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Direct Radical Polymerization of 4-Styryldiphenylphosphine: Preparation of Cross-Linked and Non-Cross-Linked Triphenylphosphine-Containing Polystyrene Polymers

Matthew Kwok Wai Choi, Helen Song He, and Patrick H. Toy*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, People's Republic of China

phtoy@hkucc.hku.hk

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Abstract: We report herein a simple synthesis of 4-styryldiphenylphosphine and the radical copolymerization of it with styrene, both with and without a cross-linker, to directly form cross-linked and non-cross-linked polystyrene supported triphenylphosphine in which the level of phosphine incorporation can be easily and accurately controlled. The utility of these polymers is demonstrated by their use in Mitsunobu and alcohol bromination reactions.

Recent years have seen a growing use of polymer-supported reagents by organic chemists in traditional solution-phase synthesis. These reagents may be used to either selectively remove impurities from synthetic products or to deliver reagents to dissolved synthesis substrates.[1] Ley and co-workers have elegantly shown the power of this later approach in their syntheses of several structurally complex natural products using exclusively polymer-supported reagents.[2] However, regardless of how they are used, all polymer-supported reagents have the effect of reducing product purification to simple filtration operations. Of the many reagents supported by polymers available, variations of triphenylphosphine are among the most broadly used. This is because triphenylphosphine is not only a reagent in a wide range of organic reactions,[3] but it also serves as a ligand in many organometallic reagents.[4] In the field of organic chemistry, attaching triphenylphosphine to a polymer has the great advantage that the byproduct of most reactions involving it, triphenylphosphine oxide, can be easily removed. When triphenylphosphine is used, the removal of this impurity from the desired synthesis product is often difficult, and therefore, alternative phosphine reagents that are more easily separated from the reaction mixture have been extensively examined.[5−8]

Despite these innovations, triphenylphosphine remains the preferred reagent in organic synthesis, and therefore, many approaches to its immobilization on a polymer support and applications of such polymer-based reagents have been reported. Many polymers with different solubility profiles have been used in this regard, including poly(ethylene glycol),[9] a ring-opened norbornene-derived polymer,[10] and most recently a non-cross-linked 4-*tert*-butylstyrene polymer.[11] However, polystyrene, both cross-linked and non-cross-linked, has been the polymer most widely used due to its inertness, low cost, and ease of preparation, and there are numerous reports regarding various strategies for the attachment of triphenylphosphine equivalents to it. Some of the earliest reports for the preparation of such polymer-bound phosphine reagents involved the radical copolymerization[12] and homopolymerization[13] of 4-styryldiphenylphosphine (**1**) (eq 1). Despite the directness of this method, and for reasons that are not clear, in recent years the most common method employed for the preparation of polymer-bound phosphine reagents involves the sequence of bromination of preformed polystyrene,[14] followed by either lithiation and subsequent reaction with electrophilic chlorodiphenylphosphine[15,16] or reaction with lithium diphenylphosphide[17] (eq 2). Recently, Charette et al. have reported a different method for the incorporation of triphenylphosphine moieties onto non-cross-linked polystyrene via an

* To whom correspondence should be addressed. Tel: (852) 2859-2167. Fax: (852) 2857-1586.

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(7) For applications of phosphines that contain fluorous tags to aid in the removal of the phosphine and phosphine oxide, see: Dandapani, S.; Curran, D. P. *Tetrahedron* **2002**, *58*, 3855−3864 and references therein.

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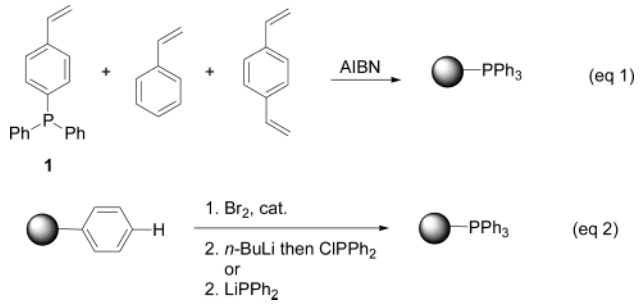
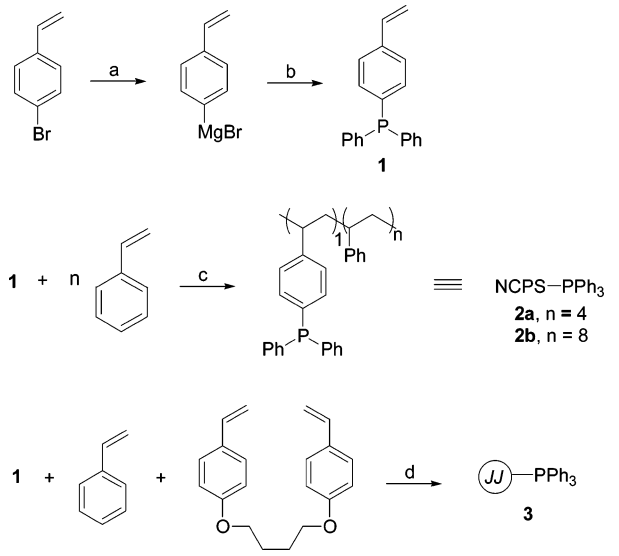
ether linkage.[18] This process is also indirect and involves the sequence of chloromethylation of preformed polystyrene followed by etherification with 4-hydroxyphenyldiphenylphosphine oxide and subsequent reduction to the phosphine.



Our interest in developing both soluble[19] and insoluble[20] polystyrene-based reagents led us to require a reliable method to prepare polystyrene polymers with varying concentrations of triphenylphosphine moieties in order to determine effects of functional group concentration on reagent utility and resin performance. The indirectness of the last two routes mentioned above made them unattractive for our use since they involve multiple reactions that need to proceed predictably and reliably in order to accurately incorporate the desired amount of phosphine groups. Therefore, we chose to examine the route shown in eq 1 that involves the direct radical copolymerization of **1**. Herein we report our results for preparing such soluble and insoluble reagents with varying but predictable loading levels by this method. For the first time, full experimental detail is provided for the one-step synthesis of **1** together with its radical copolymerization with styrene. Furthermore, we show the synthetic utility of the resulting polymer-bound triphenylphosphine reagents by applying them in Mitsunobu and alcohol bromination reactions.

To study the polymerization of **1**, we first examined several routes to prepare it on a 100 mmol scale. Recently, the synthesis of **1** in 89% yield using a modified Grignard reaction that involves potassium, magnesium chloride, potassium iodide, and 4-chlorostyrene has been reported.[21] A different synthesis of **1** that involves 4 steps in 52% overall yield has also been reported.[22] For convenience, we examined the simple Grignard reaction of 4-bromostyrene using magnesium (Scheme 1).[23] To our satisfaction, this method reproducibly produced **1** in over 50% yield on a 30 g scale.

SCHEME 1[a]



[a] Reaction conditions: (a) Mg, THF, 0 °C; (b) $ClPPh_2$, 0 °C to rt; (c) PhMe, AIBN, 85 °C; (d) PhCl, water, acacia gum, NaCl, AIBN, 85 °C.

TABLE 1. Synthesis of *JJ*-PPh_3 (3)

	1 (mmol)	styrene (mmol)	P content (%) theor	P content (%) obsd	loading (mmol/g) theor	loading (mmol/g) obsd	yield (%)
3a	35	0	10.85	9.85	3.5	3.2	96
3b	25	27	7.75	7.25	2.5	2.3	90
3c	16	52	4.96	4.80	1.6	1.5	84
3d	10	65	3.10	3.15	1.0	1.0	82
3e	5	82	1.55	1.57	0.5	0.5	75
3f	1	93	0.31	<0.5	0.1	0.1	70
3g	80	259	4.96	4.59	1.6	1.5	98

With access to adequate quantities of **1** available, we next examined conditions for the copolymerization of **1** with styrene to prepare a soluble reagent (**2**) and with styrene and the cross-linker 1,4-bis(4-vinylphenoxy)-butane, to form insoluble *J*anda*J*el-PPh_3 (*JJ*-PPh_3, **3**) (Scheme 1).[24] We found that AIBN induced radical copolymerization of 4:1 and 8:1 mixtures of styrene/**1** afforded **2** that had loadings of 1.5 and 1.2 mmol PPh_3/g, **2a** and **2b**, respectively.[25] Suspension polymerization of various molar ratios of styrene and **1**, ranging from 93:1 to 0:35, with 2 mol % of the cross-linker initiated by AIBN[26] afforded **3a**−**f** with the predicted loading levels (Table 1).[27] This procedure was used to prepare either 10 or 50 g of polymer **3** per batch. Importantly this procedure works at both extremes in terms of ratio between styrene and **1**, and allows for the production of **3a**, with the theoretical maximum possible loading level of 3.5 mmol PPh_3/g and **3f**, that contains minimal loading of approximately 0.1 mmol PPh_3/g.

To assess the synthetic utility of our polymers we chose to apply them in reactions in which commercially avail-

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(24) Janda*J*el is a registered trademark of the Aldrich Chemical Co.

(25) The loading levels of **2a** and **2b** were determined by elemental analysis. The homogeneity of the phosphine groups was determined by ^{31}P NMR spectroscopy.

(26) Attempts to use benzoyl peroxide as the initiator failed to produce any filterable polymer beads.

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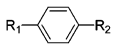
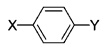
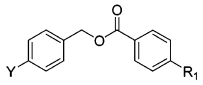
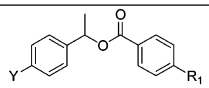
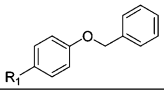
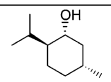
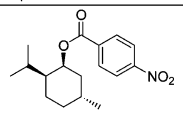
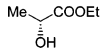
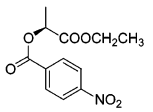
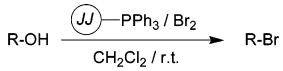
TABLE 2. Mitsunobu Reactions Using 2a

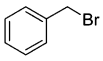
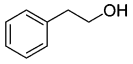
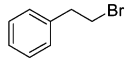
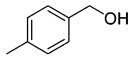
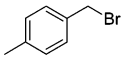
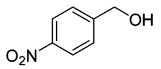
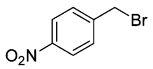
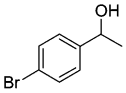
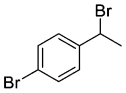
Entry	Nucleophile 	Electrophilie 	Product	Isolated Yield (%)
1	R_1 = H, R_2 = COOH	X = CH_2OH, Y= H		75
2	R_1 = H, R_2 = COOH	X = CH_2OH, Y= CH_3		81
3	R_1 = NO_2, R_2 = COOH	X = CH_2OH, Y= H		80
4	R_1 = NO_2, R_2 = COOH	X = CH_2OH, Y= CH_3		70
5	R_1 = H, R_2 = COOH	X = $CH(OH)CH_3$, Y = Br		70
6	R_1 = NO_2, R_2 = COOH	X = $CH(OH)CH_3$, Y = Br		71
7	R_1 = Br, R_2 = OH	X = CH_2OH, Y= H		83
8	R_1 = NO_2, R_2 = OH	X = CH_2OH, Y= H		70
9	R_1 = NO_2, R_2 = COOH			65
10	R_1 = NO_2, R_2 = COOH			80

able polystyrene-bound triphenylphosphine[28] has been successfully applied in, namely Mitsunobu and alcohol bromination reactions.[29,30] The Mitsunobu reactions were performed using **2a** in a 1.5-fold molar excess. The results are summarized in Table 2. As can be seen, reagent **2a** affords good isolated yields of the expected esters (entries 1−6, 9, and 10) and ethers (entries 7 and 8). Additionally, even secondary alcohols perform reasonably well with this crystalline reagent (entries 5 and 6). In these reactions, it was necessary to precipitate the polymer using diethyl ether in order to get a crystalline form of the polymer that was easy to remove by filtration.[31] After removal of the polymer, the crude material was filtered through a plug of silica gel to afford the pure product, with no trace of phosphine or phosphine oxide contaminants.

To test the performance of *JJ*-PPh_3, **3g** was used to convert alcohols to alkyl bromides (Table 3). This polymer was chosen since the 1.5 mmol/g loading level afforded reasonable resin swelling and it seemed likely to allow for efficient substrate diffusion through it. Thus, it was first reacted with bromine to form the phosphine-halogen complex in situ that converted the alcohol substrates into their corresponding alkyl bromides in quantitative yield in less than 10 min. In these reactions, the pure products were isolated in essentially quantitative yield after filtration to remove the polymer and concentration in vacuo to remove the solvent.

TABLE 3. Bromination of Alcohols Using 3g



Entry	Substrate	Product
1		
2		
3		
4		
5		
6		

In summary, we have developed a facile synthesis of **1** and used this monomer to directly prepare both non-cross-linked and cross-linked triphenylphosphine containing polystyrene polymers using homogeneous and suspension polymerization processes. It is noteworthy that monomer **1** can be incorporated into the polymers at predictable levels, depending upon the ratio of monomers used in the polymerization reaction. This allows for the facile variation of the loading levels of the polymers and thereby facilitates the study of the effects of functional group density and polymer microenvironment in polymer-assisted organic synthesis.[32] In a pioneering report by Alexandratos,[32c] it was observed that for a different polymer-bound phosphine in Mitsunobu reactions, having maximally loaded polymer is not optimal

(28) Polystyrene-bound PPh_3 is available from many suppliers with loading ranging from 1.0 to approximately 3.0 mmol PPh_3/g. Janda-Jel-PPh_3 is also commercially available with a loading of approximately 3.0 mmol PPh_3/g.

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(30) Hodge, P.; Khoshdel, E. *J. Chem. Soc., Perkin Trans. 1* **1984**, 195−198.

(31) When either methanol or hexanes was used as the precipitation solvent, the polymer formed a sticky and intractable residue that was difficult to filter.

and that resin with approximately half of the styrene monomers functionalized afforded better results. Our preparation of **3a**−**f** allows for a similar systematic examination of the effects that triarylphosphine group concentration has on resin performance.

The utility of these polymers has been demonstrated in Mitsunobu reactions and in the conversion of alcohols to alkyl bromides. While various syntheses of **1** and methods for its polymerization have been previously reported, we present here the first detailed procedures for the direct medium-scale synthesis of reagents **2** and **3** with variable and predictable loading levels. Preparation of other polymer-bound phosphine reagents using the methodology presented here is currently being investigated.

Experimental Section

4-Styryldiphenylphosphine (1). Chlorodiphenylphosphine (30 mL, 164 mmol) was added slowly at 0 °C to a solution of the Grignard reagent prepared from 4-bromostyrene (30.0 g, 164 mmol) and Mg (4.8 g, 197 mmol) in dry THF (300 mL). After the addition was complete, the reaction mixture was stirred at rt for 3 h. At this time, the reaction mixture was diluted with diethyl ether (1 L) and then washed sequentially with water (2 × 250 mL), 10% aqueous HCl (2 × 250 mL), saturated aqueous $NaHCO_3$ (2 × 250 mL), and brine (2 × 250 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by silica gel chromatography (5% EtOAc/hexanes) to afford **1** as a white solid (25.0 g, 87 mmol, 53%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.27 (dd, 1H, J = 10.9, 0.6 Hz), 5.77 (dd, 1H, J = 17.6, 0.6 Hz), 6.70 (dd, 1H, J = 17.6, 10.9 Hz), 7.25−7.44 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 114.4, 126.3 (2C), 128.5 (2C), 128.7 (4C), 133.6 (4C), 133.8 (2C), 134.0 (2C), 136.4, 137.2, 137.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ −5.12; HR EI-MS calcd for $C_{20}H_{17}P$ 288.1068, found 288.1066.

General Procedure for Preparing Non-Cross-Linked Polystyrene Reagents 2. To a solution of styrene (28.9 g, 278 mmol) and **1** (20.0 g, 69 mmol) in toluene (300 mL) was added AIBN (0.5 g, 3 mmol). The mixture was purged with N_2 for 30 min, and the solution was stirred at 90 °C for 24 h. The solution was concentrated in vacuo, and the residue was taken up in 40 mL of THF. This solution was added dropwise to a vigorously stirred cold methanol (0 °C, 1 L). The white precipitate was filtered and dried to afford **2a** as a white powder (23.4 g, 53%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01−2.36 (bm, 15 H) and 6.23−7.78 (bm, 24 H); ^{31}P NMR (162 MHz, $CDCl_3$) δ −6.22. The ratio of monomer **1** to styrene in **2a** was determined by elemental analysis to be 1:3.4 based on 4.7% P. This corresponds to a loading level of 1.5 mmol PPh_3/g of **2a**. Polymer **2b** was prepared by an analogous procedure in which the ratio of styrene to **1** was 8:1 (47%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01−2.36 (bm, 18H) and 6.23−7.78 (bm, 29H); ^{31}P NMR (162 MHz, $CDCl_3$) δ −6.22. The ratio of monomer **1** to styrene in **2b** was determined by elemental analysis to be 1:5.1 based on 3.8% P. This corresponds to a loading level of 1.2 mmol PPh_3/g of **2b**.

General Procedure for Preparing Cross-Linked Polystyrene Reagents 3 (*J*anda*J*el-PPh$_3$). A solution of acacia gum (6.0 g) and NaCl (3.8 g) in warm deionized water (45 °C, 150 mL) was placed in a 150 mL flanged reaction vessel equipped with a mechanical stirrer and deoxygenated by purging with N_2 for 2 h. A solution of approximately 10 g in total of **1**, styrene, 1,4-bis(4-vinylphenoxy)butane (2 mol % compared to the other monomers), and AIBN (0.2 g, 1.3 mmol) in chlorobenzene (10 mL) was injected into the rapidly stirred aqueous solution. The resulting suspension was heated at 85 °C for 20 h. At this time, the crude polymer was collected and washed with hot water (3 × 100 mL) and then placed in a Soxhlet extractor and washed with THF for 24 h. The beads were then washed sequentially with methanol (250 mL), diethyl ether (250 mL), and hexanes (250 mL) and then dried in vacuo for 24 h to afford **3a**−**f** (Table 1). Polymer **3g** was prepared using an analogous procedure in which a total of 50 g of the monomer mixture was suspended in 750 mL of the aqueous phase. Elemental analysis was used to determine the phosphorus content and thus the loading level of PPh_3/g for **3a**−**g**.

General Procedure for Ester-Forming Mitsunobu Reactions. To a solution of **2a** (1.0 g, 1.5 mmol, 1.5 equiv) in anhydrous THF (30 mL) was added benzoic acid (0.1 g, 1.0 mmol, 1.0 equiv) and the alcohol (1.2 mmol, 1.2 equiv). This was then cooled to 0 °C and DEAD (0.3 g, 1.5 mmol, 1.5 equiv) was added dropwise. The mixture was stirred at rt for 30 min more and then concentrated in vacuo. The resulting crude product mixture was redissolved in THF (10−15 mL) and then poured slowly into cold diethyl ether (100 mL, 0 °C). After filtration to remove the precipitated polymer, the filtrate was concentrated in vacuo and the crude residue was filtered through a plug of silica gel to provide the essentially pure product (Table 2).

General Procedure for Ether-Forming Mitsunobu Reactions. To a solution of **2a** (1.0 g, 1.5 mmol, 1.5 equiv) in anhydrous THF (30 mL) were added benzyl alcohol (0.1 g, 1 mmol, 1 equiv) and the phenol (1.0 mmol, 1 equiv). This was then cooled to 0 °C, and DEAD (0.3 g, 1.5 mmol, 1.5 equiv) was added dropwise. The mixture was stirred at rt for 30 min more and then concentrated in vacuo. The resulting crude product mixture was redissolved in THF (10−15 mL) and then poured slowly into cold diethyl ether (100 mL, 0 °C). After filtration to remove the precipiated polymer, the filtrate was concentrated in vacuo and the crude residue was filtered through a plug of silica gel to provide the essentially pure product (Table 2).

General Procedure for the Bromination of Alcohols Using *J*anda*J*el-PPh$_3$ (3g). To a magnetically stirred suspension of **3g** (1.2 g, 1.5 mmol PPh_3/g) in anhydrous CH_2Cl_2 (15 mL) at rt and under a nitrogen atmosphere was added bromine (0.3 g, 1.8 mmol, 1 equiv). The color from the bromine dissipated almost immediately. After the addition was complete, the alcohol substrate (0.6 mmol, 0.3 equiv) was added. The reactions, monitored by thin-layer chromatography, were complete within 10 min. The suspension was then filtered, and the resin was washed with additional CH_2Cl_2 (3 × 10 mL). The combined filtrate was concentrated in vacuo to afford the pure alkyl bromide product that was determined to be essentially pure by ^{1}H NMR analysis (Table 3). Since all of the products, except for entry 6, are commercially available, they were only characterized by ^{1}H NMR analysis. Our recorded ^{1}H NMR spectra matched those available from the various suppliers of authentic samples. The product from entry 6 (4-bromophenethyl bromide) was further characterized by ^{13}C NMR analysis: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01−2.02 (m, 3H), 5.12−5.17 (m, 1H), 7.28 (d, 2H, J = 8.3 Hz), 7.46 (d, 2H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.6, 48.1, 122.1, 128.4 (2C), 131.7 (2C), 142.2.

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Supporting Information Available: NMR spectra of monomer **1**, polymers **2a** and **2b**, and the Mitsunobu and bromination reaction products. This material is available free of charge via the Internet at http://pubs.acs.org.

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