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First example of 'palladium-nanoparticle'-catalyzed selective alcoholysis of polyhydrosiloxane: a new approach to macromolecular grafting†

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'Palladium-polysiloxane' nanocomposites were synthesized as stable and isolable powder by reduction of $Pd(OAc)_2$ with polymethylhydrosiloxane, which functions as a reducing agent and as a capping agent for the generation and stabilization of 'palladium'-nanoclusters. Redispersion of 'palladium-polysiloxane' nanocomposite in common organic solvents, in the presence of polymethylhydrosiloxane, yielded catalytically active polysiloxane-wrapped soluble 'palladium'-nanoclusters. Polysiloxane-encapsulated 'palladium'-nanoclusters were used as recyclable catalyst for macromolecular grafting via alcoholysis of polyhydrosiloxane. Selective alcoholysis of polyhydrosiloxane took place in fair to excellent yields under moderate reaction conditions with a variety of alcohols (primary, secondary, tertiary/sterically bulky and functional alcohols). *'In situ'* electron microscopy studies of the reaction mixtures in conjunction with controlled poisoning experiments revealed catalytic participation of 'palladium'-nanoclusters during substitution reactions.

KEYWORDS: nanoparticles; nanocomposites; polysubstitution; catalysis; alcoholysis; catalyst poisoning; poly(methylhydro) siloxane (PMHS)

INTRODUCTION

Macromolecular substitution (grafting) is a synthetic approach that involves the functionalization of a preformed polymer backbone containing reactive groups with an appropriate reagent. Using this methodology, variation of the side chains or pendant groups can be achieved, producing a family of polymers from the same parent polymer backbone. Since polymer properties are often heavily influenced by the identity of their pendant groups, a variety of different materials with a wide range of properties can be synthesized from only one antecedent (Scheme 1).

Often, a significant drawback of this concept is the requirement that the functionalization reactions be quantitative. This can be difficult and challenging to accomplish, owing to a variety of factors. Many chemical reactions are not quantitative and produce undesirable byproducts, thus severely limiting the synthetic options available. In addition, the reactivity of functional groups on a polymer backbone is often reduced compared with small molecules due to steric hindrances limiting the accessibility of the reactive site. Consequently, it is difficult for a reagent (nucleophile) to find and react with all of the reactive sites on a coiled polymer chain.

In the past few years, catalytic grafting of polyhydrosiloxane has emerged as an alternative route for the synthesis of organic–inorganic hybrid polymers, owing to the complexities involved in direct generation of well-defined linear hybrid polymers.[1–3] Low cost, easy availability, and the presence of catalytically transformable Si–H bonds in polymethylhydrosiloxane (PMHS) make it a very attractive and interesting antecedent for macromolecular grafting studies.[3] Moreover, organic functionalization of the polymer chain can lead to fine-tuning of physical and chemical properties of the resulting siloxanes. For example, appropriate substitution on the polysiloxane backbone can lead to diverse

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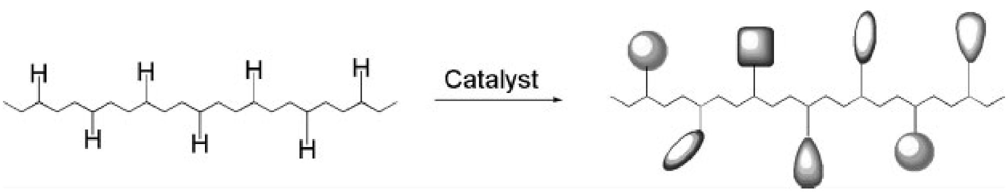
†Dedicated to the memory of Professor Colin Eaborn who made numerous important contributions to the main group chemistry.



Scheme 1. Macromolecular substitution strategy.

materials such as liquid crystals,[4–6] cross-linking agents,[7] conductive[8,9] and electroluminescent polymers,[10] non-linear optical materials,[11,12] and bactericides.[13] Poor selectivity, limited activity and non-recyclability of the catalyst remain major shortcomings of most of the catalytic routes available for macromolecular substitutions of polysiloxanes. Designing a catalyst that could provide excellent activity, selectivity and recyclability under mild reaction conditions is one of the challenges in modern catalysis chemistry.

Recently, we and others have shown that metal nanoclusters can be used as catalysts for a number of catalytic transformations and give better activity, selectivity and reusability.[14–20] Inspired by our success in designing the nanocluster catalysts for silaesterification reactions and room-temperature reduction reactions of alkenes, we initiated a systematic study to investigate whether metal nanoparticles can be used for macromolecular substitution reactions of polyhydrosiloxanes. In this publication, we report the first example of 'palladium-polysiloxane nanocomposite'-catalyzed mild, high yielding, one-pot selective alcoholysis of PMHS. In addition, we present the detailed investigations of the generation of 'palladium-polysiloxane' nanocomposites and their utility as a recyclable catalyst for the polymeric substitution reactions with functional alcohols under mild reaction conditions.

RESULTS AND DISCUSSION

Transition-metal-catalyzed condensation reactions of monomeric hydrosilanes are well documented and have been successfully applied to the synthesis of substituted silanes under mild and neutral reaction conditions. On the other hand, selective modification of Si–H bonds in a polymeric system has been a challenging problem, because of the susceptibility of these bonds towards dehydrocoupling, rearrangement, backbone degradation, and due to difficult accessibility of Si–H bonds for catalytic transformation reactions.[5] Owing to these complications, well-defined hybrid (inorganic–organic) polymers, in which organic groups are grafted onto the silicone backbone via catalytic routes, are quite rare, and the development of new synthetic concepts and their applications has been limited.

Catalysis by nanoclusters is believed to take place on active sites present on the cluster surface. Stabilization of nanoclusters by coordinating ligands normally leads to passivation of active sites, causing deterioration in catalytic activity. Thus, in our view, one of the primary challenges in nanocluster catalysis is the invention of robust and active nanocatalysts that can be bottled and used and reused for desired transformations. These characteristics, coupled with selectivity and activity provided by nanocluster catalysts, can lead to real and superior alternatives for the metal complex catalysts. Our hypothesis for such a nanocatalyst is shown in Fig. 1. The results of our studies are discussed below.

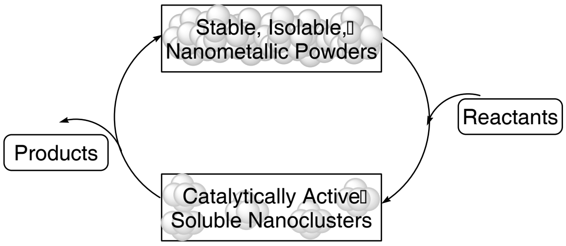


Figure 1. Pictorial presentation of the ideal recyclable nanocluster catalysts.

Synthesis of Palladium-polysiloxane nanoconjugates as stable isolable powders

The present study is inspired by our hypothesis that stabilization of catalytically active metal nanoparticles can be achieved by the 'meatball–spaghetti' analogy. In this model, preparation of functional metallic nanoparticles is viewed as the preparation of 'meatball–spaghetti' dish. This analogy is based on our proposition that the aggregation of the 'meatballs' (metal nanoclusters) can be prevented if enough 'spaghetti' (flexible polymeric structure) is present to wrap the meatballs physically during the formation process. Owing to a very weak surface passivation imparted by the stabilizing agent, such types of nanocluster are expected to show superior activity and selectivity as catalysts over those nanoparticles passivated by strong coordinating ligands. In our previous studies we have used polysiloxane polymers as reducing and stabilizing agents to generate highly active, yet stable, nanoparticles.[14,15] Polysiloxanes are particularly well suited for hosting metal nanoparticles for the following reasons: (i) the unusual freedom of rotation around the Si–O bond allows these polymers a high degree of flexibility while maintaining their integrity; (ii) polysiloxanes with Si–H functionalities act as reducing agents, thereby eliminating the need for extra reducing agents;

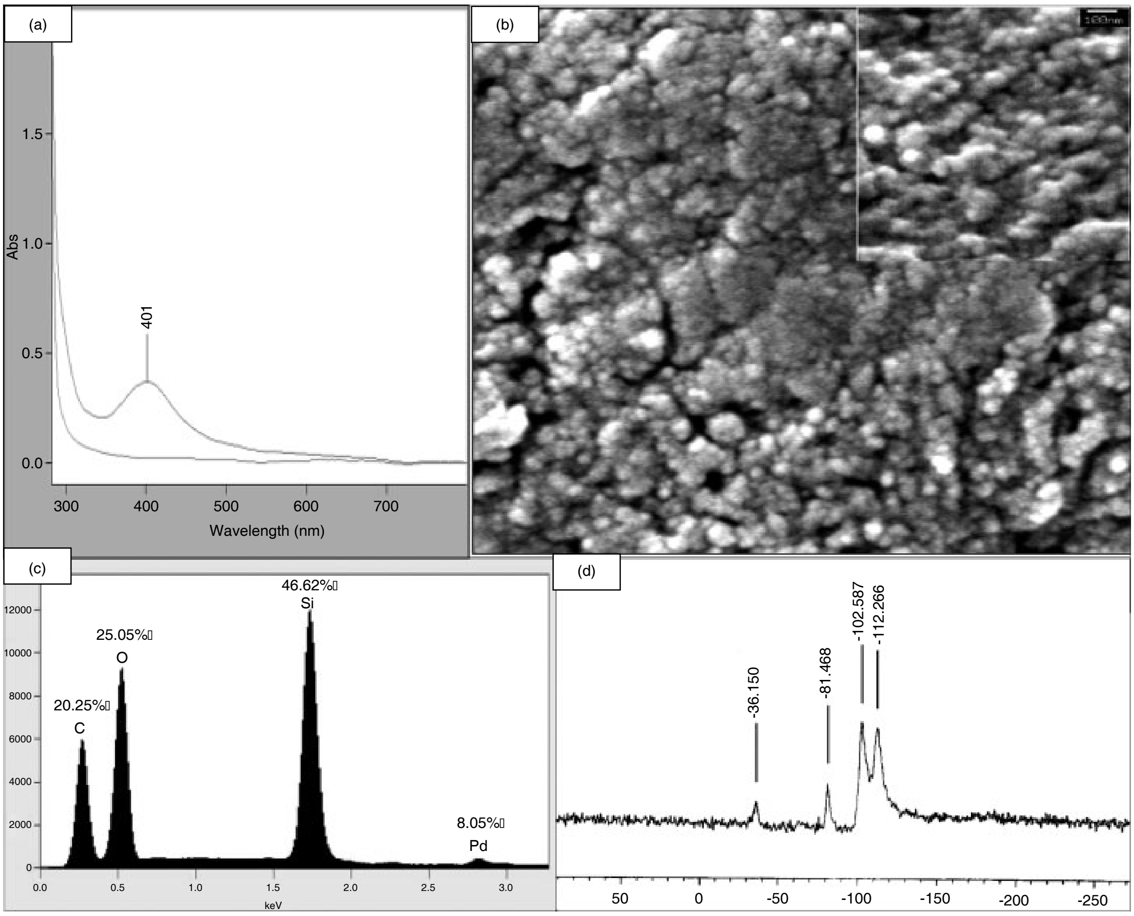


Figure 2. Characterization of palladium-polysiloxane nanoconjugates.

(iii) the encapsulated nanoparticles are confined primarily by steric effects and, therefore, a substantial fraction of their surface is unpassivated and available to participate in catalytic reactions. Thus, the studies were carried out to generate palladium-nanoclusters in presence of PMHS. Under optimized reaction conditions, the synthesis of 'palladium'-nanoclusters was carried out in a 200 Ml RB flask at room temperature. Pd(OAc)$_2$ (0.112 g, 0.5 mmol) was dissolved in 50 ml of toluene and PMHS (0.90 ml, 15.0 mmol) was added to this yellow solution. The color change from yellow to black was observed within 1 min of stirring with vigorous evolution of gas (presumably hydrogen). Color change was monitored by UV–vis analysis of the reaction mixture. A featureless UV–vis spectra (Fig. 2a) indicated conversion of palladium(II) to palladium(0).[21] After stirring the solution for 1 h, black solid began to precipitate out and the reaction mixture turned colorless after another 3–4 h of stirring. At this juncture, the black precipitate was filtered and washed with excess toluene and the resulting solid was analyzed by various techniques. Scanning electron microscopy (SEM) characterization of the solid was carried out to investigate the morphology of the solid at the nanometer size scale. Spherical particles in the 40–50 nm size range were found, as is evident from the SEM image (Fig. 2b). Energy dispersive spectroscopy (EDS) examination of the solid showed the material to be composed of 8.05 wt% palladium, 46.62 wt% silicon, 25.05 wt% carbon, and 20.25 wt% oxygen (Fig. 2c).

The presence of the above species was confirmed with CP/MAS ^{29}Si NMR spectroscopy (Fig. 2d). The ^{29}Si NMR peaks at $\delta - 36.15$, -81.46, and -102.58 and -112.26 ppm correspond to a polymeric network containing D, T and Q silicon centers respectively (Fig. 2d). FT-IR spectra also show characteristic signals associated with Si–H and Si–O–Si bonds (2162(m), 1021(b), 900.77(s), 2964.86(m)). 'Palladium-polysiloxane' nanocomposites obtained in the form of solid were air stable and can be stored at room temperature without any extra precautions for long periods of time (3–4 months). X-ray photoelectron spectroscopy (XPS) studies of the solid were also undertaken. XPS measurements of the solid showed Pd(3d$_{5/2}$) and Pd(3d$_{3/2}$) peaks at 335.9 eV and 341 eV corresponding to palladium(0) species.

Redispersion study: catalytically active soluble nanoclusters

A better catalytic efficiency of the homogeneously dispersed nanoparticles than their heterogeneous counterpart prompted us to explore the possibility of redispersion of 'palladium-polysiloxane nanoconjugates' in common organic solvents. In a typical redispersion experiment, 'palladium-polysiloxane nanoconjugates' (0.01 g) were suspended in 4 ml of benzene followed by stirring at 70 °C for 30 min. No color change was observed during this period. Electron microscopy (EM) analysis of the solution shows the absence of nanoparticles in solution. At this juncture, PMHS (0.12 ml, 2.0 mmol) was added to the above solution. The color of the solution gradually changed, yielding a homogeneous black solution after 30 min of addition of PMHS. As is evident from the EM image, polysiloxane encapsulated 'palladium'-nanoclusters, were present in the homogeneous black solution. The existence of polysiloxane-encapsulated 'palladium'-nanoclusters demonstrates unique approach for the homogenization of heterogeneous catalyst in the presence of PMHS. To investigate the redispersion phenomenon further, a separate experiment was performed with polydimethysiloxane (PDMS) as a redispersion agent under identical conditions. An EM assay of the PDMS solution confirmed no sign of nanoclusters, affirming the need of Si–H bonds for the homogenization (size reduction) process. The catalytic activity of the homogenized nanoclusters was investigated by adding *tert*-butanol to the solution containing homogeneously dispersed 'palladium'-nanoclusters. '*In situ*' EM characterization of the reaction mixture was performed after regular intervals to probe the active catalytic participation of 'palladium'-nanoclusters. EM studies of the mixture showed no visible change in the size and morphology of the nanoclusters after the addition of alcohol. Catalytic transformation was also monitored with ^{1}H NMR spectroscopy, which showed complete conversion of Si–H bonds to Si–O–*tert*-butyl bonds after 34 h of reaction at 70 °C. Complete catalytic conversion substantiates the ligand-free and physical nature of the polysiloxane interaction with 'palladium'-nanoclusters.

Catalytic application of 'palladium-polysiloxane nanoconjugates'

The catalytic efficiency of 'palladium-polysiloxane nanoconjugates' was explored by using them as catalyst for macromolecular grafting of PMHS with alcohols. In a typical alcoholysis experiment, palladium-nanoparticles (0.01 g) were suspended in 4 ml of benzene at room temperature followed by addition of PMHS (0.12 ml, 2.0 mmol) and *tert*-butanol (0.19 ml, 2.0 mmol). The colorless reaction mixture gradually turned to a homogeneous black-colored solution, indicating the generation of soluble nanoclusters. Evolution of gas (presumably hydrogen) was also observed during the reaction. A transmission EM (TEM) study of the reaction mixture during the catalysis was undertaken. Indeed the catalytic active 'palladium'-nanoclusters were present in the reaction mixture (Fig. 3). A comparatively narrow distribution of particle size (2–6 nm), with average particle size of 2.60 nm (standard deviation: 0.6 nm), was observed with 'Scion Image software'-assisted particle-size analysis of the TEM images. ^{1}H NMR examination of the reaction mixture after regular intervals shows the gradual disappearance of the Si–H signal (δ4.85) and –OH signal (δ2.09), associated with PMHS and *tert*-butanol respectively. A constant rise in the viscosity of the reaction mixture was also noticed. ^{13}C NMR spectroscopy revealed the appearance of a new peak at δ69.83 ($Me_3C{-}OSi$) representative of a silane-substituted tertiary carbon center of *tert*-butanol beside peak at δ68.02 ($Me_3C{-}OH$). After 34 h, the intensity of the silane-substituted tertiary carbon

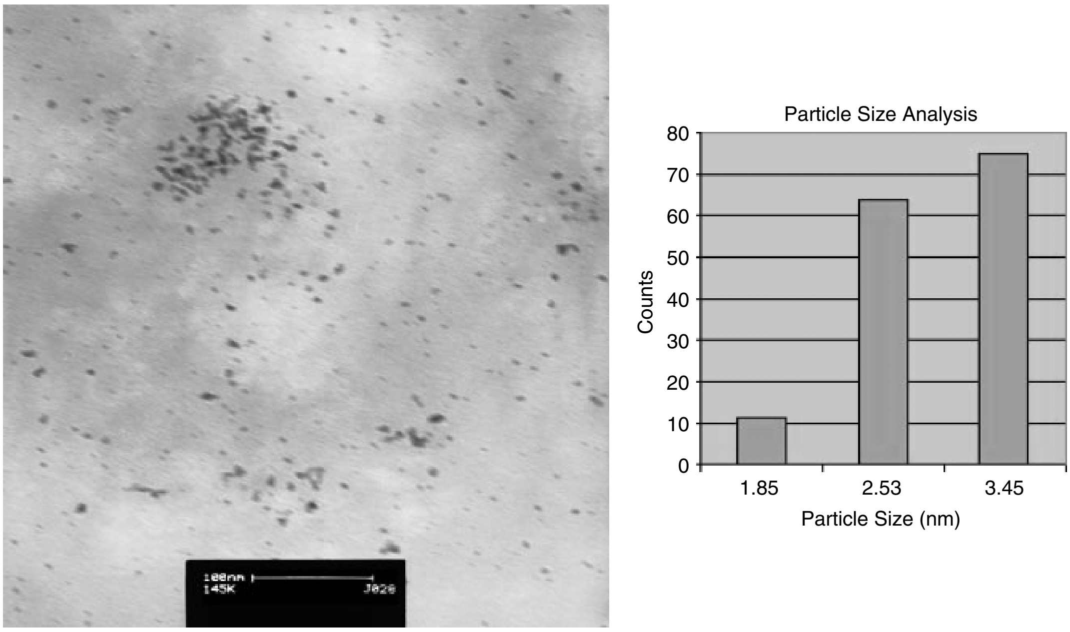


Figure 3. TEM and particle size analysis of the palladium-nanoclusters during the catalysis.

peak reached an optimum level, and the unsubstituted carbon peak disappeared completely. The ^{29}Si NMR spectra also corroborated complete transformation of Si–H bonds (δ – 36.45) to the *tert*-butoxy group (δ – 54.78, Me_3C–OSi). After complete substitution, the reaction mixture was subjected to high-speed centrifugation (15 min), which led to precipitation of 'palladium'-nanoclusters at the bottom of the centrifuge tube. Filtration of the catalysts and subsequent evaporation of solvent under reduced pressure yielded viscous *tert*-butoxy-grafted polysiloxane.

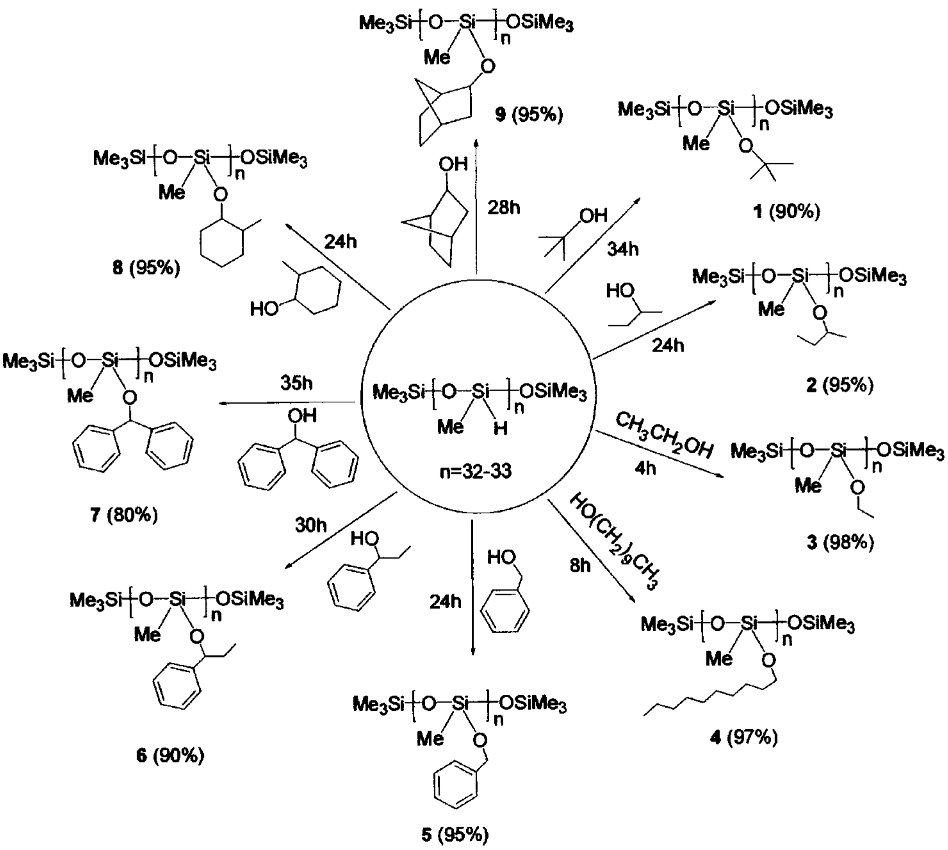
In order to investigate the utility of this catalysis process, alcoholysis of PMHS was examined in the presence of various alcohols. The method was found to be applicable to primary, secondary and tertiary alcohols, and led to selective formation of the corresponding polyalkoxysiloxanes (Scheme 2) in good yields. Macromolecular grafting of PMHS was equally successful with aromatic alcohols (**5**, **6**, and **7**; Scheme 2). Palladium-nanocluster-catalyzed reactions with sterically bulky alcohols, such as benzhydrol, were comparatively slow but led to the desired product in good yields. Depending on the electronic and/or steric nature of the alcohols, highly viscous or solid products were recovered after the evaporation of solvent in each case.

Encouraged by these results, catalysis was further extended to reactions of functional alcohols, since grafting of PMHS with functional alcohols can offer a way to further modify the polymer backbone with functionalities, which are otherwise difficult to substitute directly to the polysiloxane chain. Facile and selective reactions with 3-hydroxy-2-butanone, 4-methoxybenzyl alcohol, and 3-*tert*-butoxycyclohexanol were observed without any side reactions and led to corresponding alkoxy siloxanes in excellent yields (**10**, **14** and **15**; Scheme 3). Amino-substituted polysiloxanes are desirable products owing to their utility in various technological applications, but salt-free direct methods of their preparation are quite rare.

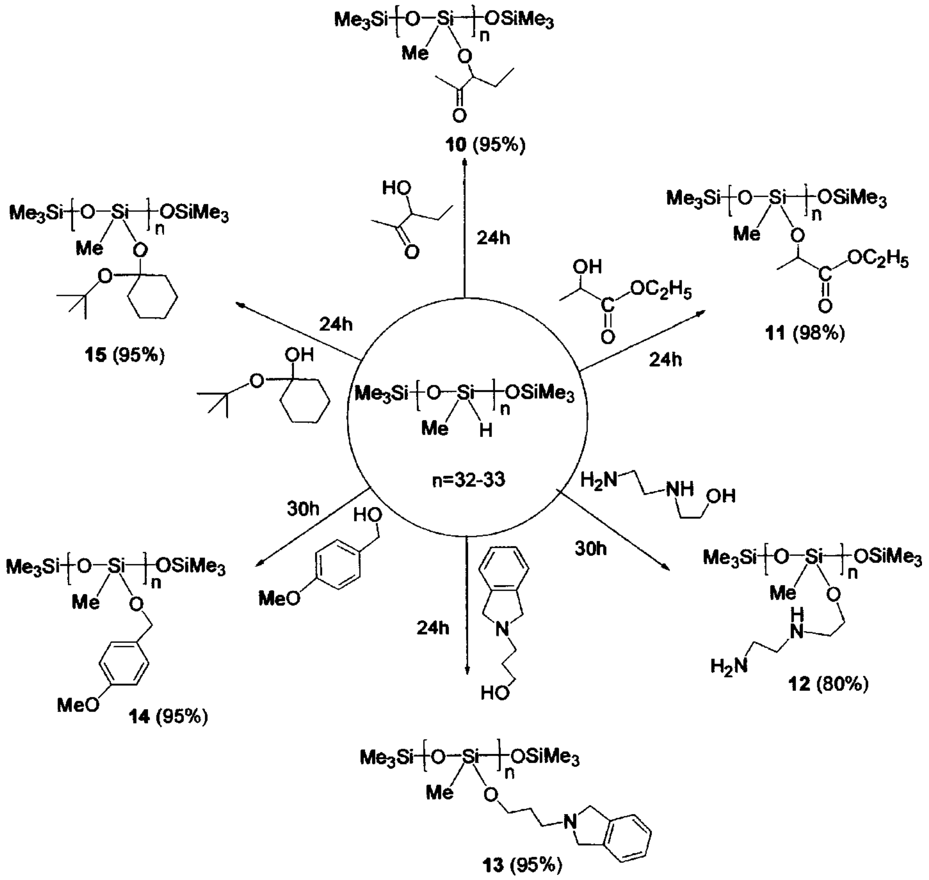
To our surprise, the Palladium-nanoclusters alcoholysis reaction of PMHS with 2-(2-aminoethylamino)ethanol furnished the corresponding amino-substituted polysiloxane (**12**, Scheme 3) in good yields without degradation or rearrangement reactions. However, it should be pointed out that double the amount of solvent was used for alcoholysis of amine-functionalized alcohols, since the viscosity of the reaction mixture rises rapidly as the reaction progresses. Similarly, hydroxypropylphthalimide reacted with PMHS to produce the aromatic amine-substituted siloxane **13** in excellent yield.

Recyclability study

Facile and efficient separation of nanoclusters from the reaction mixture led us to explore the possibility of reusability of the catalyst, recovered after the catalysis. The precipitate



Scheme 2. Palladium-nanocluster-catalyzed synthesis of poly(methylalkoxy)siloxanes.



Scheme 3. Palladium-nanocluster-catalyzed synthesis of functional poly(methylalkoxy)siloxanes.

was washed with benzene (15 ml) and reused as catalyst for another catalytic transformation. Almost identical activity and selectivity was observed, even after three recycling studies with this same batch of catalyst.

Solvent effects

A study of the solvent effect on the catalytic efficiency of 'palladium-polysiloxane nanoconjugates' was performed in common organic solvents. PMHS alcoholysis with ethanol was probed in four different solvents, i.e. tetrahydrofuran, benzene, cyclohexane and acetonitrile, under identical reaction conditions and molar ratios of the reactants. As is evident from Fig. 4, 'palladium-polysiloxane nanoconjugates' display almost similar catalytic activity in tetrahydrofuran, benzene, and cyclohexane. The rate of PMHS alcoholysis is rather sluggish in acetonitrile compared with the other solvents. The slow rate of reaction in acetonitrile can be attributed to the ligand coordination imparted to the nanoclusters by the CN-group, making them less active for the catalytic transformation.

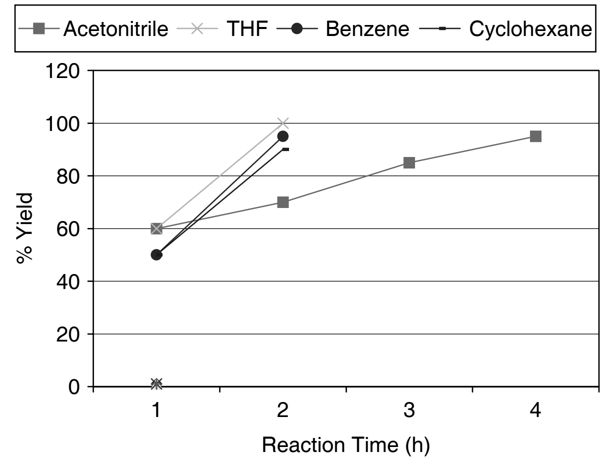


Figure 4. Plot of the reaction rates of PMHS grafting with ethanol in organic solvents.

Catalyst poisoning studies

Mercury poisoning experiment

Mercury is well known to poison metal nanoclusters such as nickel, palladium and platinum, either by forming an amalgam or by physically adsorbing onto the cluster surface. Hence, mercury can serve as a tool to probe the true nature of the catalyst during the catalytic transformations. TEM and ^{1}H NMR spectroscopy were employed to study the effects of mercury during the functionalization reactions with ethanol.

The reaction mixture was examined with TEM to establish the presence of 'palladium-polysiloxane' nanoconjugates before the addition of mercury. After confirming their existence in the reaction mixture, mercury was added to the reaction mixture. ^1H NMR spectroscopy shows only 10–15% conversion to alcoholysis product. TEM examination of the grid prepared after 30 min of addition of the mercury demonstrated complete disappearance of palladium nanoparticles from the reaction mixture. A total of 15–20% expected product was formed after addition of mercury. Stirring was continued for a further 24 h, but there was no increase in the product, indicating complete absence of catalytically active species.

Thiol poisoning study

The catalytic activity of the nanoclusters was attributed to kinks and defects present on the surface. These active sites can be passivated with strong coordinating ligands, such as thiols, which can bind strongly to the nanocluster surface and, hence, make them passive for catalytic applications. A series of experiments were carried out to find the exact amount of dodecanethiol needed to fully passivate the surface of 'palladium-nanoconjugates for the reaction of PMHS with ethanol. Only 2–6% ethanol functionalization of PMHS took place after 24 h in the presence of 0.1 mmol of dodecanethiol.

In conclusion, we have demonstrated the first example of palladium nanoparticles as a selective and recyclable catalyst for the alcoholysis of polyhydrosiloxane. A fair number of alcohols with diverse structures (primary, secondary, sterically bulky and functionalized alcohols) were selectively and efficiently grafted onto the polysiloxane backbone, without any side reactions and under moderate reaction conditions. Active participation of palladium nanoclusters during the catalytic transformations was also established by '*in situ*' EM analysis and controlled poisoning experiments. Moreover, a new approach for the synthesis and stabilization of palladium nanoclusters as a stable isolable powder and their redispersion in common solvents was presented.

EXPERIMENTAL

General information

All the experiments and manipulations were performed under a dry argon or nitrogen atmosphere using standard Schlenk-tube technique. Solvents were purchased from EM Science (Merck) and distilled over sodium–benzophenone. PMHS (M_w 2000, 32–33 Si–H units) and $Pd(OAc)_2$ were obtained from Aldrich and used as received. All alcohols used in this study were procured from Aldrich and were stored over molecular sieves prior to use. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Unity NMR instrument (200 MHz). A Varian Unity NMR instrument operating at 300 MHz and 600 MHz was used to carry out CP/MAS ^{29}Si NMR and liquid-state ^{29}Si NMR spectroscopy experiment respectively. Proton spectra were referenced internally to protonated solvent shifts. All the peaks in NMR spectra are reported in parts per million. UV–vis spectra were recorded on a Varian Cary Model 50 UV spectrophotometer. An Amray 1910 scanning electron microscope was used to conduct the morphological study of solid 'palladium-polysiloxane' nanoconjugates. The solid was mounted on the carbon tab and coated with carbon vapors before analyzing the sample using SEM. A Philips CM 100-transmission electron microscope was used to investigate the presence of 'palladium-polysiloxane' nanoconjugates during the reaction. A few drops of the reaction mixture were taken out using syringe and directly deposited on a carbon-formvar-coated copper grid at room temperature. The solvent was allowed to evaporate from the grid under normal temperature and pressure for 1 h before the TEM examination of the grid. The particle size analysis of the 'palladium nanoclusters' was carried out manually on the TEM images, using Scion Image software. Around 100–150 particles were measured using the software on each TEM image before plotting the particle size analysis plot.

Generation of 'palladium-polysiloxane nanoconjugates'

$Pd(OAc)_2$ (0.112 g, 0.5 mmol) was dissolved in 50 ml of toluene in a 200 ml round-bottom flask at room temperature in open air. PMHS (0.90 ml, 15.00 mmol) was added to this solution. A color change from yellow to black was observed within 5 min of stirring, with vigorous evolution of gas (presumably hydrogen). Black solid was observed after stirring the solution for 2–3 h, and the reaction mixture turned colorless. The stirring was stopped at this point, the reaction mixture was filtered under vacuum, and the black residue was collected after washing with an excess of toluene. The black solid obtained was characterized by CP/MAS ^{29}Si NMR spectroscopy, FT-IR spectroscopy, and SEM. ^{29}Si (CP/MAS NMR) δ, ppm: −36.15 (Me–Si–H-containing silicons), −81.46 (Me–Si–OH), −102.58 (SiO_3), 112.26 (SiO_4). FT-IR (KBr), cm^{-1} 2162(m), 1021(b), 900.77(s), 2964.86 (m).

Alcoholysis of PMHS (typical procedure)

'Palladium-polysiloxane' composite (0.010 g, 0.805 mg palladium(0)), CH_3CH_2OH (2.0 mmol, 0.12 ml), and PMHS (2.0 mmol, 0.12 ml) were mixed together with 4 ml of benzene in a 50 ml Schlenk tube. The reaction mixture was stirred at 70 °C for 2 h. The progress of the reaction was examined using ^1H and ^{29}Si NMR spectroscopy. Centrifugation of the reaction mixture yielded a black solid (which can be further utilized as catalyst) and a clear solution. Evaporation of the solvent from the clear solution yielded ethoxy-substituted polysiloxane in quantitative yields.

Poly(methyl-*tert*-butoxysiloxane) (1)

^1H NMR ($CDCl_3$, 200 MHz) δ, ppm: 0.48, 1.22(m), 1.52(m). ^{13}C NMR ($CDCl_3$, 200 MHz) δ, ppm: −0.26, 32.45, 69.83. ^{29}Si NMR ($CDCl_3$, 600 MHz) δ, ppm: −54.78 (broad, SiMe).

Poly{methyl(3-methylbutoxy)siloxane} (2)

^{1}H NMR (CDCl$_3$, 200 MHz) δ, ppm: 0.16, 1.08(m), 1.33(m), 1.45(m), 4.08(m). ^{13}C NMR (CDCl$_3$, 200 MHz) δ, ppm: −1.23, 14.00, 20.32, 61.34, 66.73. ^{29}Si NMR (CDCl$_3$, 600 MHz) δ, ppm: 57.61 (broad, SiMe).

Poly(methylethoxy)siloxane (3)

^{1}H NMR (CDCl$_3$, 200 MHz) δ, ppm: −0.04, 1.03(m), 3.48(m). ^{13}C NMR (CDCl$_3$, 200 MHz) δ, ppm: −2.97, 19.52, 59.50. ^{29}Si NMR (CDCl$_3$, 600 MHz) δ, ppm: 52.26 (broad, SiMe).

Poly(methyldecyloxy)siloxane (4)

^{1}H NMR (CDCl$_3$, 200 MHz) δ, ppm: 0.22, 0.88, 1.25(m), 1.41(m), 1.57(m), 3.47(m), 3.79(m). ^{13}C NMR (CDCl$_3$, 200 MHz) δ, ppm: −3.99, 14.35, 23.06, 26.18, 29.75, 29.88, 29.99, 30.06, 32.30, 33.09, 62.80. ^{29}Si NMR (CDCl$_3$, 600 MHz) δ, ppm: −56.46, 57.12 (broad, SiMe).

Poly(methylbenzyloxy)siloxane (5)

^{1}H NMR (CDCl$_3$, 200 MHz) δ, ppm: 0.17, 4.55, 7.16(m), 7.29(m), 7. 34(m), 7.38(m). ^{13}C NMR (CDCl$_3$, 200 MHz) δ, ppm: −2.84, 67.04, 128, 128.36, 129.57, 135.03. ^{29}Si NMR (CDCl$_3$, 600 MHz) δ, ppm: −56.81 (broad, SiMe).

Poly{methyl(1-phenyl-1-propanoxy)siloxane} (6)

^{1}H NMR (CDCl$_3$, 200 MHz) δ, ppm: 0.09, 0.82(t), 1.69(q), 4.43(t), 6.90(m), 7.16(m), 7.36(m), 7,68(m). ^{13}C NMR (CDCl$_3$, 200 MHz) δ, ppm: 0.68, 9.90, 31.66, 75.67, 125.79, 127.18, 128.12, 144.47. ^{29}Si NMR (CDCl$_3$, 600 MHz) δ, ppm: 52.26 (broad, SiMe).

Poly(methylbenzhydroxy)siloxane (7)

^{1}H NMR (CDCl$_3$, 200 MHz) δ, ppm: 0.14, 3.85, 6.85(m), 7.15(m), 7.24(m), 7.50(m), 7.64(m). ^{13}C NMR (CDCl$_3$, 200 MHz) δ, ppm: 76.00, 126.53, 127.33, 128.25, 143.96. ^{29}Si NMR (CDCl$_3$, 600 MHz) δ, ppm: −57.18, −54.03 (SiMe).

Poly{methyl(4-methylcyclohexanoxy)siloxane} (8)

^{1}H NMR (CDCl$_3$, 200 MHz) δ, ppm: 0.09, 0.76(m), 1.17(m), 1.62(m), 1.84(m), 3.39(m), 3.67(m). ^{13}C NMR (CDCl$_3$, 200 MHz) δ, ppm: −53.54 (broad, SiMe).

Poly(methylnorborneoxy)siloxane (9)

^{1}H NMR (CDCl$_3$, 200 MHz) δ, ppm: 0.12, 0.94(m), 1.35(m), 1.58(m), 2.15(m), 3.62(m), 3.89(m). ^{13}C NMR (CDCl$_3$, 200 MHz) δ, ppm: −3.57, 24.28, 28.33, 34.49, 35.26, 42.37, 44.07, 74.63. ^{29}Si NMR (CDCl$_3$, 600 MHz) δ, ppm: −59.11 (broad, SiMe).

Poly{methyl(2-butanone-3-oxy)siloxane} (10)

^{1}H NMR (CDCl$_3$, 200 MHz) δ, ppm: 0.09, 1.73(m), 2.07(m), 3.60(m). ^{13}C NMR (CDCl$_3$, 200 MHz) δ, ppm: −4.13,19.24, 25.47, 67.47, 210.13. ^{29}Si NMR (CDCl$_3$, 600 MHz) δ, ppm: −57.94 (broad, SiMe).

Poly[{methyl(butyricacidethylester)-2-oxy}siloxane] (11)

^{1}H NMR (CDCl$_3$, 200 MHz) δ, ppm: 0.24, 0.93(m), 1.19(m), 3.39(m), 3.90. ^{13}C NMR (CDCl$_3$, 200 MHz) δ, ppm: −3.37, 17.91, 18.09, 19.84, 35.01, 72.53. ^{29}Si NMR (CDCl$_3$, 600 MHz) δ, ppm: −59.21 (broad, SiMe).

Poly[methyl-{macrosleftcurlybrace2-(2-aminoethyl-amino)ethanoxy}siloxane] (12)

^{1}H NMR (CDCl$_3$, 200 MHz) δ, ppm: 0.006, 2.32(m), 2.53(m), 3.46(m). ^{13}C NMR (CDCl$_3$, 200 MHz) δ, ppm: −3.32, 41.37, 51.94, 60.24, 78.17. ^{29}Si NMR (CDCl$_3$, 600 MHz) δ, ppm: −58.30 (broad, SiMe).

Poly{methyl(phthalimide-3-propyloxy)siloxane} (13)

^{1}H NMR (CDCl$_3$, 200 MHz) δ, ppm: −0.33 (m), 1.46(m), 3.23(m), 6.75(m), 6.83(m), 6.95(m). ^{13}C NMR (CDCl$_3$, 200 MHz) δ, ppm: −4.98, 0.98, 30.57, 34.69, 59.55, 122.21, 131.53, 133.14, 167.662. ^{29}Si NMR (CDCl$_3$, 600 MHz) δ, ppm: −57.93 (broad, SiMe).

Poly{methyl(4-methoxybenzyloxy)siloxane} (14)

^{1}H NMR (CDCl$_3$, 200 MHz) δ, ppm: 0.14, 2.28, 4.45, 7.09(m), 7.11(m), 7.29(m), 7.38(m). ^{13}C NMR (CDCl$_3$, 200 MHz) δ, ppm: −2.84, 22.26, 66.09, 128.22, 129.56, 130.22, 138.08. ^{29}Si NMR (CDCl$_3$, 600 MHz) δ, ppm: −56.93 (broad, SiMe).

Poly{methyl(*tert*-butoxycyclohexanoxy) siloxane} (15)

^{1}H NMR (CDCl$_3$, 200 MHz) δ, ppm: 0.13, 0.72(m), 1.32(m), 1.63(m), 1.94(m), 3.25(m), 3.81(m), −3.57(b). ^{13}C NMR (CDCl$_3$, 200 MHz) δ, ppm: 20.65, 25.35, 27.31, 31.86, 33.52, 35.62, 47.81, 47.91, 65.26, 70.60. ^{29}Si NMR (CDCl$_3$, 600 MHz) δ, ppm: −58.80 (broad, SiMe).

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