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Functionalized hyperbranched grafts on polyethylene powder for support of Pd(0)-phosphine catalyst

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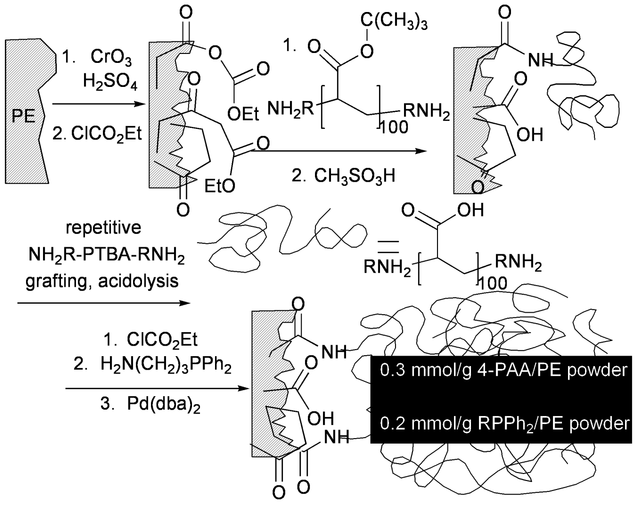
Hyperbranched grafts of poly(acrylic acid) have been modified with phosphine ligands for support of Pd(0) for use in allylic substitution chemistry.

Insoluble polymer supports are of recognized importance for the recovery of catalysts or reagents.[1] The most common such support is cross-linked polystyrene and this insoluble polymer has been used to support a variety of reagents and catalysts including palladium–phosphine complexes.[2–5] We recently described mechanically stable PE powders as alternative insoluble polymeric catalyst supports.[6] Here we show that phosphine ligands can be incorporated into hyperbranched grafts on polyethylene powder supports and that the resulting phosphinated powder can be used to prepare Pd(0)-phosphine catalysts. We further show that this chemistry can be extended to include hyperbranched surface-grafted polyethylene films and that the functionalized supports so prepared are uniformly functionalized in a 2-dimensional sense.

To prepare PE-supported phosphine-ligated Pd catalysts, we first prepared a hyperbranched poly(acrylic acid) (PE/PAA) graft on 200 μm diameter polyethylene powder. These poly(acrylic acid)-modified powders were prepared by initially oxidizing polyethylene with chromic acid.[7] Subsequent $-CO_2H$ activation with $ClCO_2Et$, followed by grafting of an amine-terminated poly(*tert*-butyl acrylate) oligomer (PTBA) produces a 1-PTBA graft. Acidolysis of the *tert*-butyl esters with $MeSO_3H$ produces a PAA graft (1-PAA/PE).[8] Repetition of this process 4 times (Scheme 1) produces a 4-PAA/PE powder with carboxylic acid loadings of *ca.* 0.3 mmol of $-CO_2H$ g^{-1} of PE powder.[6]

This hyperbranched poly(acrylic acid) graft is then modified to include phosphine ligands that were in turn used to produce a phosphine-ligated Pd(0) catalyst for allylic substitution reactions. For example, a 4-PAA/PE powder sample was first activated with $ClCO_2Et$. The resulting mixed anhydride was then allowed to react with 3-diphenylphosphinopropylamine (DPPA) to produce a hyperbranched graft containing diphenylphosphinopropyl amides.



Scheme 1

Treatment of this phosphinated powder with $Pd(dba)_2$ produced a faintly yellow catalyst for allylic substitution chemistry. Combustion of the polyethylene powder and DCP (direct current plasma) analysis of the digested residue showed that a typical sample contained *ca.* 3.95 × 10^{-2} mmol of Pd g^{-1} PE powder.

The phosphine ligands in the hyperbranched graft were characterized by ^{31}P CP-MAS NMR spectroscopy (Fig. 1). The diphenylalkylphosphino amide had a peak at δ −17.9 and was distinguishable from a small amount of phosphine oxide impurity that had a peak δ 33.3 as shown in Fig. 1. After $Pd(dba)_2$ treatment, a new peak assigned to a phosphine–palladium complex in the ^{31}P CP-MAS NMR spectrum at δ 25 in the product Pd(0)-DPPA/4-PAA catalyst (free phosphine and Pd-complexed phosphine peaks were both present in this product).

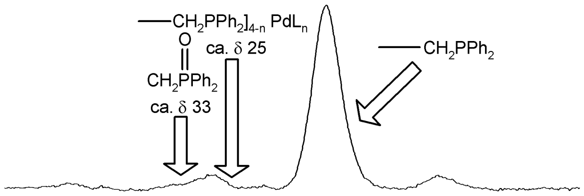


Fig. 1 ^{31}P CP-MAS NMR spectrum of phosphinoamidated 4-PAA/PE powder, DPPA modified 4-PAA/PE. Locations where phosphine oxide or Pd-complexed phosphine peaks would appear if present are noted.

This phosphinated powder was also characterized by X-ray photoelectron (XPS) (Table 1) and attenuated total reflectance infrared spectroscopy (ATR-IR) spectroscopy. ATR-IR showed *ca.* 60% conversion of $-CO_2H$ of the graft to amides. As the graft thickness increases the XPS results show the film has more poly(acrylic acid) than polyethylene character. Upon phosphination the XPS spectrum had a P peak at 130.25 eV and the palladated phosphine powder showed a P peak at 129.5 eV and a Pd 3d$_{3/2}$ peak at 335.25 eV.

The powders are irregular and 200 microns in diameter so gauging the uniformity of the surface functionalization is impractical using XPS spectroscopy with them. However, prior

Table 1 XPS analysis of the surface atomic concentration of hyperbranched polyethylene powders

Grafted PE Powder[a]	%C	%O	%N	%P	%Pd
PE	98.92	0.96	0.12	—	—
[O]-PE	91.25	8.75	—	—	—
1-PAA/PE	79.34	19.53	1.13	—	—
2-PAA/PE	72.64	25.25	2.11	—	—
3-PAA/PE	68.01	30.88	1.12	—	—
4-PAA/PE	68.27	30.80	0.93	—	—
Pd(0)-DPPA/3-PAA/PE[b]	78.90	14.38	3.57	2.35	0.80

[a] Powders were extracted in Soxhlet apparatus with CH_2Cl_2 overnight prior to analysis. [b] This sample was prepared from a PE film to facilitate analysis of the surface uniformity of $-PPh_2$ incorporation.

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work with hypberbranched grafts on gold surfaces or thiophene-containing hyperbranched grafts on PE films had indicated that these functional grafts were ultrathin (10–100 nm thick) and 2-dimensionally uniform. To determine that the chemistry above results in uniform incorporation of phosphine ligands and Pd catalysts on these surfaces, we prepared a Pd(0)-DPPA/3-PAA sample using a hyperbranched 3-PAA/PE film sample.[8] Multipoint XPS analysis over 1 mm region (Fig. 2) of the resulting film shows uniform surface functionalization. Notably, the average P/Pd ratio of *ca.* 3/1 determined with this experiment suggests that these surface-bound catalysts are similar in coordination environment to the active catalysts in a typical reaction using $(PPh_3)_4Pd$. Earlier work with thiophenes polymerization has demonstrated that these lightly crosslinked grafts are flexible enough to oligomerize so formation of bis- and tris-phosphine ligated Pd(0) catalysts seems plausible.

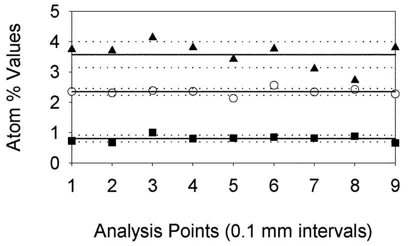
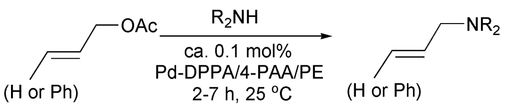


Fig. 2 Multipoint XPS analysis of a Pd(0)-DPPA/3-PAA/PE film: ■, atom% values for Pd (± 0.1); ▲, atom% values for N (± 0.1); ○, atom% values for P (± 0.4). Atom% values for C and O across this 1 cm section of film averaged 78.9 (± 1.6) and 14.4% (± 1.4), respectively.

This phosphine-ligated Pd(0) catalyst/PE powder was active for allylic substitution chemistry. These reactions (Scheme 2) were carried out at room temperature in the absence of solvent.† The regioselectivity of the reaction between cinnamyl acetate and piperidine is similar to earlier work we reported using a soluble diphenylphosphine-terminated polyethylene ligand for Pd(0).[9] The catalyst was recycled up to 5 times without a noticeable decrease in activity. If the catalysts were exposed to air, oxidation and catalyst deactivation did occur. This oxidation was verified by ^{31}P MAS NMR spectroscopy. Indeed, in all cases when catalytic activity was significantly slower and where the polymer was recovered and analyzed, ^{31}P-MAS NMR spectroscopy showed that phosphine ligand oxidation had occurred presumably due to adventitious oxidation. Such catalyst deactivation was also detectable visually—the yellow active catalyst becomes darker when the activity has noticeably decreased. This oxygen sensitivity makes recovery and reuse of these catalysts experimentally more difficult and tedious.



Scheme 2

Leaching is an important issue in any catalyst immobilization scheme. Digestion of a successful reaction mixture and DCP analysis showed that < 0.1% Pd had leached, based on loadings determined by combustion of the powder and DCP analysis of the digested residue. This catalyst was also screened as a possible catalyst for Heck coupling reactions between iodoarenes and activated olefins but was unsuccessful in our hands. Further studies will include the use of the hyperbranched grafts on polyethylene powder as supports for other ligands.

The observation of oxidation sensitivity of these catalysts is not remarkable. It is a general problem faced in recycling or using these and other Pd(0) phosphine ligated catalysts. However, the known reactivity of Pd(0) crystallites themselves in allylic substitution chemistry and the known feasibility of using added phosphine ligands to promote this reactivity led us to briefly examine the possibility that our Pd(0) catalysts were actually just Pd(0) crystallites activated by phosphine ligands in the matrix. Several experiments were performed. First, XPS analysis of Pd crystallites in a hyperbranched graft (Pd(0)-4PAA/PE, prepared by reduction of a Pd carboxylate salt) showed a Pd $3d_{3/2}$ peak at 333.25 eV. This peak was discernibly different than the peak for the molecular catalyst—a phosphine-ligated Pd (Pd(0)-DPPA/4-PAA). Next, we examined the reactivity of the crystallites with and without external triphenylphosphine in allylic substitution of allyl acetate by piperidine on a 20 mmol scale. While low activity was seen without external ligand, complete conversion to the allylic amine was seen in 16 h using 0.05 mol% Pd catalyst with 0.6 mol% added triphenylphosphine. However, unlike the results with a Pd(0)-DPPA/4-PAA catalyst, *ca.* 2–3% Pd leaching was seen. We earlier noted that molecular Pd(0)-DPPA/4-PAA catalysts could be converted to phosphine oxides and Pd(0) crystallites by refluxing the yellow Pd(0)-DPPA/4-PAA powder in methanol in air to form a grey powder. This grey powder too had low activity in allylic amination of allyl acetate. As was true with other films containing Pd(0) crystallites, activity was restored on addition of external triphenylphosphine but at the cost of probable leaching of Pd. A final experiment used DPPA to modify unreacted $-CO_2H$ groups in a hyperbranched graft containing Pd(0) crystallites (a PE/4-PAA/Pd(0) powder).[10] This powder containing both Pd crystallites and a covalently bound phosphine did have some activity in allylic amination but the activities were *ca.* 10-fold lower than those of the molecular Pd(0)-DPPA/4-PAA catalysts.

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Notes and references

† Cinnamyl acetate (1 g, 5.7 mmol) and Et_2NH (1.67 g, 22.8 mmol) were combined in a 15 mL flask and this mixture was degassed 3× by freeze/pump/thaw. A 40 mL centrifuge tube with Pd(0)-DPPA/4-PAA/PE powder catalyst (200 mg, 0.0081 mmol of Pd) was evacuated and backfilled with N_2 3×. The reaction mixture was transferred by forced syphon through cannula into the catalyst-containing tube which was degassed 3× more. This mixture was mixed for 2 h by magnetic stir bar, during which time diethylamine-HOAc salt precipitated out forming a thick mixture. The product was isolated from three 10 mL portions of distilled degassed THF that were first transferred into the centrifuge tube and then separated by centrifugation and forced siphon from the more dense powder. The THF was then removed under reduced pressure. The remaining oil was dissolved in ethyl acetate and washed with water (3×), brine, and then dried with $MgSO_4$. The ethyl acetate was removed under reduced pressure and product dried under vacuum yielding a yellow oil (89–92% isolated yield).

1 D. C. Sherrington, *J. Polym. Sci., Polym. Chem.*, 2001, **39**, 2364.
2 C. A. Parrish and S. L. Buchwald, *J. Org. Chem.*, 2001, **66**, 3820.
3 H. Danjo, D. Tanaka, T. Hayashi and Y. Uozumi, *Tetrahedron*, 1999, **55**, 14341.
4 I. Fenger and C. Le Drian, *Tetrahedron Lett.*, 1998, **39**, 4287.
5 S.-B. Jang, *Tetrahedron Lett.*, 1997, **38**, 1793.
6 D. E. Bergbreiter, G. Tao and A. M. Kippenberger, *Org. Lett.*, 2000, **2**, 2853.
7 J. R. Rasmussen, E. R. Stedronsky and G. M. Whitesides, *J. Am. Chem. Soc.*, 1977, **99**, 4736; J. R. Rasmussen, D. E. Bergbreiter and G. M. Whitesides, *J. Am. Chem. Soc.*, 1977, **99**, 4746.
8 D. E. Bergbreiter, J. G. Franchina and K. Kabza, *Macromolecules*, 1999, **32**, 4993.
9 D. E. Bergbreiter and D. A. Weatherford, *J. Org. Chem.*, 1989, **54**, 2726.
10 D. E. Bergbreiter and M. Liu, *J. Polym. Sci., Polym. Chem.*, 2001, **39**, 4119.