

# Modification of Polyethylene by Styrene Grafting Using n-Alkanes at High Pressure as Reaction Media

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## ABSTRACT

The grafting of a specific molecule onto commercial high molecular weight polymer is an interesting alternative to obtain low cost new materials with tailored properties. In this work, the copolymerization of styrene onto polyethylene (PE), using near critical n-alkanes as reaction media is proposed. The reaction is an alkylation and the catalyst was aluminum chloride (AlCl<sub>3</sub>). The reaction occurrence was assessing, varying the catalyst content between 1 to 5 %, by FTIR, <sup>13</sup>C-NMR, SEM, TEM and DSC.

## INTRODUCTION

In the last years, the most significant trends in the field of plastics are changing focusing in the final material use. The compromise between economy and technique requirement is frequently reached, by development of materials with predetermined properties, based in commodity plastics [1].

Particularly, the copolymers are molecules generated by chemical reaction, containing two or more monomers in their chains, and generally they have a synergetic combination of properties respect to the homopolymer ones. For this reason, they are used in applications as adhesives, paints, coatings, emulsifiers, biomedical materials, etc. [1, 2]. The introduction of new functional groups to a polymer can modified some properties as hydrophilicity, dyeability, permeability, antimicrobial activity, adhesion, etc. [3]. Particularly, the introduction of aromatic rings to the PE chains changes the polarity and the inert character of the material. Consequently, the material became easier to be stained, dyed and printed. Also, the permeability respect to the water, carbonic anhydride and oxygen, suffer modifications and can be tailored focusing in a specific properties desirables in the packaging and textile industries. On the other hand, in last years, the use of near and super critical fluid as solvent or as processing agent in the polymer technology area increased. The main advantages of the use of this kind of fluids are the diffusivity increment and the viscosity and superficial tension decrement [4].

In this work, the copolymerization of styrene onto polyethylene (PE), using near critical n-alkanes as reaction media is proposed. The reaction is a Friedel-Crafts alkylation and the catalyst was aluminum chloride (AlCl<sub>3</sub>). By this reaction, a hydrocarbon chain can be chemically bonded to the styrene ring through an aromatic electrophilic substitution. The principal advantage of this reaction method is that the high molecular weight PE is solubilized by alkanes at near critical conditions, consequently the polymer chains are more available to react than in a melt blend.

The reaction occurrence was corroborated by nuclear magnetic resonance (<sup>13</sup>C-NMR), Fourier transform infrared spectroscopy (FTIR), after a careful phase separation of the reaction product by selective Soxhlet extraction using tetrahydrofuran (THF). Besides of FTIR, differential scanning calorimetry (DSC), size exclusion chromatography (SEC), scanning

electron microscopy (SEM) were the techniques used for characterization of the reaction products and quantification of the polystyrene copolymerized. The effect of the amount of catalyst added was studied varying the content from 1 to 5-wt% of AlCl<sub>3</sub> at the same PE/styrene ratio.

## EXPERIMENTAL

**I. Materials:** Styrene (analytical grade) and linear low-density polyethylene from Dow-Polisur, LLDPE 6200 (Mw: 52000, Mn: 17000 g/mol) were used as reactants. The alkylation reaction was catalyzed by anhydrous Aluminum Chloride (AlCl<sub>3</sub>) (>98% purity) from Merk. N-heptane (Tc: 267.2 °C, Pc: 27 bar), with purity higher than 99 wt% was used as reaction medium.

**II. Equipment:** The reaction was carried out in a high-pressure stirred Parr reactor. The reactor also has an aluminum block heater and an automatic temperature controller. The reactor vessel is made of stainless steel with a capacity of 600 ml. It has a maximum working pressure of 200 bar. Besides, the equipment is connected to a manual pressure generator, pressure sensor and a rupture valve.

**III. Experimental Procedure:** The reactor was charged with 10 g of polyethylene films and 20 ml of styrene. After this, it was filled with n-heptane and heated, stirred and pressurized to the final conditions (T=140°C y P=150bar). These conditions were kept constant for about half an hour. To be sure that the catalyst is released when all polyethylene is solubilized, AlCl<sub>3</sub> is confined in a polyethylene capsule. In this way, when the capsule is dissolved in n-heptane, the catalyst is released and the reaction takes place. The content of catalyst added varied from 1 to 5 wt%. At the end of reaction, the reactor was cooled to room temperature and finally the vessel was opened and the product recovered. The collected sample was dried under vacuum.

**IV. Solvent Extraction:** For a complete characterization, the products were subject to a selective Soxhlet extraction with tetrahydrofuran (THF), to remove unreacted monomer and polystyrene homopolymer formed during the reaction. The extraction was performed for 15 h. Theoretically, the no copolymerized PS is extracted and the soluble fraction (SF) should be contain only PS. The insoluble fraction (IF), formed by a mixture of copolymer and homopolymer, was dried in a vacuum oven to remove any residual solvent. Both fractions were characterized by FTIR in order to analyze the chemical composition and quantify the styrene in each fraction.

**V. Solvent Etching:** In order to perform a microscopical morphological study, the reaction products were etched with THF, by sonication at room temperature to remove pure PS from the surface. The samples extracted are called ERX, where X is the wt% of AlCl<sub>3</sub>.

### VI. Characterization:

*Fourier Transformer Infrared Spectrometry (FTIR):* Qualitative identification of reaction products and quantitative measures of PS copolymerized were carried out in 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<sup>-1</sup> for PS and at 719 cm<sup>-1</sup> for PE). Previously, a calibration curve was performed with PE/PS 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. By this technique, the occurrence of secondary reactions, like chain scission, can be studied.

*Scanning Electron Microscopy (SEM):* For the morphological analysis, with the PS proportion detected by FTIR in the reaction products, a physical blend of the same PE and commercial PS was prepared in a minimixer. This blend was used for ulterior morphological comparisons. The reaction products were also melted in a minimixer at the same conditions. Either the physical blend as the reactive ones were fractured under cryogenic conditions and studied by SEM after coated by gold.

*Transmission Electron Microscopy (TEM):* the samples were analyzed in a Joel 100 CX at 100 kV. The samples were cut with a Leica ultracut with liquid nitrogen. The samples were stained with RuO<sub>4</sub>.

*Differential Scanning Calorimetry:* The thermograms of each product of reaction were obtained. Initially, the samples were heated to 180 °C and kept at this temperature for 3 min to remove all prior thermal history. Subsequently, they were quenched to 30°C and then reheated to 180 °C at a rate of 10 °C/min.

*Nuclear Magnetic Resonance (NMR):* The <sup>13</sup>C-NMR spectra of the pure polymers and reaction products were obtained in a BRUKER AVANCE II spectrometer, operating at a resonance frequency of 300.13 MHz for protons and 75.45 MHz to <sup>13</sup>C.

## RESULTS AND DISCUSSIONS

The first step in characterization is the reaction occurrence confirmation. In this sense, FTIR analysis is a direct and accurate method to confirm the chemical PS bonding in a copolymer. This technique indicates the presence of PS in the product, by following the peak at 700 cm<sup>-1</sup>. Through the calibration curve [5], the amount of PS respect of the total polymer mass is summarized in Table I. Even though, with this information, it is possible to assess the PS presence, still further characterization of the reaction products must be done for determining the copolymerization reaction itself. In this way, the insoluble fraction obtained from the THF extraction also was analyzed by FTIR. This study demonstrates the presence of PS in this insoluble fraction (IF). The results of this characterization are shown in Table I. These confirm that the polystyrene reacted with PE, at least in this proportion. The “at least” consideration proceeds from the fact that the soluble fraction contains PE and PS in proportions much greater than when the extraction was done on the pure PE homopolymer. In all of the samples the absence of oxidation reactions was corroborated following the typical peak of oxidation (1700 cm<sup>-1</sup>).

The product characterization was also carried out by DSC. It can be observed that the melting point of the products obtained was lower than the homopolymer PE. Taking into account PE chains scission is absent (demonstrated by the SEC analysis [5]), this shifting can be attributed to the incorporation of amorphous PS on the backbone of the PE polymer which builds irregularities in the overall structure of the chain. This leads to a decrease in the melting point of the product and a lower percent of crystallinity (area under the peak). It was demonstrated that a physical blending of PE and PS not changes the PE crystallinity [6]. These phenomenon increases with the amount of the catalyst added to the reaction. The values of melting temperature (T<sub>m</sub>) and the melting enthalpy (ΔH) obtained are shown in Table II.

**Table I.** PS percent detected in the reaction products and Soxhlet extraction results

Sample	PS in the prod. (%)	Soxhlet extraction		
		Extracted mass (%)	PS in insoluble fraction (%)	PS in soluble fraction (%)
PEmix	-	21.6	-	-
R1	5	31.3	2	11.7
R2	6.4	36.7	3.2	11.5
R3	10	38	5.5	17.5
R4	11	85	7.6	11.5
R5	9.5	53.3	6.2	12.5

**Table II.** PS percent detected in the reaction products and Soxhlet extraction results

Sample	Tm (°C)	$\Delta H$ (J/g)	% crystallinity
PEmix	125.42	137.13	47.5
R1	123.94	132.58	45.9
R2	123.09	122.22	42.3
R3	120.77	113.54	39.3
R4	119.8	101.21	35.0
R5	121.92	103.94	36.0

To elucidate the copolymer architecture and to have more evidences of its formation, a  $^{13}\text{C}$ -NMR study was carried out either on reaction products or pure PE. The spectrum of the reaction product with 4% of  $\text{AlCl}_3$  (R4) is compared with PE spectrum in Fig. 1. The presence of two peaks in the zone between 115 and 155 ppm in the R4 spectrum, typical of aromatic rings, indicates the PS existence. Also, it can be observed that the peak at 11 ppm in the PE spectrum disappears in the R4 one. This peak (11 ppm) is due to the methyl groups of the LLDPE pendant chains. This disappearance evidences a PE structural change, indicating reaction in these points. The 11 ppm peak disappearance and the presence of PS peaks was observed in all samples (from 1 to 5% of  $\text{AlCl}_3$ ), varying the peak intensity with the catalyst content. By this chemical change, the copolymer architecture can be deduced, proposing a main chain of PE with short chains of PS grafting onto its lateral chains, as shown the Fig. 2. An additional evidence of the copolymer generation was obtained by the SEM analysis. Fig. 3 shows the micrograph of the reaction product with 2% of  $\text{AlCl}_3$  compared with a physical blend with same PE/PS composition. Physical blend (Fig. 3a) evidences typical phase segregation and bad phase adhesion for this kind of incompatible blends. However, the total phase adhesion shown in Fig. 3b gives proof of the presence of the copolymers molecules entangled with the homopolymer ones and connecting the two immiscible components, PE and PS. The copolymer forms particles with a core consisting of the insoluble block of polystyrene and a shell consisting of the PE solubilized in the PE matrix. Then, the adhesion between phases is improved compared with the physical blend.

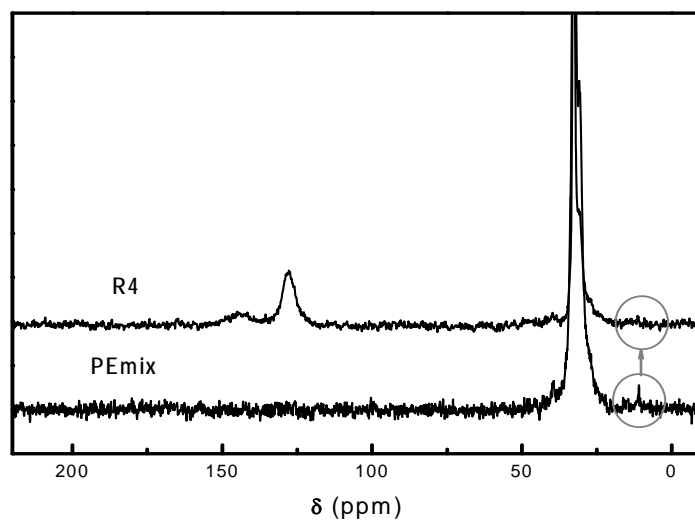


Fig. 1.  $^{13}\text{C}$ -RMN spectrum of the reaction product with 4% of  $\text{AlCl}_3$  compared with PE mix

The samples stained with  $\text{RuO}_4$  were analyzed by TEM, previous and after solvent etching with THF. The micrographs of the reaction product with 2 % of  $\text{AlCl}_3$  are shown in Fig. 4. The “dark microdomains” in it, can be attributed to PS presence because the  $\text{RuO}_4$  stain principally the aromatic rings. However, PS can be in pure state or grafting onto PE. To corroborate the copolymer formation the samples were subjected to solvent etching with THF to eliminate the PS not grafted. The micrograph of the sample after the extraction process is shown in Fig. 4 b). The “dark microdomains” are still in the sample and their size and intensity color are increased respect to the original reaction product (Fig. 4a). From these results, the copolymer formation can be assured. During the solvent etching, the PS dissolves in THF, migrates to the surface, the “microdomains” coalesces but it can't be extracted because it is grafted onto PE. This morphological study reveals that PS incorporated partly into amorphous layers of PE and partly into separate spherical microdomains.

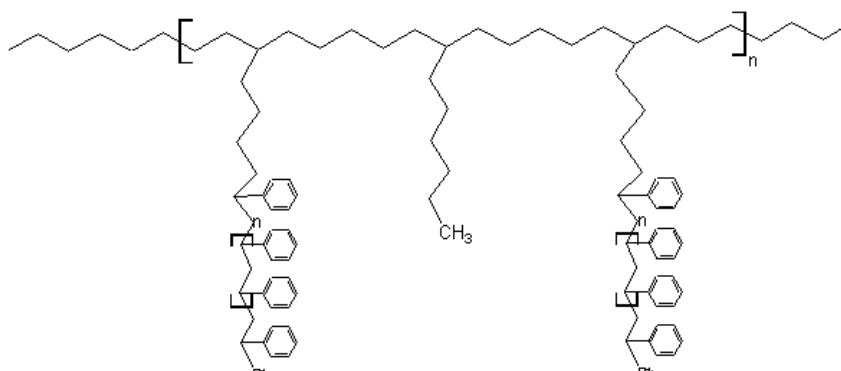
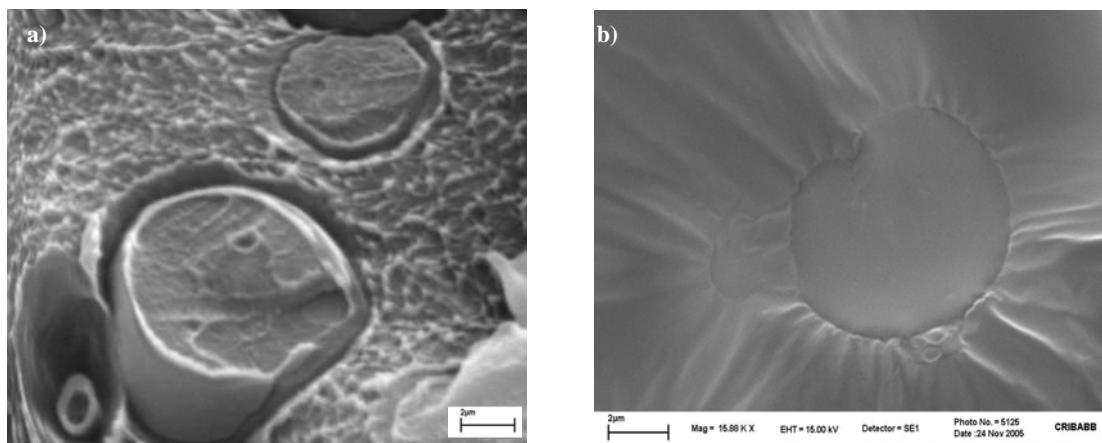
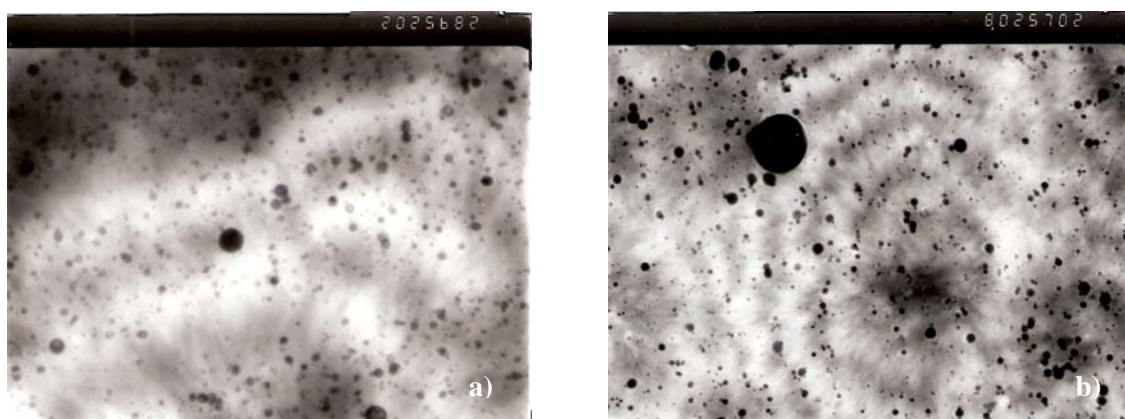


Fig. 2. Possible architecture of copolímero formed in the reaction



**Fig. 3.** SEM Micrographie of a physical blend (a) compared with the reaction product with 2% of  $\text{AlCl}_3$  (b)



**Fig. 4.** TEM Micrographie of the reaction product with 2 % of  $\text{AlCl}_3$ : a) no extracted (20000x) and b) extracted with THF (8000x)

## CONCLUSIONS

The use of high pressure-high temperature n-alkane as a reaction medium is a good alternative to carry out the copolymerization of styrene onto high molecular weight commercial PE. It was demonstrated that the PS was chemically bonded to the PE without degradation. The grafting amount increases as the catalyst concentration increases.

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