Phosphine Polymers

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Ambient-Temperature Living Anionic Polymerization of Phosphaalkenes: Homopolymers and Block Copolymers with Controlled Chain Lengths**

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Living polymerization is a powerful synthetic tool that enables the construction of well-defined macromolecules possessing controlled architectures and tailor-made properties.[1,2] Despite considerable recent activity in the synthesis of polymers composed of inorganic elements,[3,4] living polymerization methods remain primarily the domain of organic polymer chemistry.[5] The prospect of accessing macromolecules of controlled architecture possessing the unique properties imparted by inorganic functionalities is particularly attractive.[6] The addition polymerization of the C=C bond of substituted olefins (for example, styrene) is the prototypical example of a living polymerization,[7] yet the living polymerization of inorganic multiple bonds is unprecedented.

Inspired by the fascinating chemistry of phosphaalkenes and the established parallels between P=C and C=C bonds in molecular chemistry,[8] we have embarked on a program to extend this analogy to polymer science.[9] Building on the well-known addition polymerization of olefins, we have recently discovered that P=C bonds can also be polymerized to afford macromolecules with chemically functional phosphine moieties.[10,11] To polymerize phosphaalkene **1a**, high temperatures (up to 150 °C), long reaction times (about

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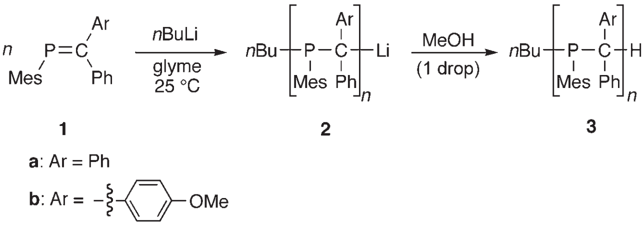
24 hours), and minimal solvent were required, even in the presence of radical or anionic initiators. Under these conditions, low monomer conversions and several unidentified phosphorus by-products are observed, thus resulting in poor yields of isolated poly(methylenephosphine). Clearly, improved methods are necessary for the polymerization of **1**. It has been noted that **1a** reacts rapidly with alkyl lithium reagents (for example, MeLi) to afford MesP(Me)CPh$_2$Li ($\delta(^{31}P) = -45$ ppm; Mes = 2,4,6-Me$_3$C$_6$H$_2$)[10,12] which in the presence of additional **1a** forms short-chain oligomers.[13] Prompted by these observations, we speculated that the anionic polymerization of **1** may be living under the right conditions.

Herein, we report the first living anionic polymerization of a heteroatom-containing multiple bond; namely, treating phosphaalkene **1** with *n*BuLi at ambient temperatures in solution gives living poly(methylenephosphine) **2** (Scheme 1). This new chemistry facilitates the construction of monodisperse homopolymers and unprecedented styrene–phosphaalkene block copolymers with controlled molecular weights.



Scheme 1. Living anionic polymerization of **1**.

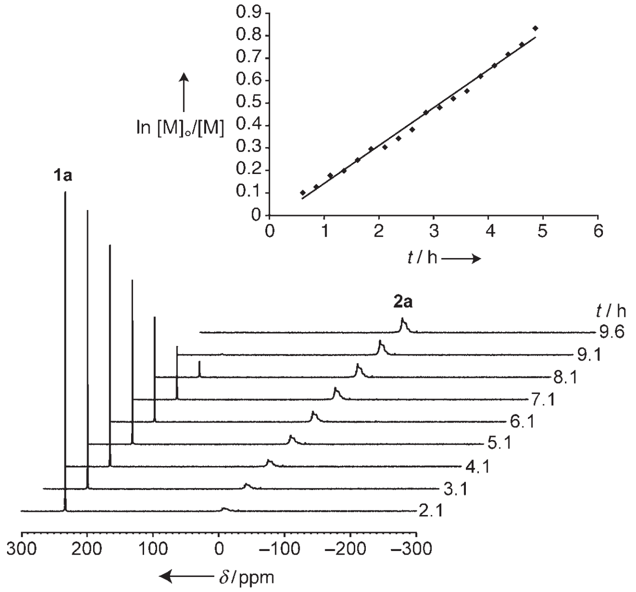


Figure 1. Selected ^{31}P NMR spectra and first-order kinetic plot (inset) showing the progress of the polymerization of **1a** in glyme using *n*BuLi (2 mol%); ^{31}P NMR measurement times are given in hours. Kinetic data: monomer/initiator (M/I) = 50:1, $k_p = 21$ L mol^{-1} h^{-1}. Concentrations determined by relative integration of the ^{31}P NMR signals for **1a** and **2a** (relaxation time (t_1) for **1a** is 1.33 s; relaxation delay for NMR experiment is 2 s with a 30° tip angle).

Monomers **1a** and **1b** are readily synthesized following literature procedures[14,15] and, for this work, must be carefully purified using distillation and recrystallization methods. The addition of the anionic initiator *n*BuLi (2 mol%) to a pale yellow solution of phosphaalkene **1a** in glyme[16] at 25 °C resulted in an immediate color change to deep red. Remarkably, monitoring the reaction progress over several hours using ^{31}P NMR spectroscopy revealed that monomer **1a** ($\delta = 234$ ppm) is entirely consumed and that polymer **2a** ($\delta = -7$ ppm) is formed quantitatively (Figure 1). The reaction is very clean and no side-products are observed. This finding is in stark contrast to our earlier investigations involving the high-temperature polymerization of neat **1a** where a number of phosphorus-containing by-products were observed.[10] Interestingly, analysis of the ^{31}P NMR spectroscopic data shows that the polymerization follows pseudo-first-order kinetics for up to 60% conversion (inset, Figure 1). This extremely slow measured propagation rate ($k_p = 21$ L mol^{-1} h^{-1}) is extraordinary. For comparison, the k_p value of styrene in glyme (1.4×10^7 L mol^{-1} h^{-1})[1] is higher by several orders of magnitude. Presumably, the small k_p value for **1a** is a consequence of the steric hindrance associated with the addition of a bulky propagating carbanion (that is, in **2a**) to bulky **1a**.

The red color of the solution of polymer **2a** persists even in the absence of monomer; however, an immediate loss of color is observed when methanol (one drop) is added. The subsequent addition of hexanes to this quenched solution results in the precipitation of H-terminated polymer **3a** (74% yield). Analysis of **3a** using triple-detection gel permeation chromatography (GPC) reveals a very narrow polydispersity index (PDI, $M_w/M_n = 1.04$). Moreover, the measured absolute molecular weight ($M_n = 14800$ g mol^{-1}) is very close to the theoretical molecular weight ($M_n = 15900$ g mol^{-1}; Table 1, entry 3). On the basis of the observed narrow PDI and the excellent correlation of the measured molecular weight of **3a** to that predicted from the ratio of **1a**/*n*BuLi, we postulate that this polymerization reaction is living.

A classic characteristic of a living polymerization is that a plot of M_n versus monomer conversion will be linear. The combination of the slow propagation rate for **1a** with the

Table 1: Synthesis of poly(methylenephosphine)s **3** with controlled molecular weight. Initiator (I) = *n*BuLi.

Entry[a]	M	M/I	M_n (calcd)[b] [g mol^{-1}]	M_n (abs)[c] [g mol^{-1}]	M_w/M_n[c]	r_{hyd}[c] [nm]
1	**1a**	25:1	8000	8900	1.08	1.8
2	**1a**	33:1	10500	10500	1.08	1.9
3	**1a**	50:1	15900	14800	1.04	2.3
4	**1a**	100:1	31700	29600	1.15	3.4
5	**1b**	33:1	11500	11500	1.09	1.8
6	**1b**	50:1	17400	14600	1.11	2.5

[a] Conditions: glyme, 25 °C in N$_2$ atmosphere (glovebox). Upon complete consumption of monomer (confirmed by ^{31}P NMR), the reactions were quenched with MeOH. [b] Predicted M_n value from M/I ratio. [c] GPC (triple detection) equipped with differential refractometer (Waters), viscometer, and laser-light-scattering detectors (Wyatt); refractive index increment (d*n*/d*c*) determined off-line (0.223 mL g^{-1} for both **1a** and **1b**); r_{hyd} = hydrodynamic radius.

^{31}P NMR handle makes this system ideal for analysis of molecular weight versus conversion. Aliquots were taken over a period of about eight hours, and each aliquot was analyzed using ^{31}P NMR spectroscopy and triple-detection GPC. The monomer conversion for each aliquot was determined from the relative integration of the signals resulting from monomer (**1a**) and polymer (**2a**) in the ^{31}P NMR spectrum. The plot of M_n versus conversion for two separate experiments correlates well with the theoretical trend line, and the polydispersities determined were below 1.05 (Figure 2). The absence of data at low monomer conversion (< 50%) is a consequence of the similar solubilities of low-molecular-weight **3a** and monomer **1a**, which renders these species inseparable using precipitation techniques. Nevertheless, the data obtained clearly support our hypothesis that the ambient-temperature anionic polymerization of **1a** is living.

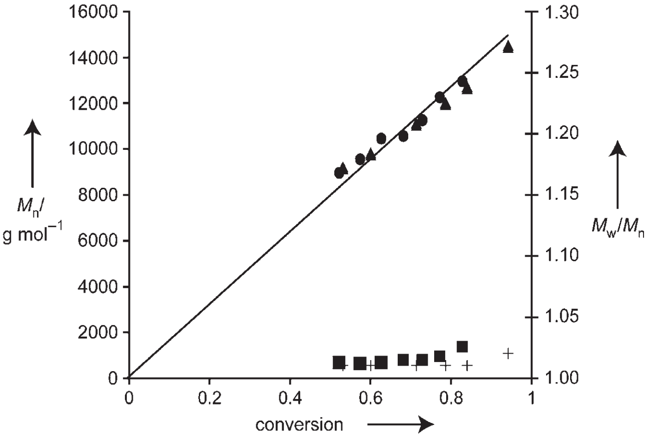
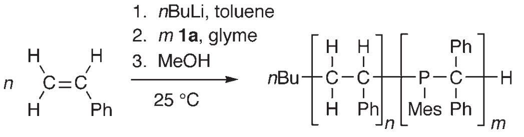


Figure 2. A graph of molecular weight (M_n) and polydispersity index (PDI, M_w/M_n) for **3a** versus conversion of monomer (conditions: glyme, 2 mol% nBuLi, 25 °C). The solid line shows the theoretical trend. Data are presented for two separate experiments with each point representing an aliquot taken from the reaction mixture (absolute M_n from GPC; % conversion from ^{31}P NMR). Experiment 1: ● (M_n) and ■ (PDI); Experiment 2: ▲ (M_n) and + (PDI).

The preparation of **3a** with molecular weights that are dependent upon the monomer-to-initiator ratio (M/I) that was used provides the final confirmation that the anionic polymerization of **1a** is living (Table 1). Importantly, all these polymers have narrow polydispersities and are isolated in high yield (≥ 70%). We have also extended this living polymerization reaction to a 4-methoxyphenyl-substituted monomer **1b** (Table 1, entries 5 and 6).

Once the living nature of the anionic polymerization of **1a** was confirmed, we attempted to prepare a block copolymer from **1a** and styrene (Scheme 2). Living polystyrene was generated by treating a solution of styrene in toluene with nBuLi (M/I = 100:1; 25 °C). An aliquot was removed from the reaction mixture, quenched with MeOH, and analyzed by GPC (M_n = 13300 g mol^{-1}, M_w/M_n = 1.07). This experimentally determined molecular weight is close to the theoretical molecular weight (M_n = 10500 g mol^{-1}). To the orange solution of living polystyrene was added a solution of **1a** (M/I = 28:1) in glyme.[17] The color of the solution immediately changed to deep red, thus suggesting rapid initiation of **1a** by the living polystyrene. After 24 hours, the ^{31}P NMR spectrum of the reaction mixture showed that **1a** had been entirely converted to polymer. The living copolymer was quenched with MeOH, and hexanes was subsequently added to precipitate block copolymer **4** (60% yield). The molecular weight of polystyrene-*block*-poly(methylenephosphine) **4**, as determined using GPC (M_n = 20900 g mol^{-1}, M_w/M_n = 1.03), correlates reasonably well with the predicted molecular weight (M_n(calcd) = 19300 g mol^{-1}). Similar results were obtained in a second experiment to prepare block copolymer **4** (n = 100, m = 50, M_n(calcd) = 26300 g mol^{-1}; GPC: M_n = 29600 g mol^{-1}; M_w/M_n = 1.06). Importantly, the block copolymers from both experiments show monomodal GPC traces, and their ^{13}C{^{1}H} and ^{1}H NMR spectra are consistent with the assigned structures.



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Scheme 2. Living anionic copolymerization of styrene and **1a**.

In conclusion, living anionic polymerization techniques, common for C=C bonds, have been extended to P=C bonds. This chemistry further illustrates the remarkable parallel between P=C and C=C bonds. Interestingly, we have utilized this new methodology to prepare unprecedented polystyrene-*block*-poly(methylenephosphine) copolymers with narrow polydispersities and controlled molecular weights. These synthetic breakthroughs pave the way to phosphorus-containing macromolecules with novel chemical functionalities and properties.

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[17] Homopolymerizations of styrene using *n*BuLi were performed in several different solvents, including glyme, THF, and toluene. We obtained the most consistent results for toluene because of the slower rate of propagation in this solvent. P=C monomer **1a** was added in glyme since polymerization of **1a** is extremely slow in toluene.