Synthesis of Polybutadiene-*graft*-poly(dimethylsiloxane) and Polyethylene-*graft*-poly(dimethylsiloxane) Copolymers with Hydrosilylation Reactions

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ABSTRACT: We report preliminary results for the synthesis of polyethylene-*graft*-poly(dimethylsiloxane) copolymers obtained by catalytic hydrogenation of polybutadiene-*graft*-poly(dimethylsiloxane) copolymers (PB-*g*-PDMS). These last copolymers were synthesized by hydrosilylation reactions between commercial polybutadiene and ω-silane poly(dimethylsiloxane). The reaction was carried in solution catalyzed by *cis*-dichloro bis(diethylsufide) platinum(II) salt. The PB-*g*-PDMS copolymers were analyzed by ^{1}H and ^{13}C NMR spectroscopies, and the relative weight percentages of the grafted poly(dimethylsiloxane) macromonomer were determined from the integrated peak areas of the spectra. © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 2920–2930, 2004

Keywords: polybutadiene; poly(dimethylsiloxane); polyethylene (PE); hydrosilylation; graft copolymers; ^{1}H and ^{13}C NMR spectroscopies; Wilkinson's catalyst; catalytic hydrogenation

INTRODUCTION

The science and technology of multiphase polymer systems have received widespread attention in the last decades.[1] In particular, graft and block copolymers are of both academical and technological interest because they can generate new materials with enhanced or specific properties. These materials are usually characterized by the presence of two or more polymeric phases in the solid state.[2]

In most cases, block and graft copolymers are made of chemically bonded glassy and rubbery segments. Almost all of them exhibit thermoplastic behavior and can be readily processed by heating above the glass-transition temperature of the glassy component.[3] Some of these copolymers offer several advantages over blends or composite materials: (1) the covalent bonds joining the copolymer blocks improve the interface behavior; and (2) the molecular architecture of the blocks can be accurately controlled to produce novel materials.

Unsaturated polymers (especially diene-based polymers) are ideal compounds for the synthesis of graft copolymers because of the technological importance associated with the parent material and the reactivities of the double bonds in the polymer chain. Conjugated 1,3-dienes [$CH_2{=}C(R){-}CH{=}CH_2$] can polymerize to form four isomeric microstructures, and in

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the particular case of butadiene (where R is equivalent to H), the corresponding homopolymer has only three isomeric microstructures. They are known as 1,4- and 1,2-addition units (1,4-cis–trans and 1,2-vinyl units, respectively).[4]

Various strategies have been developed to synthesize graft copolymers from diene-based polymers because of the reactivity of their double bonds,[5] and in the particular case of silane-modified rubbers, these polymers can be synthesized by hydrosilylation reactions.[6] This special type of reaction allows the addition of organic and inorganic silicon hydrides to multiple bonds, such as carbon–carbon, carbon–oxygen, carbon–nitrogen, nitrogen–nitrogen, and nitrogen–oxygen.[7] In particular, the addition of organic silicon hydrides to vinyl or allyl bonds is of interest because it provides a great number of useful compounds.

Poly(dimethylsiloxane) (PDMS) containing copolymers displays an unusual combination of properties. PDMS homopolymer exhibits some interesting features such as high surface tension, large permeability to gases, high hydrophobicity, and good biocompatibility, among others.[8] However, many potential applications of this polymer are hindered by its poor mechanical properties. To improve them, while keeping its other characteristics, the synthesis of block or graft copolymers in which PDMS blocks would be associated with vinylic chains has been attempted. For this purpose vinylic polymers chosen preferably among those exhibiting high glass-transition temperatures have been selected.[9] The resulting copolymers exhibit the properties of the thermoplastic elastomers with possible biomedical applications.

Nowadays, a number of special applications have arisen for siloxane-containing block or graft copolymers in mixtures with, or as additives to, other materials. One example of this kind of polymer is siloxane–ethylene oxide copolymer, which have been used as stabilizers of flexible polyurethane foams. Recently, block copolymers containing siloxane sequences have been used for specific applications such as biomaterials, fotoresistences, coatings, and adhesives.[10–15]

With the aforementioned considerations, in this work we report preliminary results for the synthesis of polyethylene-*graft*-poly(dimethylsiloxane) copolymers (PE-*g*-PDMS). They were obtained by catalytic hydrogenation of polybutadiene-*graft*-poly(dimethylsiloxane) copolymers (PB-*g*-PDMS) that were synthesized by hydrosilylation of the 1,2-addition units of a commercial polybutadiene (PB) with ω-silane PDMS. The reaction was carried out in solution catalyzed by *cis*-dichloro bis(diethylsufide) platinum(II) salt $\{Cl_2[S(CH_2CH_3)_2]Pt\}$.

EXPERIMENTAL

Materials

All solvents were distilled before use. PB-*g*-PDMS copolymers were synthesized from commercial PB (PASA S.A., Argentina), and almost monodisperse ω-silane PDMS chains were synthesized in our laboratories according to typical experimental procedures.[16] The hydrosilylation reactions were carried out in solution with toluene as a solvent. The catalyst for the reaction was *cis*-dichloro bis(diethylsufide) platinum(II) salt $\{Cl_2[S(CH_2CH_3)_2]Pt\}$, prepared in accordance with the method reported by Kauffman and Cowan.[17]

PE-*g*-PDMS copolymers were obtained by catalytic hydrogenation of PB-*g*-PDMS copolymers with chlorotris-(triphenylphosphine)rhodium(I) (Stream Chemicals Wilkinson's catalyst) and triphenylphosphine (Aldrich Chemical Co.) as a cocatalyst.

Synthesis

PB-g-PDMS Copolymers

Reactive mixtures of commercial PB and ω-silane PDMS [with different proportions of ω-silane PDMS] were prepared on the basis of 15 g of PB. From these mixtures, the hydrosilylation reactions were carried out in toluene in a three-necked flask with a nitrogen inlet and outlet and a condenser under mechanical stirring (70 rpm). The experimental conditions were as follows: solvent, toluene, 200 mL; catalyst, $Cl_2[S(CH_2CH_3)_2]Pt$ salt, 400 μL of 1 wt % solution in toluene; reaction temperature, 323 K; reaction time, 4 h. At this point, the reaction mixture is heterogeneous at the start. Despite mechanical stirring, some heterogeneity is still observed at the end of the reaction. The influence of this effect in the hydrosilylation yields is discussed in the following section of this article.

After that time, the reaction product was precipitated with cold methanol and extracted twice with methyl ethyl ketone to eliminate unreacted ω-silane PDMS and catalyst residues. Pure PB-*g*-

PDMS copolymers were dried *in vacuo* at room temperature for more than 48 h before being subjected to further analysis.

PE-g-PDMS Copolymers

The PB-*g*-PDMS copolymers were saturated catalytically. The hydrogenation reactions were carried out in a Parr reactor of 3-L capacity. In all cases, 5 g of each copolymer were dissolved in 0.7 L of toluene and were reacted with hydrogen gas (H_2) at 373 K and 4.8 MPa in the presence of Wilkinson's catalyst and triphenylphosphine (0.3-g catalyst per gram of cocatalyst).

The reaction was carried out for 72 h, and the crude reaction product was allowed to cool at room temperature. The copolymer obtained was then filtered and repeatedly washed with fresh toluene to remove catalyst residues. Finally, it was reprecipitated with cold methanol and dried *in vacuo* to constant weight.

Nomenclature

In this article, we used names for the different copolymers that indicate the ω-silane PDMS weight percentage added to the original reactive mixture. We used the term PB-*g*-PDMS *X* for a copolymer obtained from an original reactive mixture with *X* wt % of ω-silane PDMS (e.g., PB-*g*-PDMS 10 for a copolymer obtained from a reactive mixture containing 10 wt % of ω-silane PDMS).

Characterization

Low-Angle Laser Light Scattering (LALLS) and Gel Permeation Chromatography (GPC)

The weight-average molecular weight (M_w) of ω-silane PDMS was measured with a Chromatix KMX-6 LALLS equipped with a He–Ne laser operating at 633 nm. The following experimental conditions were used: toluene as a solvent; room temperature; $dn/dc = -0.0913$; concentrations range, 0.02–0.3%. The M_w values were obtained from the ($K_c/\Delta R_\theta$) versus *c* plots (where ΔR_θ is the excess Rayleigh ratio, *K* is a combination of known optical constants, and *c* is the polymer concentration).

Size exclusion chromatography of the ω-silane PDMS was performed with a Waters model 440 liquid chromatograph equipped with four μbondagel columns and was calibrated with polystyrene standards. The experimental conditions were as follows: toluene as solvent (room temperature); 0.1% (w/w) of polymer solution; flow rate, 0.5 mL/min; and 100 μL as the injection volume.

However, the weight-average and number-average molecular weights (M_w and M_n) of PB were estimated from GPC (Waters 150 C) with toluene at room temperature. The system was equipped with a set of 10-μm PL-Gel columns from Polymer Labs, having nominal porous sizes of 10^6, 10^3, and 500 Å. The average molecular weights of PB were obtained following the standard calibration procedure with monodisperse polystyrene samples.

The experimental results of these characterizations are summarized in Table 1.

Table 1. Chemical Characterization of Commercial Poly(butadiene) (PB) and ω-Silane poly(dimethylsiloxane) (PDMS-SiH)

Starting Polymers	M_nGPC (g/mol)	M_wLALLS (g/mol)	M_wGPC (g/mol)	M_w/M_n
PDMS-SiH	67,600	101,100	83,500	1.20
PB	102,500	—	206,800	2.02

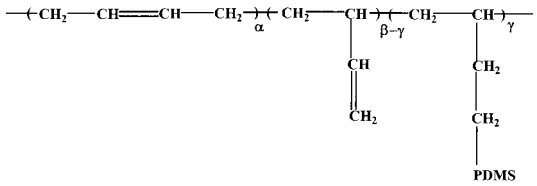
^{1}H and ^{13}C NMR Analyses

The ^{1}H and ^{13}C NMR spectra of PB, ω-silane PDMS, and PB-*g*-PDMS copolymers were recorded on a Bruker 300 spectrometer (300 MHz for proton and 75.47 MHz for carbon) with $CDCl_3$ as the solvent and tetramethylsilane as the external reference.

^{1}H NMR spectra were recorded at 300 K with an accumulation of 16 scans and a 1 wt % polymer solution. In particular, ^{1}H NMR spectroscopy was used to determine the chemical composition of PB and PB-*g*-PDMS copolymers. ^{13}C NMR spectra were recorded at 300 K with an accumulation of 1024 scans (0.29 Hz/point resolution) and a 9 wt % polymer solution. In this case, ^{13}C NMR spectroscopy was used not only to determine the chemical structure but also as evidence of siloxane grafting.

Determination of the Degree of Hydrosilylation

PB-*g*-PDMS copolymers were synthesized with the "grafting onto" technique.[18] The addition of the silane functional group to PB can potentially occur in three different ways that may result in the formation of five types of hydrosilylated microstructures in the polymer chain. However, it has been proposed that 1,2- are more reactive



PDMS: $Si(CH_3)_2OSi(CH_3)_2(CH_2)_2[Si(CH_3)_2O]_n(CH_2)_3CH_3$

Scheme 1

than 1,4-addition units and that the resulting species are anti-Markovnikov addition products.[6] Therefore, the hydrosilylation of PB with ω-silane PDMS may result in the formation of a graft copolymer whose chemical structure is shown in Scheme 1.

In this scheme, α and β represent the molar fractions of 1,4- and 1,2-addition units in the initial PB, respectively, whereas γ represents the molar fraction of hydrosilylated 1,2-addition units. According to this scheme, we calculated the chemical composition of PB-*g*-PDMS copolymers from ^{1}H NMR spectra with three alternative methods. These methods are described as follows.

Method I. The hydrosilylation degree (ξ) and the chemical composition of the PB-*g*-PDMS copolymers were estimated by an adaptation of the method described by Guo et al.[6] According to the chemical structure illustrated in Scheme 1, the total number of methyl groups in the ω-silane PDMS was equal to $(2n + 5)$, where n is the number-average degree of polymerization. Because $2n \gg 5$, we can consider that the main contribution to the integrated peak area of methyl protons is entirely due to the methyl groups of the main chain. Thus, from the ^{1}H NMR spectra of the PB-*g*-PDMS copolymers, we can establish the following relations:

$$\theta = \frac{\text{integration of methyl protons}}{\text{integration of olefinic protons}} = \frac{A_1}{A_2} = \frac{6n\gamma}{2\alpha + 3(\beta - \gamma)} \quad (1)$$

where α and β are the molar fractions of 1,4- and 1,2-addition units in the initial PB, respectively; γ is the molar fraction of hydrosilylated 1,2-addition units; n is the number-average degree of polymerization of the ω-silane PDMS; and A_1 and A_2 are the corresponding integrated peak areas. If we consider $\gamma = \xi\beta$ (where ξ is the degree of hydrosilylation), then eq 1 can be rewritten as

$$\xi = \frac{2\alpha\theta + 3\beta\theta}{3\beta(2n + \theta)} \quad (2)$$

Therefore, with the parameters α, β, and n known from eq 2, it is possible to determine the hydrosilylation degree ξ of each PB-*g*-PDMS copolymer. However, we can consider the contribution of the grafted PDMS chains to the unit molecular weight of the hydrosilylated polymer (M_0), which can be expressed as

$$M_0 = 54\alpha + 54\beta(1 - \xi) + 74n\beta\xi \quad (3)$$

Thus, according to eq 3 the mass fraction of PDMS in each PB-*g*-PDMS copolymer (ω_{PDMS}) can be calculated as

$$w_{\text{PDMS}} = \frac{74n\beta\xi}{M_0} \quad (4)$$

Consequently, from eqs 2–4 it is possible to determine the chemical composition of PB-*g*-PDMS copolymers.

Method II. We estimated the composition of the graft copolymers with the ratio of the integrated peak intensities.[19] The area of an absorption peak in the ^{1}H NMR spectrum is proportional to the number of equivalent nuclei. In the case of a polymer molecule, these nuclei are part of the chemical structure of a particular repeating unit, and we can establish that

$$\text{area} \cong \text{number of repeating units} \cong \text{weight of polymer} \quad (5)$$

Because the unit molecular weight of PB and ω-silane PDMS are known [C_4H_6 and $(CH_3)_2OSi$, respectively], the proportionality in eq 5 can be transformed in equality with the following equation:

$$\frac{\text{weight of PDMS}}{\text{weight of PB}} = \frac{\dfrac{\text{relative area of PDMS protons}}{\text{number of protons in PDMS unit}} \times 74 \text{ g/mol}}{\dfrac{\text{relative area of PB protons}}{\text{number of protons in PB unit}} \times 54 \text{ g/mol}} \quad (6)$$

Thus, from eq 6 and the corresponding integrated peak areas, we can estimate the grams of siloxane grafted per gram of PB.

Method III. The ^{1}H NMR spectra of the different copolymers were compared with those of physical mixtures of PB and ω-silane PDMS.[20] These physical mixtures were prepared in the same range of concentrations of that obtained for the siloxane-grafted copolymers calculated from Methods I and II. In particular, we compared the integrated peak areas at 0.1–0.0 ppm for the siloxane-grafted copolymers and for the physical mixtures. A linear plot of area versus concentration was obtained for the physical mixtures in the range under consideration. The linear plot-fitting equation obtained ($R^2 = 0.995$) was

$$w_{\mathrm{PDMS}} = 1.25531 \times A \tag{7}$$

where w_{PDMS} is the mass fraction of ω-silane PDMS in the mixture and A is the integrated peak area at 0.1–0.0 ppm.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of PE-*graft*-PDMS and hydrogenated PB were obtained on a Nicolet FTIR 520 spectrometer. Films of about 0.10 ± 0.01 mm in thickness were prepared by melt-pressing the materials at 423 K between the plates of a hydraulic press. The FTIR spectra were recorded at 4-cm^{-1} resolution over the range 4000–400 cm^{-1} with an accumulation of 10 scans and air as a background. The appearance of new absorbance bands between 1300 and 700 cm^{-1} in the spectra of PE-*g*-PDMS copolymers was used as evidence of grafting.

RESULTS AND DISCUSSION

^{1}H NMR Spectroscopy Characterization

The ^{1}H NMR spectrum of PB displayed two integrated peak areas. The first integrated peak area appeared as two resonance peaks between 1.4–2.0 ppm and was assigned to the aliphatic backbone of the main chain. The other area showed three resonance peaks at 4.9, 5.4, and 5.6 ppm. The resonance peak that appeared at 4.9 ppm can be assigned to the contribution of ^{1}H from vinyl groups (═C**H$_2$**) of 1,2-addition units. However, the resonance groupings centered at 5.4 and 5.6 ppm represented olefinic ^{1}H (—**H**C═C**H**—) and nonterminal vinyl ^{1}H (—**H**C═CH$_2$) from 1,4- and 1,2-addition units, respectively.[21]

As the literature suggests, the individual molar fraction of 1,4-addition units in PB could not be obtained from the ^{1}H NMR spectrum because even at 400 MHz there was no difference between ^{1}H cis and ^{1}H trans resonance.[22] However, because the peak intensity corresponded to the total number of protons in a particular group, the molar fraction of 1,2-addition related to the total amount of olefinic units can be calculated. According to this, we determined the chemical composition of the PB homopolymer as 91.78 mol % of 1,4- and 8.22 mol % of 1,2-addition units (i.e., $\alpha = 0.9178$ and $\beta = 0.0822$). This composition was further confirmed by infrared spectroscopy.

The ^{1}H NMR spectra of PB-*g*-PDMS copolymers displayed three integrated peak areas. These spectra showed not only the signals corresponding to 1,4- and 1,2-addition units (which appeared at the same position of PB) but also a new area, whose signal appeared at 0.1–0.0 ppm, and it was undoubtedly assigned to ^{1}H from the methyl groups directly bonded to silicon atoms [—OSi (C**H$_3$**)$_2$]. Qualitatively, we observed that the values of these last integrated peak areas increased with an increase in the weight percentage of ω-silane PDMS in the initial reactive mixture.

^{13}C NMR Spectroscopy Characterization

^{13}C NMR determination of the chemical structure of PB is a well established technique.[23] Figure 1 shows the ^{13}C NMR spectra of original PB, PB-*g*-PDMS 10, and PB-*g*-PDMS 70 copolymers.

In the PB spectrum, the olefinic carbons from trans 1,4-addition showed two peaks at 130.414 and 130.551 ppm, whereas cis 1,4-addition units exhibited peaks at 129.838 and 130.022 ppm. However, the 1,2-addition units signals appeared at 114.704, 114.606, and 143.059 ppm and could be assigned to methylenic (═**C**H$_2$) and methinic (—**C**H═) carbons, respectively.[24]

The copolymers' spectra showed the signals corresponding to 1,4-cis–trans and 1,2-vinyl units (which appeared at the same position of PB) and a new signal at 0 ppm. This last signal corresponded to ^{13}C from methyl groups directly bonded to silicon atoms [—OSi(**C**H$_3$)$_2$] and was evidence of siloxane grafting onto original PB. To confirm these signal assignments, we also per-

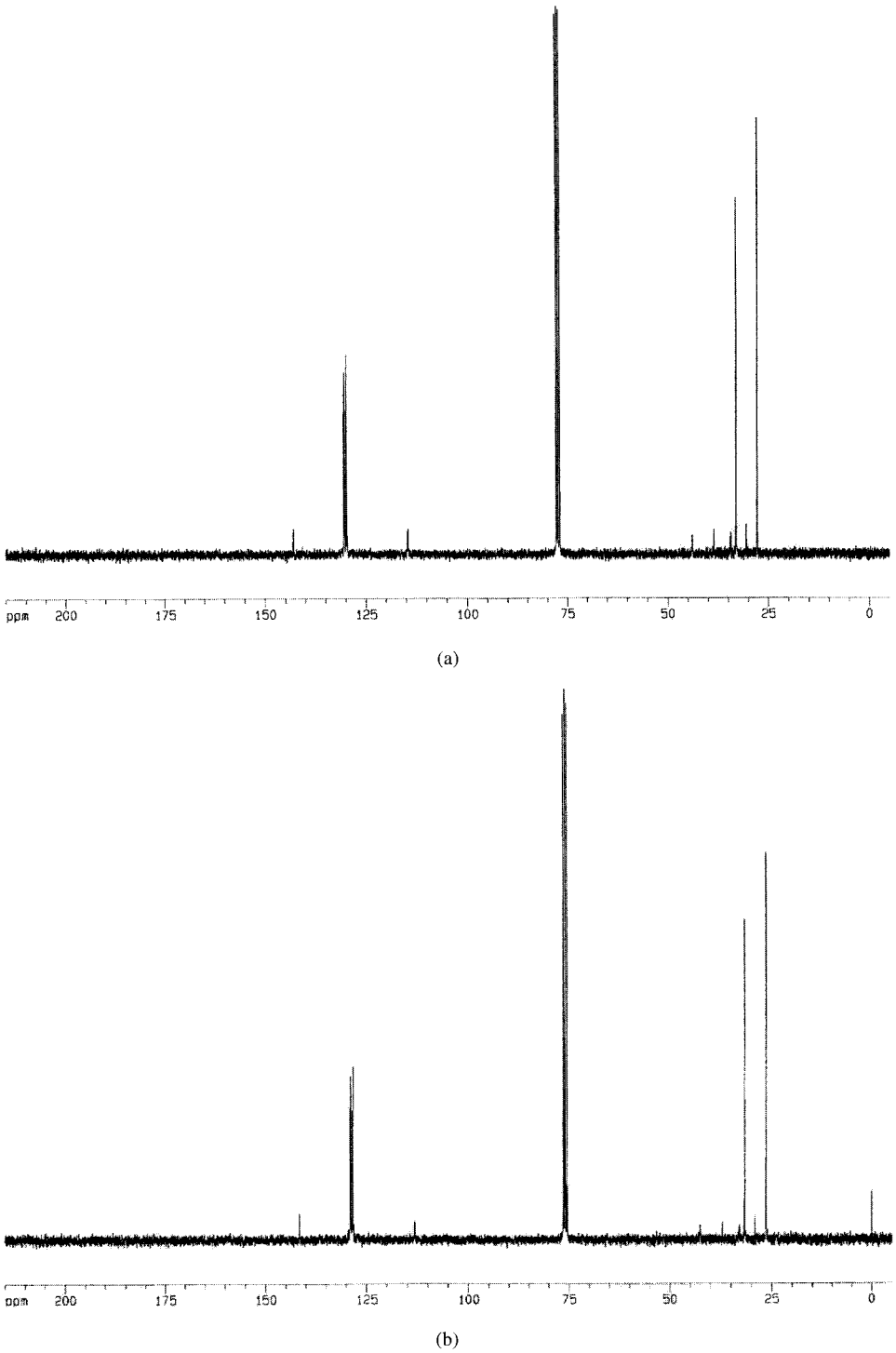
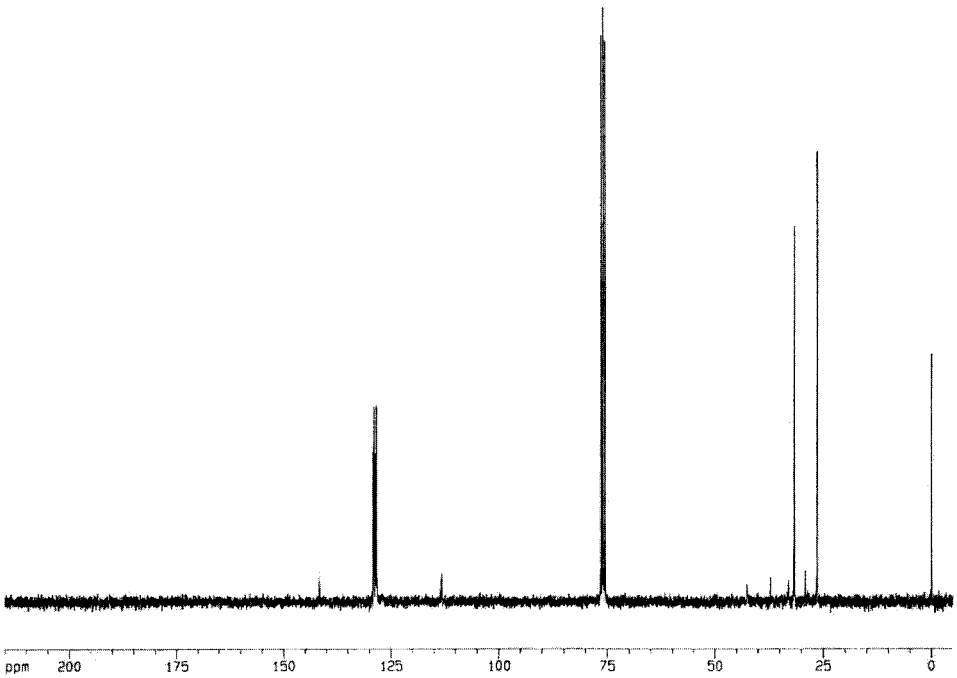


Figure 1. ^{13}C NMR spectra of the (a) original PB, (b) PB-*g*-PDMS 10 copolymer, and (c) PB-*g*-PDMS 70 copolymer.

formed a ^{13}C distortionless enhancement by polarization transfer (DEPT)-135 analysis. For example, Figure 2 shows the ^{13}C DEPT-135 spectra of PB-*g*-PDMS 70 copolymer.

The spectrum showed five positive signals between 26.394 and 37.163 ppm that corresponded to five methylenic carbons (—**C**H_2—) from cis–trans-1,4- and 1,2-addition units. A negative sig-



(c)

Figure 1. (*Continued from the previous page*)

nal at ~44.03 ppm was assigned to the methine group (—**C**H—) from the 1,2-addition units, whereas a positive signal at 113.195 ppm corresponded to their methylene carbon (=**C**H_2).

We also distinguished six negative signals: four between 128.425 and 129.125 ppm that corresponds to olefinic carbons (H**C**=) from cis–trans-1,4- and one at 141.647 ppm that corresponded to

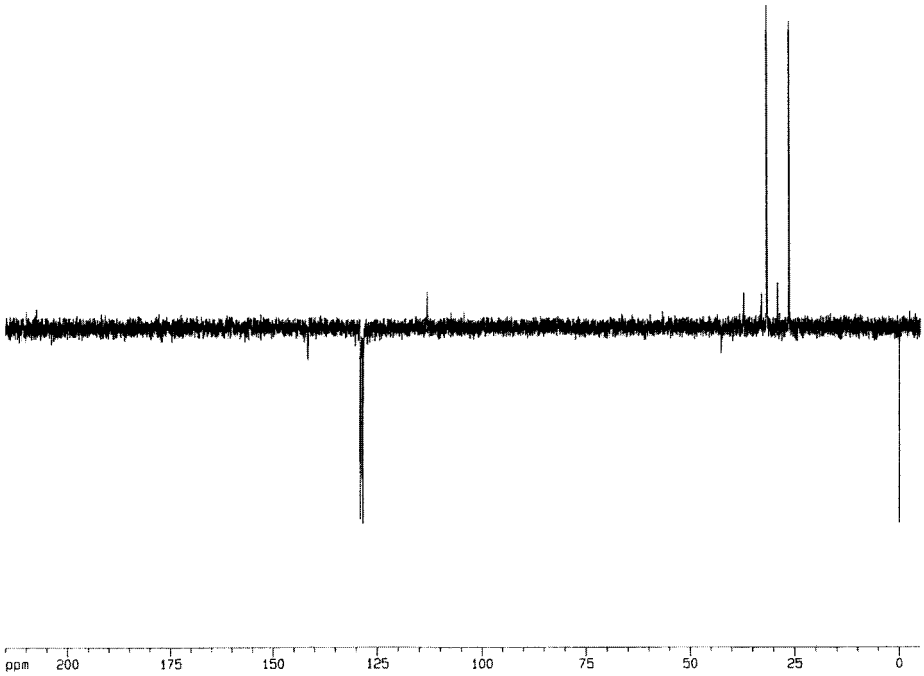


Figure 2. ^{13}C-DEPT-135 spectra of the PB-*g*-PDMS 70 copolymer.

Table 2. Integrated Peak Areas from ^{1}H NMR Spectra of PB and PB-*g*-PDMS Copolymers

Polymer[a]	^{1}H Olefinic[b]	^{1}H Aliphatic[c]	^{1}H Methylic[d]
PB	34.704	65.296	—
PB-*g*-PDMS 10	33.433	63.707	2.860
PB-*g*-PDMS 30	33.206	63.949	2.845
PB-*g*-PDMS 50	29.856	58.306	11.838
PB-*g*-PDMS 70	29.293	58.142	12.565

[a] For nomenclature, see text.
[b] Includes cis + trans + vinyl protons.
[c] Methylenic and methinic protons only.
[d] Methyl protons directly bonded to silicon.

methinic carbon (—H**C**=) from 1,2-addition units. The only signal appearing at 0 ppm corresponded to ^{13}C from methyl groups directly bonded to silicon [—OSi (**C**H$_3$)$_2$] and was assigned to equivalent methyl groups in the PDMS chain.

Determination of the Chemical Composition of PB-g-PDMS Copolymers

Table 2 shows the integrated peak areas of PB-*g*-PDMS copolymers obtained from ^{1}H NMR spectra.

From these data, we estimated the chemical composition of graft copolymers according to Methods I–III reported in the Experimental. These results are summarized in Table 3.

According to these results, ξ and w_{PDMS} increased with increasing PDMS in the initial reactive mixture. However, if we first compare the PB-*g*-PDMS 10 with the PB-*g*-PDMS 30 copolymer and then the PB-*g*-PDMS 50 with the PB-*g*-PDMS 70 copolymer, we can appreciate that the reported values are similar. These results could be explained considering various factors.

In the particular case of this article, all hydrosilylation reactions were carried out in toluene, with 4 h as the reaction time. According to Guo et al.,[6] short-chain silanes with bulky alkyl groups had an induction period of about 2 h. Then the hydrosilylation of the 1,2-addition units proceeded at a relative short speed. In our case, this induction time could be larger, and we should also consider the low silane concentrations used (particularly in the first two polymer mixtures).[25] In a previous investigation,[26] it has been proposed that the decrease of the silane concentration in the solution could also be an important factor influencing the decrease in the yield of the hydrosilylation reaction. These effects could explain the low values of ξ and w_{PDMS} reported, but we should also consider other facts, such as polymer–polymer miscibility and a "shielding effect" of the polymer chains.

Although the hydrosilylation reactions were carried out in solution, because of the drastic incompatibility between PDMS and vinyl polymers,[27] the reaction medium was quite heterogeneous. It has been demonstrated[9] that the time required to attain homogeneity increases sharply as the molecular weights of the polymers increase. Consequently, this lack of miscibility between both reagents could influence the yield of the hydrosilylation reaction. However, the reactive mixtures of PB and ω-silane PDMS were dissolved in toluene to obtain a 7.5% (w/v) polymer solution. This concentration corresponded to a semidilute solution in which polymer chains assume a random coil configuration. It is reason-

Table 3. Chemical Composition of PB-*g*-PDMS Copolymers (Data Calculated from ^{1}H NMR Spectra)

				$W_{\omega\mathrm{PDMS}}$		
Polymer	θ (.10^{-2})[a]	ξ (.10^{-4})[b]	M_0[c]	Method I[d]	Method II[e]	Method III[f]
PB	0.000	0.000	54.00	0.000	0.000	0.000
PB-*g*-PDMS 10	8.554	3.959	56.19	0.039	0.039	0.036
PB-*g*-PDMS 30	8.568	3.966	56.20	0.039	0.039	0.036
PB-*g*-PDMS 50	39.65	18.35	64.17	0.158	0.155	0.149
PB-*g*-PDMS 70	42.89	19.85	65.00	0.169	0.164	0.158

[a] Obtained from ^{1}H NMR spectra.
[b–d] Calculated according to eqs 2–4, respectively.
[e] Estimated from eq 6.
[f] Calculated from eq 7.

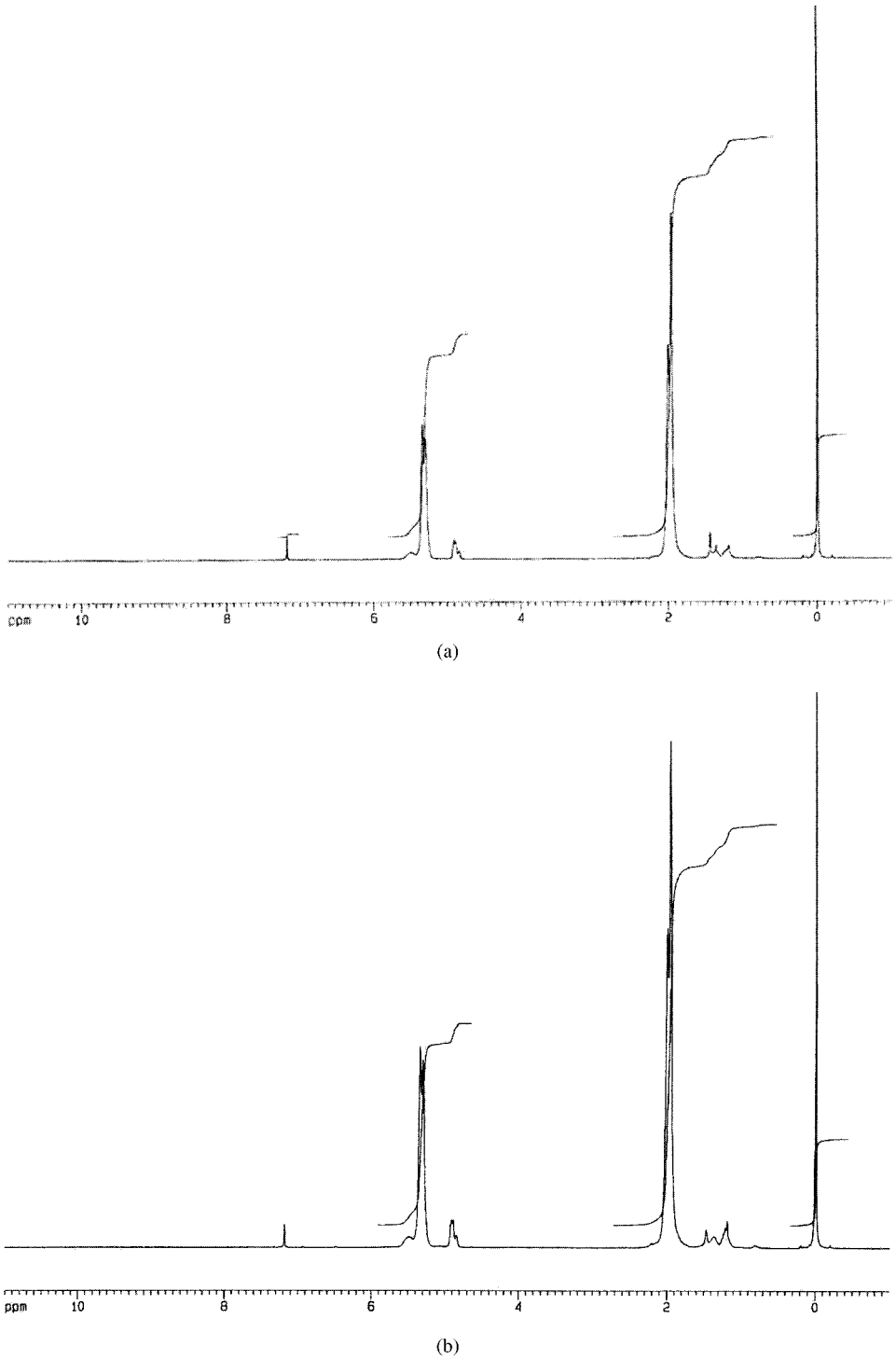


Figure 3. ^{1}H NMR spectra of a physical mixture of (a) commercial PB and ω-silane poly(dimethylsiloxane) (17 wt % of siloxane) and (b) PB-*g*-PDMS 70 copolymer.

able to suppose that the reactive groups of both polymers may be hidden (particularly, the ω-silane group), and this "shielding effect" could noticeably affect both the course of the hydrosilylation reaction and the electronic microenviroment of the carbon–carbon double bonds (C═C). According to the values of ξ and ω_{PDMS} calculated from the ^{1}H NMR spectra, this "shielding effect"

would be considerable even at low concentrations of ω-silane PDMS in the reactive mixture.

To compare the results calculated from eqs 2–6, we also registered the ^{1}H NMR spectra of physical mixtures of PB and ω-silane PDMS. For example, Figure 3 depicts the ^{1}H NMR spectrum of a physical mixture with 17 wt % of ω-silane PDMS and the spectrum corresponding to the PB-*g*-PDMS 70 copolymer.

We observed that the obtained values for the integrated peak areas of the methyl protons in both spectra were similar (14.358 in the mixture and 12.565 in the copolymer). According to the linear plot-fitting given by eq 7, this value of the integrated peak area at 0.1–0.0 ppm corresponded to a graft copolymer in which w_{PDMS} was almost 0.16. Consequently, we can conclude that the values of w_{PDMS} calculated from eqs 4 and 6 are correct. Furthermore, the same agreement between the calculated values from eqs 4 and 6 and those obtained by comparison with the physical mixtures was obtained for all the PB-*g*-PDMS copolymers synthesized, as one can observe comparing the data reported in the last three columns of Table 3.

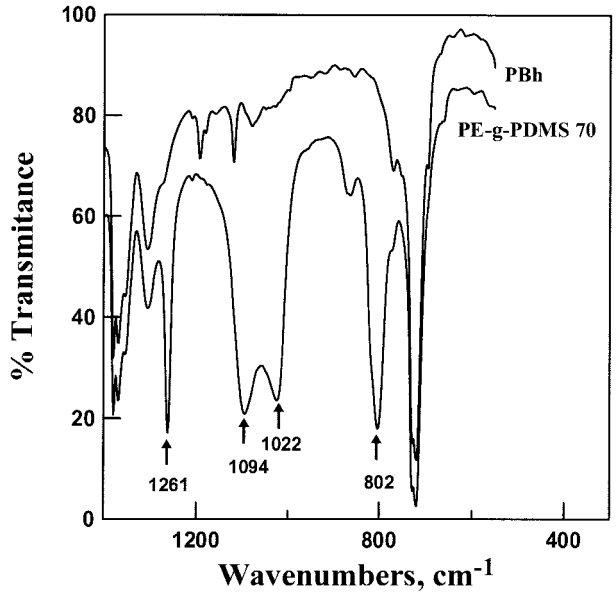


Figure 4. FTIR spectra of the hydrogenated PB (PBh) and the PE-*g*-PDMS 70 copolymer in the 1600–600 cm^{-1} wave-number range (spectra were shifted along the transmitance axis to distinguish differences between them; arrows indicate characteristic siloxane-absorption bands in the graft copolymer).

FTIR Spectroscopic Characterization

To fulfill the chemical characterization of the synthesized compounds, we registered the FTIR spectra of the hydrogenated PB and PE-*g*-PDMS copolymers. For example, Figure 4 shows the FTIR spectra of the hydrogenated PB (labeled as PBh) and the PE-*g*-PDMS 70 copolymer. Most of the bands in the FTIR spectrum of the hydrogenated PB were found in the FTIR spectrum of the PE-*g*-PDMS 70 copolymer, indicating not only structural resemblance but also complete hydrogenation with Wilkinson's catalyst, which provided a completely saturated hydrocarbon structure.

The common bands that appeared at 1301, 1362, and 1375 cm^{-1} were assigned to bending vibrations from methylene (twisting), methine (asymmetric), and methyl (symmetric) groups, respectively. However, those bands that appeared at 725 and 732 cm^{-1} (as a doublet) corresponded to methylene rocking vibrations for polymeric straight chains in planar conformation.[28,29] The inflexion at 1348 cm^{-1} over the double band at 1362–1375 cm^{-1} (observed as a medium-intensity band in both spectra) can be assigned to methylene bending vibrations inside the regular polymeric structure, closely folded in zigzag with adjacent repetitive units.[30]

Besides the aforementioned considerations, arrows in the figure show the most distinct bands in the copolymer spectrum. These bands were observed at 1261 (symmetric —CH_3 deformation in Si—CH_3 bonds), 1094 and 1022 (asymmetric Si—O—Si stretching vibrations), and 802 cm^{-1} (Si—C stretching vibration). These bands were characteristic of siloxane structures,[31] and they were absent in the hydrogenated PB spectrum, which provided additional evidence of the siloxane grafting onto original PB.

CONCLUSIONS

PB-*graft*-PDMS copolymers were synthesized by hydrosilylation reactions {catalyzed by $Cl_2[S(CH_2CH_3)_2]Pt$ salt} between commercial PB and ω-silane PDMS. These copolymers were chemically characterized by FTIR and ^{1}H and ^{13}C NMR spectroscopies. In particular, with ^{1}H NMR we determined that the mass fraction of grafted ω-silane PDMS ranged from 3 to 16 wt %. By catalytic hydrogenation of these copolymers, we obtained polyethylene-*graft*-PDMS copolymers,

and an investigation about their morphology and thermal and mechanical properties will appear in the near future.

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