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# Functionalized Hyperbranched Polyethylene Powder Supports

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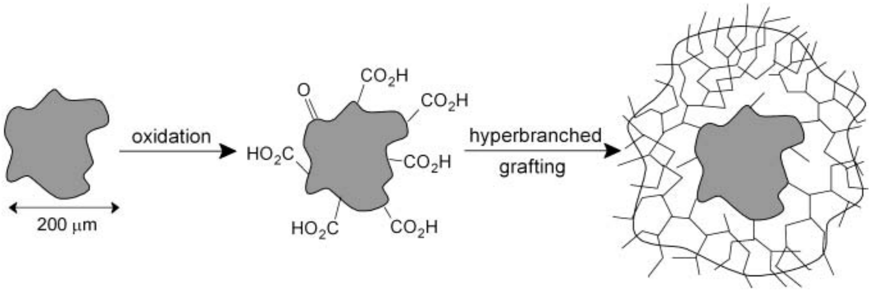
## ABSTRACT



**Polyethylene powders with useful loadings of functional groups are accessible by hyperbranched grafting chemistry. Using a 200 µm diameter high-density powder, loadings of up to 0.4 mmol/g of $CO_2H$ groups are attained. The carboxylic acid groups in the resulting powders can be further functionalized covalently or ionically and resulting powders have the physical durability and solvent resistance associated with polyethylene itself.**

Solid-phase organic synthesis is an important area in synthesis. Developments in combinatorial chemistry, drug discovery, and nucleic acid chemistry will only increase the importance of this area in organic chemistry.[1] However, while the chemistry of the underlying supports is of recognized importance, most polymer supports for synthesis still employ polystyrene. The substantial efforts that have been made to develop new supports typically focus on modification of polystyrene through incorporation of PEG tethers,[2,3] PEG cross-linking agents,[4] or dendritic grafts.[5] Other insoluble supports such as cellulosic threads have received recent attention.[6] Other polymers too have been studied, but issues of capacity, physical durability, and chemical stability remain concerns. Here we describe hyperbranched graft chemistry that leads to physically tough polyethylene supports with up to 0.4 mmol of accessible $-CO_2H$ groups/g loading, levels that could be useful in synthesis and that are useful in catalyst formation.

The polymer support used here is high-density polyethylene (PE). Surface oxidation of PE is well-known.[7] However, functional group loading on such surfaces is very low. The fractional monolayer loadings that result from such oxidations can be increased by grafting, and the resulting functionalized PE surfaces are used in synthesis.[8,9] However, even in these cases the loadings remain low. This paper describes how useful functional group loading levels on PE powders of up to 0.4 mmol/g can be attained by hyperbranched grafting.

Initial functionalization of commercially available PE powder used a chromic acid etching process.[7] The carboxylic

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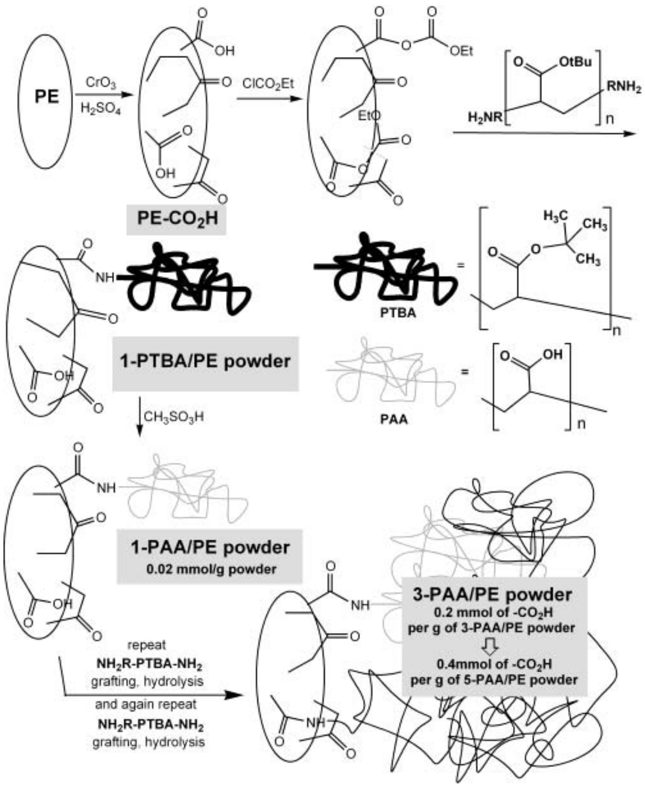
acid groups (ca. 0.01 mmol of $CO_2H$/g) on this oxidized PE polymer were activated with $ClCO_2Et$ and the resulting mixed anhydride was treated with a functional poly(*tert*-butyl acrylate) oligomer (PTBA). The *tert*-butyl esters were then converted to acids under nonaqueous conditions with $MeSO_3H$.[10] This process was repeated five times (Scheme 1) to generate 5-PAA/PE powder. The loading of $-CO_2H$ groups/g of this powder was determined to be 0.4 mmol of $-CO_2H$/g of PE powder by back-titration using first 0.01 N NaOH and then standardized HCl.

Scheme 1



As was true for grafting of poly(acrylic acid) (PAA) on insoluble gold supports,[11] grafting of PAA on PE occurred in a nonlinear fashion. Results for titrimetric analysis of the PE-bound $-CO_2H$ groups are shown in Figure 1 and are overlaid with results of an ellipsometric study of film thickness that occurred with similar hyperbranched graft chemistry on a gold surface.[10] As the results show, repetition of the grafting through several stages is required either to produce a 500 Å thick film on a gold substrate or to produce a film with useful functional capacity on a PE powder substrate. Given that the BET surface area of the oxidized PE powder used is 0.7 $m^2$/g and that the density of poly(acrylic acid) in the graft is ca. 1 g/$cm^3$, 0.4 mmol/g loading of poly(acrylic acid) on the 5-PAA/PE powder corresponds to a ca. 400 Å thick layer of poly(acrylic acid) on this 200 $\mu$m-diameter PE powder. The extent of this grafting chemistry was also followed by ATR−IR spectroscopy. At the 5-PAA/PE powder stage, the carbonyl peaks of the graft poly(acrylic acid) were the dominant peaks in the IR spectrum, a result that is analogous to what was seen in earlier work using similar grafts on PE films.[10]

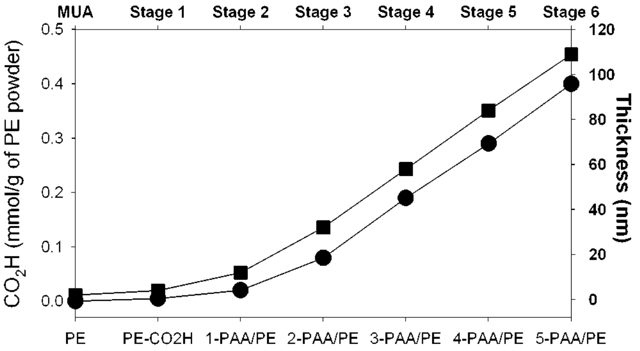


**Figure 1.** Plot of thickness increase for PAA grafts on gold (■) superimposed on a plot of $-CO_2H$ capacity (●) for successive stages of hyperbranced PAA grafting on PE.

Further modification of these surfaces is possible.[12] First, protonation/deprotonation is quantitative based on the changes in the carbonyl region in IR spectroscopy where the $-CO_2H$ $\nu_{C=O}$ peak at 1710 $cm^{-1}$ disappears on base treatment and a peak at 1560 $cm^{-1}$ appears. Esterification of the $-CO_2H$ groups of the 4-PAA/PE powder can be accomplished by activation ($ClCO_2Et$) and alcohol treatment, but is not quantitative. Higher conversions are possible using acid-catalyzed Fischer esterification. For example, using allyl alcohol or ethanol and catalytic *p*-TsOH or $H_2SO_4$, ca. 90% conversion of the $-CO_2H$ groups to $-CO_2CH_2CH{=}CH_2$ or $-CO_2CH_2CH_3$ groups was attained based on IR spectroscopy. Reduction too is feasible. While the $-CO_2H$ groups of 4-PAA/PE proved surprisingly resistant to $BH_3{\cdot}S(CH_3)_2$, they were reduced in >95% yield using activation ($ClCO_2Et$) and $BH_3{\cdot}S(CH_3)_2$ treatment based on IR spectroscopy. After reduction, a 4-PAA/PE surface with 0.29 mmol/g of $-CO_2H$ groups contained only 0.02 mmol of $-CO_2H$ groups/g (the same loading as the initial oxidized PE). We have also used activation ($ClCO_2Et$) and amine treatment ($H_2NCH(CH_3)_2$) to prepare a poly(*N*-isopropylacrylamide) graft. This amidation chemistry converts about 50−60% of the carboxylic acid groups into amides in the first cycle. Repeating this reaction produces a surface that contains >80% amides. This chemistry is summarized in Scheme 2.

Preliminary studies show that these PAA/PE powder supports we describe here can be successfully modified so as to contain useful catalysts. This premise was tested by using a variation of earlier work we reported with gel-type polystyrene resins where we entrapped Pd(0) crystallites.[13]

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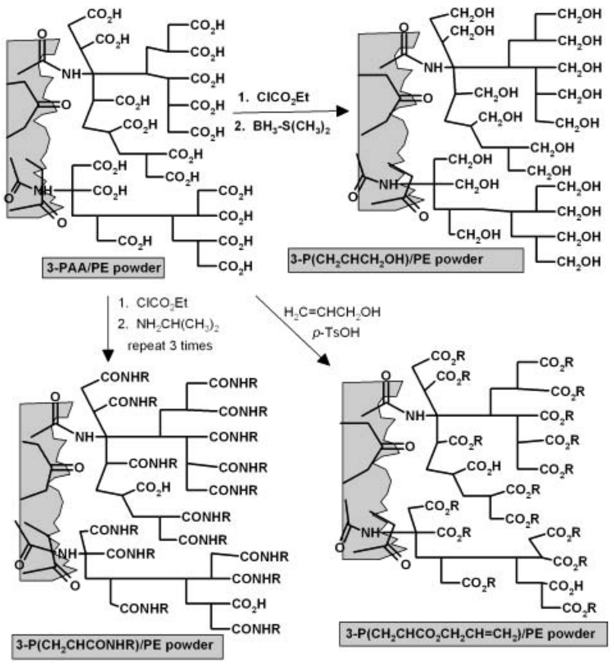
**Scheme 2**



That earlier work used a polymer-bound organometallic reagent to covalently bind monatomic Pd species, which were subsequently thermolyzed to form Pd(0) crystallites. In the case of 4-PAA/PE, Pd(II) is more simply incorporated through ion exchange, treating 4-P($CH_2CHCO_2Na$)/PE with $Pd(OAc)_2$. Subsequent reduction ($H_2$) produces a grayish powder that is an active hydrogenation catalyst. Combustion of the polyethylene followed by DCP (direct current plasma) analysis showed that a typical sample contained ca. $9.7 \times 10^{-4}$ g of Pd/g of PE powder. Turnover numbers with this catalyst and simple substrates such as allyl alcohol in water and styrene in ethanol were ca. 60,000 and 80,000 mmol of $H_2$/mg-atom of Pd, respectively. These numbers and turnover frequencies in the range 10−100 mmol of $H_2$/mg-atom of Pd/min are comparable to other Pd hydrogenation catalysts and show that Pd catalysts supported in an ultrathin hyperbranched film on a PE powder support are reasonably active. The PE-bound Pd(0) hydrogenation catalysts could be recovered and reused without any loss in activity. On a synthetic scale, 1.5 g of 10-undecenol was quantitatively reduced by 50 mg of the catalyst in 2 d to yield an 84% isolated yield of undecanol. Work in progress will assay the scope of this catalyst and the potential of this PAA ultrathin film (or its derivatives) to function as a "responsive" environment for this heterogeneous catalyst. An attractive feature of these PE powder-bound catalysts is that the PE powders used have physical properties such as ordinary PE. They do not dissolve in any solvent at room temperature (though the ultrathin graft presumably swells extensively under appropriate conditions). They are physically robust and are not damaged by extensive stirring with a stirring bar. They are easily isolated by filtration using a medium porosity fritted disk filter or can be isolated by centrifugation (their density is ca. 0.9−0.95 g/cm$^3$).

In summary, useful loadings of functional groups on tractable PE powders can be produced by hyperbranched grafting. Acid/base chemistry, esterification, reduction and amidation reactions convert the initial poly(acrylic acid) graft into a poly(acrylic acid) salt, a polyacrylate ester, a poly(allyl alcohol) or a polyacrylamide. The complete conversion of functional groups using standard solution-state reactions may be affected by neighboring groups or by the environment within the ultrathin graft. Nonetheless, the success in introduction of esters, alcohols and amides suggests that these substrates may be useful in both synthesis and catalysis. An example of Pd(0) catalyst immobilization that shows that these powders can be used as supports for alkene hydrogenation catalysts illustrates this point.

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**Supporting Information Available:** Experimental procedures for the formation of the poly(acrylic acid) grafted PE powder IR and the poly(*tert*-butyl acrylate) oligomers, along with IR spectra data for the product modified polymers are provided. This material is available free of charge via the Internet at http:pubs.acs.org.

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