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# Semicrystalline proton-conductive membranes with sulfonated amorphous phases

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## ABSTRACT

Proton-conductive membranes, exhibiting high chemical and thermomechanical resistance, have been obtained by s-PS films with the  $\beta$  crystalline phase and a sulfonated amorphous phase. These membranes can be obtained by a solid-state procedure on  $\delta$  form films, which allows an easy and uniform sulfonation of the phenyl rings of the amorphous phase and preserves the crystalline phase, followed by suitable thermal treatments leading to the  $\delta \rightarrow \beta$  crystal-to-crystal transition. The high degree of sulfonation of the amorphous phase makes this phase highly hydrophilic and proton conductive while the presence of the high melting and thermodynamically stable  $\beta$  phase assures high chemical and thermomechanical stability.

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## 1. Introduction

Ion-containing polymers (ionomers) are widely used as proton exchange membranes in fuel cells [1]. These membranes are generally exposed to very harsh environmental conditions, resulting from high local concentrations of acidic groups and from high operating temperatures, as well as from the oxidative conditions at the electrodes. Many industrially important ionomers, like e.g. Nafion are semicrystalline polymers, so that their desirable properties strongly depend on the structure and morphology of the crystalline domains.

Syndiotactic polystyrene (s-PS) is a robust polymeric material with high melting point, high chemical stability and high crystallization rate [2] and several studies have been reported in the literature describing the possible use of sulfonated s-PS as proton-conductive membranes, for fuel cells [3]. However, all the reported studies describe sulfonation procedures in solution, leading to random sulfonation of the polymer chains and hence to strong reduction of crystallinity and of related chemical and thermomechanical resistance.

In this paper we show that, by exploiting (both for the processing and the final material properties) the complex

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polymorphic behavior of s-PS, highly crystalline membranes can be achieved, which exhibit a thermal and chemical-resistant unsulfonated crystalline phases and a proton-conductive sulfonated amorphous phase.

The complex polymorphic behavior of s-PS [4], making some simplifications, can be described in terms of two highly melting ( $T_m \approx 270$  °C) crystalline forms,  $\alpha$  [5] and  $\beta$  [6] containing planar zigzag chains and of three thermally unstable forms,  $\gamma$  [4a,7],  $\delta$  [8] and  $\epsilon$ , [9] containing  $s(2/1)_2$  helical chains (helical repetition of two structural units in one turn, the structural unit being formed by two monomeric units). Beside the five crystalline phases, s-PS is able to form different kinds of co-crystalline phases with many different low-molecular-mass guest molecules [10].

Semicrystalline s-PS samples exhibiting the nanoporous  $\delta$  and  $\epsilon$  crystalline phases can rapidly and selectively absorb volatile organic compounds (mainly halogenated and aromatic) even when present at very low concentrations [11]. The thermoplastic nature of these polymers allows an easy processing to products suitable materials for several applications, like films, membranes, and foams and a number of applications in the field of chemical separations [11] and of molecular sensors [12] has been proposed.

Several guest sorption studies [11], have clearly demonstrated that for suitable guest molecules the solubility in the nanoporous crystalline phases can be much larger than the solubility in the amorphous phase. Bulky molecules, whose molecular volume and shape are unsuitable to form co-crystalline phases with s-PS, can be instead absorbed only in the amorphous phase [7b].

The molecular selectivity of the nanoporous  $\delta$  phase has been recently used to obtain efficient and selective solid-state sulfonation of the phenyl rings of the amorphous phase, also for high thickness films (at least up to 200  $\mu\text{m}$ ). In fact, by using a bulky sulfonating agent (the lauroyl sulfate), which is unable to enter in the nanoporous crystalline phase, the sulfonation can occur only in the amorphous phase [13]. Moreover, the use of chloroform as solvent which is able to easily penetrate into the nanoporous crystalline phase, makes rapid and uniform the sulfonation, for the whole film thickness. In this respect, it is worth noting that films with dense crystalline phases (e.g. the  $\beta$  phase), which are not permeable to the solvent, are sulfonated very slowly and in a highly non-uniform way [13].

In this paper we show that proton-conductive membranes, possibly suitable for fuel cells, can be obtained from these highly crystalline s-PS samples, being sulfonated only in the amorphous phase, by inducing crystal-to-crystal transition from the nanoporous  $\delta$  phase toward the thermodynamically stable  $\beta$  phase. Of course, in these membranes, the sulfonated amorphous phase assures the proton conductivity while the  $\beta$  crystalline phase assures the chemical and thermomechanical resistance.

## 2. Experimental section

### 2.1. Materials

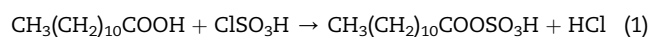
The s-PS used in this study was manufactured by Dow Chemical Company under the trademark Questra 101. The  $^{13}\text{C}$  nuclear magnetic resonance characterization showed that the

content of syndiotactic triads was over 98%. The weight-average molar mass obtained by gel permeation chromatography (GPC) in trichlorobenzene at 135 °C was found to be  $M_w = 3.2 \times 10^5$  with the polydispersity index,  $M_w/M_n = 3.9$ .

The  $\delta$ -form films subjected to the sulfonation procedure have been obtained by casting from 0.5 wt% solutions, at room temperature from chloroform [14]. The films present uniplanar  $a||c||$  orientation [14c] of nanoporous and co-crystalline phases and thickness in the range 40–60  $\mu\text{m}$ .

### 2.2. Sulfonation procedure

The acyl sulfate sulfonating reagent was prepared by mixing at room temperature an excess of dodecanoic acid (lauric acid) over chlorosulfonic acid



In particular 1.6 mol of lauric acid ( $\geq 98\%$ , Aldrich) was used per 1.0 mol of  $\text{ClSO}_3\text{H}$  (99%, Aldrich) and the reaction was conducted in Nitrogen atmosphere for a time of 24 h. All reagents were used as received.

The sulfonation of s-PS films exhibiting the nanoporous  $\delta$  phase was performed at temperature of 40 °C, by soaking for a time from 1 to 24 h in a 0.005 M acyl sulfate solution in  $\text{CHCl}_3$  (99%, Aldrich).

The sulfonated films have been purified by possible remnants of the sulfonation procedures by soaking the membranes in acetonitrile (anhydrous, 99.8%, Aldrich) for a time of 1 h, followed by extraction with carbon dioxide in supercritical conditions, with an SFX 200 supercritical carbon dioxide extractor (ISCO Inc.), by using the following conditions:  $T = 40$  °C,  $P = 200$  bar, extraction time  $t = 180$  min. As well established in the literature [15], the extraction with carbon dioxide in supercritical conditions allows complete removal of possible guest molecules from s-PS co-crystalline phases, leading to nanoporous crystalline phases.

The sulfur content in the membranes has been evaluated by elemental analysis and has been reported as fraction of sulfonated styrenic units (thereafter indicated as S).

### 2.3. Characterization methods

The films were examined with a scanning electron microscope (SEM) (Leica Cambridge Stereoscan S440) coupled with a probe for energy-dispersive scanning (EDS), and the occurrence of uniform sulfonation at different depths throughout the sample thickness was verified. The films were cryogenically fractured in liquid  $\text{N}_2$  for the SEM–EDS examinations. All films were coated with Au prior to EDX analysis. For the calibration of EDX, the following standards were used:  $\text{CaCO}_3$  (carbon standard),  $\text{SiO}_2$  (oxygen standard),  $\text{FeS}_2$  (sulfur standard).

Wide-angle X-ray diffraction patterns with nickel filtered  $\text{CuK}\alpha$  radiation were obtained, in reflection, with an automatic Bruker D8 Advance diffractometer. The spectra are reported as a function of  $2\theta$  diffraction angles.

The water uptake of the polymers was obtained by determining the weight gain of samples after soaking in water and wiping of the membranes.

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