New Functional Inorganic Polymers Containing Phosphorus

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Summary: The C=C bond plays numerous roles in polymer science. This moiety is used as a precursor to polymers by addition polymerization and has been incorporated into π-conjugated polymers. The addition polymerization reaction has been extended to P=C bonds and the first example of a poly(methylenephosphine) has been prepared. The new macromolecule is of moderate molecular weight (ca. 10^4 g/mol) and the oxidized polymers are air-stable. Poly(p-phenylenephosphaalkene), the first π-conjugated polymer containing P=C bonds in the backbone, has been prepared. The UV/Vis spectrum of this polymer shows a red shift in λ_{max} when compared with molecular model systems.

Keywords: addition polymerization; conjugated polymers; inorganic polymers; step-growth polymerization

Introduction

The development of synthetic methodologies to prepare new polymeric materials with novel structures and properties is a challenging frontier in chemistry.[1] Most known polymers contain backbones composed of combinations of carbon, nitrogen and oxygen, and their properties are tailored by structural modification of the side-group or main-chain architecture. The incorporation of inorganic elements into macromolecules is known to lead to materials possessing unique properties not obtainable by modification of known organic macromolecules. In principle, it should be possible to prepare a wide range of polymers with interesting structures and properties using various combinations of main group elements and/or transition metals. A limitation which has slowed the development of inorganic polymers has been the lack of suitable synthetic methods for their preparation.

The carbon-carbon double bond in alkenes is one of the most versatile functional groups in chemistry. The numerous transformations of this functionality form the basis for many important

CCC 1022-1360/00/$ 17,50+.50/0

industrial and academic pursuits. In polymer science, molecules containing C=C bonds are essential precursors to many commodity materials through addition polymerization processes. For example, macromolecules such as polyethylene, polypropylene, polystyrene and poly(acrylates) are prepared using this route. Recently, the incorporation of the C=C functionality into π-conjugated polymers has received significant attention due to the remarkable electronic properties exhibited by these materials.[2] For example, doped polyacetylene shows metallic conductivity and poly(p-phenylenevinylene) is an electroluminescent material.

Despite the remarkable diversity exhibited by the C=C bond in polymer synthesis, there is a virtual absence of research into using heteroatom containing (p-p)π bonds in polymer chemistry. We have embarked on a research program directed towards: (i) extending addition polymerization to other E=E' bonds (where E and E' are p-block elements); and (ii) incorporating E=E' bonds into π-conjugated macromolecules. Herein, a review of our recent work in these areas will be provided.

Addition Polymerization

The addition polymerization of olefins is the most important process for the preparation of commodity polymers. The driving force for the addition polymerization reaction is the thermodynamic preference of two sigma (σ) bonds in the polymer over a sigma (σ) plus a pi (π) bond in the alkene. This renders the process highly exothermic. For styrene, the enthalpy of polymerization (ΔH_p) is –73 kJ/mol.[3] The stability of a two σ bonds over a σ bond plus a π bond is not unique to olefins. Most element-element combinations of the heavier p-block elements (n>2) have a thermodynamic preference to form compounds with a fully sigma bonded structure rather than one containing (p-p)π bonds. Thus, by analogy to olefins, the polymerization of compounds possessing E=E' bonds should also be thermodynamically favourable.

The key feature of alkenes that makes them suitable for polymerization is that, in addition to their thermodynamic instability with respect to polyolefin, there is a large activation barrier to this reaction. This kinetic stability allows olefins to be isolated, purified and later treated with an initiator for polymerization to obtain high molecular weight polymers. Unfortunately, double bonds containing elements of the second and subsequent rows lack kinetic stability and it was long believed that heavier elements could not form stable compounds with multiple bonds involving pπ-pπ overlap.[4] For example, the structure of phosphorus is P_4 rather than P_2 and silicon dioxide (SiO_2) is polymeric whereas its congener CO_2 is molecular.

In the late seventies and early eighties methods were developed to kinetically stabilize (p-p)π bonds involving the heavier p-block elements. The employment of sterically bulky groups imposes a large activation barrier to oligomerization and facilitated the preparation of numerous compounds with (p-p)π bonds (see Figure 1). In particular, early breakthroughs in this area involved the isolation of compounds with P=N,[5] P=C,[6, 7] P≡C,[8] Si=C,[9] Si=Si[10] and P=P[11] bonds. Today, the development of multiply bonded systems containing the heavier main group elements remains an active area of investigation.[12] Like olefins, these systems are kinetically stable but thermodynamically unstable with respect to polymerization. Therefore, by employing the right combination of bulky substituents, the compounds in Figure 1 are potential monomers for the synthesis of inorganic polymers using addition polymerization.

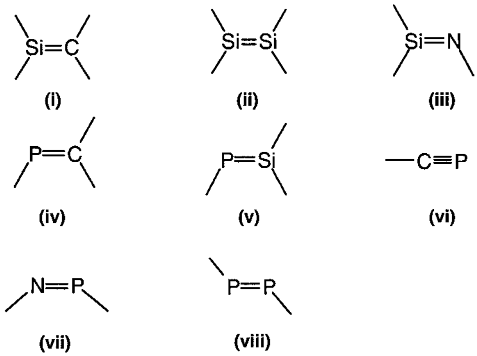
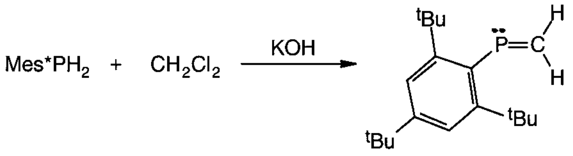


Figure 1. Examples of known systems which possess stable multiple bonds involving the heavier elements of Groups 14 and 15.

Addition Polymerization of Phosphaalkenes

As a starting point to the investigation of addition polymerization for inorganic multiple bonds, we chose to investigate the polymerization of the well-established phosphaalkenes (or methylenephosphines).[13] We have been exploring the reactions of kinetically stable phosphaalkenes with potential initiators for polymerization. Our initial studies focused on the hindered phosphaalkene (**1**) which possesses the very bulky supermesityl (Mes*=2,4,6-tri-tert-butylphenyl) substituent on phosphorus and hydrogen substituents on carbon. Compound **1** was chosen because large substituents would only be found on every second atom in a polymer which may hinder cycloaddition reactions and favour chain formation. Phosphaalkene **1** was conveniently prepared from supermesitylphosphine and CH_2Cl_2 in the presence of KOH following the literature procedure.[14]



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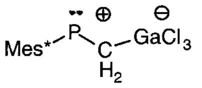
The stoichiometric reaction of **1** with Lewis and protic acids was explored as a means to understand the possible initiation step in a cationic polymerization reaction.[15] Two possible modes of coordination were considered. Based on electronegativity arguments it is possible that electrophiles would add to the double bond at carbon generating a phosphenium ion **2**. This would represent the desired initiation step in a polymerization reaction. Alternatively, due to the close energy of the (p-p)π orbital and the lone pair on phosphorus, the electophilic reagent may simply form a coordination adduct **3**. There is precedence for this mode of coordination from the reaction of the phosphaalkene $^tBuP=C(^tBu)H$ with $AlCl_3$.[16]



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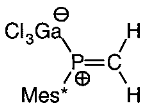

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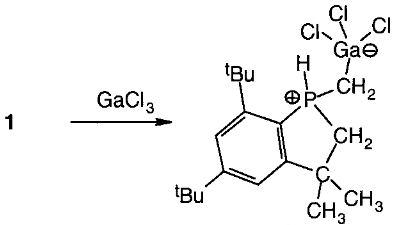
Interestingly, when **1** was treated with the Lewis acid $GaCl_3$, neither the phosphenium ion **2** nor the adduct **3** were observed.[15] An X-ray crystallographic analysis of the product **4** revealed that an intramolecular C-H activation of one of the *ortho*-^{t}Bu groups of Mes* had occurred. The organometallic compound **4** may be envisaged as a coordinated ylide. Mechanistic studies of this reaction and a related reaction of **1** with triflic acid showed that the mechanism involved initial formation of the adduct **3** followed by rearrangement to **2** and subsequent rapid intramolecular oxidative addition of the C-H bond to the divalent phosphenium centre giving **4**.



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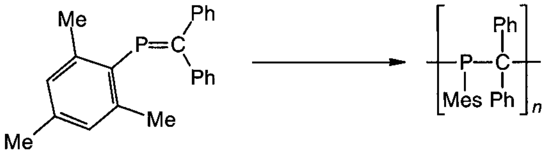
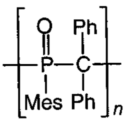
Due to the problem of C-H activation when employing the supermesityl substituent, other stable phosphaalkenes with minimal steric protection were sought which would not show the same propensity for intramolecular C-H activation. The phosphaalkene **5**, which contains the smaller mesityl substituent at phosphorus, attracted our attention. This compound was first prepared in 1978 from the base-induced dehydrochlorination of MesP(Cl)C(H)Ph_2.[7] We followed another procedure which involves the reaction of bis(trimethylsilyl)mesitylphosphine with benzophenone in the presence of a catalytic quantity of NaOH.[17] Compound **5** was vacuum distilled and the residue from distillation contained a gummy material which solidified upon cooling. The ^{31}P, ^{1}H and ^{13}C NMR spectra of the residue were consistent with a polymeric material containing trivalent phosphines. Poly(methylenephosphine) **6** was purified by precipitation with hexanes to remove molecular impurities.[18] The molecular weight of this new polymer was estimated to be about 14,000 g/mol using GPC vs. polystyrene.



5 **6**

Polymer **6** has proven to be easily functionalized.[18] An air stable phosphine oxide polymer **7** was prepared rapidly and quantitatively from **6** using hydrogen peroxide. This new material shows no weight loss until 320 °C when analyzed using TGA. The phosphine sulfide polymer **8** was prepared from the reaction of **6** with elemental sulfur. The new polymers **7** and **8** had molecular weights comparable to that of **6**.



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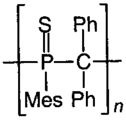

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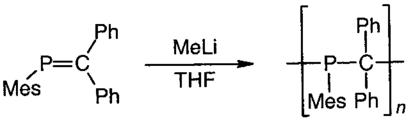
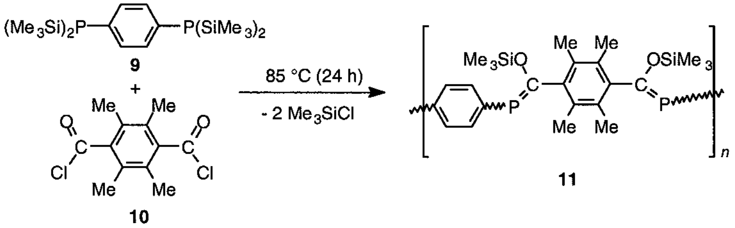
In experiments with potential initiators, we found that the polymerization of **5** can be initiated at 150 °C using anionic initiators such as MeLi or BuLi.[18] The poly(methylenephosphine) **6** was isolated in good yields and exibited spectroscopic properties identical to those for the polymer obtained by thermolysis. Reasonable molecular weights (ca. 5,000 – 10,000 g/mol) were obtained for several experiments using methyllithium as an initiator.



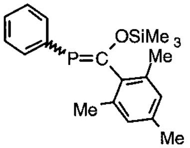
5 **6**

Incorporation of P=C Bonds into π-Conjugated Polymers

Polymers containing π-conjugated backbones are currently attracting significant attention due to their interesting properties. We have been investigating the possible incorporation of inorganic multiple bonds into π-conjugated polymers by the replacement of the C=C bonds in poly(p-phenylenevinylene) with P=C bonds. The synthetic strategy employed involves the condensation of a bis(trimethylsilyl)arylphosphine with an acid chloride followed by [1,3]-silatropic rearrangement as the key P=C bond forming step.[6, 19, 20] The thermal condensation reaction of the silylated 1,4-diphosphinobenzene **9** and the bis(acid chloride) **10** gave poly(p-phenylenephosphaalkene) **11** which was purified by precipitation with hexanes.[21] A molecular weight of ca. 6,300 g/mol was estimated for one sample of the polymer **11** by using end-group analysis. The ratio of *Z*-isomer (phenylenes are *trans*) to *E*-isomer (phenylenes are *cis*) for several samples of polymer ranged from 1.05-1.14.



Two molecular models for the polymer were prepared using the route described for the synthesis of **11**. Compounds **12** and **13** were fully characterized using NMR spectroscopy, mass spectrometry and microanalysis.[21] The *Z*/*E* ratios were 0.85 and 1.27, respectively. The electronic structure of the polymer and the two model compounds was investigated using UV/Vis spectroscopy. Absorbances were observed for **12** (λ_{max} = 310 nm) and **13** (λ_{max} = 314 nm), whilst the polymer **11** which had a molecular weight of 6,300 g/mol showed a significant red-shift in its absorbance maximum (λ_{max} = 334 nm).[21] This red-shift suggests some degree of π-conjugation through the phenylene and P=C moieties in the polymer.



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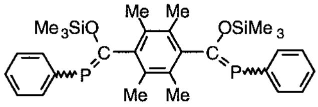

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Summary

In closing, we have shown that the addition polymerization reaction, a general method for the polymerization of alkenes, can be extended to P=C bonds. A new air-stable class of macromolecule containing phosphines in the main chain has been prepared from a phosphaalkene. The first π-conjugated polymer containing alternating phenylene and phosphaalkene moieties has been prepared and is an inorganic analogue of poly(p-phenylenevinylene).

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