initiated species could be quenched by impurities present in solution.

I speculate that the absence of polymerization is likely due to a lack of propagation. The NMR-scale experiment suggests that a lithiated species can form. However, it is possible that this species does not actually add to another monomer to propagate chain growth. Likewise, the lithiated species could be quenched by impurities in solution, consequently inhibiting polymer formation.
2.3 Summary

New phosphaalkenes 2.1 and 2.2 were successfully prepared via the base-catalyzed phospha-Peterson reaction, whereas the synthesis of 2.3 was achieved via the standard phospha-Peterson route. The molecular structures of these new phosphaalkenes were studied by X-ray diffraction analysis. Anionic polymerization of 2.1 and 2.3 afforded new polymers, 2.4 and 2.5. Attempted polymerization of 2.2 resulted in no polymer formation. The electronic properties of phosphaalkenes 2.1 and 2.3 and polymers 2.4 and 2.5, as well as the chemical functionalization of these polymers, will be discussed in Chapter 3.

2.4 Experimental section

General procedures. All manipulations of air and/or water sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques or in a glovebox. Hexanes and dichloromethane were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. THF was freshly distilled from sodium/benzophenone ketyl. KOH and NaOH were made anhydrous by following a literature procedure (recrystallization from EtOH and subsequent heating in vacuo). CDCl$_3$ and C$_6$D$_6$ were dried over molecular sieves prior to use. MesP(SiMe$_3$)$_2$, 1-benzoylnaphthalene, 2-benzoylthiophene, 9-benzoylphenanthrene were prepared following modified literature procedures. n-BuLi (1.6 M in hexanes) and MeLi (1.6 M in diethyl ether) were purchased from Aldrich and were titrated prior to use to determine the concentration.

Equipment. $^1$H, $^{31}$P, and $^{13}$C{$^1$H} NMR spectra were recorded on Bruker Avance 300 MHz or 400 MHz spectrometers. Chemical shifts are reported relative to: residual CHCl$_3$ ($\delta = 7.26$ for $^1$H); C$_6$D$_3$H ($\delta = 7.15$ for $^1$H); 85% H$_3$PO$_4$ as an external standard ($\delta = 0.0$ for $^{31}$P); CDCl$_3$ ($\delta =$ \ldots

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77.16 for $^{13}$C{$^1$H}). Molecular weights were estimated by triple detection gel permeation chromatography (GPC-LLS) using a Waters liquid chromatograph equipped with a Waters 515 HPLC pump, Waters 717 plus autosampler, Waters Styrage columns (4.6 x 300 mm) HR2, HR4, and HR5E, and a Waters 2410 differential refractometer (refractive index detector $\lambda = 940$ nm), Wyatt tristar miniDAWN (laser light scattering detector operating at $\lambda = 690$ nm) and a Wyatt ViscoStar viscometer. A flow rate of 0.5 mL min$^{-1}$ was used, and samples were dissolved in THF (ca. 2 mg mL$^{-1}$). The $dn/dc$ for each sample was determined using the software. Elemental analyses were performed in the UBC-Chemistry Microanalysis Facility. Mass Spectra were recorded on a Kratos MS 50 instrument in EI mode (70 eV).

2.4.1 Preparation of MesP=C(Naph)(Ph) (2.1). MesP(SiMe$_3$)$_2$ (8.6 g, 0.029 mol) dissolved in THF (15 mL) was treated with 1-benzoylnaphthalene (6.7 g, 0.029 mol) dissolved in minimal THF and a catalytic amount of KOH (4 mg, 0.07 mmol). The yellow mixture was stirred and the reaction progress was monitored by $^{31}$P NMR spectroscopy. After being stirred for 2 weeks at 55°C, 80% of MesP(SiMe$_3$)$_2$ had converted to the desired product ($\delta_{31P} = 251, 239; E/Z$ mixture), and the solvent was removed in vacuo. The crude product was purified by vacuum distillation at 210°C (0.01 mmHg). Recrystallization of the distillate in hexanes at room temperature afforded yellow crystals suitable for X-ray diffraction. Yield: 2.56 g (25%).

$^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta$ 251 (Z-isomer), 239 (E-isomer); $^1$H NMR (CDCl$_3$, 400 MHz) (E-isomer): $\delta$ 7.9 – 6.8 (m, 14H, Ar), 2.4 (s, 6H, o-CH$_3$), 2.3 (s, 3H, p-CH$_3$); $^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz): $\delta$ 191.1 (d, $^1$J$_{CP} = 44$ Hz, P=C), 143.3 (d, $J_{CP} = 15$ Hz), 141.7 (d, $J_{CP} = 27$ Hz), 140.5 (d, $J_{CP} = 7$ Hz), 138.9 (s), 136.7 (d, $^1$J$_{CP} = 40$ Hz, i-Mes), 134.1 (s), 132.0 (d, $J_{CP} = 9$ Hz), 129.4 – 124.8 (m), 22.2 (d, $^3$J$_{CP} = 9$ Hz, o-CH$_3$), 21.3 (s, p-CH$_3$); MS (EI, 70eV): $m/z$ [%]
Chapter Two

368, 367, 366 [2, 21, 91; M⁺]; 365 [100; M⁺ – H]; 246 [21; M⁺ – H – Mes]; 119 [8; M⁺ – H – Mes – Naph].

2.4.2 Preparation of MesP=C(C₄H₃S)(Ph) (2.2). MesP(SiMe₃)₂ (7.89 g, 0.027 mol), 2-benzoylthiophene (5.01 g, 0.027 mol), and anhydrous KOH (4 mg, 0.07 mmol) were mixed and dissolved in THF (15 mL). The reaction mixture was stirred, and the reaction progress was monitored by ³¹P NMR spectroscopy. After 5 days, MesP=C(C₄H₃S)(Ph) was formed quantitatively (δ³¹P = 227, 220; E/Z mixture). The solvent was removed in vacuo, resulting in a dark amber oil. The crude product was purified by vacuum distillation at 195 °C (0.01 mmHg). Yellow crystals suitable for X-ray diffraction were obtained from slow evaporation of a hexanes solution. Yield = 5.19 g (60%).

³¹P NMR (CDCl₃, 162 MHz) (E/Z mixture): δ 227, 220. ¹H NMR (C₆D₆, 400 MHz) (E/Z mixture): δ 7.6 – 6.4 (m, 10H, Ar), 2.39, 2.27 (s, 6H, o-CH₃), 2.14, 1.94 (s, 3H, p-CH₃). ¹³C{¹H} NMR (CDCl₃, 101 MHz) (E/Z mixture): δ 184.8 (d, ¹JCP = 40 Hz, P=C), 181.3 (d, ¹JCP = 45 Hz, P=C), 149.5 (d, ¹JCP = 28 Hz), 146.2 (d, ¹JCP = 20 Hz), 144.4 (d, ¹JCP = 26 Hz), 142.5 (d, ¹JCP = 13 Hz), 141.2 (d, ¹JCP = 7 Hz), 140.7 (d, ¹JCP = 7 Hz), 136.2 (d, ¹JCP = 46 Hz, i-Mes), 135.5 (d, ¹JCP = 40 Hz, i-Mes), 129.4 – 127.7 (m), 127.5 (s), 126.6 – 126.1 (m), 22.5 (d, ³JCP = 9 Hz, o-CH₃), 21.9 (d, ³JCP = 8 Hz, o-CH₃), 21.4 (s, p-CH₃), 21.2 (s, p-CH₃). MS (El, 70eV): m/z [%] 324, 323, 322 [6, 24, 100; M⁺]; 321 [15; M⁺ – H]; 244 [29; M⁺ – H – Ph]; 238 [73; M⁺ – H – C₄H₃S]; 202 [5; M⁺ – H – Mes]; 161 [8; M⁺ – H – C₄H₃S – Ph]; 119 [8; M⁺ – H – C₄H₃S – Mes].

2.4.3 Preparation of MesP=C(Phen)(Ph) (2.3). A stirred solution of MesP(SiMe₃)₂ (2.38 g, 8 mmol) in ¹HF was treated with MeLi in Et₂O (5.35 mL, 1.5 M, 8 mmol) at 25 °C. After heating

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the reaction mixture at 65 °C for 12 h, analysis of an aliquot removed from the reaction by $^{31}$P NMR spectroscopy suggested the complete lithiation of the starting material to MesP(SiMe$_3$)Li ($\delta_{31}P = -187$). To this reaction mixture was added 9-benzoylphenanthrene (2.27 g, 8 mmol) dissolved in THF at -78 °C. After the reaction mixture was stirred for 10 min at -78 °C, $^{31}$P NMR spectroscopic analysis of an aliquot removed from the reaction mixture suggested quantitative formation of 2.3 ($\delta_{31}P = 252, 238$; $E/Z$ mixture). The reaction mixture was then treated with Me$_3$SiCl (1.0 mL, 8 mmol) to quench LiOSiMe$_3$. After the removal of solvent, the crude oil was extracted with hexanes (3 x 40 mL) and filtered through Celite. The solvent was removed in vacuo leaving a red oil. Yellow crystals suitable for X-ray diffraction were obtained from slow evaporation of a hexanes solution. Yield: 0.50 g (15%).

$^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta$ 252 ($Z$-isomer), 238 ($E$-isomer); $^1$H NMR (C$_6$D$_6$, 400 MHz) ($Z$-isomer): $\delta$ 8.3 - 7.0 (m, 14H, Ar-H), 6.7 - 5.8 (br, 2H, Mes-H), 2.8 - 1.8 (br, 6H, o-CH$_3$), 1.6 (s, 3H, p-CH$_3$); $^{13}$C{ $^1$H} NMR (CDCl$_3$, 101 MHz) ($E/Z$ mixture): $\delta$ 193.7 (d, $^1J_{CP} = 44$ Hz, P=C), 191.0 (d, $^1J_{CP} = 44$ Hz, P=C), 144.2 (d, $^1J_{CP} = 24$ Hz), 142.7 (d, $^1J_{CP} = 15$ Hz), 140.5 (d, $^1J_{CP} = 6$ Hz), 140.1 (d, $^1J_{CP} = 28$ Hz), 138.9 (s), 138.1 (s), 138.0 (s), 136.6 (d, $^1J_{CP} = 7$ Hz), 140.7 (d, $^1J_{CP} = 7$ Hz), 136.6 (d, $^1J_{CP} = 40$ Hz, i-Mes), 135.9 (d, $^1J_{CP} = 41$ Hz, i-Mes), 131.6 - 122.5 (m), 22.6 (br, o-CH$_3$), 22.6 (d, $^3J_{CP} = 9$ Hz, o-CH$_3$), 21.3 (s, p-CH$_3$), 21.0 (s, p-CH$_3$). MS (EI, 70eV): $m/z$ [%] 418, 417, 416 [3, 29, 98; $M^+$]; 415 [100; $M^+ - H$]; 296 [29; $M^+ - H - Mes$]; 220 [5; $M^+ - Mes - Phen$]; 119 [13; $M^+ - H - Mes - Phen$]. Anal. Calcd for C$_{30}$H$_{25}$P: C, 86.51; H, 6.05. Found: C, 86.15; H, 6.09.

2.4.4 Preparation of [MesP–C(Naph)(Ph)]$_n$ (2.4). The polymerization of 2.1 was carried out inside a glovebox. To a stirred solution of 2.1 (0.84 g, 2.3 mmol) dissolved in THF (6 mL) was

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added \( n\)-BuLi (1.2 M, 38 \( \mu \)L, 0.05 mmol). The reaction mixture was stirred at room temperature and monitored by \( ^{31}P \) NMR spectroscopy, which showed an increase in intensity of a broad signal over 2 weeks. Thereafter, the reaction mixture was removed from the glovebox and quenched using methanol (3 drops). After the removal of solvent in vacuo, the polymer was isolated via hexanes precipitation (3 \( \times \) 100 mL), then dried in a vacuum oven at 65 °C for 24 h.

Yield = 327 mg (40%). \( ^{31}P \) NMR (CDCl\(_3\), 122 MHz): \( \delta = 9 \) (br). \( ^1H \) NMR (CDCl\(_3\), 300 MHz): \( \delta = 9 - 5 \) (br, Ar-H), 3.5 - 0.5 (br, CH\(_3\)). GPC-LLS (THF): \( M_n = 40,100 \), PDI = 1.42. Anal. Calcd for \((C_{26}H_{23}P)\): C, 85.22; H, 6.33. Found: C, 83.38; H, 6.45.

### 2.4.5 Attempted preparation of \([\text{MesP–C(C4H3S)(Ph)}]_n\). The polymerization of 2.2 was attempted a number of times using different monomer:initiator ratios and different temperatures inside a glovebox. The following procedure describes an attempt using 2 mol% initiator at room temperature: To a stirred solution of 2.2 (0.47 g, 1.5 mmol) dissolved in THF (3 mL) was added \( n\)-BuLi (1.2 M, 24.6 \( \mu \)L, 0.03 mmol). The reaction mixture was stirred at room temperature and monitored by \( ^{31}P \) NMR spectroscopy for 7 days by removing aliquots from the reaction mixture. The \( ^{31}P \) NMR spectra of the aliquots showed two signals that were assigned to 2.2 (\( \delta^{31P} = 227, 220 \)); there was no broad signal that would be characteristic of polymer formation.

### 2.4.6 Preparation of \([\text{MesP–C(Phen)(Ph)}]_n\) (2.5). The polymerization of 2.3 was performed inside a glovebox. A stirred solution of 2.3 (0.39 g, 1.3 mmol) dissolved in THF (3 mL) was treated with \( n\)-BuLi (1.2 M, 16 \( \mu \)L, 0.02 mmol). The reaction mixture was stirred at room temperature and monitored by \( ^{31}P \) NMR spectroscopy, which showed the gradual increase in intensity of a broad signal over 8 days. The reaction mixture was subsequently removed from
the glovebox and quenched with methanol (3 drops). The solvent was removed in vacuo, leaving an orange oil. The polymer was isolated by hexanes precipitation (3 x 100 mL), then dried in a vacuum oven at 65 °C for 24 h. Yield = 124 mg (32%). $^{31}$P NMR (CDCl$_3$, 122 MHz): δ –10 (br). $^1$H NMR (CDCl$_3$, 300 MHz): δ 9 – 5 (br, Ar), 3.5 – 0.5 (br, CH$_3$). GPC-LLS (THF): $M_n$ = 27,100, PDI = 1.39. Anal. Calcd for (C$_{30}$H$_{25}$P)$_n$: C, 86.51; H, 6.05. Found: C, 85.12; H, 6.06.

2.4.7 X-ray crystallography. All single crystals were immersed in oil and were mounted on a glass fiber. Data were collected on a Bruker X8 APEX II diffractometer with graphite Mo Kα radiation. All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms. All data sets were corrected for Lorentz and polarization effects. Refinements were performed using the SHELXTL$^{40}$ crystallographic software program of Bruker-AXS.

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Chapter Three

Chemical Modification of Poly(methylenephosphine)s with Conjugated Substituents Accompanied by Changes in Electronic Properties*

3.1 Introduction

As discussed in Chapter 2, new poly(methylenephosphine)s bearing naphthyl and phenanthrenyl substituents were successfully prepared by anionic polymerization of phosphaalkenes. The chemical equation for the reaction is shown in Scheme 3.1.

\[
\begin{align*}
\text{Mes} & \quad \text{P} = \text{C} \\
\text{Ph} & \quad \text{R} \quad \text{2 mol\% n}-\text{BuLi} \\
\text{Mes} & \quad \text{P} - \text{C} (\text{Naph})(\text{Ph})_n \\
\text{THF, RT} & \quad \text{Mes} \\
\text{R} = \text{Naph} & \quad \text{3.1a} \\
\text{R} = \text{Phen} & \quad \text{3.1b}
\end{align*}
\]

Scheme 3.1

Due to the Lewis basicity and unique reactivity of phosphorus (III) (e.g. oxidation and coordination),\textsuperscript{1,2} the chemical modification of the phosphine centres in [MesP–C(Naph)(Ph)]\textsubscript{n} (3.2a) and [MesP–C(Phen)(Ph)]\textsubscript{n} (3.2b) should be feasible. In this sense, the phosphorus atoms may act as receptor sites for analytes, possibly leading to a change in the electronic structure to give a sensor-like behavior. Following the preparation of macromolecules 3.2a and 3.2b, the

*A version of this chapter will be submitted for publication.
next goal was to chemically modify the polymers and examine the concomitant changes in the electronic properties.

Based on literature precedent,\textsuperscript{3,4} we expect that the presence of the phosphorus lone pair in \textit{3.2a} and \textit{3.2b} would lead to a fluorescence quenching effect on the polymer, resulting in weaker fluorescence intensity or no fluorescence at all. The lone pair on phosphaalkenes, \textit{3.1a} and \textit{3.1b}, is expected to invoke a similar quenching effect. We hypothesize that coordination of the phosphorus lone pairs in poly(methylene phosphine)s \textit{3.2a} and \textit{3.2b} to an electrophilic analyte (E) will eliminate the quenching effect and allow fluorescence to occur (Scheme 3.2).

![Scheme 3.2](image)

This chapter describes experiments undertaken to test the hypothesis that chemical functionalization of phosphine polymers \textit{3.2a} and \textit{3.2b} would lead to fluorescence. More specifically, this discussion entails the post-polymerization functionalization of \textit{3.2a} and \textit{3.2b} via oxidation and coordination to borane moieties. In addition, this chapter includes preliminary results from the investigation of the electronic properties of phosphaalkenes \textit{3.1a} and \textit{3.1b}, poly(methylene phosphine)s \textit{3.2a} and \textit{3.2b}, and the new chemically functionalized polymers.

\textbf{References begin on page 84}
3.2 Results and Discussion

3.2.1 Oxidation of 3.2a and 3.2b

Previous work in the Gates lab showed that $[\text{MesP}—\text{CPh}_2]_n$ can be easily oxidized using $\text{H}_2\text{O}_2$ or by exposing a solution of the polymer to air for four days. In this thesis work, the oxidation of poly(methyleneephosphine)s 3.2a and 3.2b was investigated. According to $^{31}\text{P}$ NMR spectroscopic analysis, a solution of naphthyl-derivatized polymer 3.2a did not show any evidence of oxidation after being exposed to air for one week, suggesting that 3.2a was quite air stable. Nonetheless, the oxidation of 3.2a was achieved by treating a $\text{CH}_2\text{Cl}_2$ solution of 3.2a with aqueous 30% $\text{H}_2\text{O}_2$ (Scheme 3.3). The oxidation progress was monitored by $^{31}\text{P}$ NMR spectroscopy. The complete oxidation of 3.2a required an excess of $\text{H}_2\text{O}_2$ (2.6 equiv) and the reaction mixture was stirred overnight. The $^{31}\text{P}$ NMR spectrum of the oxidized polymer $[\text{MesP(O)—C(Naph)(Ph)}]_n$ (3.3a) is shown in Figure 3.1, and for comparison the $^{31}\text{P}$ NMR spectrum of 3.2a is also included. The $^{31}\text{P}$ chemical shift of 3.3a (47 ppm) is the same as that of $[\text{MesP(O)—CPh}_2]_n$.  

![Scheme 3.3](image)

References begin on page 84
In contrast to the naphthyl-derivatized phosphine polymer 3.2a, the phenanthrenyl-derivatized poly(methylenephosphine) 3.2b oxidizes more readily in air when dissolved in THF (Scheme 3.4). After 3 hours of exposure to air, the $^{31}$P NMR spectrum of a THF solution of 3.2b showed the appearance of a new broad signal at 49 ppm (Figure 3.2b). The broad resonance at 10 ppm is assigned to unoxidized phosphorus centres in the polymer, which is consistent with the $^{31}$P NMR chemical shift of 3.2b (Figure 3.2a). After 1 week, 3.2b was completely oxidized to give $\text{[MesP(O)--C(Phen)(Ph)]_n}$ (3.3b) ($\delta_{31P} = 49$) (Figure 3.2c).

**Scheme 3.4**

Oxidized polymers 3.3a and 3.3b were isolated as white solids after the removal of solvent in vacuo. Analysis of 3.3a and 3.3b by triple detection gel permeation chromatography (GPC) showed that 3.3a exhibited an absolute number average molecular weight ($M_n$) of 43,500
Figure 3.2. $^{31}P$ NMR spectra (THF, 122 MHz) of (a) 3.2b; (b) an aliquot from the THF solution of 3.2b exposed to air for 3 h; (c) an aliquot from the same solution exposed to air for 7 d to form 3.3b.

3.2b exhibited an $M_n$ value of 31,300 g mol$^{-1}$. Both oxidized macromolecules have slightly higher $M_n$ values than their parent unoxidized polymers (3.2a: $M_n = 42,160$ g mol$^{-1}$; 3.2b: $M_n = 27,000$ g mol$^{-1}$), which is expected. According to the GPC analysis, the polydispersity index (PDI) of 3.3a is 1.16, while that of 3.3b is 1.46. Oddly, the two oxidized macromolecules 3.3a and 3.3b have narrower PDI values than their parent unoxidized polymers (3.2a: PDI = 1.40; 3.2b: PDI = 1.49). This may be due to interaction of the phosphine moieties in the unfunctionalized poly(methylene phosphine)s with the GPC columns, which has been reported for phosphine polymers in the past.$^{6,7}$ For example, the PDI of $[\text{MesP}(\text{BH}_3)-\text{CPh}_2]_n$ ($M_n = 4.13 \times 10^4$ g mol$^{-1}$) was reported to be 1.26, slightly lower than that of the parent unfunctionalized $[\text{MesP}-\text{CPh}_2]_n$ ($M_n = 3.89 \times 10^4$ g mol$^{-1}$; PDI = 1.34).$^7$

References begin on page 84
3.2.2 Boronation of 3.2a and 3.2b

Chemical functionalization of poly(methylene phosphine)s 3.2a and 3.2b can also be accomplished by using BH₃ moieties to form phosphine-borane adducts along the main chain. This was achieved by treating the polymers dissolved in THF with BH₃·SMe₂ (1.3 equiv) at −78 °C, then allowing the reaction mixtures to warm slowly to room temperature. Reaction progress was monitored by ³¹P NMR spectroscopy, which suggested that the phosphine moieties in 3.2a and 3.2b were only partially complexed with borane moieties after the first addition of BH₃·SMe₂ (1.3 equiv). Hence, additional BH₃·SMe₂ (1.3 equiv) was added to each reaction mixture at −78 °C. ³¹P NMR spectroscopic analysis suggested that 70% of the phosphorus atoms in naphthyl-derivatized polymer 3.2a were functionalized with borane moieties, giving a partially functionalized phosphine-borane polymer (3.4a) (Scheme 3.5). On the other hand, ³¹P NMR analysis revealed that 3.2b was completely functionalized to give [MesP(BH₃)–C(Phen)(Ph)]ₙ (3.4b) (Scheme 3.6). Surprisingly, it appears that phenanthrenyl-derivatized poly(methylene phosphine) 3.2b is more reactive than naphthyl-derivatized polymer 3.2a. This may be due to an effect whereby the phenanthrenyl side groups are oriented in such a way that allows easier access to the phosphorus centres and the naphthyl substituents are oriented in such a way that hinders access.

![Scheme 3.5](image)

![Scheme 3.6](image)
Figures 3.3 and 3.4 show $^{31}\text{P}$ NMR spectra of new borane-phosphine adduct polymers 3.4a and 3.4b, and for comparison, $^{31}\text{P}$ NMR spectra of the unfunctionalized macromolecules are also included. The $^{31}\text{P}$ chemical shift of 3.4b ($\delta_{31\text{P}} = 28$) and the downfield $^{31}\text{P}$ chemical shift of 3.4a ($\delta_{31\text{P}} = 27$) are similar to the $^{31}\text{P}$ chemical shift of $[\text{MesP}(-\text{BH}_3)\text{--CPh}_2]_n$ ($\delta_{31\text{P}} = 26.8$).  

![Figure 3.3. $^{31}\text{P}$ NMR spectra (THF, 122 MHz) of (a) 3.2a and (b) 3.4a.](image)

![Figure 3.4. $^{31}\text{P}$ NMR spectra (THF, 122 MHz) of (a) 3.2b and (b) 3.4b.](image)
Boronated polymers **3.4a** and **3.4b** were isolated as off-white solids after removal of solvent in vacuo, and were analyzed by triple detection GPC. According to the analysis, the $M_n$ values of **3.4a** and **3.4b** were 24,700 g mol$^{-1}$ and 27,900 g mol$^{-1}$, respectively. These values are slightly higher than the $M_n$ values of their parent unfunctionalized polymers (**3.2a**: $M_n = 22,900$ g mol$^{-1}$; **3.2b**: $M_n = 27,000$ g mol$^{-1}$). Similar to the case observed for the oxidized polymers, the PDI values of **3.4a** (PDI = 1.33) and **3.4b** (PDI = 1.32) are lower than the PDI values of their parent poly(methylene phosphine) (**3.2a**: PDI = 1.39; **3.2b**: PDI = 1.49). This effect may be attributed to interaction of the phosphine moieties in **3.2a** and **3.2b** with the GPC columns, as discussed previously.

### 3.2.3 UV/Vis and Fluorescence Measurements of 3.1a – 3.4a

The UV/Vis spectra of the naphthyl-derivatized phosphaalkene **3.1a**, the unfunctionalized naphthyl-derivatized poly(methylene phosphine) **3.2a**, and the functionalized naphthyl-derivatized polymers **3.3a** and **3.4a** are shown in Figure 3.5. THF was used as a solvent for all absorption spectra. A summary of the absorption bands and their assignments is tabulated in Table 3.1.

**Table 3.1. Summary of UV/Vis absorption bands and assignments of 3.1a – 3.4a.**

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$ (M$^{-1}$cm$^{-1}$)</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1a</td>
<td>296</td>
<td>$1.6 \times 10^4$</td>
<td>$\pi - \pi^*$ (Naph)</td>
</tr>
<tr>
<td></td>
<td>316 (shoulder)</td>
<td>$1.5 \times 10^4$</td>
<td>$\pi - \pi^*$ (P=C)</td>
</tr>
<tr>
<td>3.2a</td>
<td>290</td>
<td>$1.5 \times 10^4$</td>
<td>$\pi - \pi^*$ (Naph)</td>
</tr>
<tr>
<td>3.3a</td>
<td>272</td>
<td>$4.4 \times 10^3$</td>
<td>$\pi - \pi^*$ (Naph)</td>
</tr>
<tr>
<td></td>
<td>288</td>
<td>$7.6 \times 10^3$</td>
<td>$\pi - \pi^*$ (Naph)</td>
</tr>
<tr>
<td>3.4a</td>
<td>288</td>
<td>$1.0 \times 10^4$</td>
<td>$\pi - \pi^*$ (Naph)</td>
</tr>
</tbody>
</table>
Figure 3.5. UV/Vis spectra (THF) of 3.1a (3.1 x 10^{-5} M), 3.2a (3.1 x 10^{-5} M), 3.3a (4.3 x 10^{-5} M), and 3.4a (4.2 x 10^{-5} M).

A common absorption band shared by the naphthyl-derivatized monomer and polymers 3.1a – 3.4a occurs around 290 nm. Since these absorption bands around 290 nm nearly align with the band assigned to one of the π – π* transitions of naphthalene (λ_{max} = 286 nm), these absorptions around 290 nm are assigned to π – π* transitions of the naphthyl substituent.
Naphthalene exhibits three absorptions in the UV region assigned to $\pi - \pi^*$ transitions which include transitions that are symmetry-allowed and spin-forbidden but occur due to vibronic coupling. The oxidized polymer, 3.3a, shows an additional shoulder at 272 nm. Since the wavelength of this absorption is very similar to another band of naphthalene assigned to a $\pi - \pi^*$ transition ($\lambda_{\text{max}} = 276$ nm), the shoulder is assigned to a $\pi - \pi^*$ transition of the naphthyl substituent. A shoulder is also observed in the spectrum of phosphaalkene monomer 3.1a at 316 nm. This shoulder is assigned to the $\pi - \pi^*$ transition of the P=C bond, and is similar to that observed for MesP=CPh$_2$ ($\lambda_{\text{max}} = 324$ nm).

After obtaining the $\lambda_{\text{max}}$ values of 3.1a–3.4a by UV/Vis spectroscopy, the emissive properties of 3.1a–3.4a were examined. Dilute solutions of 3.1a–3.4a in THF (ca. $10^{-5}$ M) were excited at their $\lambda_{\text{max}}$ values. The wavelength and intensity of their emissions were recorded and these spectra are displayed in Figure 3.6. As illustrated in the spectra, naphthyl-derivatized phosphaalkene 3.1a and unfunctionalized poly(methylene phosphine) 3.2a showed no fluorescence when excited at 296 nm and 290 nm, respectively. However, oxidized polymer 3.3a and boronated polymer 3.4a were fluorescent when irradiated at 288 nm. The wavelengths of their emission bands were 329 nm and 312 nm, respectively, both in the UV region. A summary of these fluorescence measurements is presented in Table 3.2, including the values of the Stokes shifts. The Stokes shifts exhibited by 3.3a and 3.4a are 41 nm and 24 nm, respectively. The small Stokes shift exhibited by 3.4a, in comparison to the range of Stokes shifts reported in the literature, can be a sign of rigidity in the main chain.
Figure 3.6. Emission spectra (THF) of 3.1a (3.1 x 10\(^{-5}\) M), 3.2a (3.1 x 10\(^{-5}\) M), 3.3a (4.3 x 10\(^{-5}\) M), and 3.4a (4.2 x 10\(^{-5}\) M).

Table 3.2. Summary of emission measurements on 3.1a – 3.4a.

<table>
<thead>
<tr>
<th></th>
<th>(\lambda_{\text{ex}}) (nm)</th>
<th>(\lambda_{\text{em}}) (nm)</th>
<th>Stokes shift (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1a</td>
<td>296</td>
<td>none</td>
<td>-</td>
</tr>
<tr>
<td>3.2a</td>
<td>290</td>
<td>none</td>
<td>-</td>
</tr>
<tr>
<td>3.3a</td>
<td>288</td>
<td>329</td>
<td>41</td>
</tr>
<tr>
<td>3.4a</td>
<td>288</td>
<td>312</td>
<td>24</td>
</tr>
</tbody>
</table>

We have shown that the complexation of the phosphorus lone pairs in non-emissive poly(methylenephosphine) 3.2a resulted in fluorescence in the UV region. The lack of fluorescence in the 3.2a is consistent with our expectation that the unfunctionalized phosphine polymer would be non-emissive or weakly emissive, as discussed in the introduction of this chapter. The fact that 3.2a is non-emissive is likely due to a quenching effect from the lone pair electrons on phosphorus, while coordination of these lone pair electrons leads to emission. A possible mechanism to account for these observations is the photoinduced electron transport.
process, a mechanism that is commonly reported for “turn-on” chemosensors.\textsuperscript{11-26} In this process, there exists a relatively high-energy nonbonding electron pair that quenches the fluorescence of the fluorophore in the absence of an analyte (Figure 3.7).\textsuperscript{11,21,24,25} The quenching occurs by a rapid intramolecular electron transfer from the lone pair orbital to the HOMO of the fluorophore. However, coordination of the electron pair to another functionality lowers the energy of the lone pair, thus allowing fluorescence to occur from the excited fluorophore. Figure 3.7 shows a simplified depiction of the electronic processes involved in relaxation to ground state. In addition to fluorescence, relaxation to the ground state also includes internal conversion and vibrational relaxation.

\textbf{Figure 3.7.} Orbital energy diagram illustrating the process of the photoinduced electron transport mechanism and the resulting effect on fluorescence of a fluorophore.\textsuperscript{11,21,24,25} This orbital diagram carries a simplified depiction of the electronic processes involved in the relaxation to the ground state. In reality, relaxation includes internal conversion, vibrational relaxation, and fluorescence.

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3.2.4 UV/Vis and Fluorescence Measurements of 3.1b – 3.4b

The UV/Vis spectra of the phenanthrenyl-derivatized phosphaalkene monomer and polymers, 3.1b – 3.4b, dissolved in THF, are shown in Figure 3.8. A summary of the absorption bands and their assignments is presented in Table 3.3.

![Figure 3.8. UV/Vis spectra (THF) of 3.1b (3.8 x 10^-5 M), 3.2b (3.3 x 10^-5 M), 3.3b (3.7 x 10^-5 M), and 3.4b (3.0 x 10^-5 M).]
Table 3.3. Summary of UV/Vis absorption bands and assignments of 3.1b - 3.4b.

<table>
<thead>
<tr>
<th></th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>( \varepsilon ) (M(^{-1}) cm(^{-1}))</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1b</td>
<td>252 (strong)</td>
<td>5.9 x 10(^4)</td>
<td>( \pi - \pi^* ) (Phen)</td>
</tr>
<tr>
<td></td>
<td>300 (weak)</td>
<td>2.3 x 10(^4)</td>
<td>( \pi - \pi^* ) (Phen and P=C)</td>
</tr>
<tr>
<td>3.2b</td>
<td>254 (strong)</td>
<td>4.4 x 10(^4)</td>
<td>( \pi - \pi^* ) (Phen)</td>
</tr>
<tr>
<td></td>
<td>301 (weak)</td>
<td>9.5 x 10(^3)</td>
<td>( \pi - \pi^* ) (Phen)</td>
</tr>
<tr>
<td>3.3b</td>
<td>256 (strong)</td>
<td>3.7 x 10(^4)</td>
<td>( \pi - \pi^* ) (Phen)</td>
</tr>
<tr>
<td></td>
<td>301 (weak)</td>
<td>8.0 x 10(^3)</td>
<td>( \pi - \pi^* ) (Phen)</td>
</tr>
<tr>
<td>3.4b</td>
<td>254 (strong)</td>
<td>2.4 x 10(^4)</td>
<td>( \pi - \pi^* ) (Phen)</td>
</tr>
<tr>
<td></td>
<td>288 (weak)</td>
<td>5.5 x 10(^3)</td>
<td>( \pi - \pi^* ) (Phen)</td>
</tr>
<tr>
<td></td>
<td>301 (weak)</td>
<td>5.1 x 10(^3)</td>
<td>( \pi - \pi^* ) (Phen)</td>
</tr>
</tbody>
</table>

The strong absorption bands that are observed in the spectra of the phenanthrenyl-derivatized monomer and polymers, 3.1b – 3.4b, near 250 nm are assigned to \( \pi - \pi^* \) transitions of the phenanthrenyl moieties because the wavelength and strength of these bands are very similar to the \( \pi - \pi^* \) transition of phenanthrene at 252 nm.\(^8,27\) Like naphthalene, phenanthrene exhibits a number of \( \pi - \pi^* \) transitions in the UV region, some of which are symmetry-allowed and some of which are spin-forbidden but made possible due to vibronic coupling.\(^9\) The UV/Vis spectra of 3.1b – 3.4b also show weak absorption bands around 300 nm. These bands are also assigned to \( \pi - \pi^* \) transitions of the phenanthrenyl substitent, and are similar to the weak band observed in the UV/Vis spectrum of phenanthrene (\( \lambda_{\text{max}} = 293 \) nm).\(^8,27\) The UV/Vis spectrum of boronated phenanthrenyl-derivatized polymer 3.4b exhibits an additional band at 288 nm that is similar to a side band observed in the UV/Vis spectrum of phenanthrene (\( \lambda_{\text{max}} = 283 \) nm). Hence the band at 288 nm is tentatively assigned to a \( \pi - \pi^* \) transition of the phenanthrenyl moiety.

Unlike the UV/Vis spectrum of naphthyl-derivatized phosphaalkene 3.1a, the UV/Vis spectrum of phenanthrenyl-derivatized phosphaalkene 3.1b does not show a separate shoulder attributed to the \( \pi - \pi^* \) transition of the P=C bond. This transition may be completely obscured by the bands already present in the spectrum. On the other hand, its absence may suggest that the

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P=C bond is more delocalized with the aromatic C-substituents in phenanthrenyl-derivatized phosphaalkene 3.1b than in naphthyl-derivatized phosphaalkene 3.1a. Support for the latter can be obtained by comparing the angles between the best planes of the aromatic C-substituents and the P=C bond (discussed in section 2.2.4, Chapter 2). The molecular structure of 3.1a shows that the phenyl and naphthyl rings are twisted out of the plane of the P=C bond by 40° and 60°, respectively. The molecular structure of 3.1b shows that the phenanthrenyl ring is twisted out of plane of the P=C bond by 60°, but the phenyl ring is twisted only by 20°. These data suggest that there is a greater degree of π-conjugation present in 3.1b than 3.1a, at least in the solid state.

Following the UV/Vis measurements discussed above, the emissive properties of phenanthrenyl-derivatized monomer and polymers 3.1b – 3.4b were investigated. Dilute solutions of 3.1b – 3.4b in THF (ca. 10⁻⁵ M) were excited at the wavelengths of their λ_max values. Maximum emission was observed when 3.1b was excited at 300 nm, and when 3.2b – 3.4b were excited at 301 nm. The emission spectra of 3.1b – 3.4b are presented in Figure 3.9 and a summary of the data is tabulated in Table 3.4.

![Emission Spectra](image)

**Figure 3.9.** Emission spectra (THF) of 3.1b (3.8 x 10⁻⁵ M), 3.2b (3.3 x 10⁻⁵ M), 3.3b (3.7 x 10⁻⁵ M), and 3.4b (3.0 x 10⁻⁵ M).
In contrast to naphthyl-derivatized phosphaalkene 3.1a and poly(methylene phosphine) 3.2a which are non-emissive, the spectra of 3.1b and 3.2b show that the phenanthrenyl-derivatized phosphaalkene and poly(methylene phosphine) are emissive. The difference in emissive properties between the analogous species is probably due to the extra conjugation in the phenanthrenyl substituent. As shown in Figure 3.9, phenanthrenyl-derivatized phosphaalkene 3.1b, oxidized polymer 3.3b, and boronated polymer 3.4b exhibit maximum emission at 367 nm, which is the same wavelength reported for the maximum emission of phenanthrene ($\lambda_{em} = 367$ nm).27 Phenanthrene also exhibits emission bands of lower intensity at 345 nm and 385 nm, and interestingly, the emission spectrum of phenanthrenyl-derivatized poly(methylene phosphine) 3.2b shows two bands at 357 nm and 374 nm, close to those of phenanthrene. The Stokes shifts exhibited by 3.1b – 3.4b range between 56 nm and 73 nm (Table 3.4) and are within normal range compared to Stokes shifts reported in the literature.

Comparison between the spectra in Figure 3.9 shows that the fluorescence intensities of phosphaalkene monomer 3.1b and unfunctionalized poly(methylene phosphine) 3.2b are weaker than the fluorescence intensities of the functionalized polymers 3.3b and 3.4b. This observation is consistent with our hypothesis that the phosphaalkenes and unfunctionalized poly(methylene phosphine)s would be non-emissive or weakly emissive while the functionalized

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polymers would be more emissive. The weaker fluorescence intensities of phosphaalkene monomer 3.1b and unfunctionalized poly(methyleneephosphine) 3.2b are most likely due to a quenching effect from the phosphorus lone pairs. Due to the structural similarity between naphthyl-derivatized polymers 3.2a – 3.4a and phenanthrenyl-derivatized polymers 3.2b – 3.4b, the photoinduced electron transport process$^{11,21,24,25}$ (discussed in the section 3.2.3) can again be invoked to account for the emissive behaviors of 3.2b – 3.4b. To confirm the relative strengths of the fluorescence emissions, the quantum yields of 3.1b – 3.4b must be determined. This is considered as future work.

3.3 Summary

Poly(methyleneephosphine)s 3.2a and 3.2b were chemically functionalized by oxidation and boronation of the phosphorus centres to afford oxidized macromolecules 3.3a and 3.3b, and boronated polymers 3.4a and 3.4b, respectively. The electronic properties of the unfunctionalized and functionalized polymers, as well as those of phosphaalkenes 3.1a and 3.1b, were investigated by UV/Vis and fluorescence spectroscopy. For the naphthyl-derivatized species, the results showed that phosphaalkene 3.1a and unfunctionalized poly(methyleneephosphine) 3.2a were non-emissive while oxidized polymer 3.3a and boronated polymer 3.4a exhibited emissions in the UV region when irradiated at 288 nm. Similarly, for the phenanthrenyl-derivatized species, the emission intensities of phosphaalkene 3.1b and unfunctionalized poly(methyleneephosphine) 3.2b were observed to be lower than those of oxidized polymer 3.3b and boronated polymer 3.4b.

These results are consistent with our hypothesis that the chemical functionalization of the phosphorus lone pair in naphthyl-derivatized poly(methyleneephosphine) 3.2a and phenanthrenyl-
derivatized poly(methylenephosphine) 3.2b would prevent quenching of the fluorophore by the lone pair electrons and therefore allow fluorescence to occur. However, further studies are required using other phosphine polymers and different chemical modifications, in addition to measurements of quantum yields, to further generalize and test the hypothesis.

Based on the preliminary results presented in this chapter, 3.2a appears to be a better candidate as a sensor than 3.2b because 3.2a is non-emissive whereas 3.2b demonstrates an emissive behavior. It is only upon complexation of the phosphorus lone pairs in 3.2a that fluorescence occurs from this polymer. Consequently, using non-emissive 3.2a instead of 3.2b as a sensor should give a lower probability of false positive results.

3.4 Experimental section

General procedures. All manipulations of air and/or water sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques or in a glovebox. Dichloromethane was deoxygenated with nitrogen and dried by passing through a column containing activated alumina. THF was freshly distilled from sodium/benzophenone ketyl. CDC\textsubscript{3} was dried over molecular sieves prior to use. H\textsubscript{2}O\textsubscript{2} and BH\textsubscript{3}-SMe\textsubscript{2} were purchased from Aldrich and used as received.

Equipment. \textsuperscript{1}H, \textsuperscript{31}P, and \textsuperscript{13}C(\textsuperscript{1}H) NMR spectra were recorded at room temperature on Bruker Avance 300 MHz or 400 MHz spectrometers. Chemical shifts are reported relative to: residual CHCl\textsubscript{3} (\(\delta = 7.26\) for \textsuperscript{1}H); 85% H\textsubscript{3}PO\textsubscript{4} as an external standard (\(\delta = 0.0\) for \textsuperscript{31}P); CDCl\textsubscript{3} (\(\delta = 77.16\) for \textsuperscript{13}C(\textsuperscript{1}H)). Molecular weights were estimated by triple detection gel permeation chromatography (GPC-LLS) using a Waters liquid chromatograph equipped with a Waters 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel columns (4.6 x 300 mm) HR2,
HR4, and HR5E, and a Waters 2410 differential refractometer (refractive index detector $\lambda = 940$ nm), Wyatt tristar miniDAWN (laser light scattering detector operating at $\lambda = 690$ nm) and a Wyatt ViscoStar viscometer. A flow rate of 0.5 mL min$^{-1}$ was used, and samples were dissolved in THF (ca. 2 mg mL$^{-1}$). The $dn/dc$ for each sample was determined using the software. Solution absorption spectra were obtained in THF on a Varian Cary 5000 UV-vis-near-IR spectrophotometer using a 1 cm quartz cuvette. Fluorescence spectra were obtained in THF on a Photon Technology International QuantaMaster fluorimeter using a 1 cm quartz cuvette.

3.4.1 Characterization of MesP=C(Naph)(Ph) (3.1a) Experimental procedures, yield, and spectroscopic data were reported in Chapter Two (Section 2.4.1, Page 54). UV/Vis (THF):

$\lambda_{\text{max}}$/nm ($\varepsilon$/M$^{-1}$ cm$^{-1}$) = 296 (1.6 x 10$^{4}$), 216 (1.5 x 10$^{4}$).

3.4.2 Characterization of MesP=C(Phen)(Ph) (3.1b) Experimental procedures, yield, and spectroscopic data were reported in Chapter Two (Section 2.4.3, Page 55). UV/Vis (THF):

$\lambda_{\text{max}}$/nm ($\varepsilon$/M$^{-1}$ cm$^{-1}$) = 252 (5.9 x 10$^{4}$), 300 (2.3 x 10$^{4}$).

3.4.3 Characterization of [MesP−C(Naph)(Ph)]$_{n}$ (3.2a) Experimental procedures, yield, spectroscopic data, and GPC data were reported in Chapter Two (Section 2.4.4, Page 56). UV/Vis (THF): $\lambda_{\text{max}}$/nm ($\varepsilon$/M$^{-1}$ cm$^{-1}$) = 290 (1.5 x 10$^{4}$).

3.4.4 Characterization of [MesP−C(Phen)(Ph)]$_{n}$ (3.2b) Experimental procedures, yield, spectroscopic data, and GPC data were reported in Chapter Two (Section 2.4.5, Page 57). UV/Vis (THF): $\lambda_{\text{max}}$/nm ($\varepsilon$/M$^{-1}$ cm$^{-1}$) = 254 (4.4 x 10$^{4}$), 301 (9.5 x 10$^{3}$).

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3.4.5 Preparation of [MesP(O)–C(Naph)(Ph)]ₙ (3.3a) To a solution of polymer 3.2a (0.075 g, 0.20 mmol, $M_n = 42,160$ g mol⁻¹) in CH₂Cl₂ (5 mL) was added 30% H₂O₂ in water (1.5 mL). The reaction mixture was stirred vigorously for 3 h. $^31$P NMR spectroscopic analysis of an aliquot of the reaction mixture showed a partially oxidized polymer ($\delta_{^31P} = 47, 40\%$; $\delta_{^31P} = -9, 60\%$). The reaction mixture was treated with another 1.5 mL of 30% H₂O₂ in water. The reaction mixture was stirred overnight. Analysis of the reaction mixture by $^31$P NMR spectroscopy suggested complete oxidation of the polymer ($\delta_{^31P} = 47$). The layers were separated and aqueous layer was extracted with CH₂Cl₂ (2 x 3 mL). The organic layers were combined and washed with H₂O (3 x 5 mL). The organic layer was dried over MgSO₄. After evaporation of the solvent in vacuo, a white solid was obtained then dried in a vacuum oven at 65 °C. Yield = 24 mg (32%).

$^31$P NMR (CDCl₃, 162 MHz): $\delta$ 47 (br); $^1$H NMR (CDCl₃, 400 MHz): $\delta$ 9.0–5.0 (br, Ar-H), 3.3–0.5 (br, –CH₃); $^{13}$C NMR (CDCl₃, 101 MHz): $\delta$ 148–123 (br, Ar-C), 30–17 (br, CH₃); GPC-LLS (THF): $M_n = 43,500$ g mol⁻¹, PDI = 1.16. UV/Vis (THF): $\lambda_{max}$/nm (ε/M⁻¹ cm⁻¹) = 272 (4.4 x 10⁶), 288 (7.6 x 10³).

3.4.6 Preparation of [MesP(O)–C(Phen)(Ph)]ₙ (3.3b) A THF (2 mL) solution of 3.2b (0.05 g, 0.12 mmol, $M_n = 27,000$ g mol⁻¹) was left in air for oxidation of the phosphorus atoms. The oxidation progress was monitored by $^31$P NMR spectroscopy, and THF was added when there was significant solvent evaporation. After 1 week, a $^31$P NMR spectrum of the solution showed a broad signal at 49 ppm. The solvent was allowed to evaporate in air. An off-white solid remained and was dried in a vacuum oven at 65 °C for 12 hours. Yield = 0.04 g (82 %).
$^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta$ 49 (br); $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.5–6.5 (br, Ar-H), 3.0–1.5 (br, CH$_3$); GPC-LLS (THF): $M_n = 31,300$ g mol$^{-1}$, PDI = 1.46. UV/Vis (THF): $\lambda_{\max}$/nm ($\varepsilon$/M·cm$^{-1}$) = 256 (3.7 x 10$^4$), 301 (8.0 x 10$^3$).

3.4.7 Preparation of [MesP(BH$_3$)–C(Naph)(Ph)]$_n$ (3.4a) To a THF solution of 3.2a (0.30 g, 0.82 mmol, $M_n = 22,900$ g mol$^{-1}$) was added BH$_3$SMe$_2$ (0.55 mL, 2 M, 1.17 mmol) at $-78^\circ$C. The reaction mixture was allowed to warm slowly to room temperature. $^{31}$P NMR spectrum of the reaction mixture showed the presence of a new broad signal ($\delta_{31P} = 27$, 50%) in addition to the broad chemical shift of the starting material ($\delta_{31P} = -9$, 50%). The reaction mixture was treated with more BH$_3$SMe$_2$ (0.55 mL, 2 M, 1.17 mmol) at $-78^\circ$C and allowed to warm slowly to room temperature and stir overnight. After removal of solvent in vacuo, a white solid was obtained. Yield = 0.26 g (83%).

$^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta$ 27 (br), -9 (br); $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 9.0–6.0 (br, Ar-H), 3.0–0.5 (br, CH$_3$, BH$_3$); $^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta$ 137–122 (br, Ar-C), 28–18 (br, CH$_3$); GPC-LLS (THF): $M_n = 24,700$ g mol$^{-1}$, PDI = 1.33. UV/Vis (THF): $\lambda_{\max}$/nm ($\varepsilon$/M·cm$^{-1}$) = 288 (1.0 x 10$^4$).

3.4.8 Preparation of [MesP(BH$_3$)–C(Phen)(Ph)]$_n$ (3.4b) A THF solution of 3.2b (0.04 g, 0.09 mmol, $M_n = 27,000$ g mol$^{-1}$) was treated with BH$_3$SMe$_2$ (0.06 mL, 2 M, 0.12 mmol) at $-78^\circ$C. The reaction mixture was allowed to warm slowly to room temperature. An aliquot was removed from the reaction mixture and analyzed by $^{31}$P NMR spectroscopy. The spectrum showed the presence of a new broad signal ($\delta_{31P} = 28$) in addition to the broad chemical shift of the starting material ($\delta_{31P} = -10$). The reaction mixture was treated with more BH$_3$SMe$_2$ (0.06 mL, 2 M, 0.12
mmol) at –78 °C and was allowed to warm slowly to room temperature and stir overnight. After removal of solvent in vacuo, a white solid was obtained. Yield = 0.03 g (78%).

$^{31}$P NMR (CDCl$_3$, 122 MHz): $\delta$ 28 (br); $^1$H NMR (CDCl$_3$, 400 MHz): 9.0–6.5 (br, Ar-H), 3.0–1.0 (br, CH$_3$, BH$_3$); GPC-LLS (THF): $M_n = 27,900$ g mol$^{-1}$, PDI = 1.32. UV/Vis (THF): $\lambda_{\text{max}}$/nm ($\varepsilon$/M$^{-1}$ cm$^{-1}$) = 254 (2.4 x 10$^4$), 288 (5.5 x 10$^3$), 301 (5.1 x 10$^3$).

### 3.4.9 General procedure for preparing solution samples for UV/Vis and fluorescence measurements

Solution samples were prepared inside a glovebox, except for 3.3a, 3.3b, 3.4a, and 3.4b. The procedure for preparing a solution sample of 3.1a is described in the following as an example: THF was added to 3.1a (7 mg, 0.02 mmol) in a 25.0 mL volumetric flask and diluted to the mark. The volumetric flask was inverted 20 times to ensure proper mixing. Using a volumetric pipette, 1.00 mL of this solution was transferred to another 25.0 mL volumetric flask, and THF was added to dilute to the mark. Again the volumetric flask was inverted 20 times before transferring a small amount of the solution to a 1 cm quartz cuvette.

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3.5 References


*References begin on page 84*


Chapter Four

Radical Copolymerization of P=C and C=C Bonds: Reactivity Ratios of Phosphaalkene-Styrene Copolymers*

4.1 Introduction

Although synthetically challenging, the incorporation of inorganic functionalities into macromolecules is attractive because it often leads to materials with unique properties that cannot be attained using organic counterparts.\textsuperscript{1,2} Lately, the incorporation of phosphorus atoms into polymers has captured considerable attention and resulted in materials with interesting properties and important potential applications, such as chemosensors, polymer-based light emitting diodes (PLEDs), and flame-retardant materials.\textsuperscript{3-13} In 2003, the Gates group reported the addition polymerization of a phosphaalkene, MesP=CPh$_2$ (PA) (Mes = 2,4,6-trimethylphenyl) to afford poly(methylenephosphine).\textsuperscript{14} This is the first addition polymerization of a heavy-element multiple bond and represents an important step forward in the field of inorganic polymers. Previously, addition polymerization had primarily been limited to olefins.\textsuperscript{15} Our group subsequently reported the copolymerization of PA with styrene (Sty) to afford new hybrid inorganic-organic copolymers.\textsuperscript{16,17} The copolymerization can be achieved via a radical method using the radical initiator 1,1'-azobis(cyclohexanecarbonitrile) (VAZO 88) to yield a random copolymer poly(methylenephosphine)-co-polystyrene (PMP-co-PS),\textsuperscript{16} or the reaction can proceed via an anionic route using n-BuLi to give block copolymers.\textsuperscript{17} The focus of this chapter will be on the random copolymer PMP-co-PS. This hybrid inorganic-organic macromolecule is particularly attractive for its potential application in polymer-supported catalysis.\textsuperscript{16} Our group

* A version of this chapter will be submitted for publication. Chun, C. P. and Gates, D. P. Radical Copolymerization of P=C and C=C Bonds: Reactivity Ratios of Phosphaalkene-Styrene Copolymers.
showed that PMP-co-PS could be used as a ligand in the presence of \([\text{Pd}_2(\text{dba})_3]\) (dba = dibenzylideneacetone) and CsF to execute a Suzuki cross-coupling of bromobenzene and phenylboronic acid to form biphenyl with 90% yield.\(^6\) On the other hand, when the cross-coupling reaction was attempted using \([\text{Pd}_2(\text{dba})_3]\), CsF and a homopolymer of PA, the yield was the same as that in the reaction using only \([\text{Pd}_2(\text{dba})_3]\) and CsF (yield = 25%).

To better understand the microstructure of PMP-co-PS, which has not been reported, we decided to further examine the PA/Sty copolymerization system at 100 °C using VAZO 88 as the radical initiator (Scheme 4.1). The elucidation of the PMP-co-PS microstructure would require the determination of the reactivity ratios of PA \((r_{PA})\) and of Sty \((r_{Sty})\). Reactivity ratios describe the relative tendency of the growing chain to add to a particular monomer. More specifically, reactivity ratios are defined as a ratio of rate constants as shown in Scheme 4.2 using \(r_{PA}\) and \(r_{Sty}\) as examples. Starting in the 1940s, reactivity ratios have played an important role for the copolymerization of olefins to develop commercial products.\(^{18}\) They are crucial synthetic parameters in predicting predilections of a specific monomer to copolymerize with certain other monomers.\(^{19,20}\) To that end, we believe that \(r_{PA}\) and \(r_{Sty}\) may have a long term impact to the sensing work discussed in Chapters 2 and 3 if chemosensors could be realized by random copolymers derived from phosphaalkenes. It may be possible that a sensory behavior does not necessitate phosphorus at every other atomic position in the main chain.

![Scheme 4.1](image)

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Herein we describe our investigation on the reactivity ratios of PA and of Sty in the PMP-co-PS copolymerization system by following an adaptation of the Tidwell-Mortimer experimental approach,\textsuperscript{21} illustrated in Chart 4.1. The first step requires data, such as copolymer compositions, from several copolymerization experiments over a broad range of monomer feed ratios. These data are necessary for the preliminary estimation of the \( r \) values by one or more linear methods. The Fineman-Ross linearization\textsuperscript{22} and the Mayo-Lewis intersection method\textsuperscript{23} were used in this study. The second step of the experimental approach requires the input of the preliminary \( r \) values for the application of the heuristic rules introduced by Tidwell and Mortimer. These rules approximate the optimal feed compositions for further copolymerization experiments. Lastly, further experiments are performed at the optimal feed compositions, and the data are fitted to the copolymer composition equation (eq I) by nonlinear least squares regression to provide the best estimates of the reactivity ratios.

\[
\frac{m_{\text{PA}}}{m_{\text{Sy}}} = \frac{r_{\text{PA}}M_{\text{PA}} \cdot M_{\text{PA}} \cdot 2 + M_{\text{PA}}M_{\text{Sy}}}{r_{\text{Sy}}M_{\text{Sy}} \cdot 2 + M_{\text{PA}}M_{\text{Sy}}}
\]

where: \( m_{\text{monomer}} \) represents the molar fraction of PA or Sty in the copolymer; \( M_{\text{monomer}} \) represents the molar fraction of PA or Sty in the monomer feed.

Based on the best estimates of \( r_{\text{PA}} \) and \( r_{\text{Sy}} \), the microstructure of PMP-co-PS was examined and \( Q-e \) reactivity parameters of PA were computed.
Chart 4.1. Flowchart illustrating the Tidwell-Mortimer approach to determining reactivity ratios.

**Chart 4.1.** Flowchart illustrating the Tidwell-Mortimer approach to determining reactivity ratios.

**Data from copolymerization experiments**

**Step 1**

Preliminary estimation of \( r \) values by linear methods
- Fineman-Ross Linearization
- Mayo-Lewis Intersection Method

**Step 2**

Application of Tidwell and Mortimer’s heuristic rules using preliminary \( r \) values to determine optimal feed compositions for further copolymerization experiments

**Step 3**

Determination of \( r \) values by nonlinear least squares fitting of data to the copolymer composition equation

4.2 Results and Discussion

4.2.1 Analysis of Copolymer Composition by Inverse Gated Proton Decoupled \(^{13}\)C NMR Spectroscopy

Since our investigation of reactivity ratios required analysis of many copolymer samples, a simple and rapid method to analyze copolymer compositions was desired. NMR spectroscopy is commonly used for the analysis of copolymer compositions.\(^{24-31}\) Unfortunately, \(^1\)H NMR

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spectroscopy was not a feasible option in our investigation because the technique could not
differentiate changes in the copolymer composition of PMP-co-PS. Thus, we considered using
another technique, $^{13}$C NMR spectroscopy, which is a common method for the analysis of
copolymer compositions and microstructures.$^{25-27,29,30,32}$ Since $T_1$ s for macromolecules are
usually very short ($10^{-3}$ to 1s),$^{33}$ inverse gated proton decoupled $^{13}$C NMR spectroscopy may be a
viable method to measure compositions of PMP-co-PS in a quantitative fashion. In this method,
the decoupler is off during the relaxation delay and on during acquisition, thereby eliminating the
Nuclear Overhauser Effect from the protons, resulting in more quantitative integrations than the
typical $^{13}$C{H} experiment. To further ensure that the $^{13}$C NMR experiment yields results as
quantitative as possible, a $90^\circ$ pulse can be used. A $^{13}$C NMR spectrum of a sample of PMP-co-
PS, obtained via the method described above, is shown in Figure 4.1. The signals for the
aromatic carbons resonate between 155 ppm and 120 ppm, whereas the signals for the methyl
carbons resonate around 25 ppm.

To evaluate the accuracy of inverse gated proton decoupled $^{13}$C NMR spectroscopy as a
method to analyze PMP-co-PS samples, compositions of four different samples of PMP-co-PS,
prepared under conditions specified in Table 4.1, were estimated using the $^{13}$C NMR spectroscopic technique described above. These estimations were compared to compositions analyzed by elemental analysis (EA) which include phosphorus analysis, which is a service available only outside of our department (see Table 4.1). The copolymer compositions, determined by both methods, agreed within 0.05. The estimations by $^{31}$C NMR and EA for entry 3 differed by only 0.01. The maximum difference was observed in entry 2 in which the estimations differed by 0.05. Encouraged by these results and the convenience of the $^{13}$C NMR spectroscopic technique to deliver results rapidly, $^{13}$C NMR spectroscopy with inverse gated proton decoupling was chosen as the method for determining PMP-co-PS compositions.

| Table 4.1. Comparison of copolymer compositions measured by inverse gated proton decoupled $^{13}$C NMR spectroscopy and elemental analyses. |
|------------------------|------------------------|------------------------|------------------------|
| monomer feed | copolymer composition | GPC | |
| entry | $t$ (h)$^a$ | $M_{PA}$ | $M_{Sty}$ | $m_{PA}$ | $m_{Sty}$ | $m_{PA}$ | $m_{Sty}$ | $M_n$ ($10^3$ g mol$^{-1}$) | PDI |
| 1 | 2 | 0.2 | 0.8 | 0.55 | 0.45 | 0.57 | 0.43 | 14.7 | 1.17 |
| 2 | 10 | 0.4 | 0.6 | 0.36 | 0.64 | 0.41 | 0.59 | 9.6 | 1.20 |
| 3 | 16 | 0.4 | 0.6 | 0.44 | 0.56 | 0.43 | 0.57 | 8.8 | 1.29 |
| 4 | 24 | 0.4 | 0.6 | 0.35 | 0.65 | 0.38 | 0.62 | 10.4 | 1.25 |

$^a$ The duration of each copolymerization experiment conducted at 100 °C is represented by $t$. $^b$ See Experimental section.

\[
m_{PA} = \frac{(FW_{Sty})\%P_{EA}(0.01)}{100 \times AW_p - (FW_{PA} - FW_{Sty})(\%P_{EA})} \quad \text{and} \quad m_{Sty} = 1 - m_{PA}
\]

where: $FW_{Sty}$ is the molar mass of styrene; $\%P_{EA}$ is the percent of phosphorus detected by elemental analysis; $AW_p$ is the atomic mass of phosphorus; $FW_{PA}$ is the molar mass of phosphaalkene PA.
4.2.2 Experimental Design and Preliminary Estimation of $r_{\text{PA}}$ and $r_{\text{Sty}}$

All copolymerization experiments were performed by heating PA and Sty in a vacuum-sealed glass tube at 100 °C. It is critical to minimize monomer drift in studies of reactivity ratios, thus we aimed to carry all experiments to low monomer conversion ($X \leq 10\%$). To determine the number of hours of heating at 100 °C ($t$) that would minimize $X$, several copolymerization experiments were performed with variable $t$. In these experiments, we used a monomer feed ratio of $M_{\text{PA}} = 0.40$ and $M_{\text{Sty}} = 0.60$. Figure 4.2 plots the conversion of each copolymerization. Monomer conversion ($X$) was calculated based on the number of moles of each monomer in the copolymer divided by the number of moles of each monomer in the monomer feed. As illustrated in the plot, longer heating durations led to higher monomer conversions. Allowing a copolymerization experiment to proceed at 100 °C for 2 h resulted in $X_{\text{PA}} = 3\%$ and $X_{\text{Sty}} = 2\%$.

According to Figure 4.2, $t$ equal to 4 h also resulted in monomer conversions below 10%. However, $t$ of 2 h was chosen to keep monomer conversion to a minimum in order to reach more reliable results in our later calculations of $r_{\text{PA}}$ and $r_{\text{Sty}}$.

![Figure 4.2](image_url)

**Figure 4.2.** Monomer conversions of copolymerization experiments carried through different $t$. $M_{\text{PA}} = 0.40$; $M_{\text{Sty}} = 0.60$. Conversion was calculated by $X_{\text{monomer}} = \frac{\text{(moles of monomer in the copolymer)}}{\text{(moles of monomer in the monomer feed)}}$.

* Heating a reaction mixture at 100°C for 1 hour (i.e. $t = 1$ h) led to very little copolymer formation thereby rendering product isolation and analysis difficult.

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To obtain data for the first step in calculating reactivity ratios (Chart 4.1), eight different copolymerization experiments, with heating for 2 h, over a range of monomer feed ratios were conducted. Table 4.2 summarizes the data from the eight experiments. According to the data, as the monomer feed of PA (i.e. $M_{PA}$) increased, the mole fraction of PA in the isolated copolymer (i.e. $m_{PA}$) increased. This is logical and the same pattern is observed for Sty. The copolymers in Table 4.2 have $M_n$ values ranging from 7,700 g mol$^{-1}$ to 16,200 g mol$^{-1}$. In general, copolymers with higher $M_n$ values were found to have more PA in their compositions; this makes sense since the molecular weight of PA is greater than that of Sty. The GPC traces of the copolymer samples were unimodal, which gave support to the presence of PMP-co-PS, and not a polyblend of homopolymers and copolymers. The PDI values of the copolymers range between 1.11 and 1.20.

**Table 4.2. Summary of copolymerization experimental data.**

<table>
<thead>
<tr>
<th>entry</th>
<th>$M_{PA}$</th>
<th>$M_{Sty}$</th>
<th>$m_{PA}$</th>
<th>$m_{Sty}$</th>
<th>$X_{PA}^a$</th>
<th>$X_{Sty}^a$</th>
<th>$M_n$ (10$^3$ g mol$^{-1}$)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.20</td>
<td>0.80</td>
<td>0.36</td>
<td>0.64</td>
<td>5</td>
<td>2</td>
<td>8.0</td>
<td>1.11</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>0.80</td>
<td>0.39</td>
<td>0.61</td>
<td>3</td>
<td>1</td>
<td>7.7</td>
<td>1.17</td>
</tr>
<tr>
<td>3</td>
<td>0.40</td>
<td>0.60</td>
<td>0.44</td>
<td>0.56</td>
<td>4</td>
<td>3</td>
<td>10.5</td>
<td>1.13</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.60</td>
<td>0.44</td>
<td>0.56</td>
<td>2</td>
<td>2</td>
<td>11.6</td>
<td>1.15</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>0.40</td>
<td>0.46</td>
<td>0.54</td>
<td>4</td>
<td>8</td>
<td>14.1</td>
<td>1.16</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>0.40</td>
<td>0.52</td>
<td>0.48</td>
<td>4</td>
<td>6</td>
<td>11.4</td>
<td>1.18</td>
</tr>
<tr>
<td>7</td>
<td>0.80</td>
<td>0.20</td>
<td>0.55</td>
<td>0.45</td>
<td>3</td>
<td>10</td>
<td>14.7</td>
<td>1.17</td>
</tr>
<tr>
<td>8</td>
<td>0.80</td>
<td>0.20</td>
<td>0.56</td>
<td>0.44</td>
<td>3</td>
<td>10</td>
<td>16.2</td>
<td>1.20</td>
</tr>
</tbody>
</table>

$^a$ Conversion is calculated by $X_{monomer} = \text{(moles of monomer in the copolymer)/(moles of monomer in the monomer feed)}.}$

References begin on page 106
Following the first step in the Tidwell-Mortimer approach (Chart 4.1), the Fineman-Ross linearization was employed to obtain preliminary estimates of $r_{PA}$ and $r_{Sty}$. In this method, the copolymer composition equation (eq I) is rearranged to a linear form (eq II):

$$ G = F r_{PA} + r_{Sty} $$

where:

$$ G = \frac{M_{PA} (m_{Sty} - m_{PA})}{M_{Sty} m_{PA}} $$

$$ F = \frac{-m_{Sty} M_{PA}^2}{m_{PA} M_{Sty}^2} $$

Hence by plotting $G$ versus $F$, the line of best fit has a slope represented by $r_{PA}$ and a y-intercept represented by $r_{Sty}$. Figure 4.3 shows the Fineman-Ross plot generated from the data presented in Table 4.2. From the equation of the regression line (R-squared = 0.9172), the reactivity ratio values obtained are $r_{PA} = 0.07 \pm 0.02$ and $r_{Sty} = 0.21 \pm 0.12$. The results of the Fineman-Ross linearization are tabulated in Table 4.3, which summarizes the $r$ values calculated in this study.

![Figure 4.3](image)

**Figure 4.3.** Fineman-Ross plot of $G$ versus $F$ for PA/Sty copolymerization experiments. The linear least-squares function ($G = 0.07F - 0.21$) has an R-squared value of 0.9172.

\[ ^\dagger \text{The errors reported are the 95\% confidence intervals that were calculated based on the standard deviation of the slope and y-intercept of the regression function shown in the Fineman-Ross plot.} \]
Table 4.3. Approximation of $r_{PA}$ and $r_{S_y}$.

<table>
<thead>
<tr>
<th>Method</th>
<th>$r_{PA}$</th>
<th>$r_{S_y}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fineman-Ross Linearization$^a$</td>
<td>0.07±0.02</td>
<td>0.21±0.12</td>
</tr>
<tr>
<td>Mayo-Lewis Intersection Method$^b$</td>
<td>0.06±0.18</td>
<td>0.17±0.04</td>
</tr>
<tr>
<td>Average of Preliminary Estimates</td>
<td>0.065</td>
<td>0.19</td>
</tr>
<tr>
<td>Nonlinear Least-Squares Regression$^a$</td>
<td>0.11±0.01</td>
<td>0.24±0.12</td>
</tr>
</tbody>
</table>

$^a$ Errors are the 95% confidence intervals associated with the respective $r$ value.

$^b$ Errors are determined by dividing the difference between the maximum and minimum values of the intersection by two.

For comparison, we also estimated the $r$ values by the Mayo-Lewis intersection method. In this method, the copolymer composition equation (eq I) is rearranged to eq III:

$$r_{PA} = Sr_{S_y} + I$$  \hspace{1cm} (III)

where:

$$S = \frac{m_{PA}M_{S_y}^2}{m_{S_y}M_{PA}^2}$$

$$I = \left(\frac{M_{S_y}}{M_{PA}}\right)\left(\frac{m_{PA}}{m_{S_y}} - 1\right)$$

Each copolymerization experiment is represented by a straight line with a slope and y-intercept defined by $S$ and $I$, respectively, on a $r_{S_y}$, $r_{PA}$ plane. This is shown in Figure 4.4 using the data summarized in Table 4.2. There are eight straight lines, one for each copolymerization experiment. Lines representing entries 3 and 4 overlap. The $r$ values, obtained by the intersection method, are the coordinates of the centroid in the area of common intersection shown in the plot. Therefore by this method, $r_{PA} = 0.06±0.18$ and $r_{S_y} = 0.17±0.04$ (Table 4.3). The error in $r_{PA}$ is quite large, which is typical of $r$ values calculated by this method.

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$^a$ The errors are determined by dividing the difference between the maximum and minimum values of the intersection area by two.
Figure 4.4. PA/Sty copolymerization data plotted according to the Mayo-Lewis intersection method. \((r_{PA}, r_{PA}) = (0.17, 0.06)\) are the coordinates of the centroid in the area of common intersection among all the lines.

The averages of the reactivity ratios calculated from both methods (i.e. Fineman-Ross linearization and Mayo-Lewis intersection method) were taken as the preliminary estimates, giving \(r_{PA} = 0.065\) and \(r_{Sty} = 0.19\) (Table 4.3). These \(r\) values were used in the second step of the Tidwell-Mortimer approach (see Chart 4.1) which is described in the next section.

4.2.3 Application of Heuristic Rules

It has been shown and recognized that not all experimental conditions serve equally well in the determination of reactivity ratios and there are some conditions that reveal more information about the \(r\) values.\(^{19,21}\) For this reason, Tidwell and Mortimer developed heuristic rules (eq IV and eq V) that approximate the two sets of monomer feed conditions, referred to as the optimal monomer feed compositions, that lead to more accurate estimates of \(r\) values.\(^{21}\)
where: $M_{PA}'$ is the optimal monomer feed of PA for the first experiment; 
$M_{PA}''$ is the optimal monomer feed of PA for the second experiment; 
r_{Sty} and $r_{PA}$ are the preliminary estimates obtained by linear approximations

Given the preliminary estimates ($r_{PA} = 0.065$ and $r_{Sty} = 0.19$), the second step of the experimental approach involved the application of heuristic rules (eq IV and eq V). This resulted in the following set of conditions for further work in our study:

1) $M_{PA} = 0.09$, $M_{Sty} = 0.91$; and
2) $M_{PA} = 0.97$, $M_{Sty} = 0.03$.

Two additional runs were conducted at each of these conditions and their data are summarized in Table 4.4.

Table 4.4. Summary of experimental data from copolymerizations according to optimal monomer feed compositions.

<table>
<thead>
<tr>
<th>entry</th>
<th>$M_{PA}$</th>
<th>$M_{Sty}$</th>
<th>$m_{PA}$</th>
<th>$m_{Sty}$</th>
<th>$X_{PA}^a$ (%)</th>
<th>$X_{Sty}^a$ (%)</th>
<th>$M_n$ ($10^3$ g mol$^{-1}$)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.09</td>
<td>0.91</td>
<td>0.24</td>
<td>0.76</td>
<td>10</td>
<td>3</td>
<td>7.8</td>
<td>1.07</td>
</tr>
<tr>
<td>2</td>
<td>0.09</td>
<td>0.91</td>
<td>0.20</td>
<td>0.80</td>
<td>9</td>
<td>3</td>
<td>7.0</td>
<td>1.08</td>
</tr>
<tr>
<td>3</td>
<td>0.97</td>
<td>0.03</td>
<td>0.82</td>
<td>0.18</td>
<td>2</td>
<td>10</td>
<td>13.4</td>
<td>1.16</td>
</tr>
<tr>
<td>4</td>
<td>0.97</td>
<td>0.03</td>
<td>0.85</td>
<td>0.15</td>
<td>2</td>
<td>10</td>
<td>16.7</td>
<td>1.17</td>
</tr>
</tbody>
</table>

$^a$ Conversion is calculated by $X_{monomer} = (\text{moles of monomer in the copolymer})/(\text{moles of monomer in the monomer feed}).$

References begin on page 106
4.2.4 Determination of $r_{PA}$ and $r_{Sty}$ by Nonlinear Least Squares Regression

To provide the best estimates of $r_{PA}$ and $r_{Sty}$ and minimize the error associated with the solutions, nonlinear least squares regression (Step 3, Chart 4.1) was performed on both sets of data: the data presented in Table 4.2 and the data found in Table 4.4. A substitution was made to simplify the curve-fitting procedure. Since $M_{Sty} = 1 - M_{PA}$, the right hand side of the copolymer composition equation (eq I) was expressed in terms of one variable as shown in eq VI:

$$
\frac{m_{PA}}{m_{Sty}} = \frac{r_{PA} M_{PA}^2 + M_{PA}(1-M_{PA})}{r_{Sty} (1-M_{PA})^2 + M_{PA}(1-M_{PA})}
$$  \hspace{1cm} (VI)

Using the data specified, a plot of $m_{PA}/m_{Sty}$ versus $M_{PA}$ was constructed (Figure 4.5). A line of best fit, following the form of the eq VI, was obtained by using a nonlinear least squares curve-fitting tool in the MATLAB software. This function correlates well with the data points (RMSE = 0.1358). The plot shows that when $M_{PA}$ is greater than 0.8, there is a drastic increase of PA in the copolymer composition. From the equation of this line (shown in Figure 4.5), the best estimates of the reactivity ratios are $r_{PA} = 0.11 \pm 0.01$ and $r_{Sty} = 0.24 \pm 0.12$ (Table 4.3).\(^\dagger\)

\[\text{Figure 4.5. Nonlinear least squares curve fitting of copolymerization data. RMSE = 0.1353.}\]

\(^\dagger\) The errors are the 95% confidence intervals associated with the respective $r$ value.
4.2.5 Q-e values of PA and the Microstructure of PMP-co-PS

To compare the reactivity of PA to the reactivity of other monomers, it would be helpful to first assign reactivity parameters to PA following the well-known Alfrey-Price Q-e scheme. According to this framework, the Q value describes the specific reactivity of the monomer, and the e value represents the polarity of the radical adduct. Styrene was chosen as a universal standard for this scheme and hence was arbitrarily assigned the Q value of 1.0 and an e value of −0.8. To determine the Q and e values of PA, we used the Alfrey-Price formulas:

\[ r_{PA} = \exp[-(e_{monomer1} - e_{monomer2})^2] \]  
\[ r_{monomer1} = \frac{Q_{monomer1}}{Q_{monomer2}} \exp[-e_{monomer1}(e_{monomer1} - e_{monomer2})] \]

Using eq VII, eq VIII, and the Q-e values of styrene, we arrived to \( Q_{PA} = 0.9 \) and \( e_{PA} = 1.1 \). The \( Q_{PA} \) value being less than the \( Q_{Sty} \) value is consistent with our observations of a lower reactivity of PA when compared to the reactivity of Sty during polymerization. The lower reactivity of the PA monomer can be attributed to a higher degree of conjugation in PA compared to Sty thus allowing for greater radical stabilization of the PA radical adduct. It has been demonstrated that monomers with e values of opposite signs, which signifies opposite polarities, have a tendency to alternate upon copolymerization. Price rationalized this behavior by explaining that a radical species with a negative character exhibits a preference for a monomer with a positively charged double bond and vice versa. The fact that PA and Sty have e values of opposite signs (\( e_{Sty} = -0.8 \); \( e_{PA} = 1.1 \)) suggests that the PA/Sty system would exhibit an alternating behavior upon copolymerization. This suggestion coincides with our expectation based on the r values. Referring back to the definition of \( r_{PA} \) and \( r_{Sty} \) (Scheme 4.2), \( r_{PA} = k_{PP}/k_{PS} = 0.11 \) indicates that the radical of a growing chain with a terminal PA unit is more likely to attack a Sty monomer. Similarly, \( r_{Sty} = k_{SS}/k_{SP} = 0.24 \) suggests that the radical on a

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growing chain with a terminal Sty unit is more likely to add to a PA monomer. As a result, this should give rise to alternating PA and Sty monomers along the copolymer chain.

In addition to being important in kinetic aspects of copolymerization and in the determination of \( Q-e \) reactivity parameters, reactivity ratios are also key parameters to revealing monomer distribution and heterogeneity in the main chain. The microstructure of a copolymer can be deduced by formulas that are well-known and found in general polymer science textbooks.\(^{19,20}\) The average sequence length \( (l) \) of PA or Sty units linked consecutively is defined by eq IX:\(^{20}\)

\[
l_{\text{monomer}1} = 1 + r_{\text{monomer}1} \frac{M_{\text{monomer}1}}{M_{\text{monomer}2}}
\]

Using eq IX, we computed the mean sequence length of consecutive PA and Sty monomers in PMP-co-PS samples synthesized from various monomer feed ratios in this study (see Table 4.5). In entries 3–5 of Table 4.5, the copolymers have \( l_{PA} \) and \( l_{Sty} \) values slightly greater than one unit, therefore these copolymers most likely consist of alternating PA and Sty units. In the case of entry 2, the average sequence length of consecutive PA units is about 1 unit, and that of Sty is about 2 units. This would render a copolymer with a backbone of mostly repeating PA-Sty-Sty triads. In copolymers prepared from a large excess of one monomer in the monomer feed (i.e. entries 1 and 6), there is a tendency to form blocks of the monomer in excess.

Inevitably, the number of monomers in a sequence is related to the number of sequences in a given length of a copolymer chain. For example, longer sequences results in fewer sequences in a given chain length. The average number of sequences per 100 units, also known as the run number \( (R) \), can be obtained via eq X:\(^{20}\)

\[
R = \frac{200}{l_{PA} + l_{Sty}}
\]

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Table 4.5. Average sequence length of monomers units \( (l_{\text{monomer}}) \) and run number \( (R) \) of PMP-co-PS copolymers prepared from various monomer feed ratios in this study. \( t = 2 \) h.

<table>
<thead>
<tr>
<th>entry</th>
<th>( M_{PA} )</th>
<th>( M_{Sty} )</th>
<th>( l_{PA} )</th>
<th>( l_{Sty} )</th>
<th>( R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.09</td>
<td>0.91</td>
<td>1.01</td>
<td>3.43</td>
<td>45.07</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>0.80</td>
<td>1.03</td>
<td>1.96</td>
<td>66.95</td>
</tr>
<tr>
<td>3</td>
<td>0.40</td>
<td>0.60</td>
<td>1.07</td>
<td>1.36</td>
<td>82.19</td>
</tr>
<tr>
<td>4</td>
<td>0.60</td>
<td>0.40</td>
<td>1.17</td>
<td>1.16</td>
<td>86.02</td>
</tr>
<tr>
<td>5</td>
<td>0.80</td>
<td>0.20</td>
<td>1.44</td>
<td>1.06</td>
<td>80.00</td>
</tr>
<tr>
<td>6</td>
<td>0.97</td>
<td>0.03</td>
<td>4.56</td>
<td>1.01</td>
<td>35.94</td>
</tr>
</tbody>
</table>

Not surprisingly, copolymers of PMP-co-PS prepared from a large excess of one monomer have fewer sequences in a given chain length, which appears to be the case for entries 1 \( (R = 45.07) \) and 6 \( (R = 35.94) \) in Table 4.5. In other instances, PMP-co-PS contains about 67 to 86 sequences per 100 units, suggesting a large degree of heterogeneity along the copolymer backbone.

From our study, it is apparent that PMP-co-PS generally has a highly alternating PA / Sty microstructure unless prepared under monomer feed conditions of greater than 8:2. An alternating pattern leads to more open space around the phosphorus atoms in comparison to the phosphorus atoms in a homopolymer of PA. This is because phosphorus atoms in the copolymer would be preceded by CHPh moieties whereas the phosphorus atoms in the latter case would be preceded by CPh\(_2\) moieties. Returning to the observations from previously reported Suzuki cross-coupling reactions using PMP-co-PS,\(^{16}\) the open space probably facilitated the coordination of phosphorus atoms in PMP-co-PS to Pd thereby promoting coupling activity.

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4.3 Summary

In conclusion, we calculated the reactivity ratios of PA and Sty via nonlinear least squares regression and the values obtained are $r_{PA} = 0.11 \pm 0.01$ and $r_{Sty} = 0.24 \pm 0.12$. These $r$ values led us to assign $Q$-$e$ reactivity parameters to PA, which will enable reactivity comparison of PA to other monomers, and also evaluate their compatibility for copolymerization. The PMP-co-PS microstructure analysis revealed that under feed compositions of less than 8:2 an alternating pattern predominates along the copolymer chain, which allows for more open space around the phosphorus atoms in comparison to the more hindered spatial environments around the phosphorus centres in poly(methylenephosphine). This insight provides an explanation to our previously reported success of Suzuki cross-coupling reactions using PMP-co-PS.\textsuperscript{16} We have demonstrated the utility of reactivity ratios in modeling compositional heterogeneity and monomer sequence distribution along the backbone of PMP-co-PS. The architectures of PMP-co-PS ultimately influence the behavior and physical attributes of the resulting material, which will be investigated in future studies. Results from this study, particularly the $Q$-$e$ values of PA, will undoubtedly play a crucial role in the future design of copolymers composed of PA and in the evaluation of the specific applications for these tailored materials.

4.4 Experimental Section

**General procedures.** All manipulations of air and/or water sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques or in an Innovative Technology Inc. glovebox. Hexanes and dichloromethane were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. THF was distilled from sodium/benzophenone ketyl. Styrene (Aldrich) was stirred with CaH\textsubscript{2} for 24 h, distilled twice

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under partial vacuum and used immediately after distillation. 1,1’-azobis(cyclohexanecarbonitrile) (VAZO 88) (Aldrich) was recrystallized twice from ethanol (99%) and dried for at least 24 h under vacuum. Monomer MesP=CPh₂ was prepared following previously reported procedures.³⁷

**Equipment.** ¹H, ³¹P NMR and ¹³C spectra were recorded at 298 K on Bruker Avance 300 MHz or 400 MHz spectrometers. Chemical shifts are reported relative to 85% H₃PO₄ as an external standard (δ = 0.0 for ³¹P) and residual CHCl₃ (δ = 7.26 for ¹H and 77.16 for ¹³C). Samples for ¹³C NMR spectroscopy were prepared by dissolving 40 mg of PMP-co-PS samples in 0.4 mL CDCl₃. For ¹³C experiments with inverse gated proton decoupling, pulse program zgig was used. The relaxation delay (d₁) was set to 3 s, and approximately 2048 scans were used for each experiment.** Molecular weights were determined by triple detection GPC using a Waters liquid chromatograph equipped with a Waters 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel columns (4.6×300mm), HR2 × 2 and HR4, Waters 2410 differential refractometer (refractive index detector, λ = 940 nm), Wyatt tristar miniDAWN (laser light scattering detector, λ = 690 nm) and a Wyatt ViscoStar viscometer. A flow rate of 0.5 mL min⁻¹ was used and samples were dissolved in THF (ca. 2 mg/mL). The dn/dc for each sample was determined using the software. Elemental analyses were performed by the Canadian Microanalytical Service Ltd. Calculations and plots for preliminary estimates of the reactivity ratios were obtained using Microsoft Excel. Nonlinear least squares regression was performed using MATLAB V.7.0.4 R14.

** Increasing the relaxation delay to 10s and/or the number of scans does not change the relative integration of signals in the spectra, and therefore did not affect the estimations of copolymer compositions.

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4.4.1 General procedure for synthesis of PMP-co-PS. The experimental procedure for PMP-co-PS (entry 1, Table 4.2) is described in the following as an example: A pyrex tube was charged with phosphaalkene (1.14 g, 3.6 mmol), VAZO 88 (0.044 g, 0.18 mmol) and styrene (1.55 g, 14.4 mmol). The tube was flame sealed in vacuo, then heated at 100 °C in an oven equipped with a rocking tray. After 2 hours of being heated, the tube was broken. Precipitation of the copolymer was achieved by adding hexanes (100 mL) to a viscous solution of the tube’s contents dissolved in THF or CH2Cl2. Precipitation was repeated three times. The product, a white powder, was redissolved in THF (3 mL), then filtered through glass wool into a small vial. The solvent was allowed to evaporate, leaving the copolymer as a white solid, which was then dried in a vacuum oven at 60 °C for 24 hours. Yield = 0.08 g (3%).

$^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 4, -9$ (br). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.5 - 6.3$ (br, Ar-$H$), 2.5 – 1.0 (CH$_3$, CH$_2$, CH). $^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta = 155 - 120$ (br, Ar-$C$), 50, 35 (br, CH, CH$_2$), 25 (br, CH$_3$). GPC-LLS (THF): $M_n = 8.0 \times 10^3$ g mol$^{-1}$, PDI = 1.11.

4.4.2 General procedure for processing $^{13}$C NMR spectra and determining copolymer composition. The raw data, obtained via the inverse gated proton decoupled $^{13}$C NMR technique described above, were processed using the Bruker software, XWINNMR. A line-broadening setting of 25 was used, the spectrum was manually phased in zero-order and first-order, and a baseline correction was applied. The broad signals for the aromatic carbons and the methyl carbons were integrated. Each integral was phased and their values were used to calculate the copolymer composition according to the following equations:

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\[ m_{PA} = \frac{600C_{Me}}{3C_{Ar} - 12C_{Me}} \quad \text{and} \quad m_{Sy} = 1 - m_{PA} \]

where: \( C_{Me} \) represent integration value of the chemical shift assigned to methyl carbons; \( C_{Ar} \) represent integration value of the chemical shift assigned to aryl carbons.
4.5 References


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(22) Fineman, M.; Ross, S. D. *J. Polymer Sci.* 1950, 5, 259-262.


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Chapter Five

Overall Conclusions and Future Work

5.1 Summary of Thesis Work

Before I joined the Gates lab, former members had discovered the first addition polymerization of a phosphaalkene (5.1) to afford poly(methylenephosphine) (5.2).\(^1\) This can be achieved via a radical route using 1,1’-azobis(cyclohexanecarbonitrile) (VAZO 88), or via an anionic approach using an anionic initiator such as \(n\)-BuLi or MeLi. (Scheme 5.1).\(^12\)

![Scheme 5.1](image)

It has also been demonstrated by previous members of the Gates group that the phosphine centres in 5.2 can be chemically modified via oxidation reactions,\(^1\) or coordination to Lewis acids\(^3\) or transition metals.\(^4\) One of the major objectives in this thesis was to synthesize new poly(methylenephosphine)s that would manifest fluorescence upon chemical modification.

We have now successfully prepared new phosphaalkenes \(\text{MesP}=\text{C(Naph)}(\text{Ph})\) (Naph = 1-naphthyl) (5.3a), \(\text{MesP}=\text{C(Phen)}(\text{Ph})\) (Phen = 9-phenanthrenyl) (5.3b), and \(\text{MesP}=\text{C(C}_4\text{H}_3\text{S})(\text{Ph})\) (\(\text{C}_4\text{H}_3\text{S} = 2\)-thienyl) (5.3b). The syntheses of 5.3a and 5.3c were achieved by the base-catalyzed phospha-Peterson reaction (Scheme 5.2), whereas the synthesis of 5.3b was realized via the standard phospha-Peterson route (Scheme 5.3). Crystals suitable for X-ray diffraction analysis were obtained for 5.3a-c.

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Chapter Five

\[
\begin{align*}
\text{Mes-R} & \quad \text{SiMe}_3 + \quad \text{O=C} & \quad \text{KOH (cat.)} \\
\text{SiMe}_3 & \quad \text{Ph} & \quad - (\text{SiMe}_3)_2\text{O} \\
\rightarrow & \quad \text{Mes} & \quad \text{Ph} \\
\end{align*}
\]

5.3a \quad R = \text{Naph} \\
5.3c \quad R = \text{C}_4\text{H}_3\text{S}

Scheme 5.2

\[
\begin{align*}
\text{Mes-} & \quad \text{SiMe}_3 \quad \xrightarrow{\text{MeLi}} \quad \text{Mes-} & \quad \text{SiMe}_3 \\
\rightarrow & \quad \text{MeLi} & \quad \text{Mes-} & \quad \text{Li} \\
65 \, ^\circ C & \quad \text{overnight} & \quad 1) & \quad \text{PhenC(O)Ph}, -78 \, ^\circ C, 10 \, \text{min} \\
& & \quad 2) & \quad \text{SiMe}_3\text{Cl}, -78 \, ^\circ C \\
- & \quad \text{LiCl} & \quad - & \quad (\text{SiMe}_3)_2\text{O} \\
\rightarrow & \quad \text{Mes} & \quad \text{Ph} \\
\end{align*}
\]

5.3b

Scheme 5.3

Anionic polymerization of 5.3a and 5.3b afforded new poly(methylenephosphine)s 5.4a and 5.4b, respectively (Scheme 5.4). The attempted polymerization of 5.3c did not yield any polymer, presumably due to an inhibition of chain propagation. All of the synthetic work described above is presented in Chapter 2.

\[
\begin{align*}
\text{Mes-} & \quad \text{R} \quad \xrightarrow{\text{2 mol% n-BuLi}} \quad \text{Mes-} & \quad \text{P=Ca} \\
\text{SiMe}_3 & \quad \text{Ph} & \quad \text{THF, RT} \\
\rightarrow & \quad n-\text{Bu} & \quad \text{Ph} \\
\end{align*}
\]

5.3a \quad R = \text{Naph} \\
5.3b \quad R = \text{Phen} \\
5.4a \quad R = \text{Naph} \\
5.4b \quad R = \text{Phen}

Scheme 5.4

Based on literature precedent,\textsuperscript{5,6} we had expected that phosphaalkenes 5.3a and 5.3b and poly(methylenephosphine)s 5.4a and 5.4b would be either weakly fluorescent or non-emissive due to a quenching effect from the phosphorus lone pair. Thus, we hypothesized that the chemical functionalization of phosphine centres in polymers 5.4a and 5.4b would result in an increase in fluorescence. In Chapter 3, we discussed the chemical modification of 5.4a and 5.4b. This was achieved by oxidation of the phosphine centres and coordination to borane moieties to afford functionalized macromolecules 5.5a, 5.5b, 5.6a, and 5.6b (Scheme 5.5). We studied the electronic properties of 5.3a – 5.6a and 5.3b – 5.6b by UV/Vis and fluorescence spectroscopy.

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The results showed that the naphthyl-derivatized phosphaalkene 5.3a and poly(methylenephosphine) 5.4a were non-emissive, while functionalized polymers 5.5a and 5.6a fluoresced in the UV region when irradiated at 288 nm. Similarly, for the phenanthrenyl-derivatized species, the emission intensities of phosphaalkene 5.3b and poly(methylenephosphine) 5.4b were observed to be lower than those of the functionalized macromolecules 5.5b and 5.6b. These results support our hypothesis that chemical functionalization of the phosphorus centres in poly(methylenephosphine)s 5.4a and 5.4b would prevent quenching from the phosphorus lone pair and give rise to fluorescent behaviors. The long-term goal behind the work presented in Chapters 2 and 3 is to develop a poly(methylenephosphine)-based chemical sensor. The results obtained thus far builds a foundation for further work towards this ultimate goal.
While Chapters 2 and 3 focus on homopolymers with conjugated substituents, it is possible to envision analogous copolymers designed for the same sensory purpose since it may not be necessary to have phosphorus at every other atomic position in the main chain. Former members of the Gates group had studied the radical copolymerization of phosphaalkene 5.1 and styrene (Sty) to form poly(methylene phosphine)-co-polystyrene (PMP-co-PS) (Scheme 5.6).^7

\[
\text{Mes} \quad \text{Ph} \quad + \quad \text{Ph} + \quad \xrightarrow{100 \, ^\circ \text{C}} \quad \text{PMP-co-PS}
\]

\[5.1\]

\[\text{Sty} \quad \text{PMP-co-PS}\]

**Scheme 5.6**

We wanted to know more about the microstructure of PMP-co-PS, thus another objective of my work was to calculate the reactivity ratios of phosphaalkene 5.1 \(r_{PA}\) and of styrene \(r_{Sy}\) to model the microstructure of PMP-co-PS. Using data from a number of copolymerization experiments, we calculated \(r_{PA}\) and \(r_{Sy}\) by following the Tidwell-Mortimer approach.\(^8\) According to a nonlinear least squares regression of the data, the best estimates of the reactivity ratios are \(r_{PA} = 0.11\) and \(r_{Sy} = 0.24\). Using these \(r\) values, we modeled the microstructure of PMP-co-PS and showed that an alternating pattern predominates in the backbone unless the copolymer was prepared from a monomer feed ratio of greater than 8:2. We also computed the reactivity parameters of phosphaalkene 5.1 according to the widely used Alfrey-Price \(Q-e\) scheme.\(^9,10\) The reactivity parameters of 5.1 will enable us to predict compatibility of 5.1 (and other phosphaalkenes that are structurally and electronically similar) with other monomers for future copolymerization projects.

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5.2 Future Work

5.2.1 Towards Poly(methylene phosphine)-Based Chemical Sensors

While our studies have provided spectroscopic evidence to support our hypothesis that chemical functionalization of phosphorus atoms in poly(methylene phosphine)s 5.4a and 5.4b would lead to fluorescence, further studies are required to generalize and confirm this hypothesis for poly(methylene phosphine)s bearing other fluorescent groups. Future directions include:

- Prepare poly(methylene phosphine)s with fluorescent groups other than naphthyl and phenanthrenyl, preferably moieties that would emit in the visible region to give fluorescent responses that are observable to the human eye.
- Measure the quantum yield of fluorescent polymers to confirm strength of emission.

As mentioned previously, a chemosensor based on poly(methylene phosphine) may not need phosphorus at every other atomic position in the main chain. In fact, sensing behaviors may be realized by random copolymers. To this end, future work includes:

- Copolymerize phosphaalkenes bearing fluorescent groups with vinyl monomers.
- Study the electronic properties of copolymers by UV/Vis and fluorescence spectroscopy.

To evaluate the potential of new materials for sensing applications, one would need to:

- Perform studies to test sensitivity and selectivity.

5.2.2 Copolymerization of Phosphaalkenes

Using the $Q-e$ reactivity parameters of phosphaalkene 5.1, we can predict the

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predilections of 5.1 (and of structurally and electronically similar phosphaalkenes) to copolymerize with certain other monomers. It is possible to predict the microstructures prior to carrying out the copolymerization experiment. Copolymerization of phosphaalkenes with olefins offers the potential of adding new dimensions to materials available today. A few of the goals in our research include the development of water-soluble materials, macromolecular chemical sensors, and materials for polymer-supported asymmetric catalysis. Some of our targeted materials may be realized by copolymerization of phosphaalkenes with vinyl monomers. Future work involving copolymerization of 5.1 (and derivatives thereof) will be greatly aided by using the Q-e reactivity parameters of 5.1 to screen monomers for tailored applications.

5.3 Closing remarks

The preparation and chemical functionalization of new poly(methylenephosphines)s bearing fluorescent substituents was accomplished. An investigation of the electronic properties showed that chemical functionalization of the phosphorus centres in the new poly(methylenephosphines)s resulted in enhanced fluorescent properties. We also modeled the microstructure of PMP-co-PS by calculating the reactivity ratios of phosphaalkene 5.1 and of styrene. The architecture of PMP-co-PS is important as it ultimately influences the behavior, physical attributes, and function of the material. The results obtained by these studies represent the foundation towards chemical sensors based on homo- or copolymers derived from phosphaalkenes. Future development of new materials from the (co)polymerization of phosphaalkenes is an exciting and expanding area of research, and thus the story of poly(methylenephosphine)s is to be continued.

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5.4 References


