Direct Synthesis of a Di-Block Copolymer
Syndiotactic Polystyrene-b-Polyethylene

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Abstract: The direct synthesis of syndiotactic polystyrene-block-polyethylene copolymer (sPS-b-PE) with di-block structure has been achieved. The synthetic strategy consists of the sequential stereocontrolled polymerization of styrene and ethylene in presence of a single catalytic system: cyclopentadienyltitanium(IV) trichloride activated by modified methylaluminoxane (CpTiCl3/MMAO). The reaction conditions suitable for affording the partially living polymerization of these monomers were identified and the resulting copolymer, purified from contaminant homopolymers, was fully characterized. Gel permeation chromatography coupled with two-dimensional NMR spectroscopy COSY and DOSY confirmed the di-block nature of the obtained polymer whose thermal behaviour and thin film morphology were also investigated, by differential scanning calorimetry, powder wide angle x-ray diffraction and atomic force microscopy.

Keywords: Syndiotactic polystyrene; Polyinsertion Catalysis; Block copolymer; Thin Film Morphology

1. Introduction

The syndiotactic polystyrene (sPS) is one of the most relevant achievement of the homogeneous polyinsertion catalysis.[1,2] Besides its employment as engineering plastic[3] thanks to the high melting temperature joined to favourable crystallization kinetics, sPS appears also as a smart polymer due to the nanoporous crystalline structure.[4-6] In this respect, many studies have been performed to disclose its ability to selectively clathrate small molecules in order either to remove the undesirable ones from the environment or to release the useful ones into a particular context.[7,8] The permeability of the sPS to small molecules disclosed recently interesting applications of this material also as support for catalysts.[9-11]

On the other hand, the polyinsertion homogeneous catalysis opened the opportunity of copolymerizing ethylene and styrene to give chain architectures very different both in monomers sequence and in stereoregularity.[12-24] Recently some of us succeeded in the synthesis of an ethylene-styrene diblock copolymer with isotactic styrene sequence jointed to ethylene-alt-styrene isotactic sequence.[25] The tool to this achievement is the living polyinsertion that can be obtained even with traditional catalysts by working at low temperature.

In the light of the large interest for the linear diblock copolymers, mainly for their ability to give ordered nanostructures,[26-28] we addressed our efforts to the synthesis of more simple ethylene-styrene diblock copolymer with syndiotactic regularity of the styrene sequence.

The catalyst we choose is the cyclopentadienyltitanium(IV) trichloride (CpTiCl3) activated by modified methylaluminoxane (MMAO), one of the more active catalysts for the syndiotactic poly-
2. Experimental Section

2.1. General Procedures and Materials

Air- and moisture-sensitive operations were carried out in nitrogen atmosphere using standard Schlenk techniques and an MBraun glovebox. Dry solvents were freshly distilled before use. Toluene was kept under reflux in the presence of sodium for 48 h and then distilled in atmosphere of nitrogen. Styrene (99%; Sigma-Aldrich) was purified by stirring overnight in presence of calcium hydride and distillation under reduced pressure. Modified methylaluminoxane (MMAO, 7 wt% of aluminium in toluene; Sigma-Aldrich) was dried in the form of a white powder by removing in vacuo the solvent. Cyclopentadienyltitanium(IV) trichloride (97%; Sigma-Aldrich), ethylene (Linde), deuterated solvents and other reagents available from commercial suppliers, unless otherwise stated, were used without further purification.

2.2. Instruments and Measurements

NMR spectra were acquired on Bruker Avance spectrometers (250, 300, 400 or 600 MHz for 1H). Chemical shifts (δ) are reported in parts per million (ppm) and referenced using the residual solvent peaks in 1H NMR spectra at 7.27 ppm for CDCl3 and 5.80 ppm for 1,1,2,2-tetrachloroethane-d2 (TCE-d2) and in 13C NMR spectra at 77.23 ppm for CDCl3 and 73.78 ppm for TCE-d2. Diffusion ordered spectroscopy (DOSY) experiments were performed on a Bruker Avance 600 spectrometer equipped with a 5 mm PABBO 600S3 BBF-ØH-D-OS-Z-SP probe. The standard Bruker pulse program, ledbpgp2s, employing a double stimulated echo sequence and LED, bipolar gradient pulses for diffusion, and two spoil gradients was utilized. The pulse gradients (g) were increased from 5 to 95% of the maximum gradient strength in a linear ramp with a total experiment time of 45 min. Diffusion times were 2500 ms, the eddy current delay was 5 ms, the gradient recovery delay was 0.2 ms, and the gradient pulse was 1000 ms. Individual rows of the quasi-2D diffusion databases were phased and baseline corrected. After Fourier transformation and baseline correction, the diffusion dimension was processed with the software Topspin3.2 and Diffusion from Bruker. Diffusion coefficients, processed with a line broadening of 2 Hz, were calculated by Gaussian fits with the T1/T2 software of Topspin3.2. Molecular weights were calculated using a polystyrene standard for GPC (vide infra) with molecular weight of 42.6 kDa and PDI of 1.04 as internal standards, according to the procedure reported in literature.[30] Molecular weight parameters (Mw and Mn) and molecular weight distributions for all the samples were measured by using a GPC-IR apparatus from PolymerChar, which was equipped with a column set of four PLgel Olexis mixed-bed (Polymer Laboratories) and an IRS detector (PolymerChar). The dimensions of the columns were 300 × 7.5 mm and their particle size of 13 µm. The mobile phase flow rate was kept at 1.0 mL/min. All the measurements were carried out at 150°C. Solution concentrations were 1.5 mg/mL (at 150°C) and 0.3 g/L of 2,6-di-tert-butyl-p-terphenyl was added to prevent polymer degradation. For GPC calculation, a universal calibration curve was obtained using 12 polystyrene (PS) standard samples supplied by PolymerChar (molecular weights ranging from 266 to 1220000 Da). A third order polynomial fit was used for interpolating the experimental data and obtain the relevant calibration curve. Data acquisition and processing was done by using Empower 3 (Waters). The Mark-Houwink relationship was used to determine the molecular weight distribution and the relevant average molecular weights: K values were \( K_{PS} = 1.21 \times 10^4 \text{ D}_2\text{g/L} \) and \( K_{PE} = 4.06 \times 10^4 \text{ D}_2\text{g/L} \) for polystyrene (PS) and polyethylene (PE) respectively, while the Mark-Houwink exponents \( a = 0.706 \) for PS and \( a = 0.725 \) for PE were used. For PS/PE copolymers, as far as the data evaluation is concerned, it was assumed for each sample that the composition was constant in the whole range of molecular weight and the \( K \) value of the Mark-Houwink relationship was calculated using a linear combination: \( K_{PS/PE} = X_{PS}K_{PS} + X_{PE}K_{PE} \), where \( K_{PS/PE} \) is the constant of the
copolymers, \(x_{PS}\) and \(x_{PE}\) are the PS and the PE weight relative amount with \(x_{PS} + x_{PE} = 1\). Wide-angle x-ray diffraction (WAXD) diffractograms were obtained in reflection using an automatic Bruker D8 diffractometer using the Ni filtered Cu Kα radiation; the sample of Fig. 3c in a sealed vial under vacuum was kept 15 min at 270°C ten poured into liquid nitrogen before the diffraction. Differential scanning calorimetry (DSC) measurements were carried out in nitrogen on a TA Instrument DSC Q20 calorimeter (heating and cooling rate of 10 °C/min). Atomic force microscopy (AFM) images of polymer thin films were collected in air with a Dimension V microscope coupled with a Bruker Nanoscope V controller operating in tapping mode (TM). The polymers were dissolved at 130 °C in tetrachloroethane (TCE) to afford clear solutions that were deposited (30 μL) onto glass slides at 120 °C and analysed by TM-AFM. The thickness of the films (0.3–1 μm) was estimated by TM-AFM height measurements of scratches made by a sharp needle on the films. The TM-AFM micrographs were processed with the Nanoscope Analysis v1.40 r2sr1 software from Bruker.

### 2.3. Typical Procedure for Ethylene-Styrene Copolymerization

The copolymerization has been realized in a glass tube inside the stainless-steel autoclave (100 mL high-pressure autoclave model I) equipped with magnetic stirrer, pressure gauge and thermostated at 0 °C. At first a solution of toluene (10 mL), styrene (10 mL), CpTiCl\(_3\) (20 mg) and modified methylaluminoxane (650 mg) was kept to react under nitrogen for a time of 10 min; subsequently a constant ethylene pressure of 2.0 MPa replaces that of nitrogen and the system remains under stirring for further 180 minutes. At the end the gas was vented off, the solution poured into acidified methanol and the polymer collected by filtration and drying in vacuo. The copolymer fraction has been recovered by sequential extractions in Kumagawa-type extractor (see Scheme 1) with hexane and toluene. The amorphization of the hexane non-soluble fraction, by treatment of the solid at 270°C for 20 min and quenching in liquid nitrogen, improves the subsequent extractive processes. Yield: 250 mg; S/E weight ratio = 73:27.

### 3. Results and Discussion

#### 3.1. Synthesis and Characterization of sPS-b-PE Copolymer

In order to achieve the di-block structure, at first a solution of toluene, styrene, CpTiCl\(_3\) and MMAO is kept reacting under nitrogen at 0°C for 10 min; subsequently ethylene at a pressure of 2.0 MPa replaces the nitrogen and the system remains under stirring and continuous ethylene feed for further 180 minutes. At the end the gas phase is vented off, the solution poured into acidified methanol, the polymer collected by filtration, dried and finally fractionated through sequential extractions in Kumagawa-type extractor (see Scheme 1). It is worth noting that after the extraction with hexane, the insoluble fraction was dried, melted above 270°C and quenched by pouring it into liquid nitrogen. The so treated material was finally extracted with boiling toluene.

The \(^{13}\)C NMR spectra of the raw material and of the different fractions reported Figure 1 show as the fractionation was effective in isolating almost pure polyethylene (Fig. 1b, hexane soluble fraction) and syndiotactic polystyrene (Fig. 1c, toluene insoluble fraction). However our attention was devoted to the hexane insoluble-toluene soluble fraction (Fig. 1d) whose very simple pattern of signals of the aliphatic region can be safely assigned to the polyethylene sequence at 29.9 ppm and to the syndiotactic polystyrene sequence at 44.5 ppm (methine carbon) and 41.3 pm (methylene carbon).

GPC analysis of this polymer fraction revealed a \(M_n\) of 56 kDa while the monomodal shape of the curves and the value of 2.9 for the \(M_n/M_w\) ratio supports the idea that we are in presence of a diblock copolymers (see Figure S1 in the Supplementary Materials).

DOSY NMR analysis of the sPS-b-PE copolymer has evidenced that the sPS and PE segments have the same diffusion coefficient as an indication of the linkage between the homosequences (see Figure S2a), notwithstanding the different dimension of the segments as inferred from the areas of the NMR peaks.
The molecular weight of 43.8±8.1 kDa, estimated from DOSY NMR diffusion coefficients of sPS-b-PE copolymer (9.3·10^{-12}±2.7·10^{-13} m^{2}s^{-1}) in presence of a PS standard (9.4·10^{-12}±2.9·10^{-13} m^{2}s^{-1}) well compare with that determined by GPC (see Figure S2b).

The existence of the junction between the sPS and PE segments has been identified by ¹H-¹H COSY NMR. The pattern of COSY correlations due to the protons present on the E-S junction, namely those labelled as 6, 7 and 8, has been clearly identified and highlighted in Figure 2. Moreover, the same spectrum contains the pattern of correlations due to the sPS terminal, i.e. due to the initiation of the polymerization via secondary insertion of the styrene into the Ti-CH₃ bond of the activated catalytic species (see the cascade correlation of the signals 1, 2, 3 and 4), as well as shows the pattern due to the PE terminal (correlation among the signals 13-12).

It is worth recalling that relevant Ti(IV) reduction take place in these systems with possibly oxidation state of +3 in the active sites for syndiotactic styrene polymerization, on the basis of some elegant experimental evidences.[31] As a consequence, one can suppose the contemporary presence of different catalytic species, so the occurrence in the product mixture of polyethylene (hexane soluble fraction) and syndiotactic polystyrene (toluene insoluble fraction) is not surprising.

Scheme 1. Synthesis and purification of sPS-b-PE diblock copolymer.
Figure 1. $^{13}$C NMR spectra (TCE-d$_2$; 25°C) of polymer fractions deriving from the synthetic procedure adopted for the isolation of sPS-b-PE copolymer: a) crude reaction product; b) hexane soluble fraction; c) toluene insoluble fraction; d) toluene soluble fraction.

Figure 2. $^1$H-$^1$H COSY NMR spectrum of sPS-b-PE with assignments for polymer terminals and E-S junction.
3.2. Thermal and Crystalline Behavior

The copolymer material, as recovered from extraction procedure, shows the x-ray diffraction pattern typical of the δ form of sPS with toluene molecules clathrate in the crystal structure, without relevant signals of the crystallinity related to the polyethylene (Figure 3b). PE crystallinity can be detected in the crude reaction product containing the PE homopolymer (Figure 3a). When the polymer material C6-insoluble-toluene soluble is heated up to 270 °C, then quickly quenched by pouring it into liquid nitrogen and finally kept some minutes at room temperature, its diffraction spectrum clearly shows the presence of the only crystallinity due to the PE sequence (Figure 3c). The corresponding DSC analysis on such sample shows around 110 °C the overlap of the endothermal peak due to the melting of the polyethylene crystals with the exothermal peak due to the crystallization of the syndiotactic polystyrene in correspondence to its glass transition (Figure 4c). By continuing the heating one can observe an endothermic phase transition at 255 °C, well below the melting point of the syndiotactic polystyrene, usually reported around 270 °C. Probably, during the crystallization from the solution, the polystyrene can arrange its chains in the usual helices so impeding to the best organization of the polyethylene sequences into the usual lattice of planar zig-zag chains. On the other hand, the sample frozen in the amorphous state is able to develop at room temperature the polyethylene crystallinity but is unable to crystallize the polystyrene sequences as long as it is below its glass transition temperature.

The copolymer preserves the complex polymorphism of the sPS. As an example of this behavior, the δ-empty form and the β form of sPS can be obtained respectively by treatment with supercritical CO2 (Figure S3) and by heating at 170 °C for 30 min (Figure S4) the copolymer.

![Figure 3. WAXD patterns for: a) crude reaction product; b) of sPS-b-PE copolymer; c) sPS-b-PE melted and kept at 270°C for 20 min then quenched in liquid N2.](image-url)
Figure 4. DSC thermograms for: a) raw reaction product; b) sPS-b-PE (as recovered after Kumagawa extraction processes); c) sPS-b-PE melted and kept at 270°C for 20 min then quenched in liquid N₂.

3.3. Thin Film Morphology

The thin film morphology of the sPS-b-PE copolymer has been investigated by atomic force microscopy operating in tapping mode (TM-AFM). This technique has been widely adopted for the topological characterization of polymer surface as well as for identification of the distribution of the polymer phases on the base of their different mechanical properties.\cite{25,32-38} The phase of oscillation of the probe of the AFM nanoscope responds to the stiffness of the surface, allowing the discrimination of chemical phases. Atactic polystyrene (aPS) and PE present quite different stiffness in term of Young’s modulus, respectively of 2.0 GPa and 0.1 GPa, in fact they were used as standards for the calibration of AFM nanoscope (operating in HarmoniX or PeakForce mode) for the quantitative determination of mechanical properties of surface.\cite{38} This difference of stiffness is even more pronounced between syndiotactic PS and PE considered the higher modulus of the sPS of 3.0 GPa, w.r.t aPS.\cite{32,38} The specimens for AFM analyses have been prepared by dissolution of the polymer in TCE (0.2 wt%) at 130 °C and deposition (30 μL) of the polymer solution at 120 °C onto glass slides followed by quenching at room temperature. This procedure allows the accentuation of the phase separation in these materials, highlighting the eventual presence of homopolymers.\cite{38} Actually, the analysis of the thin film prepared with the raw material, prior to the isolation of the sPS-b-PE copolymer, presents soft circular regions in micrometer size embedded into an hard matrix, respectively assigned to the PE homopolymer and to the styrenic counterparts (see Figure S5). The thin films of the polymer material coming from the fractionation procedure (S/E weight ratio = 73:27) present a smooth surface, from the phase contrast analysis found consisting of a hard matrix with incorporated a soft jagged phase with nanometric scale. In this case, the PE segregates to form small nanometric domains because bounded to the sPS segments (Figure 5).
Figure 5. Height (on the left) and phase (on the right) TM-AFM micrographs of thin film of sPS-b-PE copolymer.

4. Conclusions

A unprecedented ethylene-styrene copolymer with a syndiotactic styrene sequence joined to the polyethylene chain can be obtained, although in mixture with sPS and PE homopolymers, by using the classic catalytic system CpTiCl₃/MMAO through sequential polymerization of the monomer at low temperature. The mixture can be resolved for isolating the sPS-b-PE copolymer via consecutive solvent extraction of the raw polymer material through the Kumagawa apparatus. The successful synthesis of this copolymer can be ascribed to the low reaction temperature allowing the quasi-living polymerization of the monomers whereas at a catalytic site that one could suppose based on titanium in the oxidation state III.

The in-depth characterization of the new material through gel permeation chromatography, differential scanning calorimetry, and various NMR techniques supports this di-block architecture. In addition, it has been observed that the sPS-b-PE copolymer substantially preserves the crystalline and thermal behaviors of the two polymer segments, in particular the complex and interesting nanoporosity of the syndiotactic segment. The analysis of thin film of the sPS-b-PE copolymer by TM-AFM evidenced a phase-separated morphology consisting of a hard polymer matrix of sPS with embedded jagged nanometric soft domains of PE. Finally, this new material possibly can be seen as a new member of the short list of the nanometric polymeric sieves and this perspective will be explored in the next research activity.

Supplementary Materials: Further details on the GPC, DOSY NMR, WAXD and TM-AFM analyses.

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