

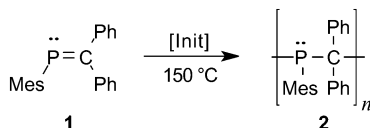
The Addition Polymerization of a P=C Bond: A Route to New Phosphine Polymers

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The preparation of macromolecules possessing inorganic elements in the backbone is an area of current interest due to the prospect of finding materials with unique properties.^{1–3} However, the design of suitable methods for their preparation has hindered their widespread development. Perhaps the most general and industrially important method of organic polymer synthesis is the addition polymerization of olefins. This method has often been ruled out as a feasible method of inorganic polymer synthesis because suitable unsaturated precursors are not readily available.^{1b,d,4} In recent years, the synthesis and study of compounds containing stable (p–p)π bonds involving the heavier elements (*n* > 2) of groups 14 and 15 has attracted considerable attention.⁵ However, their use as precursors to inorganic polymers is virtually unexplored.^{6,7} A goal of our research program is to polymerize stable heavier element-containing multiple bonds. As a starting point we have chosen P=C bonds which are known to exhibit numerous parallels to the chemistry of C=C bonds.⁸ Furthermore, as a consequence of strong, relatively nonpolar P–C bonds in the main chain, we anticipate such a polymer to be air-stable through simple chemical modification.⁹ In this work, we report the first polymerization of a phosphalkene (**1**) to give poly(methylenephosphine) **2**, a new polymer with phosphorus(III) atoms in the main chain.



The instability of phosphalkenes bearing small substituents has often been attributed to undesired “polymerization” reactions.^{8c,10} However, these reactions were likely uncontrolled, and the products were never characterized. To study reactions with polymerization initiators, isolable phosphalkenes with minimal steric protection are desired. We have reported that treating Mes*P=CH₂ (Mes* = 2,4,6-tri-*tert*-butylphenyl)¹¹ with cationic initiators (i.e., GaCl₃, AlCl₃, HOTf) results in intramolecular C–H activation of the Mes* group, effectively preventing chain growth.¹² In our search for other candidates for polymerization, phosphalkene **1** (Mes = 2,4,6-trimethylphenyl), the first stable compound with a localized P=C bond, attracted our attention.^{13,14} Interestingly, although **1** was isolable, it has been reported that employing the 2-methylphenyl substituent at P resulted in a “polymeric material” rather than phosphalkene.¹³ No spectroscopic data for this material were provided. Thus, **1** appeared to be an ideal candidate for polymerization because it is isolable but has minimal kinetic stabilization and was unlikely to undergo intramolecular C–H activation.

Monomer **1** was prepared according to a literature procedure,¹⁵ and after vacuum distillation of the crude product (bp = 150 °C; 0.1 mmHg), a gummy, pale-brown residue remained. In addition to **1** (δ = 233), the ³¹P NMR spectrum of the residue in CH₂Cl₂

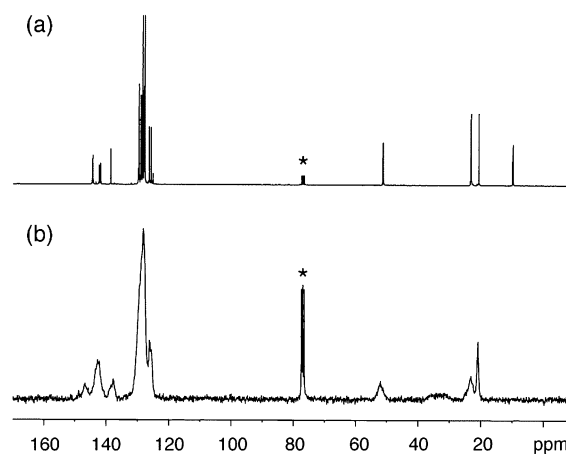
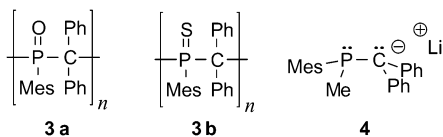


Figure 1. ¹³C NMR spectra of (a) Mes(Me)PCPh₂H in CDCl₃ and (b) **2** in CDCl₃. (*) indicates CDCl₃.

revealed several sharp resonances and a broad signal (–10 ppm) in the phosphine region. After precipitation (×4) of viscous THF solutions of the residue with hexanes, poly(methylenephosphine) **2** was obtained as a colorless solid (yield = 7%). The ¹H and ¹³C NMR spectra exhibited signals consistent with the proposed structure of **2**. The ¹³C NMR spectrum of **2** (Figure 1b) shows resonances which are remarkably similar to those of the model system Mes(Me)PCPh₂H (Figure 1a), and their breadth is consistent with the polymeric nature of **2**. In particular, the backbone quaternary P–C(Ph)₂–P moiety was detected as a broad resonance at 52 ppm (Figure 1b). Importantly, GPC (THF) analysis of the new polymer **2** resulted in an estimated *M_n* of 11500 g/mol (vs polystyrene) and a polydispersity index (PDI; *M_w/M_n*) of 1.25.

Poly(methylenephosphine) **2** is reasonably air- and moisture-stable in the solid state; however, it slowly forms phosphine oxide **3a** after 4 d in CH₂Cl₂ solution when exposed to air. The oxidized polymer **3a** can be obtained quantitatively by NMR ($\delta^{31\text{P}} = 47$), and in moderate isolated yield (60%) by treating a CH₂Cl₂ solution of **2** with excess H₂O₂ (30% in H₂O). The molecular weight of air- and moisture-stable **3a** was estimated using GPC (*M_n* = 8800; PDI = 1.27) and was similar to that for **2**. Similarly, poly(methylenephosphine) **2** reacts with elemental sulfur in CH₂Cl₂ to yield phosphine sulfide **3b** (84%; $\delta^{31\text{P}} = 52$) for which the molecular weight was estimated using GPC (*M_n* = 11900; PDI = 1.24). Due to possible inaccuracy of estimated molecular weights versus polystyrene, the polymer **3b** was analyzed using light-scattering GPC and viscometry. Significantly, the molecular weight determined for **3b** (*M_w* = 35000) using light scattering was much higher than that estimated using polystyrene standards. The thermal stability of the polymers was evaluated using TGA, and they were stable to weight loss until 265 °C (**2**), 320 °C (**3a**), and 220 °C (**3b**), whereupon they each lost 85–95% of their mass.



Although the above data supports the assigned structure of the novel poly(methylenephosphine) **2**, the mechanism of formation from **1** is not clear. We suspected that a radical impurity might have initiated polymerization at high temperatures. Therefore, samples of **1** were heated with a radical initiator (VAZO) at 200 °C. After 48 h, a polymeric material was isolated and the molecular weight estimated using GPC ($M_n = 5700$; PDI = 1.10). The ^{31}P NMR spectrum of the isolated polymer showed very broad overlapping signals with maxima at -10 and -40 ppm. This observation suggests both head-to-tail and head-to-head enchainment. Although polymer was obtained each time VAZO initiation was attempted, the ^{31}P NMR spectra varied significantly.

We shifted our attention to possible anionic initiators. When **1** and MeLi (0.05 equiv) in a minimum of THF (ca. 0.2 mL) were heated in a sealed tube at 150 °C for 24 h the solution became increasingly viscous.¹⁶ The polymer mixture was quenched with MeOH and precipitated with hexanes; the isolated polymer (**2**, yield = 30%) showed ^{31}P , ^{13}C , and ^1H NMR spectra identical to those obtained from distillation. The molecular weight of poly(methylenephosphine) **2** was estimated (vs polystyrene) using GPC ($M_n = 6600$, PDI = 1.55). The polymerization of **1** in the presence of MeLi is reproducible, and the estimated molecular weights for **2** were between 5000 and 10000 g/mol. Monomer **1** can also be polymerized using BuLi (0.05 equiv) [**2** (25%): $M_n = 5400$, PDI = 1.15].

The mechanism of the polymerization of **1** using anionic species is of interest. The addition of anionic reagents (i.e., MeLi) across P=C and P≡C bonds has been reported. For example, the linear dimer MeP=C(Mes*)P=C(Mes*)Li has been prepared by treating the phosphalkyne (Mes*C≡P; 2 equiv) with MeLi (1 equiv).¹⁷ Moreover, Mes(Me)P(O)CHPh₂ has been isolated after quenching the reaction of **1** and MeLi with MeOH. The authors concluded that carbanion **4** must be an intermediate in this transformation.¹⁸ Significantly, the formation of **4** from **1** and MeLi represents the first step in the putative anionic polymerization of **1**. We have repeated the reaction of **1** with MeLi (1 equiv) and observed **4** ($\delta^{31}\text{P} = -45$) quantitatively which, after treatment with H₂O, gave Mes(Me)PCPh₂H ($\delta^{31}\text{P} = -24$). Furthermore, monomer **1** polymerizes in the presence of **4** (0.05 equiv; 24 h; 150 °C) to yield **2** (39%; $M_n = 6200$; PDI = 1.29). Additional evidence for the involvement of **4** in the polymerization of **1** using RLi is provided by the fact that pure **1** does not polymerize at 150 °C in the absence of initiator. These results are consistent with an anionic mechanism; however, further studies must be conducted to confirm this hypothesis.¹⁹

In summary, we have reported the first polymerization of a P=C bond to yield a stable new class of functional phosphorus macromolecules.

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Supporting Information Available: Full experimental procedures, spectroscopic data, and additional figures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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