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Silyl Functionalization of Polyolefins

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Synthetic modification of polymers by introducing the functional groups is an efficient strategy to generate new materials with enhanced or specific physical and chemical properties.[1] In particular, the functionalization of diene-based polymers has generated intense interest, due to the availability of double bonds for various transformations such as oxidation,[2] epoxidation,[3] hydroboration,[4] and hydroformylation.[5] Similarly, the hydrosilylation reaction of unsaturated polymers offers a useful and convenient method for preparing silane-modified polymers which may find potential applications as rubber materials, adhesives and drug delivery agents.[6,7] Significant advances in this area have been made by groups of Rempel[8] and Cole-Hamilton,[9] who have investigated the hydrosilylation reactions of polybutadienes in the presence of $RhCl(PPh_3)_3$ and H_2PtCl_6 catalysts to generate silasubstituted polymers.

Recent disclosures from our laboratory have introduced new strategies for the generation of catalytically active metal nanoclusters and their utility as potent recyclable catalysts for various transformations.[10−12] To the best of our knowledge, metal nanocluster catalyzed functionalization of carbon-based polymers has not been reported in the literature. In this communication, we describe a first example of a highly selective, mild, and clean synthetic route to silyl-functionalized organic polymers by hydrosilylation of polybutadiene (PBD) using readily synthesized and recyclable Pt nanoclusters as catalysts.

Initial investigations of Pt nanoclusters catalyzed hydrosilylation reactions of **PBD-1** were examined in the presence of four model hydrosilanes **2a**−**2d** (Scheme 1). In an optimized procedure, a Schlenk tube was charged with presynthesized Pt nanoclusters (0.01 g, 0.001 mmol Pt),[12] and then filled with nitrogen. The **PBD-1** (0.054 g, 1 mmol) dissolved in dry benzene (2 mL) was added to the Schlenk followed by injection of **2a** (0.13 mL, 1.2 mmol) under a constant flow of nitrogen. After few minutes of stirring, the reaction mixture turned into light brown homogeneous solution, indicating the formation of soluble nanoclusters.[12] The progress of the reaction was monitored by ^1H NMR spectroscopy. After the completion of the reaction, the solid catalyst was separated by centrifugation. The filtrate was evacuated to obtain the crude product, which was purified by passing through the silica gel column (hexane). The pure product thus obtained was analyzed by GPC and ^1H, ^{13}C, DEPT, ^{29}Si NMR spectroscopies.

Gel permeation chromatography (GPC) was used to determine the molecular weight and chain length properties of functionalized polymers with reference to polystyrene standards (Figure 1). The GPC chromatograms of the products have clearly been shifted toward the high molecular weight region, while retaining a narrow molecular weight distribution ($M_w/M_n \sim 1.4−1.5$). This analysis confirmed that no other side reactions such as chain scission, cross-linking, etc. occurred during the course of the hydrosilylation reaction, leaving the large-scale molecular structure intact.

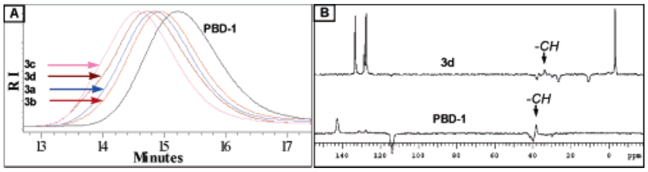
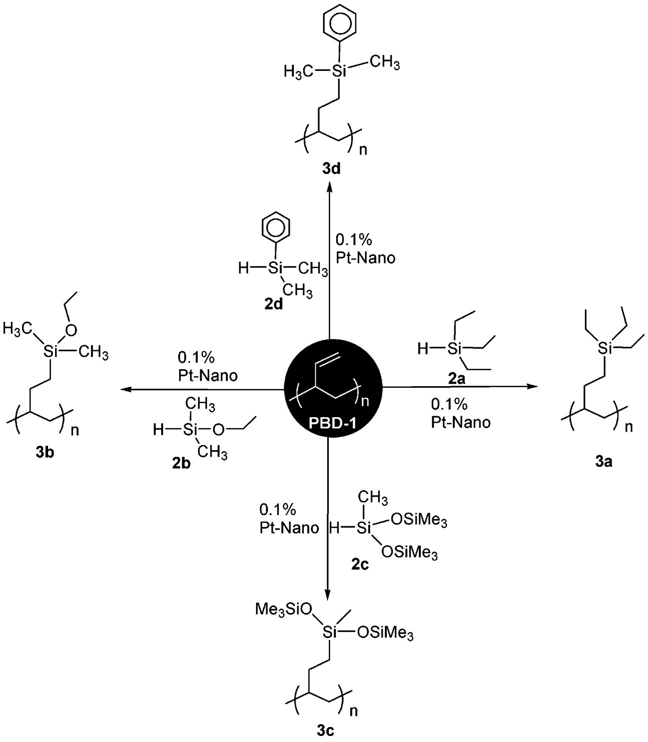
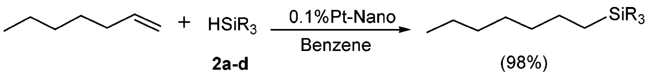


Figure 1. (A) GPC traces of the **PBD-1** and Polymers **3a**, **3b**, **3c**, and **3d** and (B) ^{13}C (DEPT) NMR spectra of **3d** and **PBD-1**.

Scheme 1. Hydrosilylation of 1,2-Polybutadiene



Scheme 2. Hydrosilylation of 1-Heptene Using Pt Nanoclusters



The structure and regioselectivity of functionalized polymers **3a**−**3d** were determined by ^1H, ^{13}C, DEPT and ^{29}Si NMR studies (Figure 1). ^1H and ^{13}C NMR studies of the products suggested that the hydrosilylation of **PBD-1** occurs selectively via an anti-Markovnikov addition, i.e., the Si-atom being attached at the terminal position of the 1,2-PBD unit (β-product). Particularly noteworthy is the hydrosilylation of **PBD-1** with silane **2d**, since silane **2d** is known to be more susceptible to provide the *Markovnikov product* as demonstrated in the presence of $RhCl(PPh_3)_3$.[8] However, the Pt nanocluster catalyzed reaction of **PBD-1** with silane **2d** still led to quantitative formation of the desired hydrosilylated product in *anti-Markovnikov* fashion.

The ^{13}C NMR was used to differentiate between α and β isomers of the hydrosilylated polymer by using the distortionless enhancement by polarization transfer (DEPT) technique. The

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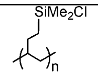
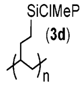
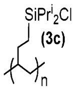
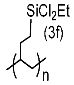
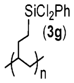
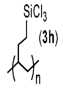
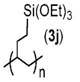
Table 1. Hydrosilylation of 1,2-Polybutadiene Using Pt Nanoclusters[a]

Silane	Product	Rx. Conditions	Yield (%)[b]	^{29}Si (δ) Silane/Poly
HSiMe$_2$Cl (**2e**)	 (**3e**)	25°C/16h	98	^{1}**HNMR** {CDCl$_3$, δ (ppm)} 0.07 (s, 6H), 0.0-2 (br, 7H); ^{13}**CNMR/DEPT:** 1.62 (-Si*CH*$_3$), 14.37 (-CH$_2$*CH*$_2$Si-), 26.1(-*CH*$_2$CH$_2$Si-), 33.6(-*CH*CH$_2$-), 38.1 (-CH*CH*$_2$-); ^{29}**SiNMR** (CDCl$_3$, 600 MHz, δ (ppm)}: 32.97.
HSiPhMeCl (**2f**)	 (**3d**)	70°C/24h	98	^{1}**HNMR** {CDCl$_3$, δ (ppm)}: 7.45, 7.23 (m, 5H), 0.49 (s, 3H), 0.0-2.0 (br, 7H); ^{13}**CNMR/DEPT**: 0.26 (-Si*CH*$_3$), 13.52 (-CH$_2$*CH*$_2$Si-), 25.83 (-*CH*$_2$CH$_2$Si-), 33.43 (-*CH*CH$_2$-), 37.86 (-CH*CH*$_2$-), 128.06 (-Si*Ph*), 130.27 (-Si*Ph*), 133.27 (-Si*Ph*), 135.24 (-Si*Ph*); ^{29}**SiNMR** {CDCl$_3$, 600 MHz, δ (ppm)}: 22.17.
HSiPr$^{i}_{2}$Cl (**2g**)	 (**3c**)	70°C/24h	98	^{1}**HNMR** {CDCl$_3$, δ (ppm)}: 0.36 (m, 14H), 0.0-2 (br 7H); ^{13}**CNMR/DEPT**: 8.05 (-CH$_2$*CH*$_2$Si-), 13.73 (-Si*CH*(CH$_3$)$_2$), 16.99 (-SiCH(*CH*$_3$)$_2$), 25.8 (-*CH*$_2$CH$_2$Si-), 33.93(-*CH*CH$_2$-), 37.61(-CH*CH*$_2$-); ^{29}**SiNMR** {CDCl$_3$, 600 MHz) δ (ppm)}: 36.8.
HSiCl$_2$Et (**2h**)	 (3f)	45°C/24h	98	^{1}**HNMR** {CDCl$_3$, δ (ppm)}: 0.91 (m, 14H) 0.0-2 (br, 7 H); ^{13}**CNMR/DEPT**: 6.16 (-Si*CH*$_2$CH$_3$), 12.52 (-SiCH$_2$*CH*$_3$), 15.52 (-CH$_2$*CH*$_2$Si-), 25.37 (-*CH*$_2$CH$_2$Si-), 33.0 (-*CH*CH2-), 37.7(-CH*CH*$_2$-); ^{29}**SiNMR** {CDCl$_3$, 600 MHz, δ (ppm)}: 35.84
HSiCl$_2$Ph (**2i**)	 (**3g**)	80°C/24h	95	^{1}**HNMR** {CDCl$_3$, δ (ppm)}: 7.39 (m, 3H), 7.62 (m, 2H), 0.0-2.0 (br, 7H). ^{13}**CNMR/DEPT**: 16.58(-CH$_2$*CH*$_2$Si-), 25.47 (-*CH*$_2$CH$_2$Si-), 33.18 (-*CH*CH$_2$-), 37.86 (-CH*CH*$_2$-), 128.34 (-Si*Ph*), 131.66 (-Si*Ph*), 132.28 (-Si*Ph*), 133.29 (-Si*Ph*); ^{29}**SiNMR** {CDCl$_3$, 600 MHz, δ (ppm)}: 20.24.
HSiCl$_3$ (**2j**)	 (**3h**)	25°C/24h	98	^{1}**HNMR** {CDCl$_3$, δ (ppm)}: 0.4-2.0 (br, 7H); ^{13}**CNMR/DEPT**: 20.2 (-CH$_2$*CH*$_2$Si-), 25.76(-*CH*$_2$CH$_2$Si-), 32.97 (-*CH*CH$_2$-), 37.83 (-CH*CH*$_2$-). ^{29}**SiNMR** {CDCl$_3$, 600 MHz, δ (ppm)}: 13.59
HSi(OEt)$_3$ (**2k**)	 (**3j**)	65/24h	98	^{1}**HNMR** {CDCl$_3$, δ (ppm)}: 3.75 (q, 6H), 1.14 (t, 9H), 0.0-2.0 (br, 7H); ^{13}**CNMR/DEPT:** 17.93 (-OCH$_2$*CH*$_3$), 5.58 (-CH$_2$*CH*$_2$Si-), 25.39 (-*CH*$_2$CH$_2$Si-), 33.7 (-*CH*CH$_2$-), 37.66 (-CH*CH*$_2$-), 57.85 (-O*CH*$_2$CH$_3$); ^{29}**SiNMR** {CDCl$_3$, 600 MHz): δ (ppm)}: -44.07.

[a] Conditions: [PBD-1] = 1.0 mmol; [silane] = 1.2 mmol; Pt-nanocluster = (0.010 g). Solvent: benzene. [b] Yields are based on isolated products.

selectivity toward β-product was verified for all the products by the DEPT technique. For instance, the DEPT spectrum of **3d** (Figure 1) shows one upward resonance at 33.70, which can be assigned to the methine carbon (CH), and three downward signals at 10.76, 26.72, and 37.85 are attributed to the three methylene (CH$_2$) carbons of polymer backbone of the β-product. This experiment clearly indicates the highly regioselective formation of the β-product, since the α-isomer would have generated two methine, one methylene carbon and one methyl group.

The regioselectivity of the products was further established by comparing the spectroscopic results with the hydrosilylation reaction of 1-heptene using four model silanes, **2a**−**2d** (Scheme 2). The ^{1}H, ^{13}C and ^{29}Si NMR analysis of hydrosilylation of 1-heptene showed formation of corresponding β-products and were in good agreement with those of hydrosilylated polymers.

For example, the hydrosilylation of **PBD-1** using silanes **2a**, **2b**, **2c**, and **2d** gave single ^{29}Si resonances at 7.06, 18.01, 7.02/−20.36, and −1.7 ppm, respectively (Figure 2), which are

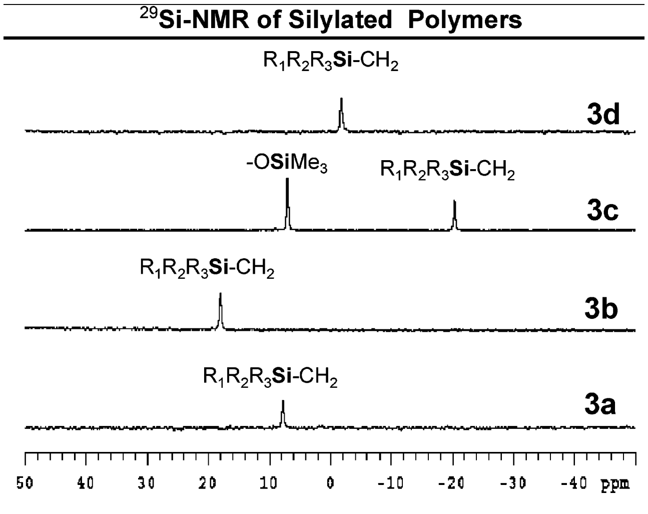


Figure 2. ^{29}Si NMR spectra of **3a**, **3b**, **3c**, and **3d**.

comparable to the Si shifts observed for the β-hydrosilylated 1-heptene (7.7, 17.46, 6.94/−21.05, −2.66). The ^{29}Si NMR, with only one detectable ^{29}Si resonance (Figure 2) in conjunction with ^{13}C NMR experiments, confirmed the high regioselectivity of these reactions toward formation of the β-adduct.

To widen the scope of hydrosilylation of polybutadienes, we have screened a variety of functional silanes, **2e**−**2l** (Table 1). Almost complete functionalization (95−98%) of the 1,2-vinyl groups of the polymer was achieved with variety of chloro- and trialkylsilanes. Regardless of the nature of the silanes, all the catalytic reactions led to high yields and selectivity to corresponding β-products as evidenced by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy.

To evaluate the stability and reactivity of Pt nanoclusters, we investigated the recyclability studies for several cycles. In every recycle, the catalyst was separated and recovered by centrifugation, washed thoroughly with fresh benzene, and dried under vacuum. We found a consistent activity and selectivity up to five recycles. The solvent effect has also been studied for the hydrosilylation of **PBD-1** using different solvents. The nonpolar solvents such as benzene, toluene, and hexane and polar solvents such as dichloromethane, ether, and chloroform were found to be equally efficient for the hydrosilylation of **PBD-1.** Exceptionally, the solvent THF (tetrahydrofuran) has shown only 50% hydrosilylation even after long reaction periods.

In view of the above-described results, the present method offers a highly efficient synthetic route to silyl-functionalized polymers in terms of high yields, selectivities, avoidance of side reactions and ease of product separation and purification. Additional investigations into their morphological studies and subsequent modifications of these polymers by other transformations are currently underway.

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Supporting Information Available: Text giving the general experimental data and data for the preparation of the Pt nanocluster catalyst, general procedure for the hydrosilation of the polybutadienes, and NMR analysis of **3a**−**3k** (including structural drawings of **3a**−**3k**). This material is available free of charge via the Internet at http://pubs.acs.org.

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