

Grafting of Styrene onto Polyethylene in Near Critical Media

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ABSTRACT: In this work, near critical *n*-heptane is used as reaction medium for the copolymerization of polyethylene with styrene monomer, using alkylation reaction with different amounts of aluminum chloride (AlCl₃) as catalyst. In this way, polyethylene chains will be more available to react with the catalyst. The reaction effect on pure reactants, as well as, the catalyst activity was previously investigated. The reaction occurrence was corroborated by analyzing the reaction products before and after careful polystyrene extraction with tetrahydrofuran. The reaction products were characterized by Fourier transform infrared spectroscopy, nuclear magnetic resonance, scanning electron microscopy, transmission electron microscopy, differ-

ential scanning calorimetry, and size exclusion chromatography. The possible architecture for the copolymer molecule was proposed from the molecular characterization results. On the other hand, the polystyrene grafting modifies final properties of polyethylene, increasing the oxygen barrier properties without deteriorating significantly the mechanical properties of the films. In this sense this reaction seems to be a promising route to modify PE films to increase the barrier properties. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2787–2799, 2012

Key words: polystyrene grafting; polyolefins; supercritical fluids; properties modifications; AlCl₃

INTRODUCTION

In the last years, the most significant trend in the field of plastics is focusing on the material application. The compromise between economy and technical properties requirements is frequently reached, by development materials with predetermined properties, based on commodity plastics.¹ In this sense, copolymers obtained by introduction of a new functional group into a polymer molecule have enhanced properties. This kind of molecules is frequently applied in diverse fields like adhesives, paints, coatings, emulsifiers, and biomedical materials. Particularly, they play an important role as compatibilizers in multiphase materials because they act as emulsifiers and phase adhesion promoters improving final properties.²

Some promising reactions begin from macromers or macromonomers. In this sense, cationic copolymerization is a growing field of synthetic polymer chemistry, which provides a variety of avenues toward a large number of unique materials with unusual combinations properties.³ In this sense, reactions involving the alkylation of an aromatic ring

and an alkyl halide using a Lewis acid catalyst are a promising route to obtain copolymers. Previous studies used this kind of reaction in molten state to graft polyolefins, like polyethylene (PE) and polypropylene (PP), onto polystyrene (PS) through an aromatic electrophilic substitution.^{4–6} They use aluminum chloride (AlCl₃) as a catalyst, because it is one of the most powerful Lewis acids, and styrene as cocatalyst.

Conversely, near critical and supercritical fluids as inert or reactive medium for synthesis, extraction and/or processing of polymers are more frequently used.⁷ Typical examples are: PE polymerization in supercritical ethylene,^{8,9} supercritical extraction of plasticizers from PVC,^{10,11} polymer plasticization using supercritical CO₂,^{12,13} etc. In supercritical fluids, a wide range of properties, from gas-like to liquid-like, become accessible by simple manipulations of pressure and temperature. As a result, a fluid can be fined-tuned to behave, as specific solvent or non-solvent for a particular substance. Furthermore of the above advantages, fluids around its critical point increase the diffusivity and decrease the viscosity and surface tension, with the consequent improvement in processing and reaction conditions.⁷

In a previous work,¹⁴ it was determined that the PE is completely soluble in *n*-heptane under high pressure-high temperature conditions. In the present work, a new method to graft styrene onto PE is proposed using near critical *n*-heptane as reaction

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TABLE I
Characteristics of Different PE Used

PE	\overline{M}_n (g/mol)	\overline{M}_w (g/mol)	Relative Proportion in Reacting PE (wt %)	T_m (°C)	Crystallinity Degree (%)
Capsule (bottom)	22,700	127,000	16.2	129.4	57.2
Capsule (cap)	16,800	46,500	4.5	122.7	44.95
PE6200	18,000	53,000	79.3	125.8	54.5
PE mix	19,200	52,100	100	124.1	47.5

medium and AlCl_3 as catalyst. Initially, reactions at high pressure and high temperature were performed over pure reactants (styrene and PE) to analyze the effect of catalyst on them. The copolymerization reactions were carried out varying the catalyst content from 1 to 4%. The reaction occurrence was assessed and quantified by Fourier Transform Infrared Spectroscopy, Nuclear Magnetic Resonance, Scanning Electron Microscopy, Transmission Electron Microscopy, Differential Scanning Calorimetry, and Size Exclusion Chromatography. Also the morphology and some final properties like mechanical properties and oxygen permeability were determined and evaluated.

EXPERIMENTAL

Materials

Styrene ($\geq 99\%$ purity) from Sigma-Aldrich and linear low-density polyethylene from Dow-Polysur, LLDPE 6200 (M_w : 52,000 g/mol, M_n : 17,000 g/mol) were used as reactants. The alkylation reaction was catalyzed with anhydrous AlCl_3 ($>98\%$ purity) from Merk. *N*-heptane from Anedra (T_c : 267.2°C, P_c : 27 bar), with purity higher than 99.5 wt % was used as reaction medium.

Equipment

The experimental system consists in a high-pressure stirred Parr reactor with temperature controller and a manual pressure generator. The reactor vessel is made of stainless steel with a capacity of 600 mL and maximum working pressure of 200 bar.

Catalyst release system

The direct catalyst addition in the reactor after pressurization and PE solubilization is very difficult because of AlCl_3 is a fine hygroscopic powder and water is a reaction inhibitor. Then, to assure that the AlCl_3 acts when the PE is completely solubilized, a catalyst release method was designed. The AlCl_3 is placed into a PE capsule, thus when the capsule is solubilized, the catalyst is released and the reaction takes place with both reactants in solution. The PE

of the capsule is similar to the LLDPE 6200, but not exactly the same, then the polymer for the reaction is a blend of different LLDPEs. The main characteristics of each PE and the blend, called *PEmix*, are summarized in Table I. In the same table the resulting blend composition is included.

On the other hand, to carry out the reactions in absence of PE, the device cannot be the same, then a little glass holder containing AlCl_3 was used. It is placed inside of reactor and it is broken by the stirrer when reaction conditions are reached. The pieces of glass are carefully separated from the reaction products.

Reaction procedure

The reaction conditions were selected based on previous studies.^{14,15} It was determined that PE can be entirely solubilized at 145°C and 150 bar, and these conditions were selected to perform the reaction. Initially, the reactor was charged with 10 g of polyethylene films ($\sim 100 \mu\text{m}$ thickness), 20 mL of styrene and the capsule with AlCl_3 . After this, it was filled with *n*-heptane, heated, stirred, and pressurized to the final conditions. The catalyst concentration varied from 1 to 4 wt %. After 1 h, the reactor was cooled to room temperature, the vessel was opened and the product was filtered to eliminate the solvent and remaining styrene. The collected sample was dried at 70°C under vacuum to remove the residual solvent and/or styrene. In this work the reaction product will be named with "R" followed with the amount of catalyst used. Thus, R1 is the reaction product prepared with 1 wt % of AlCl_3 .

For a complete characterization, the products were subject to a selective Soxhlet extraction up to constant weight (~ 15 h) with tetrahydrofuran (THF), to remove polystyrene homopolymer (PS) formed during the reaction. Also, *PEmix* and commercial PS ($\overline{M}_w = 260,000$ g/mol) were subject to extraction at the same condition to check the solvent selectivity. Complete extraction was achieved for PS while less than 22 wt % of PE appeared in the soluble fraction (SF). On the basis of these experiments, the insoluble fraction (IF) does not contain pure PS. The IF of reaction product was dried in a vacuum oven at

70°C to remove any residual solvent and then characterized.

Characterization techniques

Different techniques were applied for characterizing the raw materials and the reaction products, before and after THF extraction. These techniques are:

Fourier transform infrared spectroscopy (FTIR)

Qualitative identification of reaction products obtained at atmospheric and high pressure, as well as quantitative measures of PS copolymerized, were carried out in a Nicolet 520 FTIR equipment. The PS concentration was estimated by comparing the ratio of typical infrared absorption peaks on films samples (peak at 700 cm^{-1} for PS and at 719 cm^{-1} for PE). Previously, a calibration curve was performed with PE/PS physical blends of known concentrations.

Size exclusion chromatography (SEC)

The molecular weights distribution of the reaction products was obtained in a Waters Scientific Chromatograph model 150-CV. The samples were dissolved in 1,2,4 trichlorobenzene (0.0125% BHT), and then injected at 135°C.

Nuclear magnetic resonance (^{13}C NMR)

The ^{13}C NMR spectra of the pure polymers and reaction products were obtained by the Magic Angle Sample Spinning and Cross Polarization technique in a BRUKER AVANCE II spectrometer. The resonance frequency was 300.13 MHz for protons and 75.45 MHz to ^{13}C .

Scanning electron microscopy (SEM)

The electron microscope used was a JEOL JSM-35 CF equipped with secondary electron detection. The samples were previously coated with Au in a sputter coater PELCO 91000. Two kinds of studies were performed by this technique. For the first one, the reaction products were homogenized, melting it at 180°C during 5 min in a Maxwell minimixer. For a comparison a PE/PS physical blend with 10 wt % of PS was prepared in the same apparatus by melt blending during 15 min at the same temperature.

For the second study, the following method of sample preparation was carried out: plates of 1 mm of thickness of reaction products were molded by compression in a hydraulic press at 180°C. These samples were fractured under liquid nitrogen. One of the fracture surfaces was subjected to THF etching

under sonication at room temperature for removing pure PS. The other one was analyzed without modifications. Then, a comparative study of actual and etched fracture surfaces was carried out.

Transmission electron microscopy (TEM)

Samples etched and no-etched were analyzed in a JEOL 100 CX equipment at 100 kV. The samples were cut in a Leica Ultracryomicrotome under liquid nitrogen and then stained with ruthenium tetroxide (RuO_4). The RuO_4 was obtained from 0.02 g of ruthenium trichloride (RuCl_3) with 2 mL of sodium hypochlorite (NaOCl). The reaction was carried out in a holder hermetically closed. The polymer samples were placed into the holder, and then exposed to the RuO_4 vapor for 2 h.

Differential scanning calorimetry (DSC)

The thermograms of all samples were obtained in a Perkin-Elmer Pyris I equipment. The samples were heated to 180°C and kept 3 min at this temperature to remove all prior thermal history. Subsequently, they were quenched to 30°C and then reheated to 180°C, both steps at a rate of 10°C/min.

Oxygen permeability

The equipment used was a MOCON OX-TRAN 2/21. The oxygen barrier properties were determined at 23°C with 0% of relative humidity over films of 100 μm of thickness prepared in a hydraulic press at 180°C. Ten samples were measured for each reaction condition and for pure PE.

Mechanical properties

The tests were carried out in an INSTRON tester with pneumatic clamps over films of 200 μm of thickness prepared in a hydraulic press at 180°C. The measurements were performed at 25°C, 2 mm/min using a cell of 50N. Ten samples were measured for each reaction condition and pure PE.

RESULTS AND DISCUSSIONS

Reactions on pure reactants

The catalyst effect on pure PE was studied by carrying out a set of experiments with variable content of AlCl_3 . Neither chain scissions nor crosslinking were observed by SEC because the reacted PE SEC curve completely matches with the PEMix one for all of reaction products. This reaction neither produces PE oxidation. Typical carbonyl peak in the FTIR spectra, in the band $1650\text{--}1750\text{ cm}^{-1}$, does not appear in none of the samples.

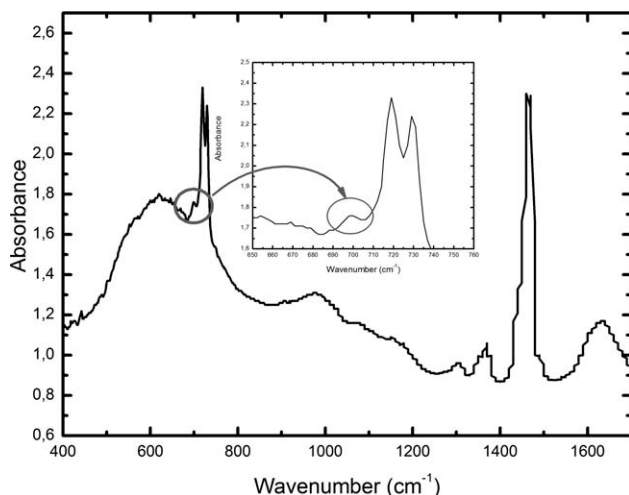


Figure 1 FTIR spectrum of insoluble fraction of R4.

The catalyst effect on pure styrene at high pressure and high temperature conditions was studied following the same procedure. The FTIR spectrum shows that the product formed is PS. Carbonyl peaks are not present evidencing that oxidation does not occur. The weight average molecular weight (\overline{M}_w) of reaction product with 4 wt % of AlCl_3 , obtained by SEC, is 974,000 g/mol and the polydispersity 2.04. The glass transition temperature (T_g) of this polymer, determined by DSC, is around of 119°C. The large \overline{M}_w agrees with the high value of the T_g and evidence the effective catalyst activity in the styrene polymerization. However, in previous works it was demonstrated that AlCl_3 also produces PS scission.^{4,6} Then, two competitive reactions could be present and, as a consequence, the resulting PS could be linear, branched, or lightly crosslinked. However, it was verified that PS is not highly cross-linked because no gels were obtained when it was dissolved in 1,2,4 trichlorobenzene at 135°C.

Copolymerization reactions

Reaction occurrence

The copolymerization reactions were carried out varying the catalyst content between 1 to 4 wt %. The first evidence of reaction occurrence was obtained by FTIR. Spectra from reaction products, after removal the residual solvent and styrene, indicate the PS presence, because the appearance of the typical aromatic rings peak at 700 cm^{-1} . The higher, the catalyst content, the higher, the aromatic rings peaks intensity, as expected. In the same spectra, no carbonyl peaks are present, demonstrating that no oxidation reaction is taken place.

In Figure 1 the FTIR spectrum of the R4 IF from THF Soxhlet extraction is presented. The presence of PS peaks (700 cm^{-1}) gives a first clear evidence of

the copolymerization reaction occurrence. As the THF extraction solubilizes all the PS homopolymer, the PS signal detected corresponds to copolymer molecules.

In SEC analysis it was observed that reactions products curves match very well with the PE one. This fact confirms that the reaction does not produce PE chain scission; however, the copolymer can not be detected by this technique. It is possible that the amount of PS grafted is under the detection limit of SEC for this kind of analysis, and then it can not be detected. Results of others authors demonstrated that the PS SEC detection limit for PE/PS blends is 20 wt %^{5,6} and according to FTIR analysis, and using a calibration curve, the amount of PS grafted in our experiments is lower than 20 wt %. A detail of detected concentrations will be presented in following sections.

To confirm the first evidences of reaction occurrence, ^{13}C NMR analysis was performed on the reaction products, SF and IF. The spectra obtained were compared with PE mix and with a commercial PS used as reference ($\overline{M}_w = 272,000$ g/mol, PD = 2.14). The pure PS spectrum is shown in Figure 2. The chemical shift observed at 146 ppm corresponds to a no protonated aromatic signal, whereas the rest of protonated aromatic signals produce the peak at 130 ppm. The methylene groups ($-\text{CH}_2-$) gives signal at 40 ppm, which is overlapped with the peak at 45.5 ppm relating with the methine group ($-\text{CH}<$). The little peak observed at 13 ppm is a rotational band of other peak. Figure 2 also includes the PE mix spectrum (named as PE). In this, the peaks at 30 and 33 ppm correspond to amorphous and crystalline components, respectively, of the methylene repetitive unit ($-\text{CH}_2-$) of the PE main chain. The signal at 39 ppm proceeds from the methylene group of the

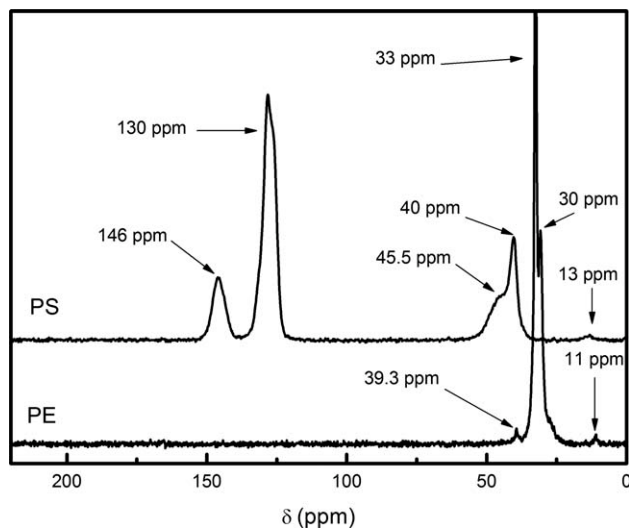


Figure 2 ^{13}C NMR spectra of reference PS and PE mix.

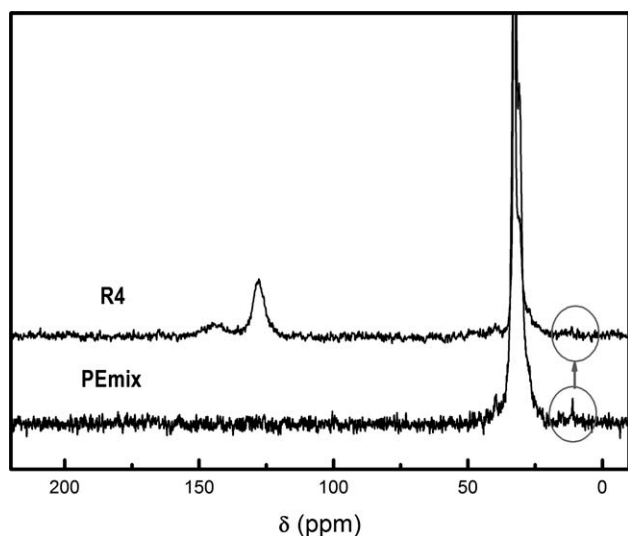


Figure 3 ^{13}C NMR spectra of PEmix and R4.

LLDPE side chains, while the end methyl groups of the PE main and side chains correspond to the peak at 11 ppm.

The ^{13}C NMR spectrum of R4 compared with the PEmix one is presented in Figure 3, with higher scale than in Fig 2. In the zone between 115 and 155 ppm of R4 spectrum, two characteristic peaks of aromatic rings are observed, indicating the PS presence in the product. As expected the intensity of these peaks varies according to the catalyst content. On the other hand, the peak at 11 ppm, detected in PEmix spectrum, disappears in R4 one. This fact evidences a change in PE structure, demonstrating the occurrence of a reaction involving the end methyl groups of LLDPE side chains. The absence of this peak and the presence of the aromatic rings characteristics peaks was observed in all of the samples (from 1 to 4 wt %).

An additional evidence of the copolymer formation was obtained by morphology comparison of the reaction products (after melt processing) with a physical blend with similar PE/PS mass ratio (obtained by direct melt mixing). Figure 4 shows SEM micrographs, performed on cryogenic fracture surfaces of R2 and a PS/PE blend containing 10 wt % of PS. The PS relative content of R2, determined by FTIR, is around 7 wt %. In the physical blend [Fig. 4(a)], the typical morphology of an immiscible blend is observed, PS spherical particles are debonded and dispersed in PE matrix. However, in R2 although phase segregation is present, particles segregated are well adhered with the matrix [Fig. 4(b)]. This adhesion confirms the presence of copolymer. It is well known that copolymers act as adhesion promoters because of their molecules contain a part affine with the matrix. Then, the copolymer forms particles with

the grafted PS chains in the core and a shell of PE entangled with the PE matrix molecules.

Reaction quantification

The catalyst content effect on PS grafting grade was followed by FTIR. The PS content, listed in Table II, was determined in the reaction product by using a FTIR calibration curve (PS/PE peak ratio versus PS content in physical blends). In this Table it is possible to note that the amount of PS increases as the catalyst content increases. However, PS molecules could proceed from homopolymer or copolymer molecules. Then, to measure the amount of PS in the copolymer molecules, the IF of Soxhlet extraction was analyzed. As THF mainly dissolves PS, the PS homopolymer is removed. The Soxhlet extraction was also performed on pure PE (PEmix), observing that some short molecules were solubilized (see Table II). These results were taken as reference due to, at least, this PE amount is solubilized during the extraction on reaction products. In Table II the mass extracted and PS content in soluble and insoluble

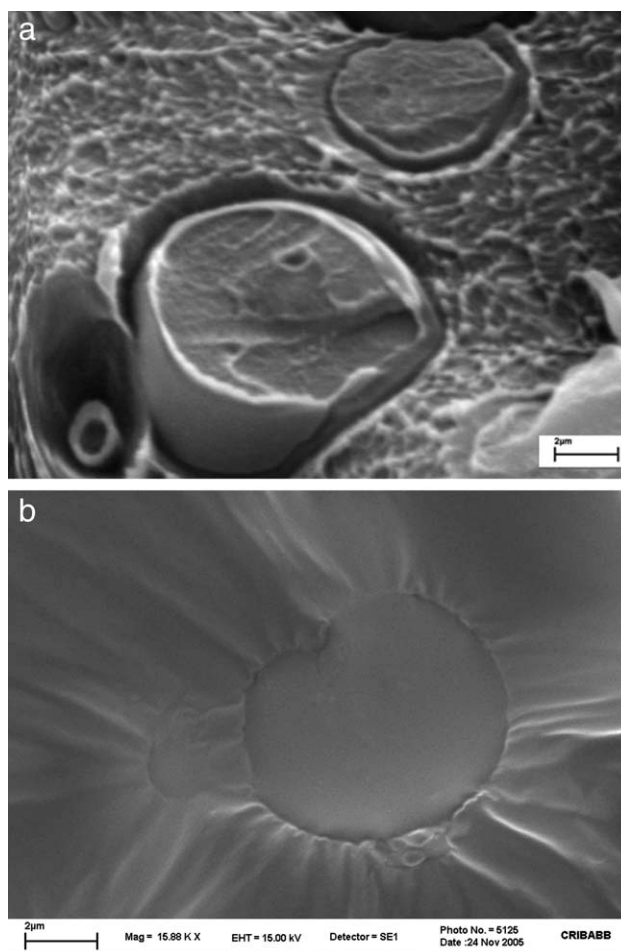


Figure 4 Micrographs of (a) PE/PS physical blend; and (b) R2.

TABLE II
PS Weight Percent, Detected by FTIR, in Reaction Products, Soluble, and Insoluble Fractions of Soxhlet Extraction (SF and IF, resp.)

Sample	PS in the Product (wt %)	Soxhlet Extraction		
		Extracted Mass (wt %)	PS in IF (wt %)	PS in SF (wt %)
PEmix	–	21.6	–	–
R1	5.0	31.3	2.0	11.7
R2	6.4	36.7	3.2	11.5
R3	10.0	38.0	5.5	17.5
R4	11.0	85.0	7.6	11.5

fractions (SF and IF respectively) are also shown for each reaction product. The mass solubilized exceeds the sum of the PS and PEmix ones for all experiments. Taking into account that PE does not suffer chain scission, it can be assumed that the mass solubilized contains three kinds of molecules, PS, PE and copolymer ones. Copolymer molecules can be solubilized by the solvent depending on the relative PS/PE content.¹⁴ Because of that, the overall PS content in copolymer molecules is at least equal to those detected in the IF. Also, it can be noted that PS content in the IF, and then, the copolymer formed increases as the catalyst content increases.

Copolymer architecture assessing

The carbocationic copolymerization reaction mechanism has not been properly explained yet. Previous studies,^{3–5,16} proposed a three steps process for the reaction of PE and PS homopolymers in molten state. A low molecular weight carbocation is firstly formed from and AlCl_3 ionic complex. Then the carbocation hits the PE molecule to yield a macrocarbocation (electrophile). Finally, this macrocarbocation produces, by electrophilic attack on the PS ring, “brush-like” molecules of graft copolymer.

The above explanation could help to understand the reaction between PE and styrene in near critical *n*-alkane. Here, two parallel reactions take place from the carbocation attack: PS homopolymerization and PE/PS copolymerization. Thus, the copolymer molecules architecture could be different. The possible molecular arrays are PE-*b*-PS, PE-*g*-PS, and PS-*g*-PE. The first possibility is ruled out after analyzing comparatively the ^{13}C NMR of pure PE and R4 (Fig. 3). In a block copolymer the spectrum of PE should match with its corresponding peaks in the copolymer one. However, the peak corresponding to the end methyl group of the lateral chains (11 ppm) disappears.

The second form (PE-*g*-PS) involves the grafting of PE chains onto a main PS one, in “para” or “meta” position of the aromatic ring. As mentioned

above, this kind of copolymer is formed by alkylation reactions in melt from PE and PS homopolymers. ^{13}C NMR spectrum of a “reactive blend” compared with the spectrum of their correspondent “physical blend” is shown in Figure 5. The reactive blend was obtained by alkylation reaction on melt PE/PS physical blend (80/20 wt %/wt %) using 0.7 wt % of AlCl_3 .⁵ Both spectra seem very similar, except for the PS peak at 128 ppm. In the spectrum of “reactive blend,” appears a new peak at 126 ppm, corresponding to “para” position in aromatic rings; and the intensity of 128 ppm peak, corresponding to the aromatic ring resonance of PS, is lower than in “physical blend.” This indicates a possible substitution in “para” position. Furthermore, it can be observed that the peak corresponding to the end methyl groups of side chains (11 ppm) remains without alteration. Because of the above evidences, it can be concluded that the copolymer obtained in the solution reaction at high pressure and high temperature has not a structure of PE-*g*-PS.

The absence of lateral methyl group signal in reaction products obtained at high pressure–high temperature reaction, and the presence of the peak at 128 ppm with the same characteristic of the pure PS, allow supposing that the copolymer obtained is a grafting of PS onto LLDPE (PS-*g*-PE). On the other hand, if the reaction product ^{13}C NMR spectra are accurately analyzed, it can be observed a change in the peak corresponding to 146 ppm. This PS characteristic peak of spectra of R4 and reference PS are compared in Figure 6(a). In this graph the data were normalized respect to the height of peak at 128 ppm. This analysis allows to compare relative height, width and position of the peaks. The peak at 128 ppm of R4 matches in width and position with the reference PS. However, the peak corresponding to monosubstituted aromatic rings (146 ppm) shifts to

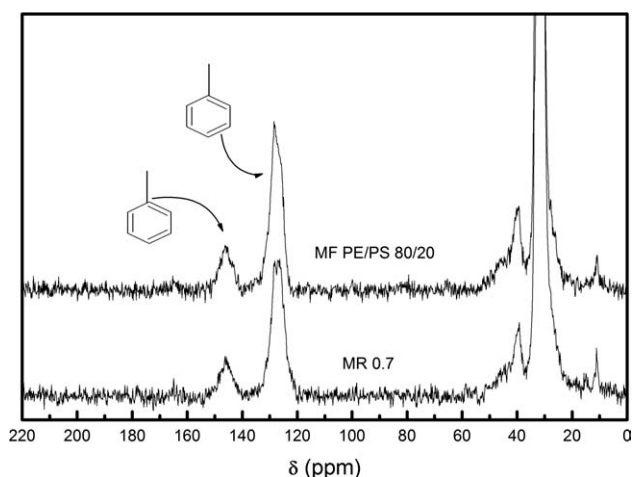


Figure 5 ^{13}C NMR spectra of physical (PE/PS 80/20) and reactive blend (PE/PS 80/20 with 0.7% de AlCl_3).

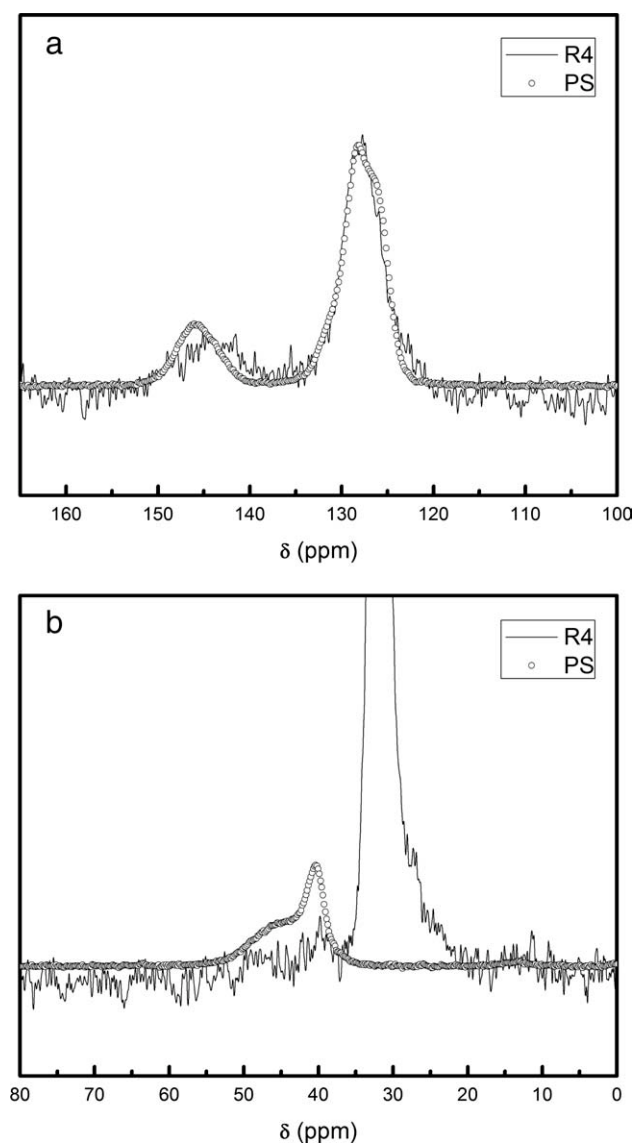


Figure 6 ^{13}C NMR spectrum (normalized respect to 128 ppm peak height) of PS compared with R4. (a) zone between 160 and 100 ppm; (b) zone between 80 and 0 ppm.

lower δ values and is wider than PS one. These effects could be due to a overlapping with the peak at 140 ppm, corresponding to a disubstituted ring contribution. The disubstituted rings could indicate the possible PS crosslinking and/or a bonding between PE chains and aromatic rings. A similar comparison of relative peak height at 40 ppm, corresponding to PS methylene groups, is shown in Figure 6(b). The peak at 128 ppm was also used as reference. In R4 reaction product spectrum, the methylene group signal is weak respect to the reference PS. It could be due to a short PS chains formation either grafted onto PE or homopolymerized. These ^{13}C NMR results and the constant hydrodynamic volume (SEC analysis) allow inferring that the

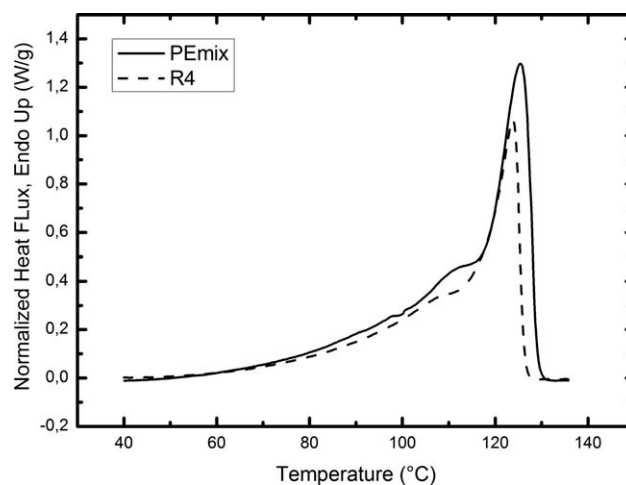


Figure 7 DSC thermogram of reaction products with different catalyst content, compared with PEmix one.

copolymer is formed by a main PE chain with short PS molecules bonded onto it.

Morphological analysis

Further evidence of the copolymer presence can be obtained from calorimetric measures. In Figure 7 the thermograms of reaction product R4 and PEmix are shown. R4 curve is shifted to lower temperatures compared with PEmix, resulting in a lower melting temperature (T_m). Also the phase transition enthalpy (ΔH) and then the crystallinity of R4 are lower than PEmix. These effects were observed in all reaction products as shown in Table III.

Taking into account that the reaction does not produce PE chain scission, and that melt blending does not produce changes in PE crystalline morphology,^{17,18} the observed changes can be attributed to the copolymer presence. The grafting of relative huge PS molecules onto PE ones introduces irregularities in the main PE chain structure decreasing its flexibility, hindering its crystallization and altering the crystal perfection. Similar results were observed by other authors when studying the influence of the copolymer formation in the PE crystallization behavior.^{19,20} Table III shows that the melting temperature

TABLE III
Temperatures and Melting Enthalpies of Polyethylene and Reaction Products

Sample	T_m (°C)	ΔH (J/g)	Crystallinity Degree (%)
PEmix	125.4	137	47.5
R1	123.9	133	45.9
R2	123.1	122	42.3
R3	120.8	114	39.3
R4	119.8	101	35.0

and crystallinity of reaction products decrease as the catalyst content increases, confirming that the amount of copolymer formed increases with the catalyst content.

The morphology of reaction products was studied by SEM and TEM microscopy. To perform an accurate study of the above observations, the SEM technique was applied on samples prepared in different ways, as explained in the experimental section. Figure 8 shows particles with different morphology in a cryogenically fractured surface of R2. This sample was previously melted and mixed in a minimixer. The particles "A" [Fig. 8(a)] could be only made of copolymer molecules, due to their homogeneous appearance and good adhesion with the matrix. As it was explained above, the copolymer places the PS grafted chains in the center, exposing the PE chains that penetrate and entangle with PE matrix. The particle "B" [Fig. 8(a)] presents two well differentiate zones, like core-shell morphology. The center (core) seems to be PS homopolymer because of the aspect, surrounded by a copolymer layer (shell) that acts as typical adhesion promoter. In this layer, PS copolymer chains penetrate in PS core and PE ones in the matrix, giving the observed good adhesion. A similar behavior is observed when copolymers are used to compatibilize PE/PS immiscible blends.¹⁷ Figure 8(b) shows a third kind of particle. It seems to be a PS homopolymer particle dispersed in a PE matrix due to the bad adhesion presented, typical of incompatible PS/PE blends.²¹

A very useful analysis for the copolymer identification is the comparison between fracture surfaces of reaction products with and without solvent etching. This set of specimens constitutes the second way to prepare the samples for microscopy study. Samples were prepared by compression molding as explained in experimental section, cryogenically fractured and one of this surfaces subject to THF extraction. The extraction of PS homopolymer is expected because THF is a good solvent for PS. It is important to note that, due to the sample preparation, the morphology observed in these samples seems to be different to the samples analyzed before (melted in a minimixer). Although the experiments were performed at the same temperature, the most important difference between them proceeds from the time and the shear fields applied. In the first case, samples were melted for five minutes in a Maxwell-type mixer under high shear fields, increasing the molecule mobility and possible coalescence. In the second one, samples were subject only to a "static" migration into a press for one minute. Micrographs of all samples processed by compression molding with and without solvent etching are included in Figure 9. In R1, the presence of well defined particles of PS and/or PS-g-PE can be

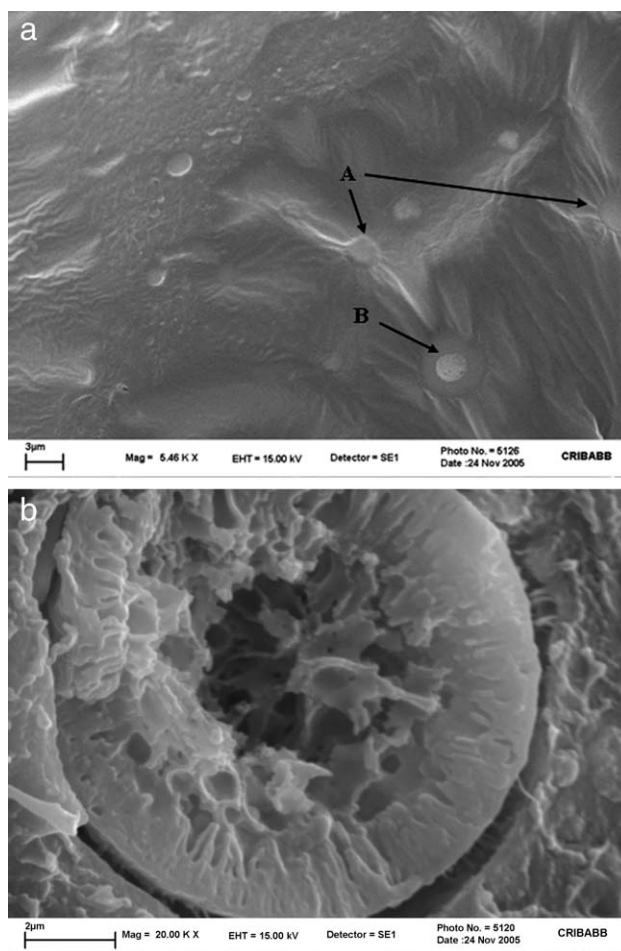


Figure 8 SEM micrographs of cryogenic fractured surface of R2 after blend mixing of R2 at different magnifications: (a) 5500 X; (b) 20000 X.

observed [Fig. 9(a)]. However, when this sample is etched [Fig. 9(b)], the major amount of particles disappears, indicating that they were removed by THF. Then, it can be concluded that the particles are mainly of PS.

In the case of the reaction product R2 [Fig. 9(c)], it can be also observed small particles but in higher amount and lower size than in R1. This fact proceeds from the higher content of PS and copolymer, as it was shown in the quantification section. In the same way, if higher amount of copolymer is present, it is expected that the particles would be smaller, due to the copolymer compatibilizer effect. On the other hand, in the micrograph of etched R2 sample [Fig. 9(d)] the particles increase their size respect to the R2 sample. This situation is different to the observed in R1. The no solubilization of the particles in THF demonstrates that the PS is bonded to PE, belonging to the copolymer. The greater particle size can be explained as follow. Favored by the sonication, the THF penetrates in the sample, swelling it. The PS rings, compatible with the solvent, acquire

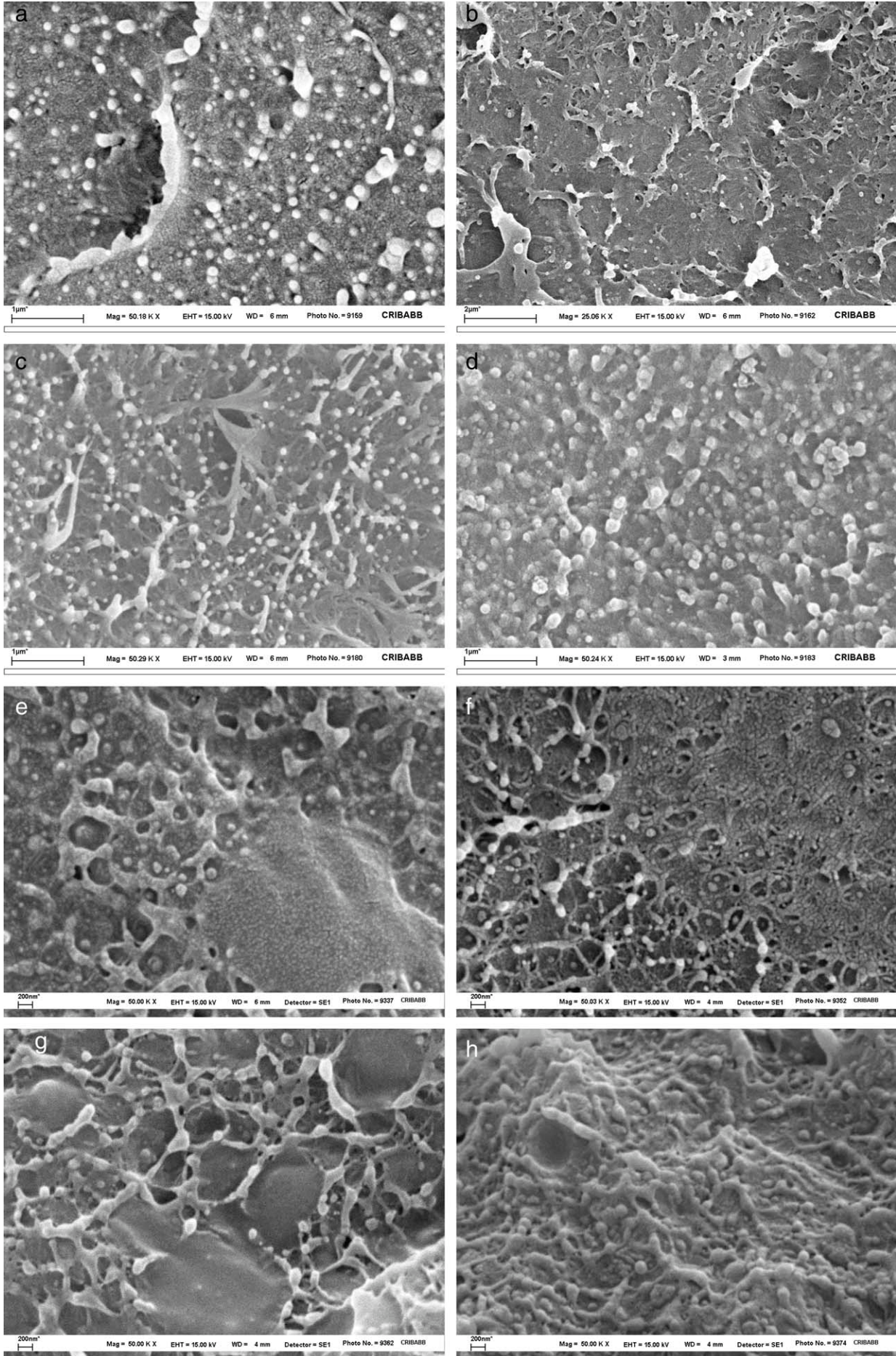


Figure 9 SEM micrographs of cryogenic fractured surface of samples processed by compression molding: (a) R1; (b) R1 after solvent etching with THF; (c) R2; (d) R2 after solvent etching with THF; (e) R3; (f) R3 after solvent etching with THF; (g) R4; (h) R4 after solvent etching with THF.

mobility and migrate to the surface. However, as the PS rings are chemically bonded to PE, they can not be solubilized and extracted by the solvent. For this reason, in the extracted product, it is observed an increase in the amount of copolymer at the surface with the consequent increment of particle size. On the other hand, the particle coalescence, proceeding from the greater molecular mobility from the combined effects of sonication and solvent action, could be another reason for the particle size increment.

The general aspect of the morphology of no etched surfaces of R3 and R4 is different [Fig. 9(e,g)]. The small particles are present, but around "clusters." The amount of clusters increases with the catalyst content. This observation agrees with the change of the relative amount of PS/PE in PS-g-PE molecules as catalyst content increases. The morphology of the corresponding etched R3 and R4 samples shows similar behavior of the etched R2, with an increase in PS "particles" coalescence. In Figure 9(f), a cluster surface after etching is shown. It seems that the cluster contains copolymer molecules that, after the etching, presents similar behavior but with smaller "particle" size.

Finally, the reaction products were analyzed by TEM, on ultra cryomicrotomed specimens stained with ruthenium tetroxide (RuO_4). In microscopy, staining involves the incorporation of electron dense atoms into the polymer, to increase its density and thus enhance the contrast. Then, this technique permits to distinguish either the chemical or the physical incorporation of a heavy atom. The RuO_4 oxidizes aromatic rings yielding either mono- or dicarboxylic acids.²² In this case, the RuO_4 is used to stain mainly the PS aromatic rings. This method was applied on samples prepared by compression molding with and without solvent etching. In Figure 10 a micrograph of R2 reaction product is shown. It can be observed the formation of concentric bands growing from a central amorphous region and dispersed dark particles. The band-like appearance is characteristic of some polyethylenes, especially LLDPE, and corresponds to a deformation of the lamellas into spherulites. The bands observed are attributed to a twist in the crystallographic orientation around the lamellas growth direction.²³ The origin of twisting is not well explained still, but some authors attribute it to avoiding tension due to tension or concentration fields.²⁴

The dark points correspond to PS particles which aromatic rings are stained by RuO_4 . In Figure 11(b) a detail of a particle is shown. In it, the dark ring in the PS particle can be attributed to the copolymer organization in the interphase. The micrographs of R2 reaction product after etching are shown in Figure 11. The whole appearance, with concentric bands

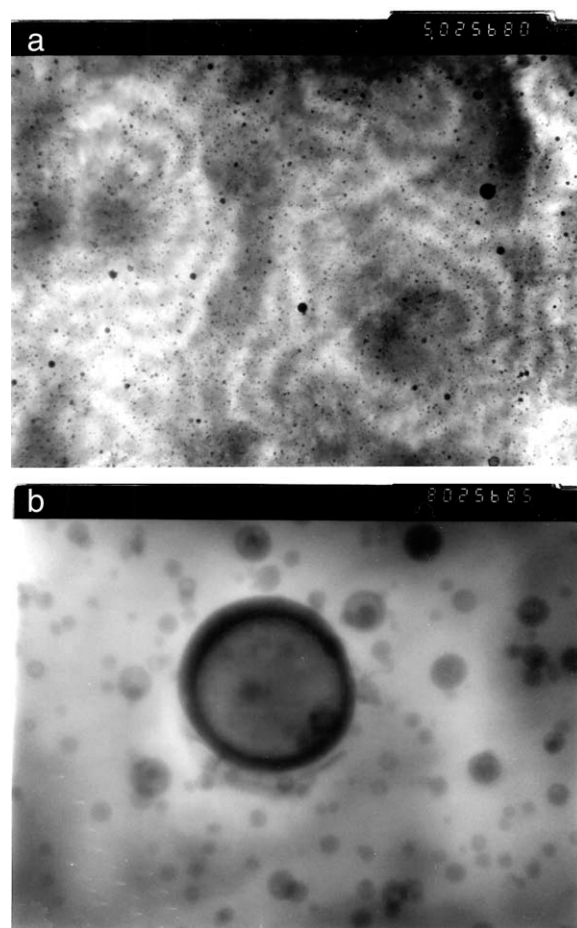


Figure 10 TEM images of ultracryomicrotomed section of R2 stained with RuO_4 : (a) 5000 X; (b) 80000 X.

and dark points, is similar to the observed in Figure 10. However, either the amount or the size of dark points is increased. This fact is in agreement with the discussion made above. Because of PS solubilization by THF, the PS chains migrate to the surface and coalesce themselves, but they can not be extracted due to the copolymer formation.

According to the observation made in TEM analysis, it can be inferred that the grafted PS is incorporated partly into amorphous layers of PE, and partly into separate PS regions placed alongside the stacks of PE crystalline lamellae. This observation is in agreement with previous studies²⁵ for the same kind of copolymer (PS-g-PE). The grafted PS located in the amorphous phase of PE increases the amount of amorphous phase. While the other PS chains form separated amorphous domains, observed by TEM as dark particles. This hypothesis agrees with the DSC results, that shows a decrement in crystallinity as the amount of catalyst increases, then the amount of PS grafted increases (Table III).

The TEM images for the product R4 without etching are shown in Figures 12. The PE band formation

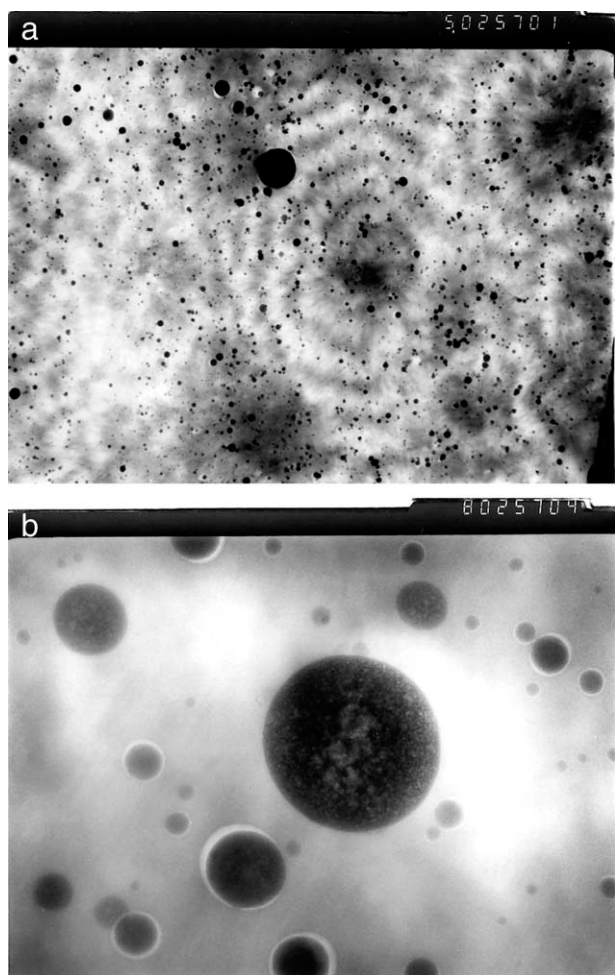


Figure 11 TEM images of ultracyromicrotomed section of R2, after solvent etching with THF, stained with RuO₄: (a) 5000 X; (b) 80000 X.

is observed again, but in general greater amorphous material proportion is detected as darker zones. At first sight, the dark spot or PS domains are more difficult to distinguish. A larger magnification [Fig. 12(b)] shows these domains but present in lower amounts. In this image, it is also observed a dark border, typical of the structural organization of the copolymer. The fact that only a few PS domains are observed can be due to a lower domain size, no distinguishable at the magnifications used, or that the PS places preferably in the amorphous part of PE, not in separately domains. Also, the cause of this less amount of PS domains can be due to the copolymer compatibilizer effect, as it was observed in SEM analysis with the presence of light particles.

Final properties

To analyze the effect of PS grafting on final properties of PE final properties, permeability and mechanical properties of reactions products were analyzed.

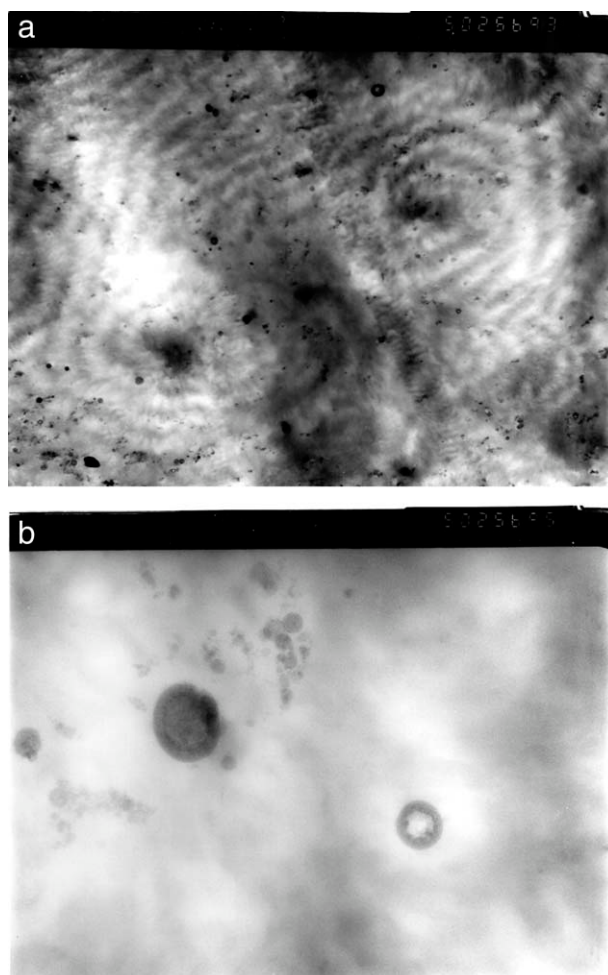


Figure 12 TEM images of ultracyromicrotomed section of R4 stained with RuO₄: (a) 5000 X; (b) 80000 X.

Oxygen barrier properties

The data of the reaction products oxygen permeability compared with pure PE are presented in Table IV. The influence of the copolymer presence, as well as of the PS molecules, is evident because the permeability decreases as the amount of catalyst increases. The reaction product R1 enhances its barrier properties in a 22% respect to pure PE, while in R4 the barrier to the oxygen increases in a 33%. Usually, the increase in barrier properties in this kind of polymers could be attributed to a decrease in the

TABLE IV
Oxygen Permeability of Pure PE and Reaction Products, Measured at 23°C and 0% of Relative Humidity

Sample	Permeability $\times 10^{13}$ (cm ³ cm/cm ² s Pa)
PEmix	2.41
R1	1.88
R2	1.80
R3	1.68
R4	1.62

TABLE V
Tensile Properties Measured from Films of Pure PE and Reaction Products

Sample	E (MPa)	Yield Stress (MPa)	Elongation at Break (%)
PEmix	246 ± 15	8.30 ± 1.20	590 ± 71
R1	300 ± 12	9.91 ± 0.60	243 ± 10
R2	306 ± 25	8.96 ± 0.82	201 ± 12
R3	344 ± 35	8.83 ± 0.90	162 ± 36
R4	330 ± 11	8.60 ± 1.01	133 ± 42

free volume and/or to the chain mobility. One factor that can modify these parameters is the crystallization. Crystal presence increases the polymer density, decreasing the free volume. Then, the "oxygen pass" through the film is hindered due to the crystallites presence.^{26,27} However, in the reaction products, the crystallization degree decreases as the catalyst content increases (see Table III) because of copolymer molecules contain aromatic rings in the pendant chains. Then, the increment in the barrier properties could be just attributed to the incorporation of these aromatic rings that impede the chain mobility and diminish the free volume of the sample. Regarding the experimental results, the last phenomena seem to be more important than crystallinity in this kind of samples. Similar results were founded by Baer et al.²⁸

Tensile behavior

Results of tensile properties from films of reaction products, compared with pure PE are shown in Table V. As expected, the rigidity of the films increases as the amount of PS increases. This increment is not remarkable, the modulus in R1 increases around 15% and in R4 25%. However, the films retain their capability to elongate. In all cases the sample forms the neck and this neck propagates up to around 200% of elongation prior to break. This is a very interesting feature because samples are complex multiphase material. The high values of elongation at break are another indication of the good phase compatibility in the material. This is in agreement with the morphology showed in the above section, where the adhesion between PS/PS-g-PE/PE seems to be very good. The increment in the yield stress is also expected because of the presence of the PS-copolymer and/or copolymer microdomains adhered to the PE matrix.²⁹

CONCLUSIONS

In this work a new grafting methodology is proposed. Near critical *n*-heptane is used as reaction medium for the copolymerization of PE with styrene

monomer using different concentrations of AlCl₃ as catalyst. The reaction occurrence was demonstrated by three independent techniques (FTIR, SEM, and ¹³C NMR), corroborating that the copolymer amount increase with catalyst content. The copolymer compatibilization effect was verified by SEM, observing a good adhesion between copolymer and PE matrix. Also a possible copolymer architecture was proposed as PS-g-PE, where the molecule is formed by a main chain of PE and short PS molecules grafted onto their side chains.

The morphological analysis shows the formation of PS and copolymer particles. The amount and size of these particles decrease as the catalyst content increases, due to the copolymer compatibilizer effect. The copolymer localize either in the amorphous PE matrix zone or in small microdomains, causing a decrement in the crystallinity of the reaction product respect to the pure PE.

The PS grafting also modifies final properties of PE, increasing the oxygen barrier properties without deteriorating significantly the mechanical properties of the films. In this sense this reaction seems to be a promising route to modify PE films to increase the barrier properties.

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