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Synthesis and Characterization of Functionalized Polysiloxane for the Stabilization of Catalytically Active Metal Nanoparticles

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Introduction. Potential applications of inorganic nanomaterials have generated a tremendous number of studies, whether to control the shape and size of the nanoparticle (NP) core and/or to choose the chemical structure of the stabilizing ligand shell. Polysiloxanes are inexpensive, commercially available polymers that are highly soluble in many organic solvents such as THF or toluene and in supercritical fluids, but are not soluble in water. They offer distinct advantages over other polymers when used as stabilizers (1) as they present a high degree of flexibility which allows them to interact strongly with NPs; (2) they can be used as templates to adjust the size, stability, and solubility of NPs ranging in diameter from less than 1 nm to up to 10 nm;[1] (3) NPs are primarily stabilized by steric effects, and therefore a substantial fraction of their surface is unpassivated and available to participate in surfactant exchange and catalytic reactions; (4) the silane function in poly(hydrogenomethylsiloxane) (PHMS) can act as a reducing agent, thus eliminating the need for extra reducing agents; it can also be easily functionalized[2] to control stabilization of the hybrid nanocomposite and used as handles for facilitating linking to surfaces or interactions with other molecules.[3−5] This last point is of special interest as it allows the tailoring of NPs' specific properties toward many predictable applications such as lock−key interaction applications (recognition, gene delivery, ...) or electron transfer applications (electronics, catalysis, electrochemistry, and photochemistry). Concerning use as catalysts, there is a strong interest in introducing chiral moieties onto the stabilizers to obtain chiral induction. Here, we report a versatile synthetic method to functionalize polysiloxane stabilizers by a cinchonidine moiety. The cinchonidine pendants confer fluorescent properties to the modified polymers,[6] and cinchonidine's extended aromatic system can adsorb to metal surfaces.[7−9] These properties were then taken into account to study the stabilization of preformed palladium nanoparticles (PdNPs) and to use these stabilized NPs in enantioselective hydrogenation.

Synthesis and Characterization of Cinchonidine-Grafted Polysiloxane. Considerable effort has been devoted to the immobilization of cinchona alkaloids on soluble[10−12] or insoluble[13] polymer supports. To graft cinchona alkaloids onto these polymers, three different sites of attachment can be potentially used, namely the most commonly used vinyl residue, the benzyl-type oxygen at C9 (see Figure 1), and the less frequently employed bridgehead nitrogen of the quiniclidine residue.[14,15] Study of the effect of the structure of chiral modifiers derived from natural cinchona alkaloids on the enantioselectivity and rate of Pt/Al_2O_3-catalyzed hydrogenation of ethyl pyruvate has shown that the modification of the vinyl function was the most appropriate to keep enantiomeric excess at the highest value (rather than modification of alcohol moiety[15]). Consequently, we decided to graft the cinchonidine onto the polymethylhydrosiloxane (PMHS) by a hydrosilylation reaction between the vinyl end group of cinchonidine (**1**) and the silane functions.

Direct hydrosylilation of PMHS with cinchonidine, in the presence of different platinum catalysts (*cis*-dichlorobis (diethyl sulfide)platinum(II), Karstedt or Speier catalysts) led to a cross-linked product due to the reaction of the double bonds on $C_{10}-C_{11}$ and the hydroxy group on C_9. Thus, prior to reaction with the polymer backbone, the alcohol function of cinchonidine was protected by TMSCl (Figure 1).[16] Hydrosilylation was then performed with **2**, in the presence of $(Et_2S)_2PtCl_2$ as catalyst at 80 °C in toluene. The efficiency of this grafting step was followed versus time by gel permeation chromatography (GPC) (Figure S1): the reaction reached completion after 4 h, and no significant increase of molar mass or decrease of polydispersity was observed later. Moreover, the ratio of silane moieties functionalized with cinchonidine compared to the unreacted ones (i.e., grafting ratio) can be controlled by adjusting the amount of **2** relative to the silane function added during the grafting step. This ratio was estimated by ^1H NMR by comparing the integration of peaks from unreacted silane groups at 4.7 ppm to those of the grafted cinchonidine moiety **2**. Similar results were obtained by using UV spectroscopy, assuming small changes in extinction coefficient of cinchonidine during the grafting process (see Figure S8 in Supporting Information). A maximum grafting ratio of about 25% was obtained: as described for other substituents,[17] the grafting of the bulky cinchonidine groups onto the polysiloxane chain greatly increased the stiffness of the polymer chain and lowered the accessibility of the reactive silane functions. Polymer **3** was isolated by preparative size exclusion chromatography as a yellow oil. Deprotection, performed in refluxing methanol, led to the final polymer **4**. Its completeness was monitored by ^1H NMR following the change in the integration ratio between H-2′ ($\delta = 8.7$ ppm) and $Si-CH_3$ broad band ($\delta = 0.1$ ppm). Moreover, ^1H NMR spectra and FTIR analysis demonstrated the reaction of the remaining silane functions of **4** with methanol, avoiding further reaction between free alcohol groups and silane functions. Two polymers with grafting ratios of 10% and 25% were isolated. Their key descriptors are reported in Table 1 (see also Figures S2−S8 for the characterization of the different compounds). Commercial PMHS has an average polymerization degree (DP_n) of about 110 and a very low glass transition temperature (−119 °C). As expected, the addition of stiff side groups to the polymer backbone drastically increases the polymer's glass transition temperature. Moreover, the changes in structural conformation and the subsequent change in hydrodynamic radius did not allow a direct

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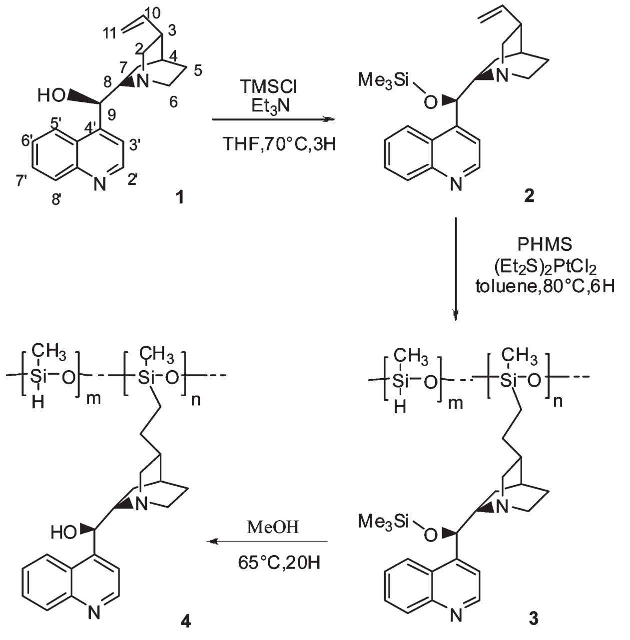

Figure 1. Grafting of cinchonidine on poly(methylhydrogeno)siloxane chain.

Table 1. Characterization of Polysiloxanes Grafted at Different Ratios with (−)-Cinchonidine

	chemical structure[a]		polymer characterization[b]			
	n (%)	*m* (%)	T_g (°C)[c]	M_n	M_w	I_p
PMHS	0	100	−119	7 000	21 000	3.0
PMHS−10% CD	10	90	−25	25 000	49 000	1.9
PMHS−25% CD	25	75	−15	29 000	79 000	2.7

[a] Determined by ^{1}H NMR and UV−vis absorbance measurements; *n* and *m* refer to the structures in Figure 1 (accuracy ±2%). [b] Evaluated from GPC data (M_n and M_w are in g mol^{-1}). In the case of PMHS $dn/dc = 0$ in THF, so measurements were carried out in toluene. [c] Evaluated by DSC (heating rate of 10 °C min^{-1}).

comparison of grafted polymers with PMHS: so average molar masses obtained from GPC measurements are only given as an indication.

Palladium Nanoparticle Stabilization. One of the most important issues in NP-based catalysis is their stabilization since aggregation would nullify the benefit of the nanosized particles used. To study the ability of the grafted polymer to interact with and to stabilize Pd NPs, we decided to use preformed NPs obtained by a novel and versatile approach to separate growth and functionalization steps in preparing functional nanomaterials (Figure 2).[18] In a first step, the control of the growth of the inorganic core is ensured in a supercritical medium without the use of stabilizing agents.[19] At the outlet of the supercritical reactor, the naked NPs are directly sprayed into a solution (room temperature and pressure) containing the stabilizer. The NPs can interact with the stabilizer to form hybrid organic−inorganic NPs.

In a typical experiment, palladium trifluoroacetate, the metal precursor, is thermally decomposed in supercritical acetone at constant pressure (20 MPa) and temperature (250 °C). The residence time in the reactor is 10 s, and the concentration of palladium is 6×10^{-3} g/$g_{acetone}$. The palladium NPs obtained are sprayed onto the functionalization vessel filled with a solution of grafted polymer (in acetone or toluene). To demonstrate the stabilizing effect of the cinchonidine-grafted polysiloxane on the palladium NPs, the same experimental procedure was performed without polymer in the functionalization vessel. After a few hours, the latter particles aggregate and precipitate, whereas in the solution of grafted polymer, the particles remain dispersed in the solvent (for periods of up to a year). Control experiments where Pd NPs are mixed with bare PMHS, free cinchonidine, or a mixture of both without any preliminary grafting also led to the formation of precipitates (Figure S9). Pd NPs were then investigated by transmission electron microscopy. Without stabilizing agent, large agglomerates with a wide size distribution of 100 ± 40 nm, composed of self-assembled palladium NPs with a mean size of 3.2 ± 0.7 nm, are formed.[18] In the presence of the cinchonidine-grafted polysiloxane, well-dispersed NPs are obtained with a fairly narrow size distribution of 2.1 ± 0.6 nm, as shown in Figure 3a. The inset of Figure 3a confirms the {200} lattice spacing of face-centered-cubic metal palladium (fringes of 1.9 Å). This confirms the ability of cinchonidine-grafted polymers to stabilize preformed Pd NPs by avoiding further NP growth and by keeping them stable in solution (acetone, toluene, THF, etc.).

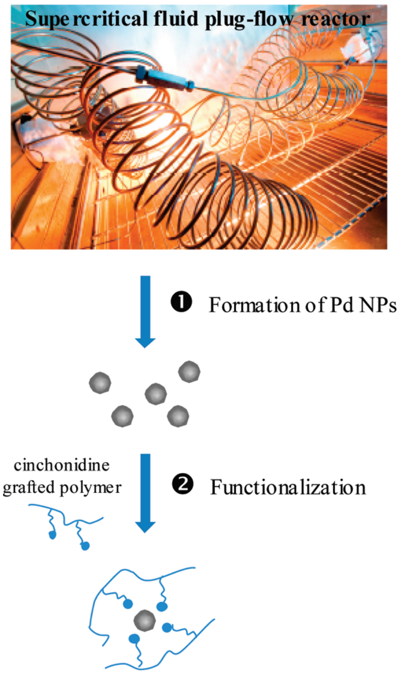

Figure 2. Illustration of the method used for the synthesis of functional NPs based on the separation of growth and functionalization steps.

Cinchonidine presents fluorescence properties: it shows a strong emission band at 355 nm upon irradiation at 329 nm. Changes in its environment, such as adsorption of the extended aromatic system on the Pd surface, can reduce the intensity of the emission peak due to the quenching of fluorescence. Thus, the cinchonidine moiety was used as a probe to investigate the interactions between NPs and the polysiloxane chain grafted with cinchonidine. First, preliminary experiments were performed with solutions of free Pd NPs in the same range of concentration. They confirmed absence of fluorescence activity of NPs, and no prefilter or postfilter effects were revealed. Then, the fluorescence intensity of samples with two different grafting ratios was monitored in toluene at 355 nm (excitation 329 nm) upon addition of NPs. A control experiment was also performed with free cinchonidine. After normalization (taking into account the dilution caused by addition of NP solution), I_0/I was plotted as a function of NP concentration, with I_0 the intensity of fluorescence without quencher and I the intensity of fluorescence at a given concentration of quencher. The relative fluorescence intensity gradually decreased

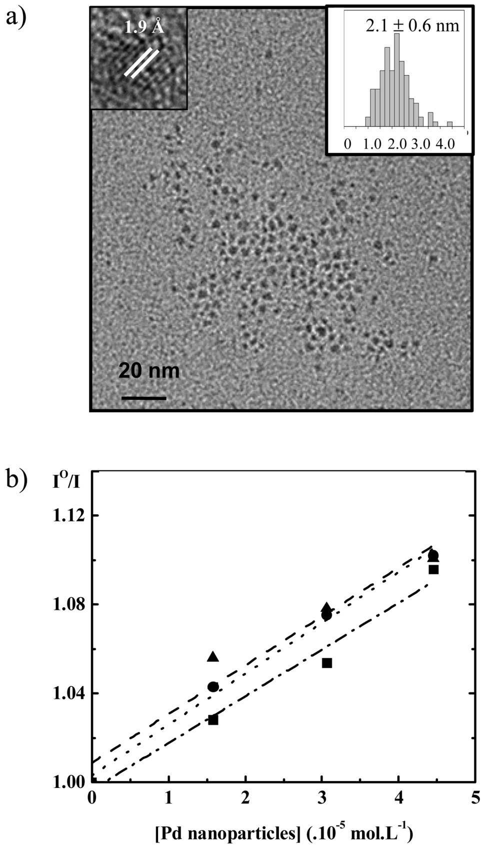

Figure 3. (a) TEM of palladium NPs functionalized with the cinchonidine-modified polymer. Inset: HRTEM micrograph and diameter distribution (in nm) of the palladium NPs. (b) Fluorescence intensity at 355 nm (excitation 329 nm) versus NPs concentration of free cinchonidine (●) and two cinchonidine-grafted polysiloxanes (grafting ratio 10% (▲) and 25% (■)). The maximum fluorescence intensity of free or polymer-grafted CD suspension was taken to be I_0, and the maximum intensity of suspensions after NP addition was taken to be I. The normalized values take into account the dilution due to addition of the NP solutions (following the Stern−Volmer law).

upon increasing the Pd NP concentration, its behavior resembling that observed with free cinchonidine (Figure 3b). This pattern follows the Stern−Volmer law. The results clearly indicate that part of the cinchonidine is interacting with the palladium NPs. This confirms that stabilization of the particles was achieved by the adsorption of the cinchonidine moiety (probably thanks to the quinoleine aromatic system)[20] to the surface of Pd NPs and by the steric hindrance of the polysiloxane chain that avoided aggregation between palladium nanoparticles.

Catalytic Properties of Stabilized Pd NPs. As mentioned below, cinchona alkaloids have been extensively used as chiral modifiers in enantioselective reactions.[21,22] They have proved to be very efficient chiral modifiers with platinum catalysts providing for instance up to 99% ee in the hydrogenation of α-keto esters. Moreover, besides platinum, the enantioselective hydrogenation of double bonds (α-keto esters, phenylcinnamic acid, ethyl pyruvate, or isophorone) by cinchonidine-modified palladium surfaces has been the subject of detailed studies.[8,15,23−26] The cinchonidine-grafted polymers presented in this paper stabilized Pd NPs in different solvents (toluene, THF, acetone, methanol). As a first probe for the applicability of these polymer-stabilized Pd NPs in catalysis, the hydrogenation of isophorone was investigated in methanol under mild conditions (Figure S10, low pressure of $H_2 = 2$ bar, room temperature). The product of the hydrogenation reaction was analyzed by monitoring the disappearance of isophorone by gas chromatography (commercial products were used as standards). Conversion rate was measured as well as the turnover number (TONs) defined as moles of isophorone consumed per mole of Pd.

3,3,5-Trimethylcyclohexan-1-one was obtained as the only product. No significant catalytic activity was observed for the naked NPs or for the NPs stabilized with only cinchonidine: moreover, they were not stable on the time scale of the experiment, and so the existence of large non-dispersed clusters in solutions decreased the Pd surface accessible to the substrate and therefore led to poor catalytic activity. The catalytic activities obtained with cinchonidine-grafted polymer (PMHS−10% CD) were moderate (TON = 30) but comparable under these mild conditions to those reported in the literature with hyperbranched poly(ethylenimine)[27] or with fourth-generation PAMAM dendrimers under similar conditions but with Pt catalysts[27] (for these systems TONs were found to be 64 and 25, respectively). An enantiomeric excess of 18%, comparable to the 20% obtained by Tungler and colleagues with the same substrate and dihydrocinchonidine-stabilized Pd NPs,[23] was obtained with the polymer-stabilized Pd NPs. After the hydrogenation reactions, the solutions of Pd NPs remained clear and there was no evidence of agglomeration. The recycling of the catalyst (by isolation as a powder) did significantly decrease activity after redispersal in solution.

Conclusion. A new family of polysiloxanes modified by a cinchonidine pendant group has been synthesized. The architecture and flexibility of the polymer allow interaction between the long dispersible polysiloxane chain and Pd NPs. The polymers were applied as stabilizers to disperse preformed metal NPs. Moreover, the interactions of this polymer with the Pd NPs was assessed by the modification of its fluorescence properties. Theoretically many other kinds of metal NPs can also be supported on these "dual-feature" polymers. Lastly, this polymer has proved to act as an efficient modifier for the enantioselective hydrogenation of isophorone. Further experiments to optimize catalytic properties by modifying structural parameters (grafting ratio, amount of stabilizer) and experimental conditions are in progress.

Supporting Information Available: Materials and methods, polymers synthesis, and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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