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Catalytic Hydrosilylation of Diene-Based Polymers. 2. Hydrosilylation of Styrene–Butadiene Copolymer and Nitrile–Butadiene Copolymer

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ABSTRACT: The hydrosilylation of styrene–butadiene copolymer (SBR) and nitrile–butadiene copolymer (NBR) using triethylsilane in the presence of $RhCl(PPh_3)_3$ was investigated at 110 °C in toluene under Ar. The hydrosilylation products were characterized by IR and ^{13}C NMR. It was found that the reaction mechanism was markedly influenced by the nature of the functional groups in the polymer chain. In the case of SBR, the reaction occurred via a typical anti-Markovnikov addition leading to a linear adduct. However, when strong electronegative groups such as nitrile were present (i.e., in the case of NBR), the addition appeared to occur via a Markovnikov addition mechanism which led to a branched adduct. The styrene units in SBR appeared to retard the hydrosilylation, compared with pure polybutadiene, while the nitrile groups of NBR appeared to have less of an effect.

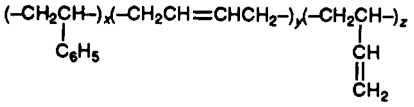
Introduction

Hydrosilylation of unsaturated polymers has recently been used to prepare polymers with special properties.[1-4] In addition, a considerable number of patents have been granted on the hydrosilylation of polymers. Due to the potential important applications of such polymers, there is a great need for a better understanding of those factors which influence the mode of this reaction. We have recently reported a detailed investigation on the hydrosilylation of polybutadiene (PBD) in the presence of $RhCl(PPh_3)_3$.[4] It was found 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 hydrosilylation mechanism. However, the choice of substituents in the silanes had an important effect on the hydrosilylation mechanism. This raised an important question: Is the effect of functional groups in the copolymer chain important to the mode of hydrosilylation?

The following work was devoted to determining the influence of the functional groups of the copolymer substrates on the hydrosilylation mechanism. In this study, SBR and NBR copolymers were used as substrates to react with triethylsilane in the presence of $RhCl(PPh_3)_3$.

Experimental Section

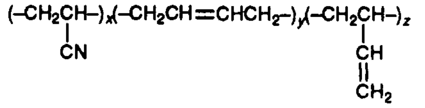
Polymer Substrates. Two types of SBR copolymers were used for this study. Type A (Finaprene 414 obtained from Petrofina) is a radial copolymer with 60 wt % butadiene content and 7.7 wt % pendent vinyl (of total butadiene) content; type B (Finaprene 410 obtained from Petrofina) is a tapered diblock AB copolymer with 52 wt % butadiene content and 8.4 wt % pendent vinyl (of total butadiene) content (see I for repeating unit structure).



$$(\text{–}CH_2\underset{\substack{|\\ C_6H_5}}{CH}\text{–})_x(\text{–}CH_2CH{=}CHCH_2\text{–})_y(\text{–}CH_2\underset{\substack{|\\ CH\\ \|\\ CH_2}}{CH}\text{–})_z$$

I

The NBR used for this study was Krynac 38.50, which was supplied by Polysar Rubber Corp. Krynac 38.50 has about 62 wt % butadiene content with 5% pendent vinyl group (see II for repeating unit structure).



$$(\text{–}CH_2\underset{\substack{|\\ CN}}{CH}\text{–})_x(\text{–}CH_2CH{=}CHCH_2\text{–})_y(\text{–}CH_2\underset{\substack{|\\ CH\\ \|\\ CH_2}}{CH}\text{–})_z$$

II

The polymers were purified by dissolution in toluene with subsequent precipitation effected by addition of methanol.

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

NMR Spectroscopic Analysis. NMR spectra were recorded on a Bruker AM 250-MHz instrument and a Bruker AC 200-MHz instrument. All the analysis were carried out in $CDCl_3$ solvent.

Synthetic Method. The hydrosilylation of SBR and NBR was carried out in toluene under argon at the following reaction conditions: $[C{=}C]$ = 200–290 mM, T = 109–110 °C, volume of toluene 40 mL, $[RhCl(PPh_3)_3]$ = 0.54 mM, $[HSi(CH_2CH_3)_3]$ = 10–35 mM, reaction time 20 h.

Results and Discussion

1. Hydrosilylation of Styrene–Butadiene Copolymer by Triethylsilane in the Presence of $RhCl(PPh_3)_3$.

The study on the hydrosilylation of polybutadiene polymers has revealed that $RhCl(PPh_3)_3$ is highly selective toward catalyzing the hydrosilylation of the pendent vinyl $C{=}C$ of the polymer due to the steric effect of the polymer chain.[4] Therefore, it is reasonable to assume that the hydrosilylation of a SBR copolymer will probably occur only on the pendent vinyl $C{=}C$ of the copolymer. The addition of triethylsilane to the SBR copolymer chain thus could potentially result in two types of possible microstructures as shown in eq 1. Species III is an anti-Markovnikov addition product, and species IV is a Markovnikov addition product.

The hydrosilylation of SBR was carried out at a silane to vinyl ratio of 1 under Ar for 20 h. The IR spectrum of the SBR (A) substrate is given in Figure 1. The peak at 3060 cm^{-1} is assigned for $=CH$ stretching of the pendent vinyl $C{=}C$ bonds. The absorbance at 915 cm^{-1} is assigned to the $=CH_2$ wagging of these vinyl units. The absorbances at 970 and 995 cm^{-1} are attributed to the internal $C{=}C$ bonds in the 1,4-addition units of the butadiene content. The absorbances at 705 and 765 cm^{-1} are

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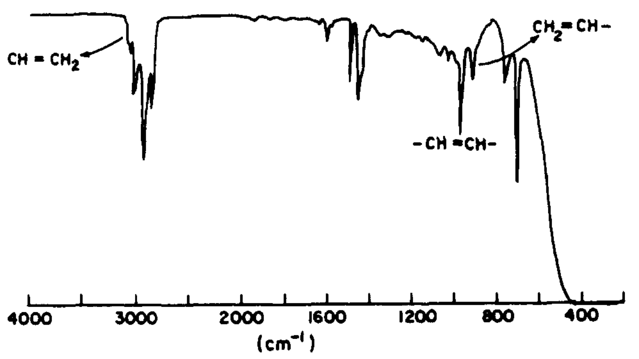
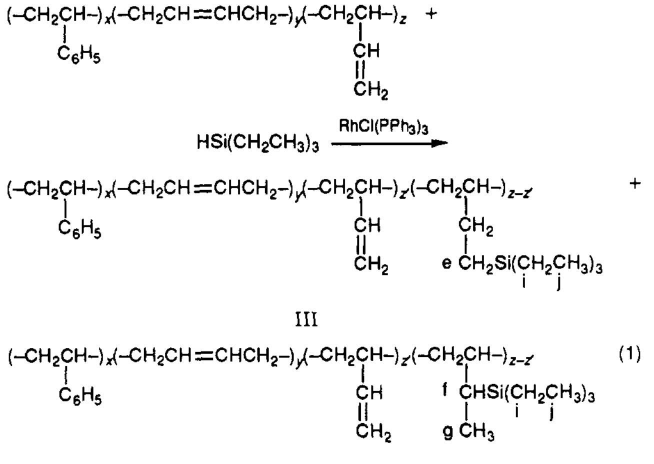


Figure 1. IR spectrum for SBR copolymer A.



$$(\text{–}\underset{C_6H_5}{CH_2CH}\text{–})_x(\text{–}CH_2CH{=}CHCH_2\text{–})_y(\text{–}\underset{\underset{CH_2}{\overset{\|}{CH}}}{CH_2CH}\text{–})_z + HSi(CH_2CH_3)_3 \xrightarrow{RhCl(PPh_3)_3}$$

$$(\text{–}\underset{C_6H_5}{CH_2CH}\text{–})_x(\text{–}CH_2CH{=}CHCH_2\text{–})_y(\text{–}\underset{\underset{CH_2}{\overset{\|}{CH}}}{CH_2CH}\text{–})_{z'}(\text{–}\underset{\underset{e\ CH_2Si(\underset{i}{CH_2}\underset{j}{CH_3})_3}{CH_2}}{CH_2CH}\text{–})_{z-z'} +$$

III

$$(\text{–}\underset{C_6H_5}{CH_2CH}\text{–})_x(\text{–}CH_2CH{=}CHCH_2\text{–})_y(\text{–}\underset{\underset{CH_2}{\overset{\|}{CH}}}{CH_2CH}\text{–})_{z'}(\text{–}\underset{\underset{g\ CH_3}{f\ CHSi(\underset{i}{CH_2}\underset{j}{CH_3})_3}}{CH_2CH}\text{–})_{z-z'} \quad (1)$$

IV

attributed to the out-of-plane C–H bending vibrations of the aromatic ring of the styrene content. The sample of the product polymer used for IR analysis was cast on a NaCl diskette and dried in vacuum. Figure 2 shows the IR spectrum for the hydrosilylation product of SBR (A). The intensities of the peak at 915 cm^{-1} (=CH_2 wagging) and the peak at 3060 cm^{-1} decrease substantially compared with its parent polymer as seen in Figure 1. However, there is still a small amount of residual pendent vinyl C=C in the product polymer. The new peak near 1220 cm^{-1} is due to CH_2 wagging of the –$SiCH_2$– structure, and the peak at 1005 cm^{-1} is also attributed to the newly introduced –$SiCH_2$– structure. The IR analysis results confirm that the hydrosilylation of SBR catalyzed by RhCl(PPh$_3$)$_3$ is selective toward hydrosilylating the vinyl units in the copolymer, as was the case for the PBD homopolymer hydrosilylation.[4] However, the reaction with the SBR copolymer seems to proceed with greater difficulty than was the case for the hydrosilylation of the PBD polymer. For example, in the presence of excess silane, there were still vinyl units left in the SBR copolymer system after 20-h reaction. One of the reasons for this is probably due to the presence of the aromatic ring in the copolymer chain which can create a different electronic environment as well as a different steric environment for the reaction centre in the polymer chain. Another possible reason is the lower pendent vinyl content in each copolymer chain.

The hydrosilylation product polymer was precipitated from methanol and dried in vacuum for NMR analysis. The attached proton test (APT) technique can show methine and methyl carbons as downward signals and methylene and quaternary carbons as upward signals. Therefore, it was used for the ^{13}C NMR analysis in this investigation. The ^{13}C NMR (APT) spectrum of the SBR (A) starting material is shown in Figure 3. The upward

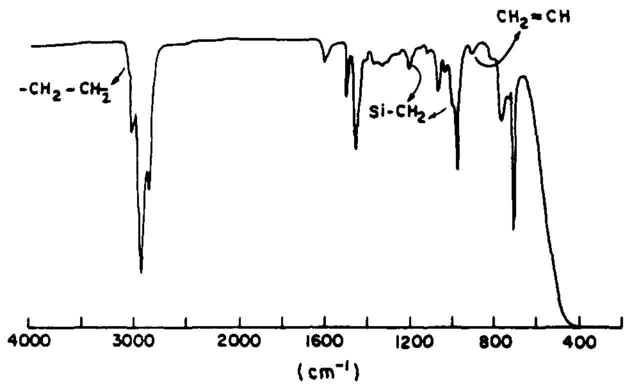


Figure 2. IR spectrum for "SBR copolymer A + HSi(C_2H_5)$_3$" product.

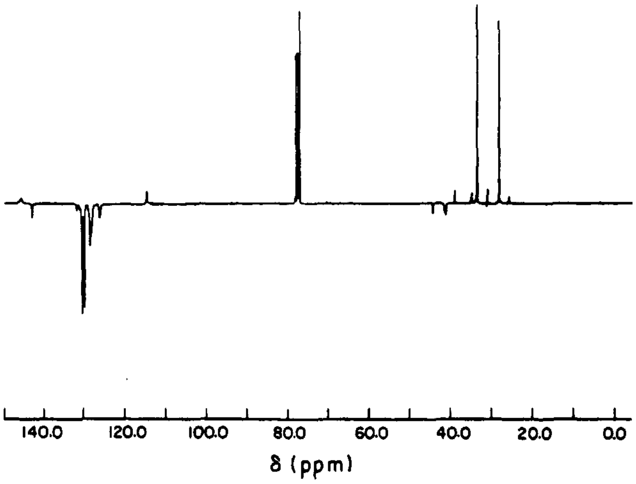


Figure 3. ^{13}C NMR (APT) spectrum for SBR copolymer A.

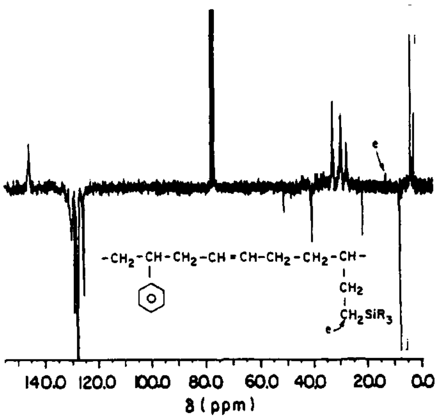
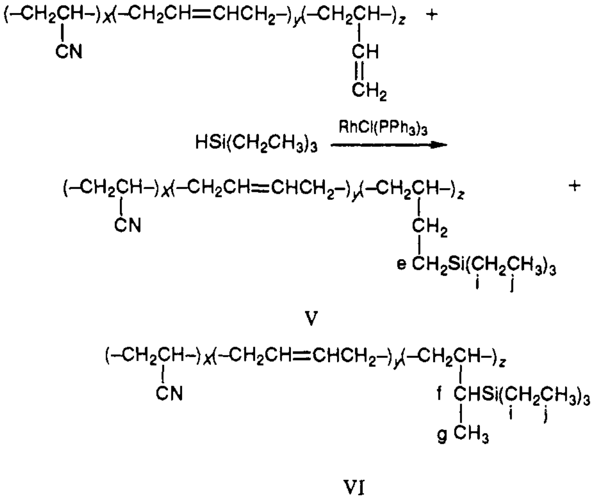


Figure 4. ^{13}C NMR (APT) spectrum for "SBR copolymer A + HSi(C_2H_5)$_3$" product.

peak at 145.2 ppm is attributed to the substituted aromatic carbon of the styrene content of the copolymer; the unsubstituted aromatic carbon atoms have downward signals in the region 125–131 ppm, which are mixed with the resonances of the olefinic methine carbons of the 1,4-addition units (–CH_2*CH*=*CH*CH_2–) of the butadiene content. The upward signal at 114.2 ppm and the downward signal at 142.5 ppm are assigned, respectively, to the olefinic methylene carbon (*C*H_2=CH–) and the olefinic methine carbon (CH_2=*C*H–) of the pendent vinyl C=C bonds. Figure 4 shows the ^{13}C NMR (APT) spectrum for the hydrosilylated SBR. From the IR result, it is known that the amount of unreacted pendent vinyl C=C in the hydrosilylation product polymer is very small. Thus, the peaks at 114.2 and 142.5 ppm, which are due to the olefinic carbon atoms in these pendent vinyl units, are almost totally absent in the spectrum shown in Figure 4. The resonances for the aromatic carbons and the internal olefinic carbon atoms remain in the same position as in the spectrum of the starting copolymer. In the high-field region near 0 ppm, there are peaks at 3.6, 7.6, and 12.5 ppm as upward, downward, and upward signals, respectively. These three peaks are assigned, respectively, to the i, j, and e carbon atoms of structure III. The downward signals at 21.4 and 50.9 ppm are due to the methyl carbon atoms of toluene ($CH_3C_6H_5$, reaction solvent) and methanol (CH_3OH, precipitating solvent), respectively. In the high-field region near 0.0 ppm, the upward signal at 2.54 ppm is due to the methylene carbon ($HSiCH_2CH_3$) of the unreacted triethylsilane reactant which was trapped in the product polymer during the precipitation. The resonance for the methyl carbon ($HSiCH_2CH_3$) of the unreacted triethylsilane is the downward signal at 8.0 ppm. These results suggest that the reaction between triethylsilane and SBR occurred only on the vinyl C=C bonds via an anti-Markovnikov addition mechanism. This also indicates that the presence of the styrene functional groups, although significantly reducing the hydrosilylation rate, has no effect in changing the addition mechanism which is observed for PBD.[4]

Another SBR copolymer used for this hydrosilylation reaction was B, which has a different amount of butadiene content. IR and NMR analysis for the product polymer from this reaction showed similar results as in the case of the reaction between triethylsilane and SBR (A).

2. Hydrosilylation of NBR Using Triethylsilane Catalyzed by $RhCl(PPh_3)_3$. If the hydrosilylation of NBR copolymer can only take place on the pendent vinyl C=C bonds of this copolymer, there are two possible hydrosilylated copolymer structures as shown as V (the anti-Markovnikov addition product) and VI (the Markovnikov addition product).



$$(\text{-CH}_2\underset{\text{CN}}{\text{CH}}\text{-})_x(\text{-CH}_2\text{CH=CHCH}_2\text{-})_y(\text{-CH}_2\underset{\underset{\text{CH}_2}{\|}}{\underset{\text{CH}}{\text{CH}}}\text{-})_z + \text{HSi(CH}_2\text{CH}_3)_3 \xrightarrow{\text{RhCl(PPh}_3)_3}$$

$$(\text{-CH}_2\underset{\text{CN}}{\text{CH}}\text{-})_x(\text{-CH}_2\text{CH=CHCH}_2\text{-})_y(\text{-CH}_2\underset{\underset{\text{CH}_2\text{Si(CH}_2\text{CH}_3)_3}{|}}{\underset{\text{CH}_2}{\text{CH}}}\text{-})_z \quad \text{V}$$

$$+ \quad (\text{-CH}_2\underset{\text{CN}}{\text{CH}}\text{-})_x(\text{-CH}_2\text{CH=CHCH}_2\text{-})_y(\text{-CH}_2\underset{\underset{\text{CH}_3}{|}}{\underset{\text{CHSi(CH}_2\text{CH}_3)_3}{\text{CH}}}\text{-})_z \quad \text{VI} \qquad (2)$$

The reaction between triethylsilane and NBR was conducted in toluene under Ar with a silane to vinyl ratio of 1. The sample of product polymer used for IR analysis was cast on a NaCl diskette and dried in vacuum. The product polymer was precipitated from methanol and dried in vacuum for NMR analysis.

The IR results for the starting NMR and hydrosilylated NBR are shown in Figures 5 and 6, respectively. In the IR spectrum of NBR, the small peaks at 3090 and 910 cm^{-1} are attributed to the 5% pendent vinyl units in the butadiene content of the NBR copolymer. It is found that, after hydrosilylation, the characteristic peaks attributed to the pendent vinyl C=C are not present in the spectrum. There are new peaks at 1250 and 1015 cm^{-1} due to the introduction of the triethylsilane group into the polymer. Calculation from the ^1H NMR result showed about 4–5% hydrosilylation, which is about the total content of vinyl group in the NBR polymer. These results show that the hydrosilylation of NBR catalyzed by $RhCl(PPh_3)_3$ is indeed highly selective to the pendent vinyl C=C bonds of the copolymer; the unsaturation in the 1,4-addition units remained unreacted during the reaction.

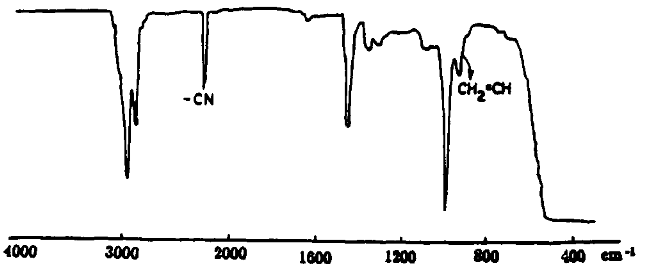


Figure 5. IR spectrum for NBR copolymer.

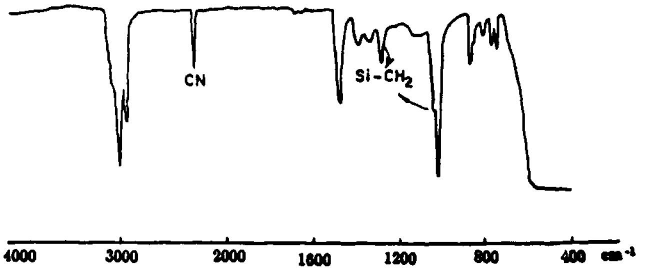


Figure 6. IR spectrum for "NBR copolymer + $HSi(C_2H_5)_3$" product.

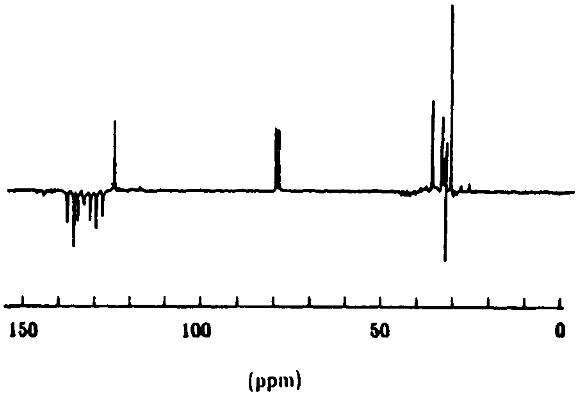


Figure 7. ^{13}C NMR (APT) spectrum for NBR copolymer.

The direction of the addition of silyl hydride to the pendant vinyl units in NBR is of interest here. Figure 7 shows the ^{13}C NMR (APT) for the starting NBR and Figure 8 the ^{13}C NMR (APT) spectrum for triethylsilane hydrosilylated NBR. In Figure 7, the upward signal at 121.7 ppm is due to the quaternary carbon atom in the nitrile group. The small downward peaks at 141 and 138 ppm are assigned for the methine carbon atom ($-CH=CH_2$) of the 5% vinyl units, and the very small upward signal at 116 ppm is assigned to the methylene carbon atom ($-CH=CH_2$) of the vinyl units. In Figure 8, the resonance for the quaternary carbons of the nitrile group is shown in the same position as an upward signal as in the starting NBR, which indicates that the nitrile groups remained unattacked during the hydrosilylation reaction. As shown in eq 2, the possible product polymer would be expected to have a structure like V or VI. The downward signal at

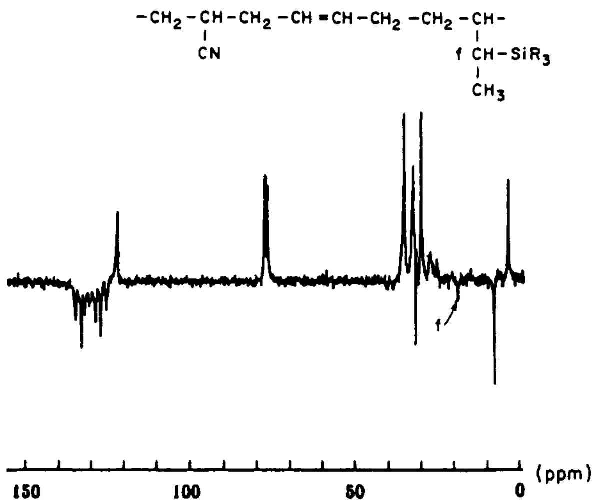


Figure 8. ^{13}C NMR (APT) spectrum for "NBR copolymer + $HSi(C_2H_5)_3$" product.

18.3 ppm can be assigned to the methine carbon f, which connects the silyl group with the polymer chain as shown in structure VI. There is no upward resonance near 11.0 ppm which can be assigned to the e carbon atom of structure V. In the high-field region of the spectrum shown in Figure 8, the resonance at 3.2 ppm is due to carbon i of the triethylsilane group. The methyl carbon in the β-position to the silicon atom (i.e., carbon j) is characterized by a resonance at 7.4 ppm. The resonance for the g carbon is expected near 10.0 ppm according to the ^{13}C NMR result previously reported.[4] In fact, there is a weak downward signal at 9.2 ppm in Figure 8 which can be attributed to the g carbon atom. This result suggests that the hydrosilylation of NBR occurs via a Markovnikov addition mechanism to form adduct VI. Similar results have been obtained for the hydrosilylation of acrylonitrile catalyzed by $RhCl(PPh_3)_3$.[5] This different mechanism for the hydrosilylation in the presence of the nitrile group is possibly caused by the strong coordination ability of nitrile to the transition metal which may change the reaction intermediate for the hydrosilylation.[5,6] Further studies need to be carried out in order to gain a full understanding of this phenomenon.

Conclusions

The studies of the hydrosilylation of SBR and NBR copolymers catalyzed by $RhCl(PPh_3)_3$ were successfully performed at mild reaction conditions under Ar. The results of the studies suggest that $RhCl(PPh_3)_3$ is highly selective toward hydrosilylating the pendent vinyl C=C bonds of the diene polymers. In the presence of styrene functional groups, the hydrosilylation on the vinyl C=C occurred by a typical anti-Markovnikov addition mechanism as observed for PBD. In the presence of nitrile functional groups, the reaction on the vinyl C=C bonds occurred via a Markovnikov addition mechanism.

References and Notes

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Registry No. Et_3SiH, 617-86-7; $RhCl(PPh_3)_3$, 14694-95-2.