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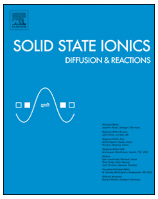

Structure and morphology of model polymer electrolyte membranes based on sulfonated syndiotactic-polystyrene in the δ co-crystalline phase resolved by small-angle neutron scattering

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ABSTRACT

Syndiotactic polystyrene (s-PS) is able to form different kinds of co-crystalline phases with guest molecules of different size, shape and property. Several advanced materials have been produced starting from s-PS co-crystalline films. In particular, sulfonated s-PS (s-sPS) can be used as proton-conductive membrane in some fuel cells applications, as it presents high proton conductivity (comparable with Nafion). Besides, it shows a high chemical and thermo-mechanical stability and a low cost. The morphology of different s-PS clathrates and the structural behavior of s-sPS upon hydration can be thoroughly understood by SANS. In fact, exploiting the neutron contrast variation between various hydrogenated and deuterated components of s-PS and s-sPS clathrates, additional and unique information about the distribution of guest molecules in the crystalline and amorphous regions and about the hydrated domains of the polymer were obtained. Moreover, using uni-axially deformed films the occurrence and distribution of scattering features from typical morphologies on specific directions and sectors of detection plan enable an accurate structural study of such complex polymeric systems. We report in the present paper a detailed SANS investigation of s-PS films, starting from their crystallization with guest molecules to the subsequent sulfonation and hydration. FT-IR, neutron PGAA, WAXD and cryo-TEM were used complementary to SANS to check the state of the samples after each step of the treatment process and to obtain additional structural information as support for the understanding of the SANS data. The current experimental analysis has highlighted that the morphology of these polymeric films is characterized by hydrated channels in the bulk amorphous phase alternated to stacks of crystalline lamellae, oriented along the stretching direction.

1. Introduction

Polymer electrolyte membranes (PEMs, also called proton exchange membranes) are typically ionomers of interest for applications such as fuel cells [1], solar energy conversion devices [2] and water filtration [3]. PEM for fuel cells (PEMFC) [4] are considered today as one of the most promising technologies in the field of renewable power sources and environmentally friendly energy generation, to solve the problems of oil shortage and global warming due to their high efficiency and the clean exhausts [5]. To be considered a good candidate as membrane for fuel cell applications, specially designed polymers and copolymers have to present different properties, such as: high ionic conductivity, resistance to dehydration, adequate mechanical strength, chemical and electrochemical stability under operating conditions, low gas permeability, moisture control in stack, low cost production and good capability for fabrication into membrane electrode assemblies. Currently, the most used material for such applications is the Nafion (N115, N117 and N1110, chemically stabilized perfluorosulfonic acid/polytetrafluoroethylene [PFSA/PTFE] copolymers in the acid (H^+) form), produced for the first time in the 1970s by Du Pont™. However, despite the excellent properties of the Nafion membranes, there are several disadvantages such as the high cost, the lack of safety during its manufacture and use, requirement of supporting equipment and temperature related limitations [4–8]. Moreover, under the more stringent operating conditions requested by industry ($T > 100$ °C and $RH < 50\%$), proton conductivity for PFSA membranes drops significantly, leading to a

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decrease in fuel cell performance [9]. This has prompted the research towards the analysis of alternative polymers that could be used as PEMFCs. In this regard, non-fluorinated membranes with aromatic backbone, non-fluorinated hydrocarbons, acid-base blends and partially sulfonated polymers have become the subject of numerous scientific investigations in the industry and academic world [4,6–8,10]. Recently some authors [11–14] have proposed a proton-conductive membrane based on sulfonated syndiotactic polystyrene (s-sPS), which presents a high proton conductivity, high chemical and thermo-mechanical stability and a low cost. Moreover, its thermoplastic nature allows for easy processing in forms suitable for several applications, like films, membranes, and foams, as well as their recycling. At the same time, the very complex polymorphic behavior and the extreme sensitivity to the processing conditions spurred many investigations on it [15].

The sPS can crystallize in many crystal forms as well non-equilibrium structures depending on the thermo-mechanical processing conditions [16–22]. The most stable α and β forms are characterized by chains in *trans*-planar (zig-zag) conformation and principally obtained by melt crystallization or by annealing at the appropriate temperature, whereas the γ form [23] is characterized by chains in helical conformation and can be prepared through solvent treatments of the amorphous phases or α form followed by annealing at high temperatures. Two nanoporous crystalline phase, called δ [23–25] and ε [26–32], have been discovered for this polymer (with the same helical conformation $s(2/1)2$ of the γ form), which can absorb several guest molecules so producing clathrate and intercalate co-crystals [29–32]. In particular, different advanced materials [33–35] have been already produced starting from s-PS co-crystalline films.

As previously mentioned, a field in which sPS may be employed is that of PEMs, once appropriately functionalized [36,37]. However, a number of issues related to the practical use of the sulfonated hydrocarbon polymer PEMs in fuel cell applications were reported in various publications. Thus, a strong reduction of the sPS crystallinity as a consequence of sulfonation procedure in solution was observed [38,39]. Another problem is related to the durability of the sPS PEMs. Several studies reported degradation of polystyrene based membranes at high temperatures, due to their oxidation decomposition in practical fuel cell systems conditions [40–42]. Anyway, recent developments have shown that, at least at the laboratory scale, these problems can be successfully tackled. In their study, Fasano et al. [14] have set up a method of using a bulky sulfonating agent which, when applied to δ form sPS samples, leads to an efficient and uniform phenyl ring sulfonation only in the amorphous phase, without disturbing the polymer crystallinity. Such membranes were prepared and characterized from a macroscopic point of view and a value of proton conductivity of 10^{-3} to 10^{-2} S/cm, comparable with that exhibited by Nafion membranes [4,13,14], was reported. On the other hand, Saga et al. [43] prepared composite polyelectrolyte membranes from sulfonated polystyrene and fullerenes and concluded that the addition of fullerenes improved the oxidation resistance of the membranes due to the radical scavenging role played by the fullerenes. More recently, aiming to increase the operating temperature of Li-ion batteries (LIB), Raut et al. [44] fabricated and characterized sPS ionogel membranes for use in such applications. The membranes were found to be stable over a long time in high temperature electrochemical operations, such in LIBs.

It is generally accepted that the properties of PEMs derive from the microphase separation of a hydrophilic ionic material from a hydrophobic substance. Therefore, to design new PEMs, one should not only consider the architecture of the molecule itself, but also understand the microphase separation structures of membranes, such as the crystalline domains, the formation of conducting regions, and the distribution of ionic groups and water in the conducting regions. Even the microstructure of the Nafion is still debatable, as shown by the continuous interest raised by this material regarding the microstructural investigations by small-angle scattering techniques, either X-ray (SAXS) or neutrons (SANS). Several morphologies involved in the microstructural conduction mechanisms were proposed for Nafion along the time: from Gierke's model of inverted-micelle water clusters [45–48], through layered structures [49,50], channel networks [45,51,52], polymer bundles [53–55], parallel randomly packed water channels [56] until the most recently proposed flat and narrow water domains yielding “water films” [57]. A comprehensive summary of PSFAs, including Nafion, with a detailed description of their nanomorphology and transport properties is reported in [58].

In this paper we report a detailed microstructural characterization of membranes based on sulfonated syndiotactic polystyrene (s-sPS) in the δ-clathrate co-crystalline phases carried out by using primarily SANS with contrast variation. The investigation on the structural behavior of s-sPS films was done upon their clathration, sulfonation and subsequent hydration either by dipping in water or by exposing them to controlled relative humidity (RH) by means of a humidity chamber (Anton Paar). Complementary techniques like FT-IR spectroscopy, neutrons prompt gamma activation analysis (PGAA), wide angle X-ray scattering (WAXS) and transmission electron microscopy using the cryo option (cryo-TEM) were used before or after film hydration to enable a complete system characterization prior to SANS investigations or as support for the interpretation of the SANS observations. Neutron contrast variation was used to emphasize or to mask different regions of the complex s-sPS system. By clathration, crystalline regions showing cages that are filled with certain guest molecules were generated in the sPS films as dispersed in an otherwise amorphous phase. The crystalline region itself consists of crystalline lamellae alternating with amorphous inter-lamellar regions. The reported crystallinity of such sPS samples was about 40% [59]. Therefore, the neutron contrast between the crystalline and amorphous regions can be varied by loading either hydrogenated or deuterated guest molecules into the crystalline regions [60]. The sulfonation of sPS films affects exclusively the amorphous regions, which can thus change further the neutron contrast between the amorphous and crystalline regions. Furthermore, exploring the hydration of the samples for different D_2O/H_2O ratios, we aimed for another contrast manipulation between the crystalline and amorphous regions. Particular interest was focused on the investigation whether the hydration will affect both the inter-lamellar and bulk amorphous regions or only the bulk amorphous region of the system.

Finally, in order to be able to analyze better all scattering features yielded by such a complex system we used uni-axially deformed (oriented) sPS films to separate the scattering signals from different regions of the film morphology on different sectors of the two-dimensional position sensitive detector used for SANS [59]. A schematic design of the SANS investigation geometry is shown in Fig. 1. Following this experimental approach we were able to characterize in details the complex morphology of s-sPS films in dry or hydrated state and to evidence the water one-dimensional regions, which possibly emerge at a later stage by linking together initially formed water clusters in the bulk amorphous region of the films.

2. Experimental part

2.1. Synthesis

The deuterated syndiotactic polystyrene (d_8-sPS) sample was prepared using the homogeneous catalytic system composed of pentamethylcyclopentadienyltitanium trichloride (Cp^*TiCl_3) and methylalumoxane (MAO) in toluene. All manipulations of air- and/or water-sensitive compounds were carried out under dry nitrogen atmosphere using a Braun Labmaster drybox or standard Schlenk line techniques. Glassware and vials used in the polymerization were dried in an oven at 120 °C overnight and exposed to vacuum-nitrogen cycle, three times.

d_8-Styrene (Aldrich, isotopic purity 98% atom% D) was purified by distillation under reduced pressure over CaH_2. Cp^*TiCl_3 was purchased from Stream and used as received. MAO was purchased from Chemtura. Toluene was refluxed 48 h over metallic sodium and distilled under a