Novel Synthesis of Polyethylene–Poly(dimethylsiloxane) Copolymers with a Metallocene Catalyst

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ABSTRACT: Polyethylene–poly(dimethylsiloxane) copolymers were synthesized in solution from an ethylene monomer and an ω-vinyl poly(dimethylsiloxane) (PDMS) macromonomer at 363 and 383 K with $EtInd_2ZrCl_2$/methylaluminoxane as a catalyst. The copolymers obtained were characterized with Fourier transform infrared spectroscopy, ^1H and ^{13}C NMR, size exclusion chromatography, and differential scanning calorimetry. The rheological properties of the molten polymers were determined under dynamic shear flow tests at small-amplitude oscillations, whereas the physical arrangement of the phase domains was analyzed with scanning electron microscopy (SEM)/energy dispersive X-ray (EDX). The analysis of the catalyst activity and the resulting polymers supported the idea of PDMS blocks or chains grafted to polyethylene. The changes in the rheological behavior and the changes in the Fourier transform infrared and NMR spectra were in agreement with this proposal. © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 2462–2473, 2004

Keywords: $EtInd_2ZrCl_2$/methylaluminoxane catalyst system; copolymers; ethylene; poly(dimethylsiloxane); graft copolymers; macromonomers; functionalization of polyolefins; metallocene catalysts

INTRODUCTION

The synthesis of functionalized polymers with specific properties is very important for the development of new materials.[1] In the particular case of ethylene-based polymers, some specific characteristics (e.g., good mechanical and electrical properties, ease of processing, and an excellent cost–performance relationship) have generated great interest in the development of polyethylene (PE) blends or copolymers with other materials for the improvement of some properties or its range of use.[2]

Metallocene catalysts have been shown to be effective for this propose because these single-site catalysts offer the possibility of producing polymers with controlled molecular structures and narrow molecular weight distributions,[3] along with the possibility of copolymerizing vinyl monomers with dienes or polar monomers.[4] For example, organolanthanide complexes favor the polymerization of a wide variety of polar monomers,[5,6] and zirconocenes have recently been used to polymerize methyl methacrylate (MMA).[7,8] Moreover, metallocenes have been reported as active catalysts in the hydrosilylation reaction of olefins.[9]

Among the great diversity of metallocene catalyst systems, $EtInd_2ZrCl_2$/methylaluminoxane (EBI/MAO) is one of the most studied.[10] However, the polymerization of ethylene at low temperatures, such as 313 K, with EBI/MAO produces a polymer with a complex rheological behavior because of the presence of long-chain branching (LCB). Apparently, this LCB is due to the insertion of PE molecules with terminal vinyl groups (macromonomers) during the polymerization process at temperatures lower than 333 K.[11] However, LCB has also been observed at elevated temperatures in the gas phase or in a slurry with hydroxylated silica and alumina supports.[12]

Metallocene catalyst systems have also been used to obtain graft or block copolymers.[13] Because the main chain and branched chains are generally thermodynamically incompatible, most graft and block copolymers are multiphase materials. For this reason, these copolymers are useful as emulsifiers, surface-modifying agents, coating materials, adhesives, and compatibilizing agents for polymer blends.[14] For example, the copolymerization of vinyl monomers (e.g., ethylene or propylene) with polar monomers (e.g., MMA or caprolactone) allows the introduction of polar functional groups into the structures of polyolefins.[15]

The copolymers obtained by this reaction are very attractive as new engineering plastics with specific applications, such as printable or dyeable resins and adhesive materials. In addition, degradable copolymers can be synthesized with this method. However, the copolymerization of ethylene with polar monomers drastically reduces the catalytic activity of the EBI/MAO system because these compounds can react with the cationic zirconium, which is the reactive site of the catalyst. Because the same behavior has been observed for ethyl benzoate (EB) and tetramethylpiperidine, a plausible explanation is that polar monomers behave like Lewis base compounds.[16]

Polyorganosiloxanes have a number of outstanding properties, such as thermal and oxidation stability, a low glass-transition temperature, water and chemical resistance, water repellency, and biocompatibility.[17] However, the major drawback of these compounds is their high immiscibility with carbon-based polymers. An effective alternative is the synthesis of graft or block copolymers.

The modification of ethylene homopolymerization by siloxane grafting would result in the synthesis of an organic hybrid material, which could be useful in a wide range of applications. Although the scientific literature (journal articles and patents) includes reports on the synthesis of polyethylene–poly(dimethylsiloxane) (PE–PDMS) copolymers with different techniques,[18–20] as far as we are concerned, poly(dimethylsiloxane) macromonomers and metallocene catalysts have not been used for this purpose. Therefore, we report preliminary results for the copolymerization reaction between an ethylene monomer and an ω-vinyl poly(dimethylsiloxane) (PDMS) macromonomer at 363 and 383 K with EBI/MAO. To the best of our knowledge, the copolymerization reaction between ethylene and a macromonomer such as PDMS with a metallocene catalyst system has not yet been reported. Because this macromonomer can be synthesized with anionic polymerization procedures, this kind of copolymerization would provide a novel method of tailoring the properties of the resulting copolymers.

EXPERIMENTAL

Materials

Toluene, chloroform, and methanol (Dorwill) were purified according to the usual experimental procedures. The PDMS macromonomer was previously synthesized in our laboratories with typical anionic polymerization techniques.[21] The weight-average molecular weight (M_w) of this homopolymer was 21,700 Da, and its polydispersity index [weight-average molecular weight/number-average molecular weight (M_w/M_n)] was 1.28. Research-grade ethylene (Matheson Co.) was purified with 13 X molecular sieves and MnO_2/Al_2O_3 before use. Methylaluminoxane (MAO; 10% MAO in toluene; Witco) was used without further purification. $EtInd_2ZrCl_2$ (EBI; Aldrich), a catalyst, was used as received.

Homopolymerization of Ethylene and Copolymerization Reaction of Ethylene with the PDMS Macromonomer

A 0.6-L semibatch steel reactor equipped with a magnetic stirrer was used. Gaseous ethylene (0.172 MPa) and 0.2 L of toluene were introduced. The system was heated, and the temperature was stabilized at 363 or 383 K. Then, 0.5–1 mg of EBI and 2–3 cm^3 of MAO (10% w/v in toluene) were added.

After 15–20 min, a sample of the pure ethylene homopolymer was taken. Subsequently, 0.4 g of

the PDMS macromonomer was added to the reactor by syringe techniques (ethylene/PDMS = 300) as a solution in toluene (400 mg of PDMS in 2 mL). The copolymerization reaction proceeded for another 20 min. Both compounds (the ethylene homopolymer sample and the crude copolymerization product) were precipitated by the addition of acidic ethanol, gently stirred, and filtered.

For the elimination of the unreacted PDMS, the crude copolymerization products were dissolved first in hot xylene and then reprecipitated in cold methanol. The fine powder obtained was then extracted in hot chloroform and reprecipitated again in cold methanol. By this sequential purification procedure, we assumed that all the unreacted PDMS macromonomer was eliminated.

The PE samples were purified with the same experimental conditions. The resulting pure products were adequately washed with additional methanol and dried *in vacuo* at 323 K for more than 48 h before being subjected to further analysis. The ethylene homopolymers are named PE *X*, and the PE–PDMS copolymers are named PE–PDMS *X*. In both cases, *X* denotes the polymerization temperature (363 or 383 K).

Characterization

Low-Angle Laser Light Scattering (LALLS) and Size Exclusion Chromatography (SEC)

M_w of the PDMS macromonomer was measured with a Chromatix KMX-6 LALLS instrument equipped with a He–Ne laser operating at 633 nm under the following experimental conditions: toluene was the solvent (room temperature), *dn/dc* was −0.0913, and the concentration range was 0.02–0.3 wt %. The M_w values were obtained from $Kc/\Delta R_\theta$-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).

SEC of the PDMS macromonomer was performed with a Watters 440 liquid chromatograph equipped with four *μ*-bondagel columns and calibrated with polystyrene standards. The experimental conditions were as follows: toluene was the solvent (room temperature), the polymer concentration was 0.1% (w/w), the flow rate was 0.5 mL/min, and the injection volume was 100 *μ*L.

The average molecular weights (M_w and M_n) of the PE and PE–PDMS copolymers were estimated by gel permeation chromatography (GPC; Waters 150C) with 1,2,4-trichlorobenzene at 408 K. The system was equipped with a set of 10-*μ*m

PL-gel columns from Polymer Labs with nominal pore sizes of 10^6, 10^3, and 500 Å. The molecular weights of the copolymer were estimated as equivalent to PE according to the standard calibration procedure with monodisperse polystyrene samples.

Differential Scanning Calorimetry (DSC)

The thermal transitions of the PE and PE–PDMS copolymers were determined with DSC with a PerkinElmer Pyris 1 calorimeter. To ensure the same thermal history for all samples, we melted each sample in the calorimeter at 423 K and then cooled it to 303 K at the fastest cooling rate permitted by the calorimeter. After this treatment, the melting endotherm was recorded between 303 and 423 K at a heating rate of 10 K/min. The melting peak and the area of the thermogram were measured to determine the temperature and enthalpy of fusion, respectively. The reported values are averages of three to four samples of each material.

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra of the resulting polymers were obtained on a Nicolet FTIR 520 spectrometer. Films about 0.10 ± 0.01 mm thick were prepared by the melt pressing of the materials at 393 K between the plates of a hydraulic press. The FTIR spectra were recorded at a 4-cm^{-1} resolution over the range of 4000–400 cm^{-1} with an accumulation of 10 scans and with air as a background. In the particular case of PE–PDMS *X* copolymers, the appearance of new absorbance bands between 1400 and 400 cm^{-1} in the spectra was used as evidence of grafting.

FTIR spectroscopy was also used to determine the vinyl content (C=C/1000 C) of the obtained homopolymers and copolymers.[22] This parameter was calculated from the FTIR spectrum of each particular sample as follows:

$$\text{C=C/1000 C} = \frac{A}{\epsilon \times b} \qquad (1)$$

where A is the height of the 908-cm^{-1} absorption peak, b is the thickness of the sample (mm), and ϵ is the molar coefficient factor (in this particular case, $\epsilon = 1.087$).

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

^{1}H and ^{13}C NMR spectra of the PE and PE–PDMS copolymer were recorded at 125 °C on a Varian

Inova 300 spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C) with o-dichlorobenzene with 20 vol % benzene-d_6 as an internal lock.

^{1}H NMR spectra were used not only to determine the chemical structure but also as evidence of siloxane grafting. In particular, the region of the ^{1}H NMR spectrum from 1.0 to 0.0 ppm was used to determine the presence of siloxane in the copolymer.

Calculation of the Grafting Degree of the PE–PDMS Copolymers with NMR Data

Generally, the amount of the inserted comonomer is obtained directly from the areas of different ^{1}H's in the NMR spectrum. The main fact here is that the total molecular weight of the copolymer is the same for both comonomers. However, in our particular case, we have two different comonomers considered as two different macrocomonomers: PE and PDMS. Consequently, the amount of the inserted comonomer should be calculated with certain assumptions.

Considering the wide dispersion of results from published data in terms of the reported amounts of the grafted comonomer, we defined a quantity of grafted PDMS in the ethylene homopolymer, considering the average molecular weights and polydispersity indices of both homopolymers. The proposed method is described next.

It is well known that 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

$$Area \cong Number\ of\ protons$$
$$\cong Number\ of\ repeating\ units \quad (2)$$

Because the chemical structure of the repeating units of both the PE and PDMS macromonomer are known, eq 2 can be written as follows:

$$Area \cong Number\ of\ repeating\ units$$
$$\cong Moles\ of\ polymer \quad (3)$$

In our particular case, we have assumed that the main contribution of the grafted PDMS macromonomer to the ^{1}H NMR spectrum is due to the methyl groups directly bonded to silicon atoms from the repeating unit, $[-(CH_3)_2SiO]_n-$. In the ^{1}H NMR spectra of the PE–PDMS copolymers, a

resonance peak appears at 0.2–0.0 ppm, and it can undoubtedly be assigned to $[-(CH_3)_2SiO]_n-$. Consequently, any other signal in the spectra should be assigned to the contribution of the ^{1}H atoms from PE units.

In light of these considerations, the molar ratio of grafted PDMS to PE can be calculated, by the rewriting of eq 3, as follows:

$$\frac{Moles\ of\ PDMS}{Moles\ of\ PE}$$
$$\cong \frac{Relative\ area\ of\ PDMS\ protons}{Relative\ area\ of\ PE\ protons} \quad (4)$$

The proportionality in eq 4 can be transformed in equality by the consideration of the average molecular weight and the number of ^{1}H in the repeating unit of both homopolymers, PDMS and PE (6 and 4, respectively):

$$\frac{Moles\ of\ PDMS}{Moles\ of\ PE}$$
$$= \frac{\dfrac{Relative\ area\ of\ PDMS\ protons}{6 \times PD_{PDMS}}}{\dfrac{Relative\ area\ of\ PE\ protons}{4 \times PD_{PE}}}$$
$$= \frac{2 \times PD_{PE} \times A_{PDMS}}{3 \times PD_{PDMS} \times A_{PE}} \quad (5)$$

where PD_{PDMS} and PD_{PE} are the average degrees of polymerization of PDMS and PE, respectively, and A_{PDMS} and A_{PE} are the corresponding areas. Considering both average molecular weights, for the copolymers we can define the following grafting degrees:

$$GD_n = \frac{2 \times PD_{PE_n} \times A_{PDMS}}{3 \times PD_{PDMS_n} \times A_{PE}} \quad (6)$$

$$GD_w = \frac{2 \times PD_{PE_w} \times A_{PDMS}}{3 \times PD_{PDMS_w} \times A_{PE}} \quad (7)$$

where PD_{PDMS_n} and PD_{PE_n} are the number-average degrees of polymerization of PDMS and PE, respectively; PD_{PDMS_w} and PD_{PE_w} are the corresponding weight-average degrees of polymerization; and GD_n and GD_w are the number-average and weight-average degrees of grafting, respectively.

Table 1. Average Molecular Weights and Thermal Properties of the PDMS Macromonomer and PE and PE–PDMS Polymers

Polymer	M_n (Da)	M_w (Da)	M_w/M_n	$T_{m,peak}$ (K)	ΔH_m (J/g)	X_c (%)
PDMS	17,000	21,700	1.28			
PE 363	22,700	50,800	1.91	404.4	208.2	72.1
PE 383	16,300	31,300	2.15	404.7	240.1	83.2
PE–PDMS 363	20,700	49,300	2.19	403.9	209.6	72.6
PE–PDMS 383	14,100	31,000	2.38	404.9	221.5	76.7

$T_{m,peak}$: peak melting temperature.
ΔH_m: enthalpy of fusion.
X_c: degree of cystallinity.

Scanning Electron Microscopy/Energy Dispersive X-ray (SEM–EDX)

Copolymers samples were observed and analyzed in a JEOL 35 CF scanning electron microscope equipped with secondary electron detection and X-ray disperse energy microanalysis (EDX DX4 was used to detect elements from B to U). EDX and scanning electron microscopy (SEM) analysis were performed simultaneously. All samples were coated with Au in a vacuum chamber. The microscope was operated at 15 kV. SEM was performed at different magnifications, whereas EDX was performed at 10,000×; this allowed a surface penetration of 1 μm.

Rheology

The dynamic properties of the molten polymers were studied on a Rheometrics RDA-II rotational rheometer in the parallel-plate mode. For this purpose, samples of the PE and PE–PDMS copolymer were molded into discs 25 mm in diameter and about 1 mm thick with a hydraulic press at 423 K.

The rheological characterization was performed in small-amplitude oscillatory shear flow tests. The dynamic elastic moduli, $G'(\omega)$, and loss moduli, $G''(\omega)$, were determined in the linear viscoelastic range of strain under a nitrogen atmosphere at temperatures between 423 and 473 K by frequency (ω) sweeps in the range of 0.1–500 s^{-1}.

RESULTS AND DISCUSSION

Copolymerization Reaction

The copolymerization reaction between gaseous ethylene and the PDMS macromonomer was carried out at 363 and 383 K over an EBI/MAO catalyst system according to the experimental conditions described previously. The PDMS macromonomer was added after 15–20 min of ethylene homopolymerization because this macromonomer could behave as a Lewis base compound (mainly because of the presence of the oxygen atom in the Si—O—Si bonds).

According to the experimental results obtained, the addition of the PDMS macromonomer does not inhibit the EBI/MAO system but clearly reduces its catalytic activity. This effect is particularly important at 383 K. However, at a polymerization temperature of 363 K, the activity after the addition of the PDMS macromonomer is partially recovered, and the ethylene consumption shows an increasing trend. This trend has also been found in the polymerization of ethylene with EBI/MAO at a lower temperature (313 K), with EB as an MAO modifier.[16]

SEC and DSC Characterization

M_n, M_w, and polydispersity values of the synthesized polymers are shown in Table 1. The molecular weight and polydispersity of the PE homopolymers are related to the polymerization conditions.

The lowest polymerization temperature gives the highest molecular weight with the lowest polydispersity index. PE–PDMS copolymers (calculated as the PE homopolymer) show lower molecular weights and higher polydispersity indices than the parent homopolymer, and this indicates the presence of PDMS molecules incorporated into some PE chains.

The melting temperature and melting enthalpy of the PE and PE–PDMS copolymers indicate that the PE homopolymers obtained at both
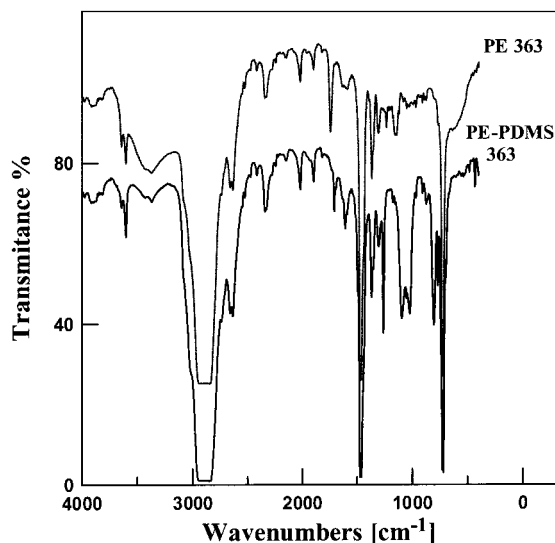
Figure 1. FTIR spectra of PE 363 (top line) and the PE–PDMS 363 copolymer (bottom line) in the 4000–400-cm^{-1} wave-number range. The spectra have been shifted along the transmittance axis to distinguish the differences between them.

temperatures are similar to a high-density PE. The presence of PDMS chains in the copolymers does not lead to an important decrease in the degree of crystallinity of the PE block, as shown in Table 1.

FTIR Characterization

PE 363 and PE–PDMS 363 Copolymer

The FTIR spectra of the PE 363 and PE–PDMS 363 copolymer in the 4000–400-cm^{-1} range are shown in Figure 1.

The spectra in Figure 1 have been chosen as examples to illustrate the differences and changes between the obtained PEs and their derived copolymers. To further interpret the differences between the PE homopolymer and its respective PE–PDMS copolymer, we first discuss the common absorption bands that appear in both spectra.

The broad absorption bands appearing at 2960–2830 cm^{-1} can certainly be assigned to symmetrical and asymmetrical stretching bands of methyl (ν CH$_3$), methylene (ν CH$_2$), and methine (ν CRH) groups from the main chain, which corresponds to the PE structure.[23] The band that appears at 1641 cm^{-1} can be assigned to stretching vibrations of carbon–carbon double bonds (ν C=C), especially vinyl groups (—CH=CH$_2$), the maximum absorption of which appears at 1640 cm^{-1}.[24]

Two absorption bands could confirm the presence of high-crystallinity zones present in these polymers: the low-intensity band at 1896 cm^{-1} and the band that appears at 1049 cm^{-1}. However, the broad band at 1306 cm^{-1} shows that amorphous zones are also present.[23] From an analysis of the FTIR spectrum, we have concluded that the structure of PE 363 is similar to that of a high-density PE.[25] Short branches (e.g., methyl branches) in the PE structure could be confirmed through the band at 1119 cm^{-1}, which corresponds to the deformation of C—H bond in a tertiary carbon. Finally, two sharp absorption bands between 730 and 720 cm^{-1} appear in both FTIR spectra. These bands can undoubtedly be assigned to methylene rocking bands (ρ CH$_2$) and are indicative of the crystalline structure of PE.[26]

The most important differences between the PE 363 homopolymer and the PE–PDMS 363 copolymer can be appreciated in the 2000–400-cm^{-1} range. Figure 2 displays both FTIR spectra in this zone.

The PE 363 spectrum shows an absorption band at 1742 cm^{-1} that can be assigned to the presence of oxidation products formed during the polymerization or purification processes. The absorption band that appears between 1180 and 1130 cm^{-1} (which is not longer noticeable in the copolymer spectrum) can be assigned to terminal methyl groups.[27]

In the PE–PDMS 363 spectrum, we can observe four characteristic absorption bands from
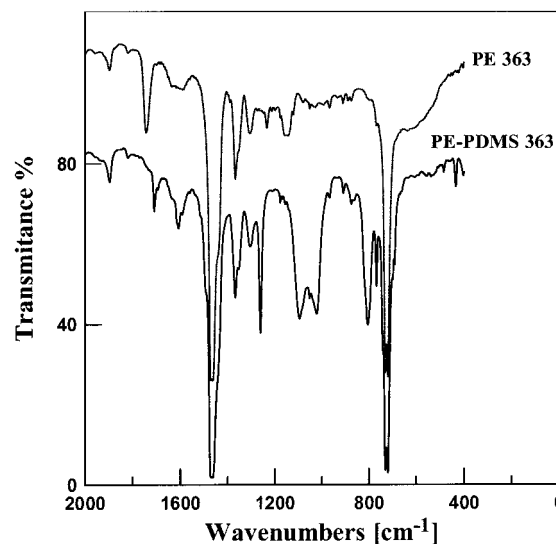
Figure 2. FTIR spectra of PE 363 (top line) and the PE–PDMS 363 copolymer (bottom line) in the 2000–400-cm^{-1} wave-number range.

siloxane structures: the band at 1261 cm^{-1} (symmetric deformation of —CH$_3$ in Si—CH$_3$), the bands at 1094 and 1022 cm^{-1} (asymmetric Si—O—Si stretching vibrations); and the band at 802 cm^{-1} (Si—C stretching vibration).[28] They are absent in the PE spectrum. Consequently, the presence of these bands provides decisive evidence of siloxane grafting. However, analyzing both spectra, we have observed that the absorption band at 767 cm^{-1} shows a noticeable increase in the copolymer spectrum. This band could denote the presence of long branches in the PE–PDMS 363 copolymer structure, which would be assigned to the grafted PDMS chains.

Another important band that appears in the PE–PDMS 363 spectrum is the band at 1607 cm^{-1}. Carbon–carbon double bonds (—C=C—) are classified as terminal or vinyl, vinylidene, and internal (cis and trans) double bonds.[23] Consequently, the band at 1607 cm^{-1} could be assigned to vinyl and vinylidene double bonds, the presence of which seems to be much more important here than in the PE 363 homopolymer. Moreover, two bands increase their intensity in the copolymer spectrum: the bands at 873 and 908 cm^{-1}. The first one is assigned to deformation vibrations from vinylidene groups (δ RR′CH=CH$_2$),[29] whereas the band at 908 cm^{-1} (as well as the band at 993 cm^{-1}) confirms the presence of vinyl double bonds. In addition, we also distinguish an absorption band at 993 cm^{-1}, which should be assigned to γ =CH in these chemical groups.

Finally, the band that appears at 767 cm^{-1} has been assigned to branches (mainly ethyl branches) in the PE homopolymer structure, but its increase is noticeable in the copolymer spectrum. If we consider correct the presented assignment, this band would indicate an important degree of branching in this copolymer, necessarily assigned to the grafted PDMS chains.

PE 383 and PE–PDMS 383 Copolymer

Most of the absorption bands observed in the PE 383 and PE–PDMS 383 copolymer are identical to those already reported for the PE 363 and PE–PDMS 363 copolymer. However, we observed some differences between them.

The FTIR spectrum of PE 383 is practically identical to that of PE 363. Despite this, the band that appears at 767 cm^{-1} (which has already been assigned to ethyl branches in the PE structure) is no longer noticeable in the PE 383 homopolymer spectrum. This is the most important difference between these homopolymers, and it could denote some effect of the reaction temperature during the polymerization process. On the contrary, the presence of this band in the copolymer is noticeable.

The position of this band is unexpected for a double bond, but if an alternative explanation is necessary, it should be assigned to trisubstituted double bonds (R$_1$CH=CR$_2$R$_3$), the bands of which appear between 840 and 790 cm^{-1}. If we assume that ethyl branches are absent in the structure of the main chain, the absorption band could be shifted to lower wave numbers. This fact could be explained if we consider that one of the substituents is the PDMS chain.

In contrast to the PE–PDMS 363 copolymer, the absorption band at 908 cm^{-1} (which has been already assigned to the presence of vinyl double bonds) diminishes its absorptivity in the PE–PDMS 383 FTIR spectrum. This fact could denote differences between the termination reactions of both copolymers, and this is discussed in the next section. Finally, in the PE–PDMS 383 copolymer spectrum, we have also observed the four characteristic bands from siloxane structures at 1261, 1094, 1022, and 802 cm^{-1}. However, the intensity of these bands is lower than that of PE–PDMS 363.

Grafting Reactions: Proposed Mechanism for the Termination Reactions

The vinyl content (C=C/1000 C) of the PE homopolymers and PE–PDMS copolymers was calculated from the FTIR spectrum of each sample according to eq 1. The obtained values for C=C/1000 C are summarized in Table 2.

According to these data, the vinyl content of the PE–PDMS 363 copolymer is higher than that of the PE 363 homopolymer, whereas the opposite tendency is observed when we compare PE 383 and PE–PDMS 383. We can provide a reasonable explanation for these facts of we consider two different termination mechanisms.

If we consider termination after 1,2-insertion of PDMS in some PE chains, all the growing chains at both reaction temperatures (363 and 383 K) are available to copolymerize with PDMS. Consequently, no changes in the C=C concentration would be found, and homopolymers and copolymers should have almost equivalent values for C=C/1000 C. In this case, H transfer to Zr would be the main termination reaction, and the

Table 2. Vinyl Content (C=C/1000 C) of the Synthesized Polymers according to FTIR Spectroscopy Data

Polymer	A_{908}	Thickness (mm)	C=C/1000 C[a]
PE 363	0.011 ± 0.001	0.10 ± 0.01	0.113 ± 0.020
PE–PDMS 363	0.024 ± 0.001	0.11 ± 0.00	0.200 ± 0.010
PE 383	0.038 ± 0.001	0.11 ± 0.01	0.338 ± 0.012
PE–PDMS 383	0.030 ± 0.001	0.10 ± 0.01	0.285 ± 0.020

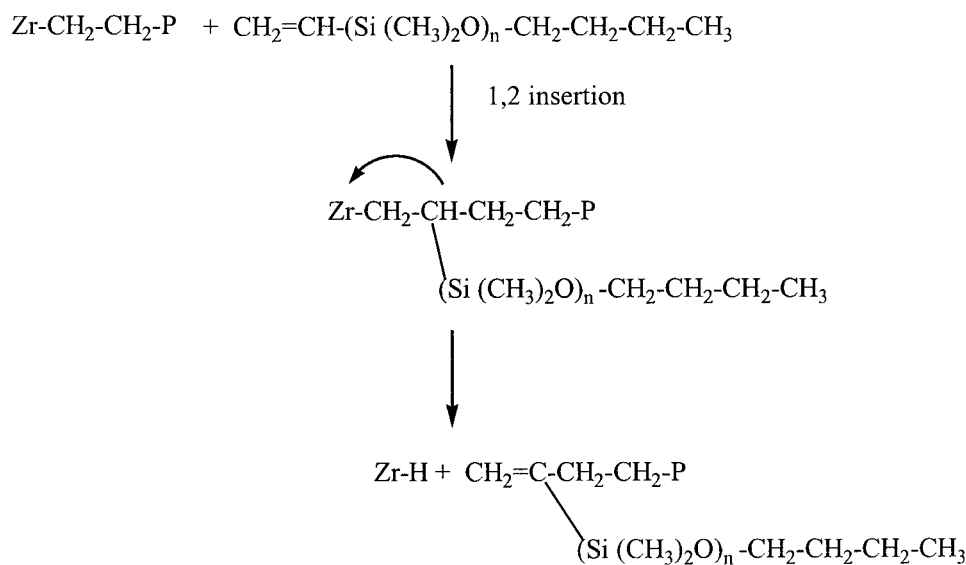[a] Calculated according to eq 1.

hypothetical reaction scheme after 1,2-PDMS insertion is shown in Scheme 1.

Transfer to the monomer has been proposed as the main termination reaction when ethylene is polymerized with EBI/MAO.[30] In this particular case, when the copolymerization reaction occurs at 363 K, the copolymer has a higher vinyl concentration. In addition, analyzing its FTIR spectrum, we have observed *trans*-vinylenes and vinylidene double-bond absorption bands. At 363 K, the data are in line with the copolymerization of PDMS without suppression of ethylene insertion. Scheme 2 shows hypothetical copolymerization with ethylene after 1,2-PDMS insertion and subsequent termination by transfer to the ethylene monomer.
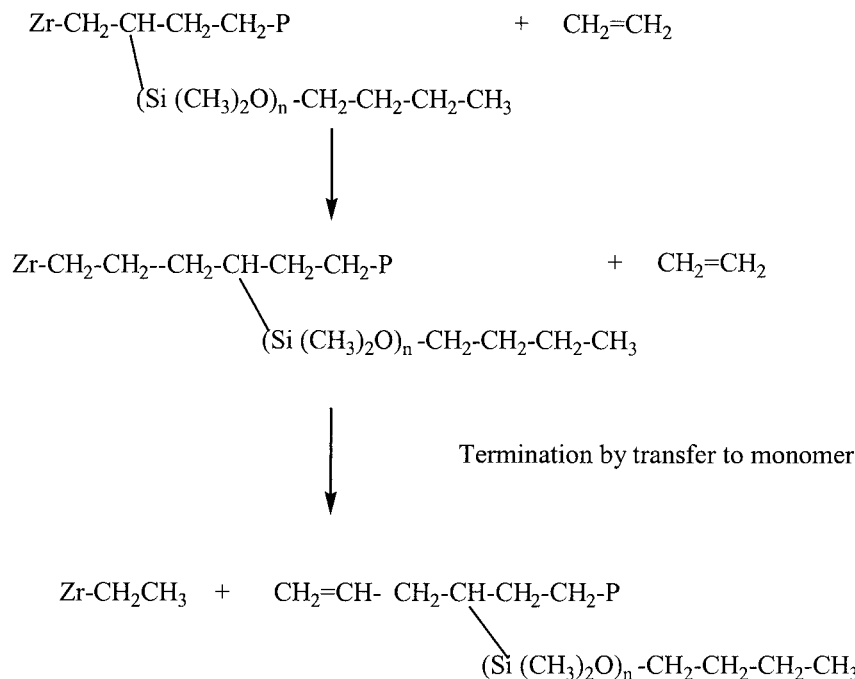
We suppose that changes in the reaction medium viscosity (because of PDMS) increases the monomer coefficient diffusion and the termination reaction constant with respect to the propagation constant, resulting in a lower molecular weight for the fraction of molecules that do not insert into PDMS but terminate with transfer to the monomer. Because PDMS is copolymerized in some of the remaining PE molecules, this last effect is compensated by the fraction of molecules with a higher molecular weight.

The results for the copolymerization at 383 K are more easily explained if we consider that the increase in the temperature has different effects. One of these effect is the reduction of M_w (compared with PE 363, from 50,800 to 33,300 Da), which explains the increase in the C=C/1000C concentration in the PE 383 homopolymer. However, diffusional problems are less important than those present at lower temperatures. Because PE is dissolved in the reaction media, the transfer constant to the monomer would probably increase with respect to the propagation constant. For the PE–PDMS 383 copolymer, the possibility of 2,1-insertion of PDMS and then β-H termination would explain the lower vinyl content. This hypothetical termination mechanism is illustrated in Scheme 3.
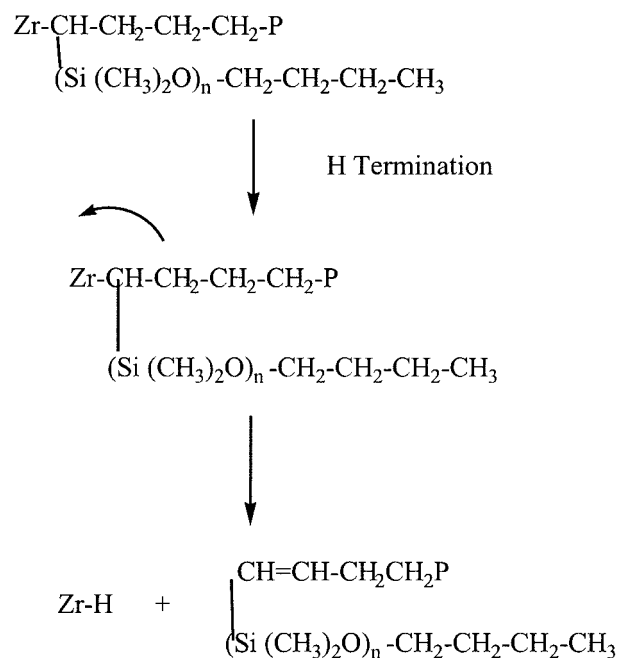
Zr-CH$_2$-CH$_2$-P + CH$_2$=CH-(Si (CH$_3$)$_2$O)$_n$-CH$_2$-CH$_2$-CH$_2$-CH$_3$

1,2 insertion

Zr-CH$_2$-CH-CH$_2$-CH$_2$-P

(Si (CH$_3$)$_2$O)$_n$-CH$_2$-CH$_2$-CH$_2$-CH$_3$

Zr-H + CH$_2$=C-CH$_2$-CH$_2$-P

(Si (CH$_3$)$_2$O)$_n$-CH$_2$-CH$_2$-CH$_2$-CH$_3$

Scheme 1. Hypothetical termination reaction after 1,2-PDMS insertion.

Zr-CH$_2$-CH-CH$_2$-CH$_2$-P   +   CH$_2$=CH$_2$

|

(Si (CH$_3$)$_2$O)$_n$ -CH$_2$-CH$_2$-CH$_2$-CH$_3$

↓

Zr-CH$_2$-CH$_2$--CH$_2$-CH-CH$_2$-CH$_2$-P   +   CH$_2$=CH$_2$

|

(Si (CH$_3$)$_2$O)$_n$ -CH$_2$-CH$_2$-CH$_2$-CH$_3$

↓ Termination by transfer to monomer

Zr-CH$_2$CH$_3$ +   CH$_2$=CH- CH$_2$-CH-CH$_2$-CH$_2$-P

|

(Si (CH$_3$)$_2$O)$_n$ -CH$_2$-CH$_2$-CH$_2$-CH$_3$

Scheme 2. Hypothetical copolymerization reaction between the PE–PDMS 363 copolymer and ethylene monomer after 1,2-PDMS insertion.

The terminal *n*-butyl string due to 2,1-insertion of PDMS and β-H transfer to the end of the chain reduces the relative concentration of terminal vinyl groups in the copolymer. When copolymerization is performed at 383 K, an increase in both the termination reaction constant and the wrong insertion of PDMS can be sought. However, if PDMS (or PE) 2,1-insertion on a particular PE growing chain is possible, the result would be an increase in the nonterminal vinyl groups (especially *trans*-vinylenes).

Zr-CH-CH$_2$-CH$_2$-CH$_2$-P

|

(Si (CH$_3$)$_2$O)$_n$ -CH$_2$-CH$_2$-CH$_2$-CH$_3$

↓ H Termination

Zr-CH-CH$_2$-CH$_2$-CH$_2$-P

|

(Si (CH$_3$)$_2$O)$_n$ -CH$_2$-CH$_2$-CH$_2$-CH$_3$

↓

Zr-H   +   CH=CH-CH$_2$CH$_2$P

|

(Si (CH$_3$)$_2$O)$_n$ -CH$_2$-CH$_2$-CH$_2$-CH$_3$

Scheme 3. Hypothetical termination reaction after 2,1-PDMS insertion.

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

Although the ^{13}C NMR spectra did not demonstrate significant incorporation of PDMS at the range of detection of the equipment used, in the case of ^{1}H NMR spectra, we could distinguish different ^{1}H resonance peaks. The positions of these peaks, as well as the values obtained for their integrated peak areas, are presented in Table 3. From these values, we calculated the amount of grafted PDMS according to eqs 6 and 7 reported in the Experimental section.

According to the data obtained, for PE–PDMS 363, we found 0.9 mol % grafted PDMS, whereas for the PE–PDMS 383 copolymer, the total amount of grafted PDMS is 0.3 mol %. These results clearly show that the grafting efficiency is higher at the lowest reaction temperature studied. However, they agree with the FTIR analysis

Table 3. PE–PDMS Copolymers: ^{1}H NMR Data Analysis

Copolymer	[1]H Resonance	ppm	Area	GD_n $(\times 10^3)^a$	GD_w $(\times 10^3)^b$	mol %	wt %
PE–PDMS 363	—[(CH$_3$)$_2$SiO]$_n$—	0.16	0.38	9.0	15.9	0.89	0.67
	CH$_3$—P	0.82	0.31				
	—(CH$_2$)$_n$—	1.25	98.66				
	R—CH(R')—P	1.42	0.53				
	R—CH$_2$—CH=CH—P	2.00–2.15	0.43				
PE–PDMS 383	—[(CH$_3$)$_2$SiO]$_n$—	0.16	0.19	3.3	4.9	0.33	0.34
	CH$_3$—P	0.82	0.66				
	—(CH$_2$)$_n$—	1.30	97.72				
	R—CH(R')—P	1.45	0.84				
	R—CH$_2$—CH=CH—P	2.00–2.15	0.71				

[a] Calculated according to eq 6.
[b] Calculated according to eq 7.

reported and with the termination mechanisms proposed in the previous section of this article.

Rheological Characterization

Figures 3 and 4 show the master curves of the melt viscosity for polymers synthesized at 363 and 383 K, respectively. The PE–PDMS copolymer synthesized at 383 K has viscosity values higher than those of the corresponding homopolymer. This can be attributed to the incorporation of PDMS into some PE chains. However, at 363 K, the opposite situation can be observed, even when the degree of PDMS incorporation is higher at this temperature. This fact can be attributed to the higher degree of branching present in the PE homopolymer obtained at lower temperatures.

All the analyzed polymers obey the time–temperature principle, and so curves of $G'(\omega)$ and $G''(\omega)$ measured at different temperatures can be superposed through shifting along the frequency axis with a temperature shift factor (a_T). The values of the flow activation energy (ΔH), in an Arrhenius-type dependence of a_T with the temperature, for the PE homopolymers and PDMS copolymers synthesized in this work are shown in Table 4.
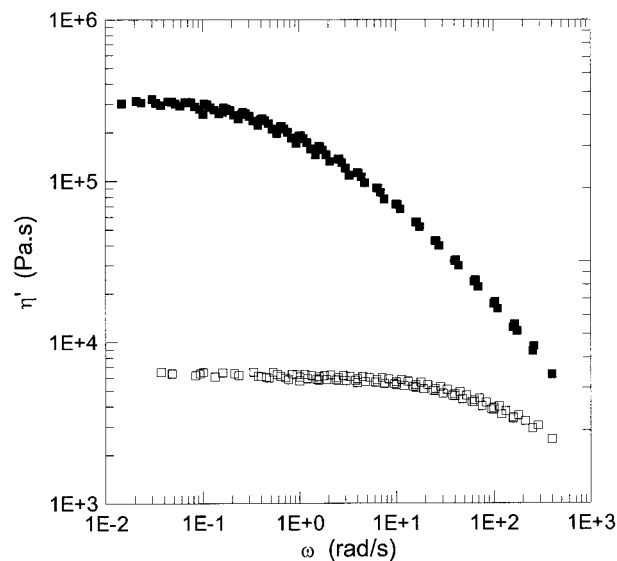
Figure 3. Master curves of the melt viscosity for PEs at reference temperature T_0 = 323 K: (■) PE 363, and (□) PE 383.
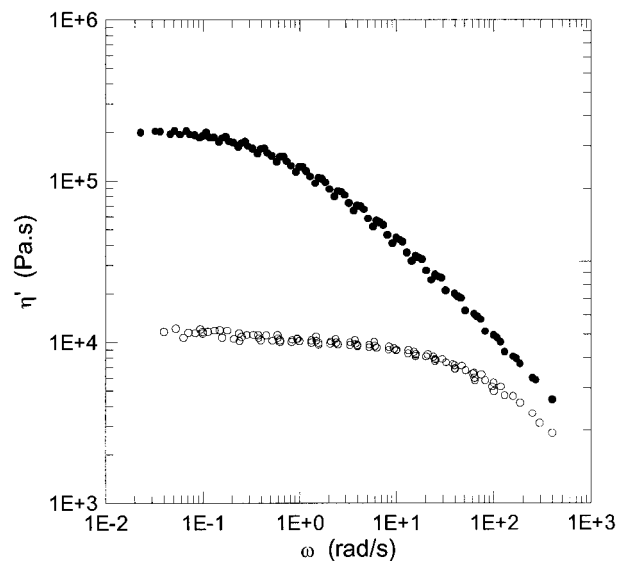
Figure 4. Master curves of the melt viscosity for PE–PDMS copolymers at reference temperature T_0 = 323 K: (●) PE–PDMS 363 and (○) PE–PDMS 383.

Table 4. ΔH and η_0 Data

Polymer	ΔH (kJ/mol)	η_0 exp (Pa s) at $T_0 = 463$ K	η_0 calc (Pa s) at $T_0 = 463$ K[a]
PE 363	63.7	105,820	297
PE 383	48.1	3,530	52
PE–PDMS 363	59.5	86,320	
PE–PDMS 383	47.8	4,580	

[a] Calculated according to $\eta_0 = 3.4 \times 10^{-15} M_w{}^{3.6}$.[31]

ΔH for the PE homopolymer increases as the temperature of the reaction decreases. The ΔH values of the PE homopolymer are comparable to those obtained for a high-density PE modified with a low concentration of peroxide.[32] However, ΔH of the copolymers decreases with respect to ΔH of the parent homopolymer. The decrease is higher for the copolymer PE–PDMS 363; this indicates a higher incorporation of PDMS, which agrees with the FTIR and ^{1}H NMR results.

EBI/MAO, like other ansa metallocenes, produces LCB PE.[33] It has been reported that 0.2 LCB/1000 C can be obtained with this metallocene,[34] and branching increases the zero shear rate viscosity (η_0) dramatically. However, ΔH is a very sensitive measure of LCB in PE. Linear (high-density) PEs have ΔH values of 25–30 kJ/mol, a small amount of short-chain branching increases those values to 30–36 kJ/mol, and LCB PEs have values of 40–60 kJ/mol. The ΔH values of PE 363 and PE 383 indicate that they have LCB in their structures.

If PDMS is incorporated, and this produces an LCB-PE/PDMS block copolymer, a decrease in ΔH should be expected. The incorporation of PDMS reduces the relative proportion of LCB in PE–PDMS and also increases the molecular weight. This is in agreement with the experimental values obtained in this work. The decrease in ΔH is less noticeable for PE–PDMS 383 because the degree of incorporation is lower than the corresponding value of PE–PDMS 363.

SEM–EDX

Figures 5 and 6 show SEM microphotographs of the copolymer surfaces; they are shown to illustrate the observed morphologies.

According to these microphotographs, two different morphologies are evident: fibrils and globules. The amorphous nature of PDMS seems evi-
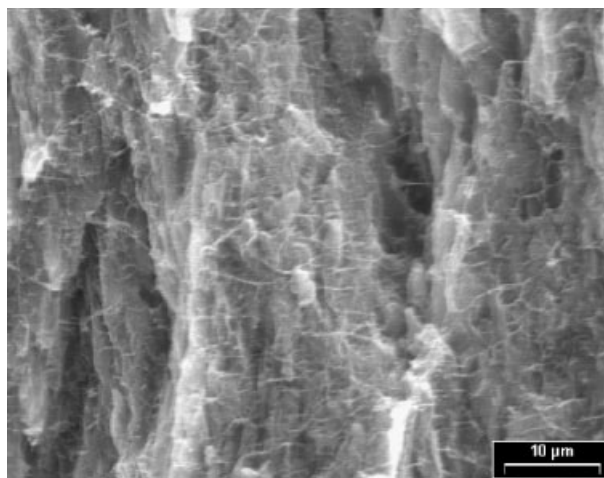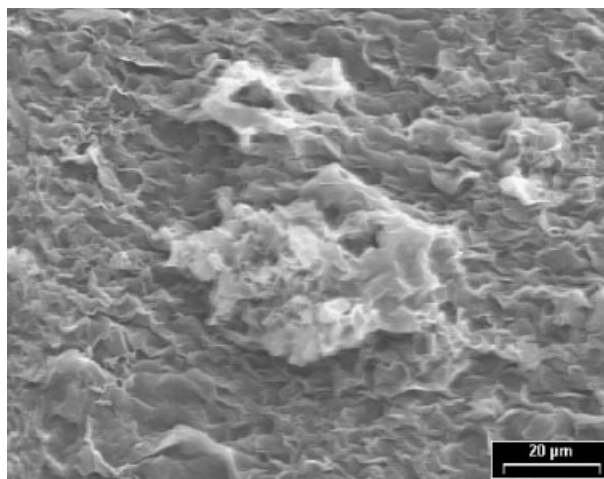

Figure 5. SEM–EDX microphotograph of the surface of the PE–PDMS 363 copolymer.

dent in the microphotographs, and because of its low surface tension, it will be preferentially located at the surface.[35] In addition, the EDX analysis shows evidence of the presence of Si.

CONCLUSIONS

PE–PDMS copolymers have been synthesized in solution from an ethylene monomer and a PDMS macromonomer at 363 and 383 K with EBI/MAO as a catalyst. The copolymer obtained at 363 K shows a higher content of PDMS than that obtained at 383 K. However, the degree of grafting of the PDMS macromonomer to the PE chains

Figure 6. SEM–EDX microphotograph of the surface of the PE–PDMS 383 copolymer.

seems to be low for the experimental conditions studied. With EBI/MAO, it has been demonstrated that M_n is independent of the ethylene concentration, the chain transfer to the monomer being the predominant termination reaction. However, when PDMS is present, the predominant termination reaction becomes β H-termination.

The FTIR spectra of the copolymers show four absorption bands at 1261, 1094, 1022, and 802 cm^{-1}, which are characteristic of siloxane structures. The presence of these bands provides, among other things, decisive evidence of siloxane grafting. In addition, SEM–EDX, ^{1}H NMR spectroscopy, GPC data, and rheological measurements support the idea of the real copolymerization of PDMS and PE. However, the PE homopolymers obtained under our experimental conditions have LCB, particularly the polymer obtained at 363 K. Rheological measurements show that ΔH decreases after copolymerization with PDMS.

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