



Rhodium-complexed hyperbranched poly(ethyleneimine) and polyamidoamine and their non-covalent immobilization on magnetic nanoparticles



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ABSTRACT

We describe a synthetic strategy for the synthesis and functionalization of hyperbranched poly(ethyleneimine) (**H-PEI**) and polyamidoamine (**H-PAMAM**) with phosphine ligands and their non-covalent immobilization on magnetic nanosupports. Treatment of these functionalized hyperbranched polymers with $\text{Rh}(\text{COD})_2\text{BF}_4$ affords polymer-bound Rh(I) complexes that can be utilized in the hydroformylation of alkenes and in one pot hydroformylation-Knoevenagel-hydrogenation reactions. These functionalized hyperbranched polymers are linked to magnetic nanoparticles that are modified with carboxylic acid groups *via* ionic interactions resulting from the acid-base reactions, and are responsible for facilitating the separation of the polymeric catalysts. These magnetically retrievable polymeric catalysts can be reused for up to four cycles.

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1. Introduction

Over the last few decades, many intensive studies have been directed to the field of hyperbranched polymers (HBP), which became inherent in different areas and applications due to their unique properties and functions [1–8]. These polymers, as well as dendrimers, belong to a synthetic tree-like macromolecules family called dendritic polymers [9]. They are simply synthesized by a single step direct polymerization of an AB_x type monomer, based on various synthetic techniques including condensation polymerization, self-condensing vinyl polymerization and ring-opening polymerization [4,10–14]. Even though their synthesis lacks the production of a well-defined structure, and affords a broad molecular weight product rather than a monodispersed one, HBPs still

possess similar properties to dendrimers, such as low viscosity, high solubility and inexhaustible functionality [15–17]. Moreover, the simplicity of their preparation in comparison to dendrimers makes them cost and time effective substitutes. Thus, in most cases, there is no need for tedious isolations and cumbersome purification steps during the synthesis of HBP. Therefore, these polymers could easily be very attractive for numerous industrial applications as favored alternative dendrimers analogues [18]. In addition, hyperbranched polymers attracted a great deal of interests in different fields including biology [19] or drug delivery [20,21], bioimaging [22] and catalysis [23–27]. Due to the fact that hyperbranched polymers are capable of enhancing chemical reactivity and solubility because of their intrinsic high degree of branching (DB), which can reach up to 100% [28], these dendritic molecules have been adopted for many catalytic applications [29–32]. The judicious choice of a peripheral functionality is considered as an essential parameter for tuning their chemical properties, when being utilized as ligands for various metal catalyzed reactions [33–37], or for the stabilization of metal nanoparticles [38–43].

In recent years, dendritic catalysts immobilized on organic [44–48] or inorganic [49–52] supports have been investigated intensively, and applied to several catalytic organic transformations. These new catalytic materials are sometimes highly

Abbreviations: H-PEI, hyperbranched poly(ethyleneimine); H-PAMAM, hyperbranched polyamidoamine; HBP, hyperbranched polymers; DB, degree of branching; MNPs, magnetic nanoparticles; DCC, *N,N'*-Dicyclohexylcarbodiimide; H-PAMAM-PPH₂, phosphinated hyperbranched poly(amidoamine); H-PEI-PPH₂, phosphinated hyperbranched poly(ethyleneimine); TEM, transmission electron microscopy; TGA, thermogravimetric analysis; DCM, dichloromethane.

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efficient in terms of reactivity and selectivity, easily recyclable and have unusual stability [53].

In the last decade, magnetic nanoparticles (MNPs) have been investigated intensively as nanosupports of catalysts that can be isolated from the reaction medium by the application of an external magnetic field [54–60]. In this regard, magnetic nanoparticles have also been utilized in the immobilization of dendrimers *via* step-by-step divergent synthesis or grafting presynthesized dendrimers on their surfaces [32,37,52,61–63].

We report here a facile preparation of rhodium-based hyperbranched polymeric catalysts, and their non-covalent immobilization onto magnetic nanoparticles simply *via* ionic interactions. The catalytic activity of the obtained materials was evaluated in hydroformylation reactions and in one-pot hydroformylation-Knoevenagel-hydrogenation reactions. After reaction completion, the catalysts were easily retrieved by applying an external magnetic field and recycled for four consequent cycles without a significant loss in their activity.

2. Results and discussion

2.1. Synthesis and functionalization of hyperbranched polymers (HBP)

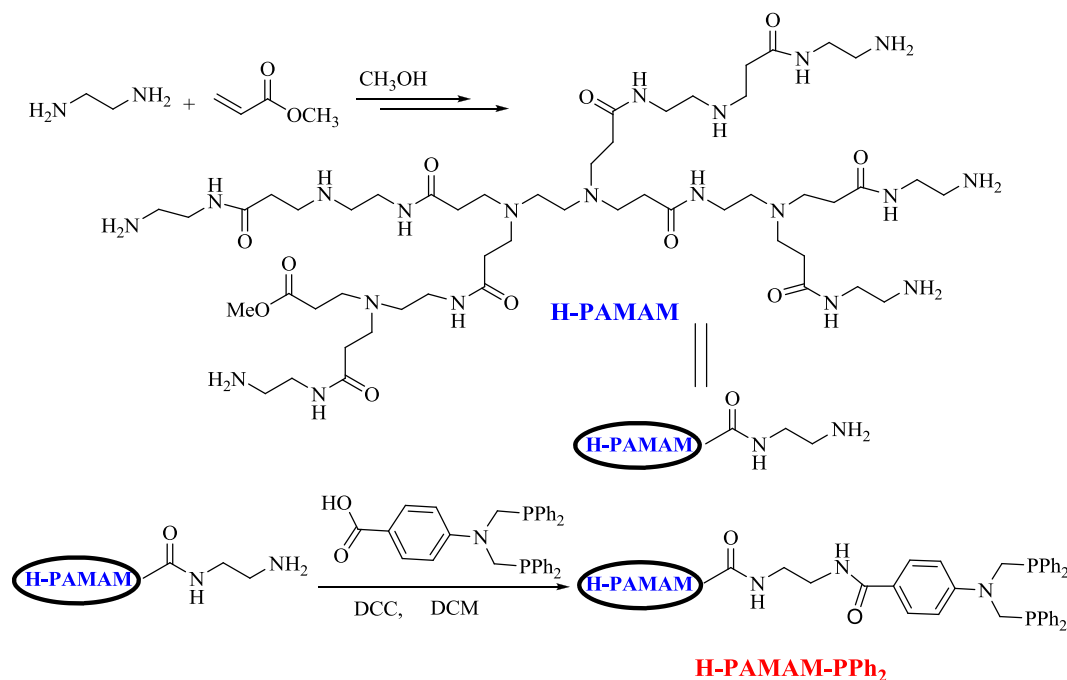
Hyperbranched poly(amidoamine) (**H-PAMAM**) is one of the most investigated materials in the hyperbranched polymers family. In our research, **H-PAMAM** was synthesized from methylacrylate and ethylenediamine in a one-pot reaction according to a double monomer methodology [43,64–66]. By this synthesis, Michael-type addition of methyl acrylate produces the amino propionate ester followed by amidation reaction with ethylenediamine resulting in **H-PAMAM** polymer (Scheme 1). Subsequently, the peripheral primary amino groups on the **H-PAMAM** were substituted with phosphine groups through an amidation reaction with 4-[bis[(diphenylphosphino)methyl]amino]-benzoic acid that was mediated by *N,N'*-dicyclohexylcarbodiimide (DCC), to afford chelate phosphines on the periphery of the hyperbranched

polymer (**H-PAMAM-PPh₂**). By the same manner, a commercially available hyperbranched poly(ethyleneimine) (**H-PEI**) was also functionalized with phosphine groups to yield **H-PEI-PPh₂** (Scheme 2). The phosphinated hyperbranched polymers were treated with Rh(COD)₂BF₄ by mixing at room temperature in dry dichloromethane for 30 min, to yield rhodium complexed hyperbranched polymers **2a** and **2b** (Schemes 3 and 4).

Inductively coupled plasma mass spectrometry (ICP-MS) measurements were utilized for determining the loading of the rhodium in both complexes. The homogeneously prepared **H-PEI-PPh₂-Rh (2a)** and **H-PAMAM-PPh₂-Rh (2b)** catalyst yielded a loading of 0.42 mmol/g and 0.65 mmol/g respectively. While the phosphorous content was found to be 0.916 mmol/g and 1.43 mmol/g, in a good correlation with the rhodium loading in **2a** and **2b** catalysts, respectively.

2.2. Catalysis

The catalytic performance of the resultant Rh(I) complexed phosphine functionalized HBPs was examined in the hydroformylation of styrene as a model reaction using a 1:1 mixture of carbon monoxide and hydrogen pressurized to 1000 psi. For initial examination, the reaction was mediated by catalyst **2a** and performed in various solvents. It was observed that the solvent polarity could highly affect the reaction progress. Thus, polar solvents could negatively affect the catalyst reactivity while nonpolar solvents could smoothly increase catalyst reactivity. Dichloromethane solvent afforded full conversion with high regioselectivity towards the branched aldehyde (B:L = 20:1) (Table 1, entry 7). The reaction in methanol was pretty slow, and was not completed probably due to the restricted solubility of the metal complex in this medium (Table 1, entry 1). Furthermore, when the polar tetrahydrofuran was used as a solvent, it showed good regioselectivity for the branched aldehyde accompanied with poor conversion, whereas at elevated temperatures the conversion of the reaction was increased and the selectivity was decreased considerably (Table 1, entries 2–3). In acetonitrile, high selectivity was obtained in spite of the low



Scheme 1. Preparation of (a) hyperbranched poly(amidoamine) (**H-PAMAM**) and phosphinated hyperbranched poly(amidoamine) (**H-PAMAM-PPh₂**).

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