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Hydroformylation of octene-1 with a poly(arylene ether triaryl phosphine) rhodium complex

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Poly(arylene ether triaryl phosphine oxide)s were synthesized by nucleophilic aromatic substitution reaction of bisphenolates and bis(4,4′-fluorophenyl)phenyl phosphine oxide. Amorphous, transparent, high glass transition temperature materials are produced that are soluble in a number of solvents. The macromolecular aryl phosphine oxide structure was successfully reduced with phenylsilane in chlorobenzene at 110°C to produce the corresponding poly(arylene ether triphenyl phosphine). The model precursor polymer was soluble in toluene and was used as a ligand for the hydroformylation of octene-1. The soluble rhodium species was based upon $Rh(acac)(CO)_2$. When the two component solutions were combined they produced a heterogeneous catalyst which was reacted with octene-1 and purified synthesis gas in a pressure reactor. Various ratios of polymeric phosphene ligands were investigated and an 8 : 1 ratio produced 95% conversion in 3 h at 120°C. The polymeric catalyst demonstrated improved selectivity of normal to branched aldehydes relative to a control conventional catalyst.

(Keywords: hydroformylation; poly(aryl phosphine oxide); catalyst)

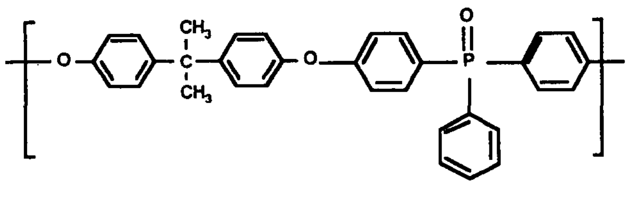
Introduction

The synthesis of poly(arylene ether triaryl phosphine oxide)s (PEPO) (*Scheme 1*), by nucleophilic aromatic substitution of bis(4,4′-fluorophenyl)phenyl phosphine oxide with bisphenol-A phenolates has been previously reported from our laboratory[1–3]. These polymers have several attractive physical properties such as toughness, high thermo-oxidative and hydrolytic stability, flame resistance, high transparency and potential for metal complexation through the phosphine oxide moiety.

With respect to metal complex formation[4], we have recently demonstrated[5–7] that composite films of poly(arylene ether triarylphosphine oxide) containing up to 20 mol% metal salt, based on the repeat unit of the polymer, can be cast from amide solvents to allow for uniform incoporation of the metal salts $CoCl_2$, $FeCl_3$ and $CuCl_2$ into the films. The films are homogeneous, clear and tough; characterization of the materials by *FT*i.r. as well as relaxation time measurements by solid-state phosphorus (^{31}P) n.m.r. confirm that the metal salts are complexed to the polymer and homogeneously dispersed throughout the polymer matrix. The formation of stable complexes of low molecular weight organophosphine oxides with a large variety of metals was reviewed by Karayannis and co-workers[4]. It is well known that phosphines are even better ligands for metal complex formation and it was thus of interest to investigate the formation of the novel polyphosphines by reduction of the phosphine oxide polymer described above.

Triphenylphosphine is widely used as a ligand in organometallic chemistry and homogeneous catalysis. Good reaction selectivity and activity are often obtained for catalysts derived from PPh_3. The relatively large size of the ligand together with its low basicity define triphenylphosphine as an ideal ligand. Complexes such as $RhH(CO)(PPh_3)$, $PtH(CO)(SnCl_3(PPh_3)_2)$, $RuCl(PPh_3)_3$ and $RhC(PPh_3)_3$ have been used in a number of catalytic reactions including the decarbonylation of aldehydes, acyl and aroyl halides, the hydrogenation of unsaturated compounds such as alkenes and alkynes and hydroformylation of alkenes[8].

Although phosphine-based catalysts are widely used industrially, there are problems associated with the design of chemical processes that use homogeneous catalysts. Most notably, a separation step must be included to remove the catalyst from the product. For this reason, there is an extensive literature on the immobilization of homogeneous catalysts[9–14]. With a few exceptions, immobilized catalysts generally suffer compared to their homogeneous counterparts with respect to reactivity and selectivity[15]. In several cases, polymer supports have been shown to enhance reaction rates relative to their homogeneous counterparts by retarding the agglomeration of the catalyst and



Scheme 1 Bisphenol-A-based poly(arylene ether phosphine oxide)

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stabilizing reactive coordinatively unsaturated metallic sites. For instance, Pittman and Ng demonstrated a remarkable rate enhancement in the dimerization–methoxylation of butadiene to 1-methoxyocta-2,7-diene by anchoring a palladium(0) complex on to a styrene resin with 1% divinylbenzene crosslinking[11]. The improved activity was attributed to site isolation, as well as the promotion of coordinative unsaturation by the polymer support. In other cases, securing the catalytic complex with a polymer anchor has resulted in a change in selectivity of the catalyst. For example, the selectivity to aldehydes in the catalysed hydroformylation reaction of hexene-1 was enhanced by anchoring the $Rh(CO)_2(acac)$ complex to a styrene/divinylbenzene copolymer modified with a phosphine ligand[16]. In a separate experiment, Pd(II)chloride bound to a phosphinated polystyrene was found to be more active in the heterogeneous catalysis of the hydrogenation of a series of conjugated dienes than an analogous homogeneous catalyst[13].

In this paper we describe the synthesis of a novel polymeric ligand, poly(arylene ether triaryl phosphine), which contains the triphenylphosphine moiety in the backbone. Typically, polymer-bound catalysts are prepared by attaching a ligand group, such as a phosphine, to an organic polymer onto which the soluble metal complex is bound. Ligand-functionalized polymers can be obtained via modification of a preformed polymer, as well as via polymerization of a monomer with a pendent ligand. Phosphine-modified polystyrene is by far the most commonly used organic support, but other modified polymers, such as poly(vinyl chloride), soluble polysiloxanes and poly(phenylene isophthalamide), have also been described. The polymer-bound complexes can be linear, soluble materials or crosslinked systems. Of the reported polymer anchors containing the phosphine ligand, only a few contain the phosphine in the polymer backbone and those which do generally have very low molecular weights and lack thermal as well as mechanical stability.

The synthesis of the polymer support and its application to catalysis of the hydroformylation of octene-1 by a rhodium complex formed *in situ* with this ligand are reported in this paper.

Experimental

Sufficiently pure and dry *N,N*-dimethylacetamide (DMAc) for the step polymerizations was obtained by stirring over calcium hydride overnight, followed by distillation at around 60°C using a vacuum aspirator. Typically, DMAc was stored in a round-bottomed flask fitted with a rubber septum under anhydrous nitrogen pressure. For the reduction of the phosphine oxide polymer, chlorobenzene was dried over calcium hydride for 24 h, vacuum distilled, and stored under N_2. Phenylsilane was purchased from Aldrich, and stored under nitrogen. The following solvents were used as received from Fisher Scientific: methanol, toluene, chloroform and hexanes.

Phosphorus (^{31}P) n.m.r. spectra were obtained on a Varian RU 400 MHz instrument. All spectra were referenced to 85% H_3PO_4 at 0 ppm and dichlorophenyl phosphine sulfide was used as a standard. Intrinsic viscosities were measured at 25°C in a Cannon-Ubbelohde viscometer, generally using chloroform as the solvent. Thermogravimetric analysis (t.g.a.) was conducted in air on the Perkin–Elmer 7 series thermal analysis instrument. The samples were heated to 800°C at a rate of $10°C\ min^{-1}$. The 5% weight loss temperature and the char yield at 750°C were recorded. Differential scanning calorimetry (d.s.c.) was also performed on a Perkin–Elmer 7 series instrument. The samples were typically heated from 100 to 300°C at a heating rate of $10°C\ min^{-1}$, rapidly cooled to 100°C, and subsequently reheated to 300°C at $10°C\ min^{-1}$. The glass transition temperature was recorded for the second heat.

All catalytic reactions and measurements were carried out using standard Schlenk techniques under an atmosphere of purified synthesis gas, $CO:H_2$, 1:1. Toluene was distilled from sodium benzophenone ketyl and stored under dry conditions. Octene-1, nonane standard and $Rh(acac)(CO)_2$ were obtained from Aldrich and used as received. The high pressure catalysed hydroformylation was carried out in a 30 ml reactor equipped with a pressure gauge. A Varian 3300 gas chromatograph equipped with an HP1 column (25 m × 0.32 mm × 0.52 mm) and flame ionization detector was used to analyse the reaction products. The carrier gas was He; the temperature programme was from 50°C (4 min) to 200°C (4 min), at a heating rate of $10°C\ min^{-1}$.

Synthesis and reduction of the poly(arylene ether triaryl phosphine) ligand. A linear $15\,000\ g\ mol^{-1}$ poly(arylene ether phosphine oxide) precursor was based on bis(4-fluorophenyl)phenyl phosphine oxide (BFPPO). The BFPPO monomer was prepared and purified by known Grignard techniques[17–19] and reacted with a slight excess of bisphenol-A in order to produce phenolic end groups. The monomers were dissolved in DMAc (20% (w/w) solids) at room temperature along with 15% excess of K_2CO_3 and toluene, which was used to azeotropically remove water. The system was dehydrated by heating at approximately 145°C for 4–6 h. The temperature was then raised to 165°C and maintained there for 16 h. The mixture was then allowed to cool, diluted with chloroform, filtered to remove the inorganic salts formed and neutralized with dilute acetic acid. The polymer was precipitated into a 75:25 methanol/water mixture and dried in the vacuum oven up to 150°C for 12 h. It was subsequently redissolved in chloroform, and reprecipitated into a 90:10 methanol/water mixture and similarly redried. The intrinsic viscosity in chloroform at 25°C was found to be $0.29\ dl\ g^{-1}$, which indicated a sufficiently high molecular weight to produce creasable cast films[17–19].

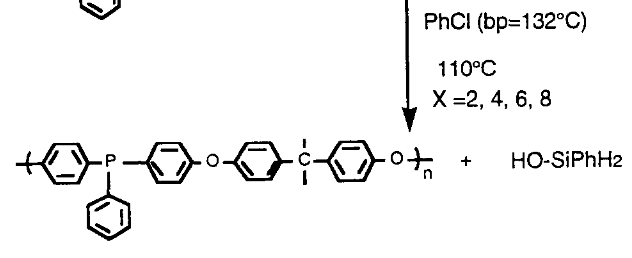
The reduction was conducted in a three-necked round-bottomed flask under a nitrogen atmosphere. First, the precursor polymer was dissolved in previously distilled chlorobenzene. At room temperature and while stirring, freshly distilled phenylsilane was syringed dropwise into the reaction flask and the mixture was heated slowly using an oil bath. Molar ratios of the silane/polymer from less than one to about two were employed. The spontaneous evolution of hydrogen, signalling the onset of the reaction, was observed at about 90°C. The reduction was allowed to proceed at approximately 110°C and was monitored by ^{31}P n.m.r. until essentially complete. An insoluble glass-like solid was occasionally observed as a by-product. The solution was filtered and the polymer was precipitated by adding to a 90:10 methanol/H_2O mixture, then filtered and dried in a vacuum oven up to 150°C for 12 h. It was subsequently redissolved in chloroform, washed with 5% HCl (aqueous), reprecipitated with hexanes, and redried under similar conditions.

Catalytic hydroformylation of octene-1. The catalytic reactions were carried out at 120°C in 30 ml stainless steel reaction vessels equipped with high pressure gauges. The ratio of the aldehyde products (normal/branched, n/b) was determined using gas chromatography. The catalyst was generated *in situ* by mixing a rhodium precursor, $Rh(acac)(CO)_2$, with the phosphine polymer. In order to ensure good reproducibility in a series of catalytic reactions, two separate stock solutions of $Rh(acac)(CO)_2$ were prepared: 0.01 M in toluene and polymer, and 0.100 M in toluene. The corresponding volumes of these stock solutions were combined in the reactor at room temperature under CO and allowed to mix for 3 min, producing a heterogeneous catalyst. Then, octene-1, 0.34 ml of nonane (internal standard), and toluene were added such that the octene-1/Rh molar ratio was 500 to 1, and the total volume was 2.5 ml. The reaction vessel was then closed, pressurized with CO/H_2 (1 : 1) gas and placed in a silicone oil bath at 120°C. The initial pressure at room temperature was 200 psig, and at the reaction temperature this increased to 230 psig. After the desired reaction time the vessel was removed from the bath, cooled to room temperature and depressurized. The products were then analysed by gas chromatography.

Results and discussion

The ligand in the polymer-bound rhodium catalyst used in this study of the hydroformylation of octene-1 is a poly(arylene ether triaryl phosphine) in which the phosphine is part of the polymer backbone. It was synthesized via the phenylsilane reduction of BisA-PEPO in chlorobenzene (*Scheme 2*).

Silanes are commonly used for the reduction of low molecular weight phosphine oxides due to their wide scope, easy use, clean stereochemistry and high yields[20]. The most frequently used silanes are trichlorosilane, hexachlorodisilane and phenylsilane. In our case, phenylsilane was the reagent of choice since it results in the highest yields (~ 90%), it is commercially available and, unlike trichlorosilane, it does not require the use of an amine scavenger, which may be difficult to remove[20,21]. By varying the molar ratio of phosphine oxide to phosphine, the per cent solids of the polymer solution and the reaction time, it was possible to control the reduction of the 15 000 g mol^{-1} BisA-PEPO. The degree of reduction of the polymer was determined by ^{31}P n.m.r. from the integrated peak areas of the $R_3P{=}O$ (25 ppm) and PR_3 (7.5 ppm) units in the polymer. The phosphine concentration in the polymer can thus be varied by the extent of phosphine oxide reduction.



Scheme 2 Phenylsilane reduction of a poly(arylene ether phosphine

The intrinsic viscosity ([η]) in chloroform at room temperature, the thermo-oxidative stability via dynamic t.g.a. and the glass transition temperature (T_g) of these triarylphosphine-containing polymers were studied as a function of backbone phosphine content. These results are summarized in *Table 1*.

In general, the thermo-oxidative dynamic t.g.a. stability, as judged by the 5% weight loss temperature, was found to decrease relative to the starting poly(arylene ether phosphine oxide) as a function of the incorporation of the phosphine unit in the chain. This was somewhat surprising since it was anticipated that the phosphine might reoxidize under the t.g.a. conditions. Apparently other unknown chain scission processes are occurring. The intrinsic viscosity in chloroform increases somewhat with phosphine content and the 94% reduced polymer was found to be only partially soluble in the relatively polar chloroform. It was soluble in toluene and this no doubt reflects the reduced polymer polarity. The glass transition temperature decreased with increasing per cent phosphine, as determined by d.s.c. In the case of the 54% phosphine polymer, two distinct softening temperatures were found, suggesting a blocky sequence or at least non-random chain architecture. Quantitative reduction might be possible under harsher conditions, but this was not investigated.

Transformation of the triaryl phosphine oxide to the corresponding phosphine alters both the molecular structure of the chain and the intermolecular interactions. The geometry of tricoordinate phosphorus is pyramidal, whereas that of pentacoordinate phosphorus is tetrahedral. This stereochemistry difference may produce very different polymer chain configurations. The polarity of the chain also decreases upon reduction to the phosphine. The polymer–polymer intermolecular forces, polymer–solvent intermolecular interactions and the intramolecular chain stiffness characteristics related to resonance possibilities are influenced by these variations. As noted, the intrinsic viscosity in chloroform at 25°C and the glass transition are influenced by the combination of these factors. The general decrease in the oxidative stability with increasing phosphine content is consistent with the generally greater stability of monomeric phosphine oxides relative to the corresponding phosphines.

The 94% reduced BisA-PEPO polymer was used as a ligand in the investigation of the catalytic activity and selectivity of a rhodium complex in the hydroformylation of octene-1.

Hydroformylation involves the conversion of an olefin to an aldehyde by the addition of carbon monoxide and hydrogen to the double bond. The reaction is catalysed by a wide variety of homogeneous transition metal complexes. The process has received considerable attention owing to its industrial and commercial importance[8]. The hydroformylation of octene-1 in the absence of isomerization yields two products, resulting

Table 1 Influence of phenylsilane reduction conditions on the characteristics of a poly(arylene ether phosphine oxide)

$POR_3 : SiPhH_3$	Solids (%)	Final phosphine content (mol%)	Total reaction time (h)	$[\eta]$ 25°C, $CHCl_3$ ($dl\,g^{-1}$)	5% weight loss temp. (°C)[a]	T_g (°C)[b]
15 k BisA-PEPO	–	0	–	0.28	511	194
3:2	20	9	28	0.27	525	192
3:4	20	28	38	0.33	513	185
3:6	20	54	48	0.36	443	158/174
3:6	10	94	88	–	418	155

[a] Dynamic t.g.a., 10°C, in air

[b] D.s.c., second scan, 10°C min^{-1}

from the Markovinkov and anti-Markovnikov addition to the double bond (*Scheme 3*).

Reaction selectivity is reported as the normal/branched (n/b) ratio and includes all possible branched isomers. Catalysts can be prepared *in situ* from $Rh(acac)(CO)_2$ and an appropriate ligand, as shown generally in *Scheme 4*[22,23], and this was the method of choice in the present study.

The ligand/rhodium ratio was varied from two to ten while other reaction conditions were held constant. Each reaction was carried out for 3 h at 120°C and initial pressure of 230 psi in toluene. The total volume inside the reactor and the octene-1/rhodium ratio were also constant. The catalytic activity and selectivity of the poly(arylene ether triaryl phosphine)–rhodium complex was reported as per cent yield of aldehydes and n/b ratio. A control based on triphenyl phosphine was included.

The influence of the phosphorus/rhodium ratio on the octene-1 hydroformylation with this new rhodium–phosphine polymer complex is presented graphically in *Figure 1*.

The ligand/rhodium variation experiments, which were conducted at a constant reaction time of 3 h, show that the per cent conversion increases with increasing phosphorus/rhodium (P/Rh) ratio until it reaches a plateau at approximately 95% conversion, corresponding to a P/Rh ratio of approximately 8/1. Thus, at these P/Rh ratios the reaction is almost quantitative after only 3 h at 120°C. The ratio of normal to branched aldehyde products also increases with increasing phosphine ligand and attains a maximum value of ~ 5.5 at a P/Rh ratio of 10. At low P/Rh ratios these heterogeneous catalysts suffer in terms of reaction rate compared to their homogeneous counterparts. However, at higher P/Rh ratios the reaction is almost quantitative, and substantially greater selectivity is obtained relative to homogeneous systems at comparable P/Rh levels.

Previous comprehensive studies of microporous phosphinated styrene–divinylbenzene resins have revealed that the n/b aldehyde selectivity in the hydroformylation of olefins is determined by the phosphine loading of the support, the phosphine/rhodium ratio, and the crosslink density of the resin[24]. These factors are suggested to alter the ligand equilibria within the swollen resin such that high phosphine loadings and high phosphine/rhodium ratios promote the formation of the more crowded bisphosphine species, thus resulting in a higher yield of the normal aldehyde. In our case, greater selectivity was observed at high phosphine/rhodium ratios and therefore may be influenced by the steric requirements of the polymeric ligand that facilitates the formation of the linear aldehyde.

$$Rh(acac)(CO_2) + 3L + H_2/CO \rightarrow HRh(CO)(L)_3$$

$$+ \text{acetyl acetate} + CO$$

$$L = \text{phosphine ligand}$$

Scheme 4 *In situ* generation of the active rhodium catalyst

Conclusions

The supported heterogeneous rhodium complex generated from the novel triarylphosphine polymeric ligand appears to offer several important advantages over conventional homogeneous catalysts. At high phosphine/rhodium ratios, the selectivity and activity of the catalyst are high. Additionally, the heterogeneous

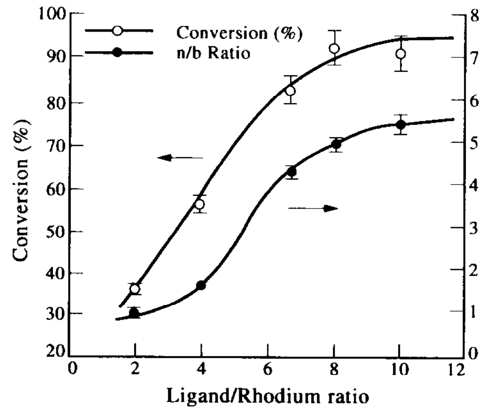
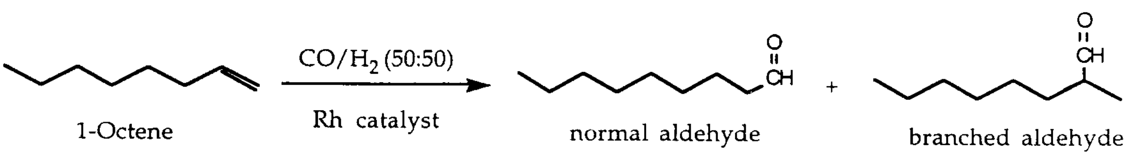


Figure 1 Effect of phosphorus/rhodium ratio on the hydroformylation of octene-1



Scheme 3 Hydroformylation of octene-1

nature of the polymeric catalyst potentially allows for the easy separation of the product and the recovery of the catalyst, which are of considerable commercial importance. The mechanical strength and thermal stability of the polymer is very good and may allow the use of these materials in reactions in which strong agitation is required and higher temperatures can be employed to enhance the rate of the reaction.

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