Macromolecules

Volume 23, Number 24 November 26, 1990

Catalytic Hydrosilylation of Diene-Based Polymers. 1. Hydrosilylation of Polybutadiene

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Received January 3, 1990; Revised Manuscript Received April 30, 1990

ABSTRACT: The chemical modification of unsaturated polymers via catalytic hydrosilylation offers an efficient synthetic route to novel polymers containing silane functional groups. A study involving the hydrosilylation of polybutadiene polymers has been carried out in the presence of $RhCl(PPh_3)_3$. Under mild reaction conditions, $RhCl(PPh_3)_3$ is highly selective toward catalyzing the hydrosilylation of the vinyl C=C bonds of the polymers. The degree of hydrosilylation can be controlled by appropriate adjustment of the [silane]:[C=C] ratio. In the case of alkyl- and alkoxysilanes, the reaction mechanism involves an anti-Markovnikov addition leading to a linear adduct. The microstructure of the product polymers was characterized by IR, ^1H NMR, ^{13}C NMR, and ^{29}Si NMR. In addition, vapor phase osmometry and gel permeation chromatography were used to determine the chain-length properties of the product polymers.

Introduction

Chemical modification of polymers has recently emerged as a field of increasing importance in macromolecular chemistry. It is considered as an efficient alternative synthetic route to novel polymers with desirable physical properties and functional groups, which are otherwise inaccessible, difficult or too expensive to prepare by conventional polymerization techniques.

Unsaturated polymers, especially diene polymers, are ideal polymers for chemical modification because of the technological importance associated with the parent materials and the reactivities of the double bonds in the polymer chain. A variety of such possibilities have been explored by Schulz, Turner, and Golub.[1] A particularly interesting reaction involves the hydrosilylation of diene polymers to obtain a silane-modified rubber material. This reaction has potential application since silane-modified rubber has been claimed to show improved adhesion to fillers and better heat resistance and to serve as a reactive substrate for grafting or moisture-catalyzed room-temperature vulcanization.[2-5] More recently, hydrosilylation has been used to prepare polymers with special properties.[6,7] In 1986, Lien and Humphreys patented a process for preparing polyphotoinitiators by hydrosilylating unsaturated polymers with silane-bearing photoinitiating groups.[8] At the same time, Fontanille and coworkers reported a method for the preparation of polymers with enhanced conductivity by utilizing hydrosilylation of unsaturated polymers.[9]

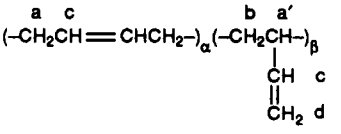
Although there have been only a few papers published on the hydrosilylation of polymers,[6] a considerable number of patents have been granted.[2,3,5,7-12] In most of the cases, Pt complexes were used and the hydrosilylation took place on the chain end groups. There appears to be no detailed characterization of the hydrosilylated polymers reported. Our own particular interest has involved the hydrosilylation of polybutadiene (PBD) catalyzed by chlorotris(triphenylphosphine)rhodium(I) and the characterization of the microstructure of the product polymer by IR, ^1H NMR, ^{13}C NMR, and ^{29}Si NMR. In addition, vapor phase osmometry (VPO) and gel permeation chromatography (GPC) were used to determine the chain-length properties of the product polymers.

Experimental Section

Apparatus. For the reaction between gaseous silane and PBD, a constant-pressure gas uptake system previously described[13] was used. For the reactions between other silanes and PBD, a three-neck flask with an argon inlet and outlet and a condenser was used together with a magnetic stirrer and a heating mantle.

Materials. Toluene (Fisher Scientific & Allied Co.) was treated with 4-Å molecular sieves. *o*-Dichlorobenzene (Aldrich) was stored under argon in the dark. All liquid silanes (Aldrich) were stored under nitrogen. $RhCl(PPh_3)_3$ was prepared by the reaction of rhodium trichloride trihydrate (Johnson Matthey Chemicals Limited) with excess freshly recrystallized triphenylphosphine (Aldrich) in hot ethanol under nitrogen.[14]

Three different PBD polymers having the basic structure as shown in I were used for this study where α represents the mole



I

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fraction of 1,4-addition units in PBD polymer and β represents the mole fraction of 1,2-addition units, and a, a', b, c, and d represent protons in five different chemical environments.

The three PBD polymers used were as follows:

(A) M_n = 4500; terminal vinyl content (or 1,2-addition units) $\cong$ 45%, obtained from Aldrich; i.e., α = 0.55, β = 0.45.

(B) M_n = 10 000; terminal vinyl content (or 1,2-addition units) $\cong$ 90%, obtained from Goodyear Tire and Rubber Co.; i.e., α = 0.10, β = 0.90.

(C) M_n = 30 000; terminal vinyl content (or 1,2-addition units) $\cong$ 90%, obtained from Goodyear Tire and Rubber Co.; i.e., α = 0.10, β = 0.90.

Polymer Characterization. Infrared Spectroscopic Analysis. The IR spectra were recorded on a Perkin-Elmer 1330 infrared spectrophotometer. The samples were prepared by casting polymer films on sodium chloride plates.

NMR Spectroscopic Analysis. The ^1H NMR spectra were obtained by using a Bruker AM 250-MHz instrument. $^{29}Si\{H\}$ NMR spectra were recorded on a Bruker WH 400-MHz instrument operating at 79.51 MHz over the range of −196.5 to 196.5 ppm; TMS was used as external reference standard (0.00 ppm). ^{13}C NMR spectra were recorded with a Bruker WH 400-MHz spectrometer at 100.6 MHz and a Bruker AM 250-MHz instrument at 62.8 MHz; in most of the cases, proton-noise-decoupled mode was used with the attached proton test (APT)[15] to identify the various ^{13}C as methyl, methine, methylene, and quaternary carbons. All the analyses were carried out in $CDCl_3$ solvent.

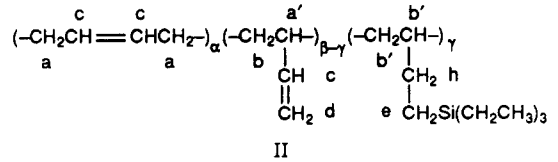
Vapor Phase Osmometry (VPO). The number-average molecular weights of polymers with M_n < 70 000 were determined by using a Model 232A molecular weight apparatus, Wescan Instruments, Inc. (3018 Scott Blvd., Santa Clara, CA 950950). Toluene was used as solvent and the instrument was calibrated by using polystyrene of M_n 9000 and 20 400.

Gel Permeation Chromatography (GPC). The gel permeation chromatograms were obtained by using a Waters GPC ALC/301 instrument. The conditions used were as follows: solvent, tetrahydrofuran; column, Styragel; permeability range, 10^3–10^6; temperature, 25 °C; detector, differential refractometer.

Synthetic Method. The hydrosilylation of polybutadienes was carried out in toluene in a three-neck flask with an argon inlet and outlet and a condenser, under the following conditions: [C=C] = 300–740 mM, T = 109–110 °C, toluene = 30–50 mL, [$RhCl(PPh_3)_3$] = 0.54–1.08 mM, [$HSiR_3$] = 100–600 mM (the concentration of $HSi(CH_3)_3$ is not in this range), reaction time = 10–20 h; $HSiR_3$ = 1, $HSi(CH_2CH_3)_3$; **2** (*o*-dichlorobenzene was used as a solvent for this gas consumption reaction since it has a boiling point of 178 °C), $HSi(CH_3)_3$; **3**, $HSi(CH_2CH_2CH_2CH_3)_3$; **4**, $HSi(OCH_2CH_3)_3$; **5**, $HSi(C_6H_5)(CH_3)_2$.

On termination of the reactions, the product polymers were precipitated from methanol under N_2 and dried in vacuo for more than 15 h before being subjected to further analyses.

Determination of the Degree of Hydrosilylation (γ). The extent of hydrosilylation, which was estimated from the integration of ^1H NMR spectra, was further confirmed by elemental analysis. One example of this calculation for product polymer II is given as follows:



II

a, a', b, b', c, d, e, and h are eight types of protons in different chemical environments. The degree of unsaturation, ζ, for the starting PBD (I) is calculated as in eq 1.

$$\zeta = \frac{\text{integration of olefinic protons}}{\text{integration of (aliphatic protons + olefinic protons)}} \quad (1)$$

$$\zeta = \frac{2\alpha + 3\beta}{2\alpha + 3\beta + 4\alpha + 3\beta} \quad (1')$$

Similarly, the degree of the unsaturation, η, of the hydrosilylated polymer II can be calculated as in eq 2.

$$\eta = \frac{\text{integration of olefinic protons}}{\text{integration of (olefinic protons + aliphatic protons)}} \quad (2)$$

$$\eta = \frac{2\alpha + 3(\beta - \gamma)}{2\alpha + 3(\beta - \gamma) + 4\alpha + 3\beta} \quad (2')$$

e and h types of aliphatic protons and the protons in the triethylsilane group were not included since they can be integrated separately from the aliphatic protons from the main chain. Therefore the degree of hydrosilylation, γ, can be calculated from the rearrangement of eq 2 providing that η can be obtained from the integration results:

$$\gamma = \frac{(6\alpha + 6\beta)\eta - 2\alpha - 2\beta}{3\eta - 3} \quad (3)$$

With known γ, the amount of carbon, hydrogen, and silicon elements in polymer II can be calculated from eqs 4–6

$$C\% = \frac{(4\alpha + 4(\beta - \gamma) + 10\gamma)(12)}{M_0} \quad (4)$$

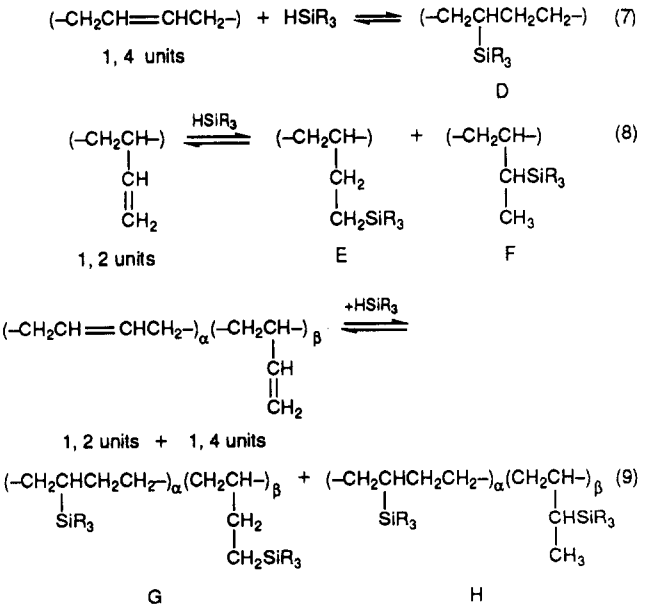
$$H\% = \frac{(6\alpha + 6(\beta - \gamma) + 22\gamma)(1)}{M_0} \quad (5)$$

$$Si\% = 100\% - C\% - H\% \quad (6)$$

where M_0 is the unit molecular weight of the hydrosilylated polymer.

Results and Discussion

As shown in eqs 7–9 the addition of silane functional group to PBD can potentially occur in three different ways, which results in the formation of five types of hydrosilylated microstructures in the polymer chain as shown by species D–H:



Species D is formed when the hydrosilylation only occurs on the 1,4-addition units. Species E is an anti-Markovnikov addition product, and species F is a Markovnikov addition product resulting from hydrosilylation, which takes place only on the terminal C=C bonds in PBD. Structures G and H are formed when both the internal C=C bonds and the terminal C=C bonds are attacked by the silane.

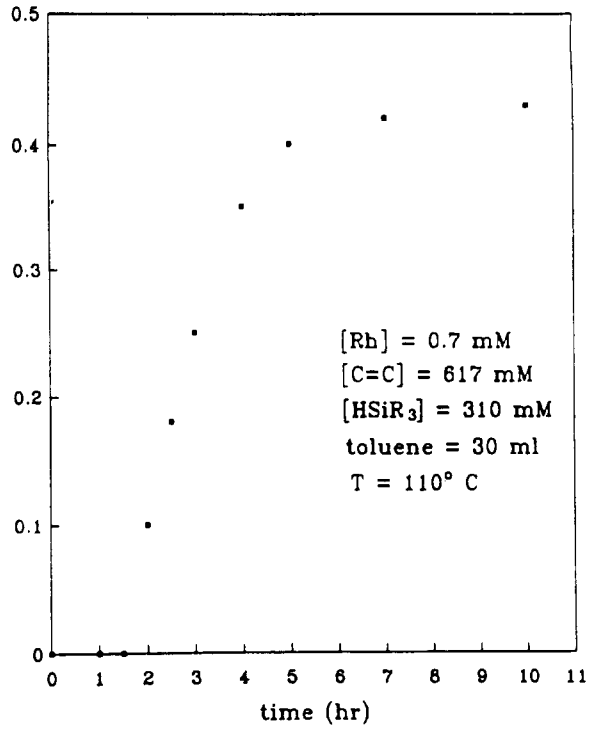


Figure 1. Hydrosilylation of PBD (A) with $HSi(C_2H_5)_3$ (1) catalyzed by $RhCl(PPh_3)_3$.

Hydrosilylation of PBD Using Silanes 1–4. The reaction between PBD (A) and 1 (triethylsilane) catalyzed by $RhCl(PPh_3)_3$ was followed by ^1H NMR analysis of samples taken during the course of reaction (see Figure 1). There was an induction period of about 1.5 h, followed by a very rapid reaction, which achieved more than 30% hydrosilylation in the following 1.5 h. After that the reaction became much slower. After 10 h the total hydrosilylation achieved was about 43%. It was believed that the increased loading of the triethylsilane group in the polymer chain could cause a change in the mobility of the polymer chain as well as a change in the electronic microenvironment of the C=C of the polymer, thus leading to a decrease in hydrosilylation rate. The decrease of the silane concentration in the solution could also be an important factor influencing the decrease in hydrosilylation rate. However, further addition of 1 to the reaction system did not increase the degree of hydrosilylation. This suggests that $RhCl(PPh_3)_3$ under the reaction conditions used only catalyzed the hydrosilylation of the monosubstituted vinyl double bonds of PBD (A). This is consistent with the observed results for the hydrosilylation of small olefin molecules.[16-19] It was reported that the reaction of 1 with 2-pentene was very much slower than with 1-pentene,[16] and there was no hydrosilylation on the C=C bonds of cyclohexene.[17]

The reaction of 1 with PBD was found to be much slower than that of small olefin molecules. For 1-pentene, the hydrosilylation degree achieved was 80% in 2 h under comparable reaction conditions.[16] It is considered that the lower reactivity of PBD toward hydrosilylation is due to the steric effect of the bulky polymer chains. Similar results were obtained for the hydrosilylation of polymers B and C.

The IR spectra of PBD (A) and the corresponding hydrosilylated polymer using 1 are given in parts a and b of Figure 2, respectively. Figure 2b shows a complete disappearance of the absorbances due to the terminal C=C bonds (3100 and 910 cm^{-1}). There are also new absorbances at 1235 cm^{-1} due to CH_2 wagging and at 1410 cm^{-1}

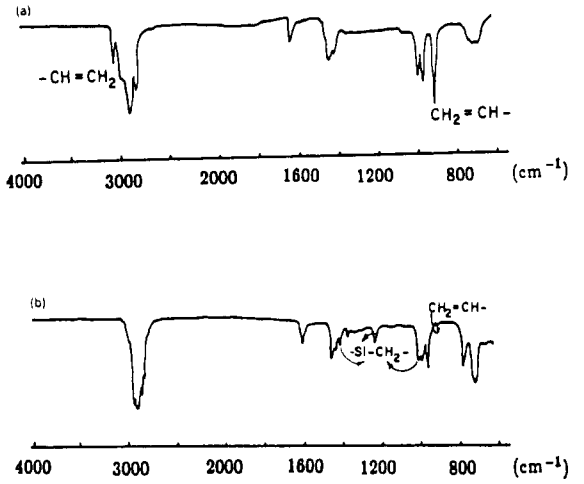


Figure 2. (a) IR spectrum for PBD (A). (b) IR spectrum for "PBD (A) + $HSi(C_2H_5)_3$ (1)" product.

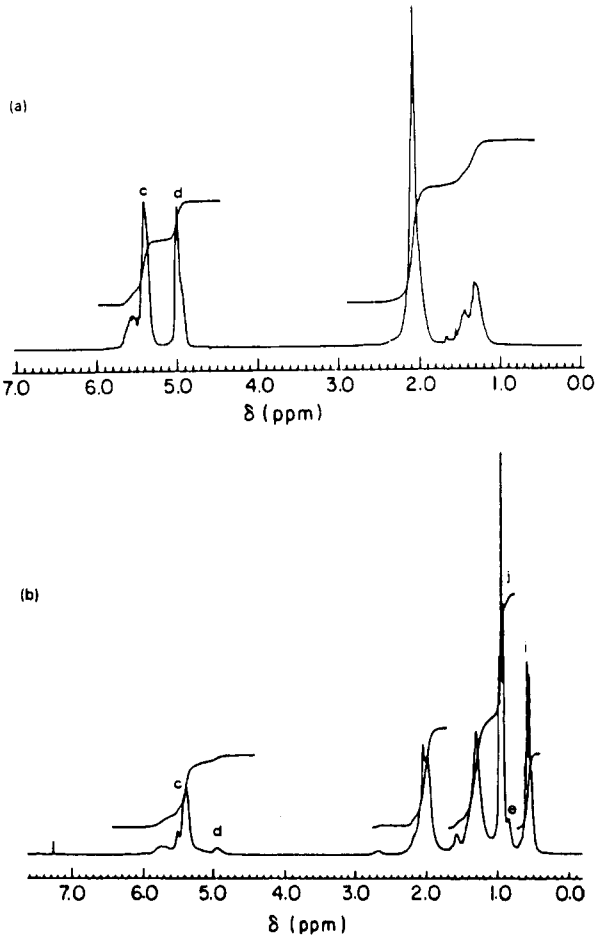


Figure 3. (a) ^1H NMR spectrum for PBD (A). (b) ^1H NMR spectrum for "PBD (A) + $HSi(C_2H_5)_3$ (1)" product.

due to CH_2 scissoring for the $-SiCH_2-$ structure in the hydrosilylated polymer. The ^1H NMR spectra for PBD (A) and the hydrosilylated PBD (A) using 1 are shown in parts a and b of Figure 3. The calculation based on integration, showed 43% hydrosilylation. The disappearance of the resonance centered at 5.0 ppm ($-CH=CH_2$) suggests that the hydrosilylation takes place only on 1,2 units, thus eliminating D, G, and H as possible product polymers. The methylene and methyl protons of a triethylsilyl group appear at 0.5 ppm (polymer-$SiCH_2-$) and 0.93 ppm (polymer-$SiCH_2CH_3$) as a quartet and a triplet, respectively. The small peak at 0.83 ppm is believed to be the signal for the methylene protons of the polymer-CH_2SiR_3

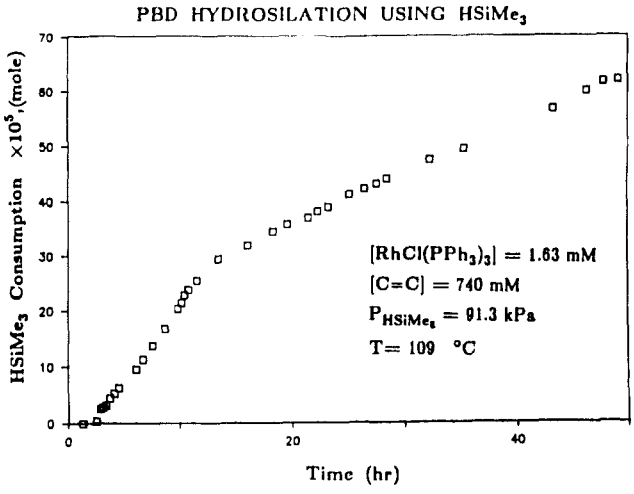


Figure 4. Gas uptake plot for the reaction between PBD (A) and $HSi(CH_3)_3$ (2) catalyzed by $RhCl(PPh_3)_3$.

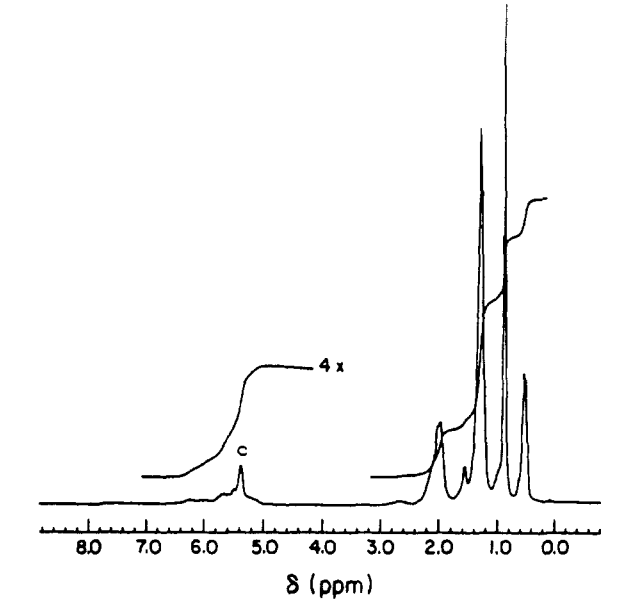


Figure 5. ^1H NMR spectrum for "PBD (A) + $HSi(n\text{-}Bu)_3$ (3)" product.

structure (E) or the methine proton of polymer–C*H*-$(CH_3)SiR_3$ structure (F).

To investigate the steric effect of the alkyl group of the silanes, **2** (trimethylsilane) and **3** (tri-*n*-butylsilane) were used to react with PBD (A). In Figure 4, a gas uptake plot for the reaction between PBD (A) and **2** is shown. The reaction had an induction period of about 2.0 h and then proceeded at a relatively slow speed. After achieving about 4% of hydrosilylation in about 10 h, the reaction became very slow and it only achieved about 9% of hydrosilylation in 50 h of reaction. The real reason(s) for the unusually slow reaction between trimethylsilane and PBD is not clear. However the reduced concentration of the $HSi(CH_3)_3$ due to its solubility relative to the higher concentration of other liquid silanes could be one of the reasons. Another possible reason for the very slow reaction rate of trimethylsilane with PBD could be due to the fact that $(PPh_3)_2RhHSi(CH_3)_3Cl$ has a low equilibrium concentration at the reaction temperature of 109 °C. It has been reported that the complex $(PPh_3)_2RhHSi(CH_3)_3Cl$ decomposed completely on heating at 100 °C, giving trimethylsilane and $\{(PPh_3)_2RhCl\}_2$.[18] Figure 5 shows the ^1H NMR spectrum for the product polymer obtained from the reaction between PBD (A) and **3**. There is no resonance at 5.0 ppm (–CH=CH_2), and the integration shows about 45% hydrosilylation after 12 h of reaction for this product polymer. This suggests that the relatively bulky *n*-butyl group in the silane probably has no significant effect on the hydrosilylation rate and the reaction mechanism.

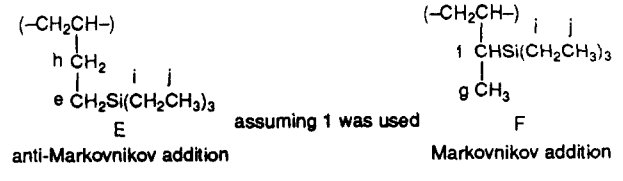
The reaction between PBD (A) and **4** (triethoxysilane) seemed to be much slower relative to that observed for the alkylsilanes as shown in Table I. Under the same reaction conditions as those in the reaction between **1** and PBD (A), this reaction only achieved 25% hydrosilylation ($\gamma = 0.25$) in 20 h. After being precipitated out from solution, this product polymer cross-links even under vacuum.

It was reported that the ease with which addition of silane to C=C takes place can be related to the stability of the corresponding hydrido(silyl)rhodium(III) complex formed.[20] The reactivity of the silane decreases with increasing stability of the respective hydrido(silyl)rhodium-(III) complex. Thus it is believed that the possible reason for the lower reactivity of triethoxysilane is due to the greater stability of its hydrido(silyl)rhodium(III) complex compared with that of alkylsilanes.[16,20]

Figure 6 shows the ^1H NMR spectrum for the product polymer obtained from this reaction. In comparison with the ^1H NMR spectrum for PBD (A) in Figure 3a, it can be seen that there is an obvious decrease in the intensity of the resonance at 5.0 ppm for the methylene protons (–CH=CH_2) of the terminal C=C bonds. The integration of the resonances at 5.0 and 5.5 ppm suggests that the hydrosilylation only occurred on the terminal C=C bonds. The characteristic resonance of the methylene protons in the polymer–$SiOCH_2CH_3$ group is centered at 3.8 ppm as a quartet. The triplet centered at 1.25 ppm is assigned to the methyl protons in the polymer–$SiOCH_2CH_3$ group. Part of the resonances of the aliphatic protons in the product polymers were also buried under this triplet. The signal for the methylene or methine proton(s) in polymer–$CH_2Si(OC_2H_5)_3$ or polymer–$CH(CH_3)Si(OC_2H_5)_3$ is attributed to the small peak at 0.82 ppm.

Some representative results for the catalytic hydrosilylation of polybutadiene are listed in Table I. It is found that, in most cases, quantitative hydrosilylation can be achieved for the terminal vinyl content in the polymers. This suggests that it is possible to control the degree of hydrosilylation by controlling the [silane]:[C=C] ratio. Elemental analysis results shown in Table I are in reasonably good agreement with the values calculated from the degree of hydrosilylation (γ).

The IR and ^1H NMR spectra discussed above indicate that the addition of silanes (1–4) to PBD polymers only occcurred on the terminal C=C bonds. However, two possibilities exist for the mode of addition of the silane to these terminal C=C bonds; i.e., a Markovnikov addition mechanism or an anti-Markovnikov addition mechanism:



The $^{13}C\{H\}$ NMR for the hydrosilylated polymer from the reaction between PBD (A) and **1** is shown in Figure 7. With the help of proton-coupled spectrum and attached proton test (APT) technique,[15] the resonance at 11 ppm is assigned to the methylene carbon (e carbon in structure E). The resonance at 3.6 ppm is due to methylene carbon i. The methyl carbon j is characterized by a resonance at 7.4 ppm. There is no resonance for carbon f, which

Table I
Representative Results for the Hydrosilylation of PBD by $RhCl(PPh_3)_3$[a]

polymer	silane	silane/[C=C]	hydrosilylation degree γ	elem anal. % calcd C	calcd H	calcd Si	found C	found H	found Si
PBD (A)	1, $HSi(C_2H_5)_3$	0.5	43.0	75.9	11.4	12.7	77.5	11.9	11.6
PBD (A)	1, $HSi(C_2H_5)_3$	0.3	30.0	79.3	12.0	8.7	80.8	11.1	8.1
PBD (A)	1, $HSi(C_2H_5)_3$	1.0	*b*	*c*	*c*	*c*	*c*	*c*	*c*
PBD (A)	2, $HSi(CH_3)_3$	*c*	9.7	84.0	11.2	4.8	84.2	10.2	5.6
PBD (A)	3, $HSi(n\text{-}Bu)_3$	0.5	46.0	78.1	12.8	9.1	80.0	12.0	7.2
PBD (A)	4, $HSi(OC_2H_3)_3$	0.5	23.0[b]	69.3	10.4	*c*	73.2	9.9	*c*
PBD (A)	5, $HSi(CH_3)_2C_6H_5$	0.5	43.0	77.2	11.6	11.2	79.3	9.9	10.8
PBD (B)	1, $HSi(C_2H_5)_3$	0.5	51.2	74.5	12.5	13.0	74.5	12.6	13.1
PBD (C)	1, $HSi(C_2H_5)_3$	0.5	41.4	75.0	12.3	11.7	74.5	12.6	12.9
PBD (C)	1, $HSi(C_2H_5)_3$	1.0	85.0	*c*	*c*	*c*	*c*	*c*	*c*

[a] Reaction conditions: $[RhCl(PPh_3)_3]$ = 0.54–1.08 mM; [C=C] = 300–740 mM; T = 109–110 °C; toluene = 30–50 mL, $[HSiR_3]$ = 100–600 mM (liquid silanes). [b] Product polymer cross-linked. [c] Data not available.

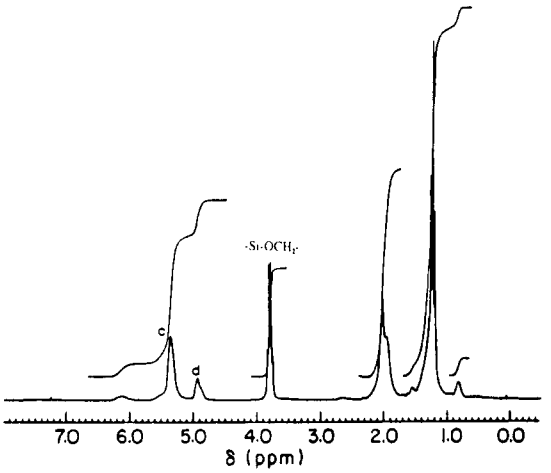


Figure 6. ^1H NMR spectrum for "PBD (A) + $HSi(OC_2H_5)_3$ (4)" product.

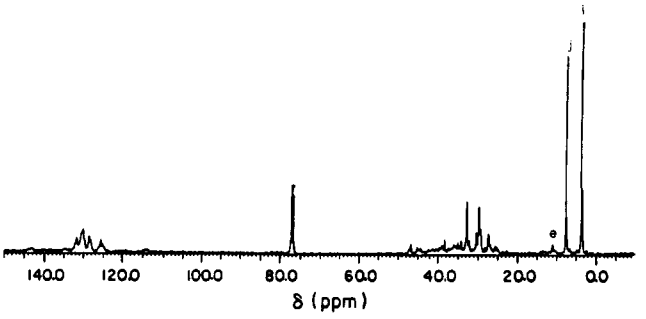


Figure 7. $^{13}C\{H\}$ NMR spectrum for "PBD (A) + $HSi(C_2H_5)_3$ (1)" product.

Table II
^{13}C NMR (APT) Results for Silane-Modified PBD

PBD	silane	δ for carbons near to Si (*C*)
A	1	7.40 (j, $-SiCH_2CH_3$), 3.58 (i, $-SiCH_2CH_3$), 11.0 (e, Pol–CH_2CH_2Si–)
B	1	7.47 (j, $-SiCH_2CH_3$), 3.61 (i, $-SiCH_2CH_3$), 11.2 (e, Pol–CH_2CH_2Si–)
C	1	7.51 (j, $-SiCH_2CH_3$), 3.64 (i, $-SiCH_2CH_3$), 11.3 (e, Pol–CH_2CH_2Si–)
A	4	58.20[a] ($-SiOCH_2CH_3$), 18.20 ($-SiOCH_2CH_3$), 12.1 (e, Pol–CCH_2CH_2Si–)
A	5	−2.30 and −3.1 ($-Si(CH_3)_2$), 10.3 (g, Pol–$CH(CH_3)Si$), 11.2 (e, Pol–CH_2CH_2Si), 18.5 (f, Pol–$CH(CH_3)Si$–)
C	3	26.8 ($-SiCH_2CH_2CH_2CH_3$), 26.2 ($-SiCH_2CH_2CH_2CH_3$), 13.8 ($-SiCH_2CH_2CH_2CH_3$), 12.5 ($-SiCH_2CH_2CH_2CH_3$), 10.8 (e, Pol–CH_2CH_2Si–)

free silane	δ of carbon atoms (*C*)
1, $HSi(CH_2CH_3)_3$	8.05 ($HSiCH_2CH_3$), 2.54 ($HSiCH_2CH_3$)
3, $HSi(CH_2CH_2CH_2CH_3)_3$	27.0 ($HSiCH_2CH_2CH_2CH_3$), 26.4 ($HSiCH_2CH_2CH_2CH_3$), 13.8 ($HSiCH_2CH_2CH_2CH_3$), 12.5 ($HSiCH_2CH_2CH_2CH_3$)
4, $HSi(OCH_2CH_3)_3$	58.17 ($HSiOCH_2CH_3$), 18.01 ($HSiOCH_2CH_3$)
5, $HSi(CH_3)_2C_6H_5$	−3.9 ($HSi(CH_3)_2$)

[a] Product polymer cross-linked.

eliminates the Markovnikov addition product (F). This result suggests that the hydrosilylation of PBD (A) using 1 occurs regioselectively via an anti-Markovnikov addition to form product E. However, in the case of hydrosilylation of 1-hexene with 1 using $RhCl(PPh_3)_3$, only 60% *n*-hexyltriethylsilane was obtained.[17] The higher regioselectivity of PBD is believed to be mainly due to the presence of bulky polymer chains.

The $^{29}Si\{H\}$ NMR for the above hydrosilylated polymer shows a single resonance at −1.5 ppm. This further supports the suggestion that only one type of hydrosilylated polymer (structure E) was produced.

The reactions of silane 3 and 4 with PBD (A) followed the same course of reaction as that observed for reaction between 1 and PBD (A). The results for ^{13}C NMR (APT) and $^{29}Si\{H\}$ NMR of the product polymers are listed in Tables II and III. It was also found that changing the molecular weight of PBD from 4500 to 30 000 has no obvious effect on the course of the hydrosilylation reaction (see Tables II and III).

Chain-length properties of the representative hydrosilylated polymers were determined by VPO and GPC.

The addition of silane to the terminal C=C bonds in PBD is expected to cause a certain degree of increase in the molecular weight of the product polymer. Theoretically, assuming the degree of polymerization of the polymer (n) does not change during the hydrosilylation reaction, the number-average molecular weight (M_n) for the hydrosilylation product polymer at a certain degree of hydrosilylation (γ) can be calculated. Table IV shows the VPO measurement results for different product polymers. As seen from the results, reasonable agreement between calculated and observed M_n values was obtained. This implies that little change in large-scale molecular structure (chain scission, cross-linking, etc.) occurred during the course of the hydrosilylation reaction.

Table III
^{29}Si NMR Results for Silane-Modified PBD

PBD	silane	^{29}Si NMR, ppm
A	1	-1.52
A	5	-2.55, -12.05
A	4	-44.06[a]
A	3	-5.78
B	1	-1.78
C	1	-1.74
C	3	-5.70

free silane	^{29}Si NMR, ppm
1, $HSi(CH_2CH_3)_3$	0.23
5, $HSi(CH_3)_2C_6H_5$	-17.19
4, $HSi(OCH_2CH_3)_3$	-58.35
3, $HSi(n\text{-}Bu)_3$	-6.26

[a] Product polymer cross-linked.

Table IV
VPO Results for Silane-Modified PBD

PBD	silane	degree of hydrosilylation (γ)	M_n(calc)	M_n(obs)
A	1, $HSi(CH_2CH_3)_3$	43.0	8 342	9 050
B	1, $HSi(CH_2CH_3)_3$	51.2	21 090	24 920
C	1, $HSi(CH_2CH_3)_3$	41.4	56 920	62 790

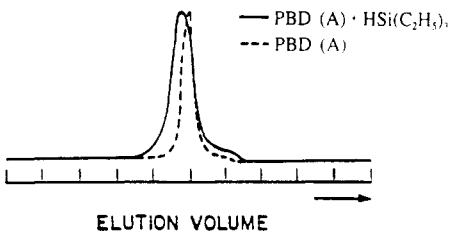


Figure 8. Gel permeation chromatograms for PBD (A) and "PBD (A) + $HSi(C_2H_5)_3$ (1)" product.

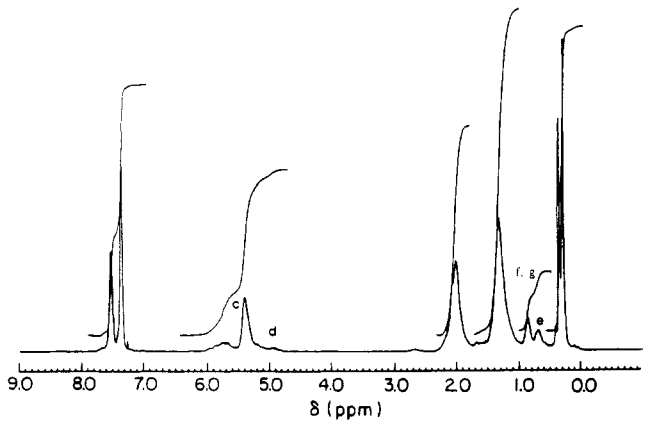


Figure 9. ^{1}H NMR spectrum for "PBD (A) + $HSi(CH_3)_2C_6H_5$ (5)" product.

Figure 8 shows GPC traces of the original PBD (A) and "PBD + 1" product. The product polymer has a molecular weight distribution similar to its parent polymer and shows a higher molar mass than the original polymer as expected.

Hydrosilylation of PBD Using 5. The ^{1}H NMR spectrum for the product polymer of the reaction between PBD (A) and **5** (dimethylphenylsilane) is given in Figure 9. The resonance of the olefinic protons of the terminal vinyl units at 5.0 ppm is almost totally absent from the spectrum. Integration shows that the hydrosilylation degree γ is about 0.43. This result strongly suggests that the hydrosilylation of PBD (A) using **5** only takes place on the terminal C=C bonds of the polymer. The possible structures for the product polymer(s) for this reaction are

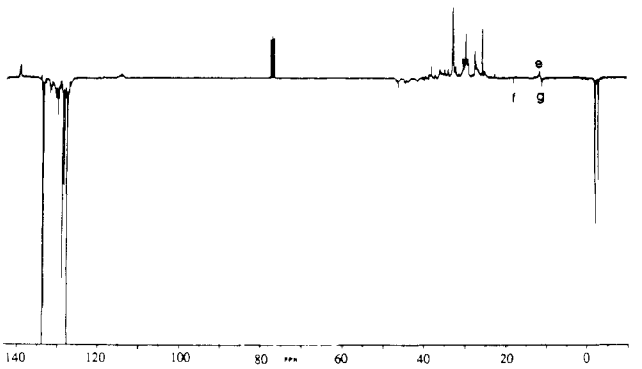
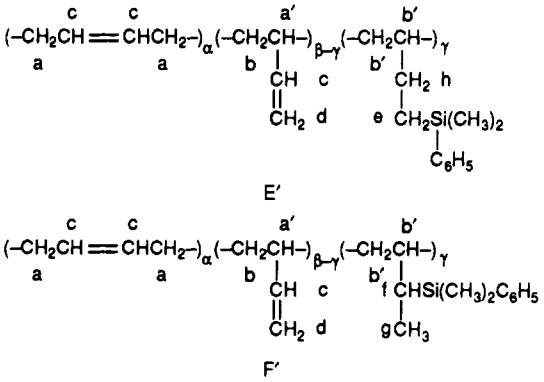


Figure 10. ^{13}C NMR (APT) spectrum for "PBD (A) + $HSi(CH_3)_2C_6H_5$ (**5**)" product.

shown as E′ and F′. In Figure 9, the peaks centered at 7.35 ppm are attributed to the ortho and para position protons, and the peaks centered at 7.41 ppm are assigned to the meta position protons of the phenyl ring. The two peaks at 0.35 and 0.31 ppm are assigned to the characteristic resonances of the methyl protons of the polymer-$CH_2Si(CH_3)_2(C_6H_5)$ group (structure E′) and possibly the methyl protons of polymer-$CH(CH_3)Si(CH_3)_2(C_6H_5)$ (structure F). The small broad peak at 0.7 ppm is assigned as the characteristic peak of the methylene protons e of structure E′. The small broad peak at 0.87 ppm is considered as the characteristic peak of the methine proton f of structure F′ and the resonances of the g protons of structure F′ are possibly hidden under this signal.



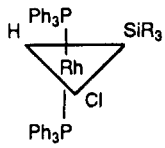
a, a′, b, b′, c, d, e, f, g, and h are 10 types of protons in different chemical environments.

The product polymer(s) of the reaction between **5** and PBD (A) was analyzed by ^{13}C NMR with off-resonance decoupling, proton-noise-decoupling, and APT techniques using a Bruker WH-400-MHz spectrometer. Figure 10 shows the ^{13}C(APT) NMR spectrum for this product polymer(s). As in the case of the reaction between **1** (triethylsilane) and PBD (A), all the signals for terminal C=C carbons have almost totally disappeared. There are new peaks in the region of aromatic protons (127–140 ppm) due to the introduction of the dimethylphenylsilane group into the polymer. In the high-field region near 0 ppm, the downward resonances at -2.3 and -3.1 ppm are assigned to the methyl carbons of the dimethylphenylsilane group in structures E′ and F′, respectively. The downward signal at 10.3 ppm is likely to be the resonance for the g methyl carbon of the F′ structure. The upward signal at 11.7 ppm is attributed to the e methylene carbon of the E′ structure. The small downward signal at 18.5 ppm is attributed to the f methine carbon of the F′ structure. This ^{13}C NMR analysis suggests that the reaction between **5** and PBD (A) is not regioselective and both anti-Markovnikov addition and Markovnikov addition were involved.

The $^{29}Si\{H\}$ NMR for the product polymer(s) of reaction between 5 and PBD (A) shows two signals at −2.55 ppm (structure F′) and −12.05 ppm (structure E′). This result again suggests that there are two types of product polymers produced for this reaction.

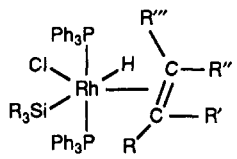
Further studies need to be carried out in order to fully understand the lower selectivity of this reaction system. It is possible that the presence of an aromatic ring in the silane molecule might cause some change in the reaction mechanism.

Mechanistic Considerations. The exclusive formation of anti-Markovnikov addition product E for the reactions of PBD with silanes 1–4 can be rationalized by examining the mechanism that has been previously reported for $RhCl(PPh_3)_3$ catalyzed hydrosilylation of olefins.[17-21] It was reported that the main product for the hydrosilylation of 1-hexene was $(n\text{-Hex})SiR_3$, and in some cases, isomerization of the 1-hexene was observed, which was postulated as the reason for a slower reaction and lower reaction yield.[17] In another paper, hydrosilylation of internal olefins with this catalyst has been reported, but the reaction was much slower compared with terminal olefins.[19] It was proposed that a five-coordinate, monomeric complex of the type $(Ph_3P)_2RhH(SiR_3)Cl$ with a trigonal-bipyramidal configuration (III) was formed when treating the $RhCl(PPh_3)_3$ with an excess of a silane at room temperature for several days to months.[17] The regioselective hydrosilylation giving straight-chain hydrosilylated products is thought to arise from the inability of the sterically hindered



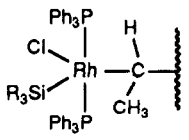
III

internal olefins to form the alkenylrhodium intermediate (structure IV) as required by the catalytic cycle. It can be visualized from structure IV that, for the 1,4-addition units where R′ and R″ are polymer chains, the transition state is sterically crowded and the formation of the Rh complex is inhibited.

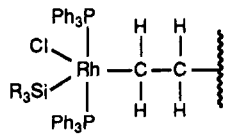


IV

In the case of pendant C=C, i.e., when R = R′ = R‴ = H and R″ = polymer chain, two possible modes of hydride transfer are possible, which are (1) Markovnikov addition, which leads to the formation of structure V, and



V



VI

(2) anti-Markovnikov addition, which results in the formation of structure VI. It can be seen that intermediate V is sterically less favorable due to bulky polymer chain, silyl group, and triphenylphosphines surrounding the Rh. In structure VI the straight chain alkylrhodium complex allows the main bulky polymer chain to remain outside

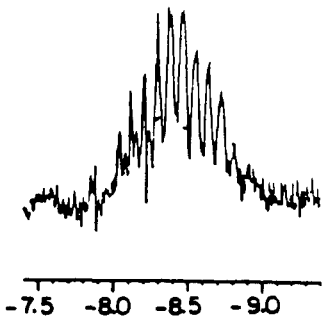
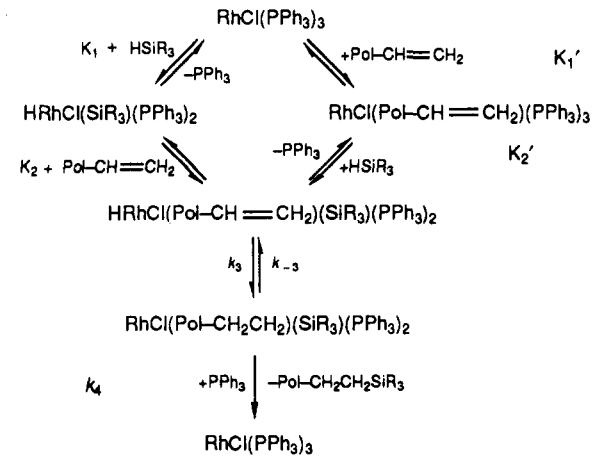


Figure 11. Upfield ^1H NMR for "$RhCl(PPh_3)_3$ + $HSi(C_2H_5)_3$ (1)" product(s).

Scheme I[a]



[a] Pol represents a polymer chain.

of the coordination sphere of Rh. Reductive elimination from structure VI would result in the formation of product E. In an attempt to confirm the formation of a rhodium–silane complex, the upfield ^1H NMR for the reaction solution of $HSi(C_2H_5)_3$ with $RhCl(PPh_3)_3$ which was sealed in a 5-mm NMR tube and heated for 3 h was investigated. The high-field region of the spectrum, which was recorded at 25 °C in C_6H_6, is shown in Figure 11. This concentrated solution has a brownish color. The resonance of Rh–H is identified as a multiplet centered at −8.33 ppm. The complicated pattern for this Rh–H signal is caused by the coupling between Rh and H and the coupling between P and H.

When 5 (dimethylphenylsilane) was used to react with PBD, both anti-Markovnikov and Markovnikov addition products were produced. Besides steric effects, an electronic effect due to the phenyl group in the silane is believed to complicate the reaction.

As in the case of olefin hydrogenation, the hydrosilylation reaction might be expected to follow either a hydride pathway (Scheme I, step 1 → 2 → 3 → 4) or an unsaturated pathway (Scheme I, step 1′ → 2′ → 3 → 4), or perhaps concurrently both.

In the case where $k_4 > k_{-3}$, no isomerization would be expected, but if $k_{-3} > k_4$, isomerization may be possible.

Two experiments were conducted in an attempt to gain further insight into the various processes shown in Scheme I.

In reaction A, 0.020 g (2.16×10^{-5} mol) of $RhCl(PPh_3)_3$ and 4.0 mL (0.025 mol) of $HSi(C_2H_5)_3$ was initially reacted in 45 mL of toluene under N_2 for about 20 h. Then 1.5 g (0.028 mol in C=C) of PBD (C) was added to the reaction mixture. In reaction B, 0.020 g (2.16×10^{-5} mol) of $RhCl(PPh_3)_3$ and 1.5 g (0.028 mol in C=C) of PBD (C) was initially heated in 45 mL of toluene under N_2 at 110

°C for about 20 h. A total of 4.0 mL (0.025 mol) of triethylsilane was then added to the reaction mixture. Sampling and ^1H NMR were carried out to follow the extent of the hydrosilylation reactions. There is no significant difference between these two reactions. In both cases, there is no induction time; and the final reaction mixture had a light yellow color. This result suggests that the equilibria processes in Scheme I are probably quite fast and/or that both hydride and unsaturated paths may be involved in the hydrosilylation process.

Conclusions

The above detailed investigation on the hydrosilylation of PBD in the presence of $RhCl(PPh_3)_3$ indicated that hydrosilylation of PBD using trialkylsilanes resulted in the exclusive formation of anti-Markovnikov addition product(s). The steric effect of the alkyl groups in the silanes seemed to have no significant effect on the regioselectivity of the hydrosilylation. However, when triethoxysilane was used, the reaction did not occur as readily. When dimethylphenylsilane was used, the reaction was not regioselective, producing both the anti-Markovnikov addition product and Markovnikov addition product. This result suggests that the nature of the substituents in the silanes has an important effect on the hydrosilylation mechanism.

Acknowledgment. Financial support of the research from the University Research Incentitive Fund of the Ministry of Colleges and Universities of Ontario (URIF Project WA10-002) is gratefully acknowledged. We thank Dr. A. F. Halasa of Goodyear Tire and Rubber Co. (Akron, OH) for supplying the 90% terminal vinyl content polybutadiene, which helped make this work possible.

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Registry No. 1, 617-86-7; 2, 993-07-7; 3, 998-41-4; 4, 998-30-1; 5, 766-77-8; PBD, 9003-17-2; $RhCl(PPh_3)_3$, 14694-95-2.