Abstract

The synthesis of polymeric materials by modification method, to obtain the desired properties in polymers, is an important topic in polymer chemistry and technology. Quite often, desired properties are not attainable by the properties of a single homopolymer. A strategy commonly used to achieve this purpose is the anchoring of specific functional groups along the polymer chains

In this context that the interest in the functionalization of syndiotactic polystyrene (s-PS) arises, a semi-crystalline thermoplastic polymer that has low cost and excellent mechanical and dielectric properties, excellent heat resistance and solvent resistance.

In addition, the sPS has a complex polymorphism and the peculiarity that two of his note crystalline forms are nanoporous that are characterized of the presence of empty spaces (cavities in the δ-form and channels in the ε form) within the crystal lattice, able to accommodate small molecules.

This thesis presents new selective functionalization strategy for only amorphous phase of s-PS that at the same time does not change the crystalline phase and therefore all the characteristics of the s-PS.

In particular, in Chapter 3 the sulfonation of s-PS films and their characterization is reported.

The sulfonation allows to introduce a polar acid group on the polymer chains of the amorphous phase of s-PS, which makes the hydrophilic polymer, with a capacity of proton exchange, from here the idea of using sulfonated films of sPS as polyelectrolytic membranes in fuel cells.

In chapter 3 is reported proton conductivity and the capacity to absorb water from the sulfonated sPS films at varying of sulfonation. Degree. It was also well describes the behavior of sulfonated s-PS films after the Fenton's test. In Fenton's test membranes are exposed to drastic oxidizing conditions, similar to those that develop in fuel cells. The ability of sulfonated s-PS films to resist the oxidizing conditions of Fenton test while maintaining good values of conductivity, reveals a possible practical application of this material as polyelectrolytic membrane in fuel cells.

The addition of hydrophilic properties of the amorphous phase of the polymer has the additional effect of improving the properties of nanoporous crystalline phases of the sPS to absorb VOCs from aqueous environments.

Indeed, it is expected that hydrophilic amorphous phases rapidly absorb aqueous solutions containing organic compounds, VOCs, making these (usually nonpolar) more easily available to the absorption in crystalline nonoporose phases of sPS.

In Chapter 4, the sulfonation of s-PS aerogels and their characterization are reported. In particular we have studied the sorption kinetics of a molecule model (1,2-dichloroethane, DCE that is representative of VOC category), from dilute aqueous solutions (50-100 ppm), in the nanoporous δ phase of sPS sulfonated aerogels, to vary the of sulfonation degree. The data indicate that the sulfonation of the only amorphous phase of s-PS increases the sorption kinetics of DCE. This behavior suggests potential practical use of sPS sulfonated aerogels systems for the purification of water or air from volatile organic compounds.

In Chapter 5 the chloromethylation of sPS δ-films and their characterization of are reported.

The introduction of chloromethyl groups on the polymer chains of the amorphous phase of s-PS allows to obtain a highly versatile polymer that by simple nucleophilic reaction with appropriate reagents can give numerous other functionalized polymers.

In this regard, in the chapter 6 the amination reaction of chloromethyl sPS is shown. The aminated polymer contains another polar groups with anion exchange capacity. This property, limited to the amorphous phase, allows the use of aminated sPS semi-crystalline membranes as anion exchange membranes in fuel cells.

In chapter 5, the anionic conductivity and the capacity to absorb water of aminated sPS membranes are reported, these membranes a discrete ability to absorb water and anionic conductivity show.

Finally it should be noted that the characterization of samples functionalized s-PS (sulphonated, chloromethyl, amines), effected by infrared spectroscopy and X-ray diffraction, indicates that the presence of functional groups in the only amorphous phase leaves essentially unchanged the

crystallinity and the orientation of the nanoporous δ crystalline phase of the SPS up to high degrees of functionalization.

In conclusion, the proposed functionalization techniques allow to increase the properties and applications of s-PS respecting the already note characteristics of the polymer.