Organophosphine Polymers

Radical Copolymerization of a Phosphaalkene with Styrene: New Phosphine-Containing Macromolecules and Their Use in Polymer-Supported Catalysis**

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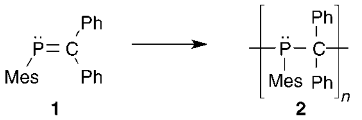
Since Becker's synthesis of the first stable phosphaalkene in 1976,[1] these compounds, which contain a P=C bond and were once considered exotic, now constitute a major branch of phosphorus chemistry. Applications for these compounds are even being developed.[2–4] The ability of P=C bonds, in many instances, to "copy" the well-established chemistry of isolobal C=C bonds has attracted considerable attention.[2,3a,d] In molecular chemistry, the remarkable analogy between phosphaalkenes and alkenes is evidenced by phospha variants of a number of reactions, including 1,2-addition, [4+2]cycloaddition, Peterson and Wittig olefination, η^2 coordination to metal centers, and Cope and allylic rearrangements. One of the most important reactions of C=C bonds is the addition polymerization of olefins, which is used to produce many commodity polymers. The absence of an analogous polymer chemistry for P=C bonds prompted us to investigate addition polymerization as a potential route to new phosphine polymers. We recently reported the first addition polymerization of the phosphaalkene **1**[5] (Mes = 2,4,6-trimethylphenyl) to give the poly(methylenephosphine) **2** ($\bar{M}_w \approx 10^4\,\mathrm{g\,mol^{-1}}$ by GPC versus polystyrene), an alternating P–C polymer.[6]



1 **2**

The development of synthetic methodologies to incorporate phosphorus into the backbone of macromolecules or into dendrimers is a challenging frontier in polymer chemistry

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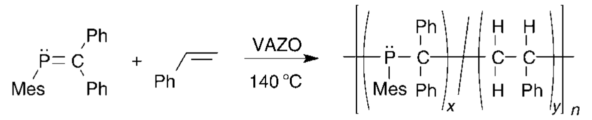
because of the novel properties and chemical functionality phosphorus can impart to such materials.[7,8] Now that we have homopolymerized a phosphaalkene by using conventional methods of initiation, an exciting possibility would be to prepare copolymers from compounds with P=C and C=C bonds by taking advantage of their similarity. From the perspective of the synthesis of phosphorus polymers, this would represent a new and convenient chain-growth method to incorporate functional phosphine moieties directly into the backbone of polyolefins.

Herein we report the first copolymerization of a phosphaalkene, **1**, with styrene to afford hybrid inorganic–organic copolymers **3**. Importantly, the presence of phosphine moieties in the main chain of **3** imparts chemical functionality to the polymer and may ultimately lead to applications of the polymer. As an example, we show that **3** can be employed as a polymer support for palladium-catalyzed Suzuki coupling.



1 **3**

Homopolymers of **1** can be prepared by using thermal, radical, and anionic initiation methods.[6] For the present copolymerization studies, we favored conventional radical over anionic initiation methods, since they are convenient to perform and do not have the same strict purity requirements of anionic polymerization. Therefore, we decided to investigate the copolymerization of **1** and styrene with 1,1′-azobis(cyclohexanecarbonitrile) [VAZO, catalyst 88] as the free-radical source. All copolymerization experiments were conducted at 140 °C for 14 h with monomer **1** dissolved in neat styrene in the presence of a trace amount of VAZO. Typical results for three trials are given in Table 1. Each trial was reproducible, although there was some variation in the molecular weight of **3** as is common for uncontrolled radical polymerization. In each trial molecular impurities were removed by precipitation of a solution of **3** in CH_2Cl_2 into hexanes (repeated twice). The poly(methylenephosphine)–polystyrene **3** is soluble in common organic solvents, such as CH_2Cl_2, THF, and toluene. Copolymer **3** is stable towards hydrolysis and oxidizes slowly in air. Complete oxidation to give an air- and moisture-stable phosphine oxide polymer occurs readily upon treatment with H_2O_2.

Table 1: Selected data for copolymers **3**.

Entry	**1** [%][a]	VAZO [%][b]	$\bar{M}_w$[c]	PDI[d]	Yield [%]	Incorporated P [wt%]	Incorporated **1** [mol%][e]
1	10	0.5	9000	1.7	37	1.28	5
2	20	1.0	7000[f]	1.7	48	2.16	9
3	40	2.0	3600	1.4	18	6.44	39

[a] % **1** = mol **1**/(mol **1**+mol styrene) 100. [b] % VAZO = mol VAZO/(mol **1**+mol styrene) 100. [c] Molecular weights were estimated by gel-permeation chromatography (GPC) versus polystyrene standards. [d] PDI = polydispersity index (estimated by GPC). [e] Estimated from wt% of phosphorus measured by elemental analysis (see Supporting Information for an equation). [f] Triple-detection GPC of an oxidized sample gave $\bar{M}_w = 12000\,\mathrm{g\,mol^{-1}}$, thus suggesting that conventional GPC may underestimate the actual molecular weight.

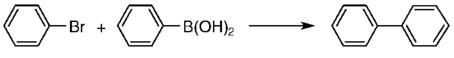
The unoxidized copolymer **3** was analyzed by conventional GPC (THF), and moderate molecular weights (M_w = 3600–9000 $\mathrm{g\,mol^{-1}}$) were estimated relative to polystyrene standards. Importantly, in all cases a monomodal molecular-weight distribution (PDI = 1.4–1.7) was observed, thus providing strong support for the formulation of **3** as a copolymer. A bimodal distribution would be likely if a blend of homopolystyrene and **2** was obtained. Broad overlapping signals in the aromatic and aliphatic regions of the ^{1}H NMR spectra of **3** can be attributed to phosphaalkene and styrene moieties in the polymer. In principle, it is possible to use the ratio of aromatic to aliphatic resonances to estimate the degree of phosphorus incorporation into **3**; however, we have found that this analysis does not give accurate results.[9] Therefore, the phosphorus content determined by elemental analysis was used to estimate the degree of incorporation of the phosphaalkene into **3**. The results are shown in Table 1. For example, the copolymerization of 20 mol% of **1** and 80 mol% of styrene afforded **3** with 2.16 wt% phosphorus, which corresponds to approximately 9% (i.e. $x = 0.09n$ in **3**) incorporation of the phosphaalkene and 91% (i.e. $y = 0.91n$ in **3**) styrene into **3**. Detailed analysis of the outcome of many copolymerization experiments to determine monomer-reactivity ratios would be required to help understand the observed trend in % incorporation versus monomer feed, and this will be the subject of future investigations.

The ^{31}P NMR spectra of **3** are quite interesting and show two major broad signals at $\delta = -9$ and 4 ppm, along with several smaller resonances in the same region. The question arises: why are two signals observed for **3**, whereas only one is observed for **2** ($\delta_{^{31}P} = -9$ ppm)? We speculate that the signals in the region of $\delta = -9$ ppm may result from regions of the polymer with (styrene)–(P–C)–(P–C) and/or (P–C)–(P–C)–(P–C) segments, whereas those at 4 ppm are (styrene)–(P–C)–(styrene) fragments. This is difficult to prove given the expected complex microstructure in **3**; however, the fact that the intensity of the signal at $\delta = 4$ ppm decreases relative to that at $\delta = -9$ ppm as the phosphaalkene content in **3** increases lends support to our hypothesis (see Supporting Information). We note that partial regioirregular enchainment (i.e. P–CH_2 and P–CHPh linkages) and polymer tacticity may contribute to minor signals in the ^{31}P NMR spectra. However, relative intensities of these minor signals would not be expected to change dramatically with phosphorus concentration. Furthermore, it is possible that some phosphorus may be incorporated at or near the polymer chain end and would lead to additional signals. Although further studies are required to fully elucidate the microstructure of **3**, the NMR spectroscopic and GPC data are entirely consistent with our conclusion that this is a random copolymer.

To investigate the chemical functionality of **3**, we have undertaken a preliminary examination of its potential use as a phosphine ligand for polymer-supported metal catalysis. Motivated by the facile separation of the organic product from the polymer/catalyst, researchers have developed a large number of phosphine-containing macromolecules for these applications.[10] As an entry point to this area, we decided to study the Pd-catalyzed Suzuki cross-coupling reaction, a powerful carbon–carbon bond-forming reaction.[11] Polymer-supported Suzuki couplings have been performed with either insoluble phosphine-functionalized resins[12] or soluble polymer-supported phosphines.[13]

To test the feasibility of using our polymers in catalysis, several Pd-catalyzed coupling reactions of bromobenzene and phenylboronic acid were conducted in the presence of $[Pd_2(dba)_3]$ with CsF as a base. The results are shown in Table 2 and the yields reported are averages of at least two runs. Surprisingly, reactions with homopolymer **2** ($\bar{M}_w = 7200$, PDI = 1.5) gave low yields of biphenyl (Table 2, entry 1), possibly because of the congested environment of the phosphorus centers.[14] In contrast, when the copolymer **3** with a lower concentration of phosphine moieties was used, biphenyl was obtained in moderate yield (62%) at room temperature (Table 2, entry 2). For comparison, a control experiment (no added phosphine) and an experiment with $PPh_3/[Pd_2(dba)_3]$ (Table 2, entries 5 and 6) each gave poor yields of biphenyl under very similar conditions. Therefore, we conclude that copolymer **3** is directly involved in the generation of an active catalyst. To garner evidence that **3** interacts with palladium, we treated it with $[Pd_2(dba)_3]$ (P/Pd = 1:1) in THF, and the ^{31}P NMR spectrum of the reaction mixture revealed a very broad resonance between 80 and 0 ppm, as well as broadened signals for uncomplexed **3**. We presume that the broad resonance is an indication of interaction between the phosphine moieties and palladium although the breadth of the signal suggests some ligand exchange.

Table 2: Results of Suzuki cross-coupling reactions with **2** and **3**.[a]



Entry	Ligand	P/Pd	T [°C]	Yield [%][b]
1	**2**	2.0:1	25	23
2	**3**	1.4:1	25	62
3	**3**	1.4:1	80	83
4	**3**	2.8:1	80	90
5	none		25	22
6	PPh_3	1.0:1	25	30

[a] General conditions: bromobenzene (100 mg), phenyl boronic acid (116 mg, 1.5 equiv), base: CsF (3.3 equiv), $[Pd_2(dba)_3]$ (5 mol%), copolymer **3** (for consistency, molar ratio in Table 1, entry 2 used for all experiments), and freshly distilled THF (2.0 mL). [b] Yield of isolated product (an average of two runs; entry 3: average of four runs), purity of biphenyl confirmed by ^1H NMR spectroscopy (all runs) and GC (representative runs).

We have begun to optimize the conditions for Suzuki coupling with **3**. Significantly, at higher temperatures in the presence of **3** (P/Pd = 1.4:1; 80 °C) the yield of biphenyl improved to 83%, and at higher phosphine loading (P/Pd = 2.8:1; 80 °C) we isolated biphenyl in 90% yield (Table 2, entries 5 and 6). These results are very encouraging and are comparable with those obtained in the presence of $[Pd(PPh_3)_4]$.[11a] Furthermore, they demonstrate the potential use of P=C/C=C hybrid copolymers as ligands for Pd-catalyzed reactions. Moreover, the polymer/catalyst could easily be removed by precipitation with hexanes to afford pure biphenyl (by GC and NMR spectroscopy) without the need for column chromatography.

In closing, this paper discloses two significant advances: 1) The remarkable ability of P=C bonds to mimic the chemistry of C=C bonds has been applied to copolymerization, and 2) new hybrid inorganic–organic macromolecules were prepared that can be used in polymer-supported catalysis. We have laid the foundation for the future development of numerous copolymers from a range of phosphaalkenes[15] and olefins by this convenient, one-step methodology. Future work will also explore the possible application of these copolymers in other catalytic processes and attempt catalyst recycling.

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