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Potential contact and intraocular lenses based on hydrophilic/hydrophobic sulfonated syndiotactic polystyrene membranes

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ABSTRACT

Crystalline films of syndiotactic polystyrene (s-PS), a commercially available thermoplastic polymer, having a highly hydrophilic amorphous phase, were achieved by using a mild solid-state sulfonation procedure. Despite the used mild process conditions, an easy and uniform sulfonation of the phenyl rings of the amorphous phase is obtained. The crystallinity of the polymer was not affected by the sulfonation degree (S), at least at S less than 20%, and the obtained polymer films show the nanoporous crystalline form of s-PS. As widely reported in literature, the nanoporous nature of the polymer crystalline phase gives to these materials the ability to absorb and release organic molecules of appropriate size and polarity. This property, coupled to transparency, makes these materials potentially useful intraocular lens (IOLs) and contact lens applications. Sulfonation procedure and sulfonated film samples characterization by using wide-angle X-ray diffraction (WAXD), Fourier-transform infrared (FTIR) and ultraviolet-visible (UV-vis) spectroscopy techniques and water sorption tests were reported. Furthermore, the biocompatibility study demonstrated no cytotoxicity and appropriate cell interaction properties for the specific applications.

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1. Introduction

In the last century the field of contact lens materials has been continuously evolving. The technology of vision correction uses a lens in intimate contact with the cornea which is anterior part of the eye shell (Lepore et al., 2002). The cornea is a multilayer tissue with a high water content (65–75%) whose structure is complex and mechanical properties are mainly correlated to collagen fibrils tridimensional distribution. In this context, the ocular environment places high demands on the performance of contact lenses as biomaterials. Therefore, biomaterial science has led to the

development of a variety of intraocular lens (IOLs) and contact lenses biomaterials (Chehade and Elder, 1997; Kodjikian et al., 2004; Nicolson and Vogt, 2001). Main chemical-physical characteristics of these materials are optical transmittance, dimensional stability and chemical stability. Moreover, materials used in ophthalmic devices have to be non-toxic, biocompatible and anti-adhesive to avoid the lens opacification due to the adhesion, proliferation and migration of cells.

Recently, novel anti-adhesive materials have been developed to reduce the collateral effects due to cell-material interaction without affect optical properties (Lee et al., 2007). Hydrogel, soft acrylic and silicone IOLs have gradually displaced poly(methyl methacrylate) (PMMA) lenses. Silicone has the lowest threshold for YAG laser damage of all IOLs materials but, due to its hydrophobic surface, it gives a high risk of cellular reactions. Hydrogel lenses are very biocompatible and resistant to YAG laser, but pigment adheres to their surface. Soft acrylic IOLs unfold slowly, resulting in controlled insertion, but it is possible to crack the lens or develop glaucomas due to water accumulation. s-PS is a commercial thermoplastic semicrystalline polymer presenting

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high robustness, durability, and low cost associated with easy processing. The mild conditions of the used sulfonation procedure (Borriello et al., 2009; Venditto et al., 2015), allow to selectively sulfonate only amorphous phase of s-PS leaving intact the crystalline phase. At the end of the sulfonation procedure, the polymer is in the nanoporous crystalline phase, which inside the crystal lattice presents empty spaces distributed in all identical cavities of nanometric dimensions (micropores, according to IUPAC classification). It is well known that s-PS nanoporous crystal forms, named δ (De Rosa et al., 1997) and ϵ (Petraccone et al., 2008), are able to absorb organic molecules of appropriate size and polarity, even if present in traces in air or water (Daniel et al., 2011, 2013a, 2013b; Guerra et al., 2012; Manfredi et al., 1997; Mensitieri et al., 2008). Moreover, the capacity of the s-PS nanoporous crystal δ form to release previously absorbed guests has been extensively studied, for gases (e.g., CO₂, ethylene, propene, and butadiene) (Albunia et al., 2012; Annunziata et al., 2006) and organic molecules (e.g., 1,2-dichloroethylene, carvacrol) (Albunia et al., 2014; Venditto et al., 2006).

In this work we summarize the preliminary characterization results on a new hydrophilic-hydrophobic membrane as potential IOLs and contact lenses material based on semicrystalline s-PS film having sulfonated amorphous phase.

2. Materials and methods

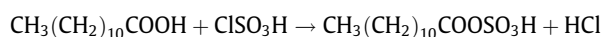
2.1. Materials

The s-PS used in this study was manufactured by Dow Chemical Company under the trademark Questra 101. The ¹³C-NMR characterization showed that the content of syndiotactic triads was over 98%. The weight-average molar mass obtained by gel permeation chromatography (GPC) in 1,3,5-trichlorobenzene at 135 °C was found to be $M_w = 3.210^5$ with the polydispersity index $M_w/M_n = 3.9$ (Rizzo et al., 2002a).

All films considered in this paper have been obtained by casting from 0.5 wt% solutions, at room temperature from chloroform (Rizzo et al., 2002b). The films present uniplanar orientation of crystalline phases and thickness in the 30–70 μm range.

2.2. Sulfonation procedure

The sulfonation reagent was prepared by mixing an excess of lauric acid with chlorosulfonic acid (ClSO₃H) at room temperature, for 24 h:



In detail, 1.6 mol of lauric acid (Aldrich, ≥98%) was used per 1.0 mol of ClSO₃H (Sigma-Aldrich, 99%). The sulfonating solution was obtained by mixing 40 ml di CHCl₃ (Aldrich, 99%) and 4.2 g of the solution containing the acyl sulfate sulfonating reagent. The polymer sulfonation was performed by soaking s-PS films in the sulfonating solution, at temperature of 40 °C, for times from 2 to 24 h. The sulfonated films (Ss-PS) have been purified by possible residuals of the sulfonation process by washing with ethanol and CHCl₃, and then the solvents were extracted with carbon dioxide in supercritical conditions. The extractions were performed by using a SFX 200 supercritical carbon dioxide extractor (ISCO Inc.) using the following conditions: T = 40 °C, P = 200 bar, extraction time t = 180 min. As well established in the literature, (Ma et al., 2005; Reverchon et al., 1999) this procedure leads to δ form of s-PS.

The S has been evaluated by elemental analysis on the whole semicrystalline samples, by using a Flash EA 1112 analyzer from Thermo Fisher Scientific, and is reported as molar fraction of sulfonated monomeric units:

$$S = \frac{[(\text{sulfur moles by elemental analysis}) / (\text{moles of polymer styrenic units})] \times 100}{}$$

The membrane were examined with a scanning electron microscope (SEM) (Leica Cambridge Stereoscan S440) coupled with a probe for energy-dispersive scanning (EDS) to evaluate the S at different depths of films Ss-PS throughout the sample thickness. The membranes were cryogenically fractured in liquid N₂ and silver coated prior to EDS analysis. For the EDS calibration, the following standards were used: CaCO₃ (carbon standard), SiO₂ (oxygen standard), FeS₂ (sulfur standard). The EDS was performed with a beam current of 100 pA and a 20 kV acceleration voltage. As expected, only the peaks of S, C, O and Ag atoms, the latter being used as a coating element, were observed in this range of energy. The observed peaks do not have any overlaps between them. The sulfur percentage present on sample surfaces was evaluated by comparing the S and C content and using a relationship similar to that shown above.

2.3. Characterization methods

2.3.1. Wide-angle X-ray diffraction

Wide-angle X-ray diffraction (WAXD) patterns were obtained with an automatic Theta-Theta Bruker D8 Advance powder diffractometer, equipped with a Vantec PSD (multi strip position sensitive) detector, by using a nickel filtered CuKα radiation (λ = 1.5418 Å). Measurements were made in reflection, on films horizontally mounted on sample holder, in the range 2θ = 4–40°, by using 1° soller slits both on incident and diffracted beams. The correlation length of the crystalline domains, perpendicular to the (010) crystal planes was evaluated using the Scherrer formula

$$D_{hkl} = 0.9\lambda / (\beta_{hkl} \cos \theta_{hkl})$$

where β_{hkl} is the full width at half-maximum expressed in radiant units, λ is the wavelength, and θ_{hkl} the diffraction angle.

2.3.2. FT-IR spectroscopy

Infrared spectra were obtained at a resolution of 2.0 cm^{−1} by a Tensor 27 Bruker spectrometer equipped with deuterated triglycine sulphate (DTGS) detector and a Ge/KBr beam splitter. The frequency scale was internally calibrated at 0.01 cm^{−1} using a He-Ne laser. Measurements were made in transmission on dry films vertically mounted on sample holder, and 16 scans were signal averaged in order to reduce the signal-to-noise ratio. The degree of crystallinity (X_c) has been evaluated by the FT-IR spectral subtraction procedure, as described by Musto et al. (1997). In detail, the spectrum of a fully amorphous s-PS film was subtracted to the spectra of semicrystalline samples ensuring that the 1379 cm^{−1} peak, related to only the amorphous phase, was reduced close to the baseline (Albunia et al., 2006).

2.3.3. Water sorption measurements

The water content for Ss-PS with different S was measured as follows: the dried polymer film was immersed in distilled water at room temperature, for 24 h. The excess water on the surface of the swollen hydrogel was gently removed with a filter paper before to measure its weight, and the water content in the film was determined from an increase in the film weight. The water content responsible for the swelling of the film is expressed from following equation:

$$\text{Water content (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \times 100$$

where W_{wet} and W_{dry} are the weights of the wet and dry samples, respectively.

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