Communication

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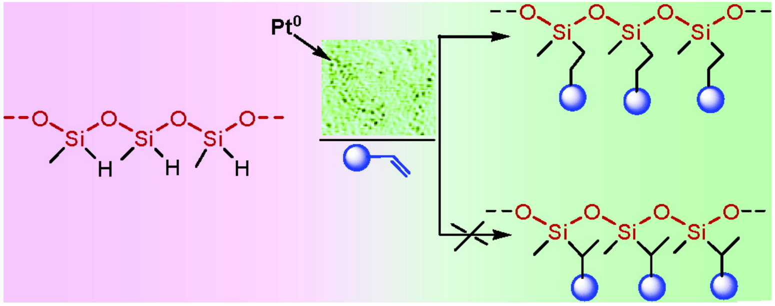

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Regioselective Synthesis of Multifunctional Hybrid Polysiloxanes Achieved by Pt−Nanocluster Catalysis

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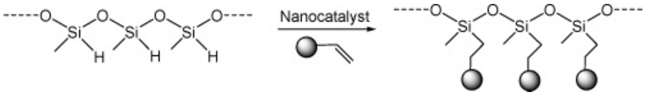
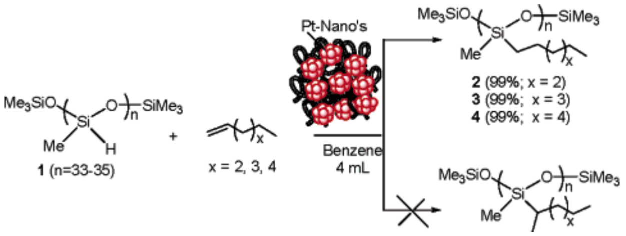
Combining inorganic and organic functionalities to form well-defined hybrid polymer composites[1−5] is a challenging task, and catalytic routes to such macromolecules are highly desirable. Poly(methylhydro)siloxane (PMHS) is an excellent inorganic template due to its availability in various molecular weight ranges and well-defined microstructures. Moreover, evenly distributed Si−H bonds in PMHS can be viewed as chemical handles on which organic groups can be catalytically attached to generate hybrid polymers not achievable by physical mixing of individual phases. Catalytic hydrosilylation, that is, the addition of Si−H bonds across the carbon−carbon multiple bonds, can be employed as a tool to organically tailor the silicones. Although selective hydrosilylation of monomeric species is well-documented,[6−8] selective hydrosilylation of polyhydrosiloxanes is a challenging task due to side reactions, such as redistribution of functional groups, self-dehydrocoupling, and cross-linking reactions to name a few.

Recently, our laboratory has been developing new strategies for the generation of catalytically active metal nanoclusters and successfully demonstrated their utility as potent catalysts for silaesterification[9] and chemoselective hydrogenation[10] reactions. Herein, we report the first example of "Pt"−nanocluster-catalyzed regioselective organic modification of PMHS to generate hybrid polymers (Scheme 1). In addition, we also probe Pt−nanoclusters as catalysts of choice for polyhydrosilylation reactions with a unique combination of reactivity, stability, selectivity, and recyclability.

Scheme 1. Modification of Silicones via Nanocluster Catalysis



Scheme 2. Pt−Nanocluster-Catalyzed Regioselective Modification of PMHS



To examine Pt−nanocluster-catalyzed hydrosilylation reactions of PMHS **1** (0.06 mL, 1.0 mmol; $M_w \sim 2000$), Pt−nanoclusters (0.01 g, 0.001 mmol Pt) and 1-hexene (0.13 mL, 1.0 mmol) were mixed together in 4 mL of benzene and stirred at room temperature (Scheme 2). After 1 h of the reaction, the colorless mixture gradually turned to homogeneous brownish−yellow solution, indicating the generation of soluble nanoclusters (see Supporting Information). The progress of the reaction was monitored with ^{1}H NMR spectroscopy, which revealed gradual disappearance of peaks associated with Si−H (δ 4.58) and olefinic protons (δ 4.8−5.9) and appearance of the new peaks in the methylene region (δ 0.4−1.2). Total disappearance of peaks associated with starting materials was observed after 20 h of the reaction. Isolation of product was carried out by the high-speed centrifugation (20 min) of reaction mixture, which led to precipitation of Pt−nanoclusters. After separation of the catalyst, evaporation of the solvent furnished polymer **2** as a viscous liquid. The molecular weight analysis by gel permeation chromatography (GPC) of **2** ($M_w \sim 4600$ and $M_w/M_n = 1.2$) was consistent with the proposed structure and in good agreement with the calculated value ($M_w \sim 4500$). Detailed NMR analysis of polymer **2** was carried out to elucidate the regiospecificity of the addition reaction (see Supporting Information). Since addition of Si−H bonds to alkene can take place either in an anti-Markovnikov (β-addition) fashion resulting in the silicon being attached at the terminal position or in a Markovnikov (α-addition) fashion resulting in silicon being attached at the iso position of the 1,2 alkene. ^{13}C NMR spectra of the solution revealed two new peaks at δ 23.31 ($-CH_2CH_2Si$) and δ 14.31 ($-CH_2CH_2Si$), indicating exclusive β-silylation of 1-hexene at terminal carbons. Furthermore, ^{29}Si NMR analysis of the reaction mixture showed only a single peak at δ −22.40 ($-CH_2SiMe$) corresponding to hexyl-substituted silicon centers beside the peak at δ −7.28 originating from the terminal $-OSiMe_3$ groups. The reaction was found to be quite general for other linear alkenes and provided corresponding β-adducts **3** and **4** very selectively.

Hydrosilylation of functionalized olefins is often accompanied by side reactions. For example, epoxy-containing olefins are susceptible to ring opening polymerization,[11] while carbonyl-bearing olefins often yield a mixture of C- and O-silylated products. Regioselectivity of organic incorporations into the silicones also plays a vital role in defining the property profile in terms of durability, flexibility, and film toughness of the composites.[12,13] In present catalysis, epoxy- and carbonyl-containing olefins were silylated with **1** without any side reactions. A high degree of regioselectivity was achieved by Pt−nanoclusters during the hydrosilylation of functional linear olefins. Regioselectivity of the product remained unaffected by varying the functional groups (carbonyl, ether, epoxide, and hydroxyl groups) on the olefins (Table 1).

A noticeable regioselectivity pattern was observed for the hydrosilylation of aromatic olefins with **1** (entries 6−8, Table 1). Hydrosilylation of styrene yielded polymer **10**, which was a mixture of regioisomers (β/α:55/45).[14] An improvement in the selectivity toward β-silylated product (β/α:65/35) was observed when 2-vinylnaphthalene was used. A further increase in the size of the aromatic ring by employing 9-vinylanthracene led to exclusive β-silylated polymer (entry 8, Table 1). It should be pointed out that polyhydrosilylation of vinylanthracene is not known.[15] In view

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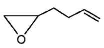
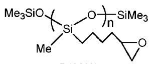
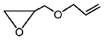
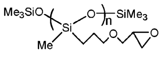
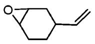
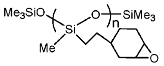
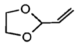
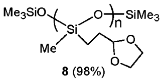
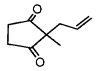
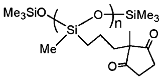
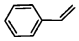
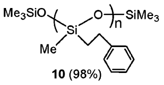
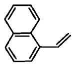
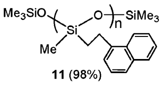
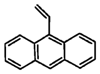
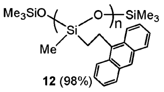
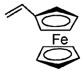
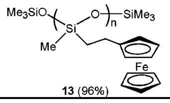
Table 1. Regioselectively Substituted Functional Polysiloxanes

Entry	Alkene	Conditions	Product	Ratio (β:α)
1		32h/RT	 **5** (98%)	99:traces
2		32h/RT	 **6** (98%)	99:traces
3		34h/RT	 **7** (98%)	99:traces
4		34h/RT	 **8** (98%)	99:traces
5		38h/RT	 **9** (92%)	99:traces
6		36h/RT	 **10** (98%)	55:45
7		72h/RT	 **11** (98%)	65:35
8		78h/RT	 **12** (98%)	95:traces
9		78h/RT	 **13** (96%)	98:traces

of widespread utility of the metal-containing polysiloxanes, reactions of metal-containing alkenes were also investigated. Reaction of vinylferrocene with PMHS **1** (entry 9) led to the corresponding β-addition product in near quantitative yield without any side reaction on the metallocene ring.

To gain insight into the catalysis, Transmission Electron Microscopy (EM) studies and UV−vis studies were performed during the catalysis. Thus, during the catalysis (typically after 2 h of reaction), one drop of solution was deposited on a Formvar-coated carbon grid and examined by TEM. Pt−nanoclusters in the size-regime of 1−3 nm were found to be present in the reaction mixture. Additionally, UV−vis analysis of the reaction mixture was performed at regular intervals and showed featureless spectra, a characteristic of Pt−nanoclusters.[16]

Recyclability of the catalyst was also investigated after washing the separated catalyst with benzene and recharging the Schlenk with reactants (entry 6, Table 1). A comparable catalytic activity and selectivity was observed. The same batch of catalyst was investigated for seven runs and always yielded the desired product with almost the same regiospecificity and activity (Figure 1).

In conclusion, PMHS backbone was regiospecifically tailored with a fair number of sterically and electronically varied alkenes to furnish hybrid polysiloxanes under mild conditions. A high degree of activity, selectivity, and recyclability was achieved in the presence of the Pt−nanocluster catalyst. In situ analysis of the reaction mixtures with various spectroscopic techniques strongly supports active participation of Pt−nanoclusters as the real catalyst during the transformations. Research is underway to study nanocluster catalysis on various polymer templates, which may lead to polymers with desired densities of one or more functional groups for custom designing of specialty polymer systems.

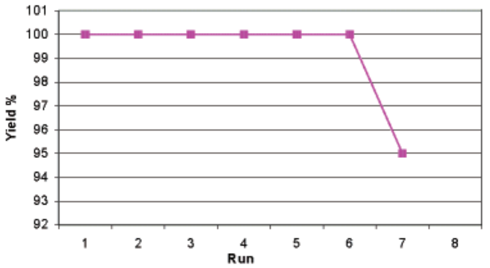


Figure 1. Recyclability studies (product was identified but not isolated).

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Supporting Information Available: Experimental details, NMR and TEM analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) In a comparative experiment, (cod)PtMe$_2$ (precursor) catalyzed hydrosilylation of styrene was examined under identical reaction conditions and molar ratios at room temperature. After 36 h, only 16% (β/α: 50/50) conversion to product was observed by ^{1}H NMR spectroscopy. Under the identical conditions and molar ratios, total conversion to product was achieved when Pt−nanoclusters were used as catalyst.

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