

Small angle X-ray scattering of polystyrene grafted and sulfonated poly(ethylene-co-tetrafluoroethylene) membranes.

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Radiation-induced graft copolymerization can be used to prepare various types of polymeric membranes; however, most of the membranes have ion exchange capacity, as functional monomers can be easily grafted onto pre-made polymeric films without altering their inherent properties. The membranes physico-chemical properties depend on the structure and morphology of the branches grafted onto polymer substrate. Thus, a better structural and morphological understanding of the graft before and after the insertion of ionic groups (sulfonic groups) in the nanoscale is essential to improve the performance of ion exchange membranes.

In this work Small-angle X ray scattering (SAXS) has been used to investigate the morphology of the microdomains of radiation grafted membranes based on poly(ethylene-co-tetrafluoroethylene) (ETFE) obtained by pre-irradiation method. The ETFE film (125 μ m) was irradiated in an inert atmosphere in bottle containing the solvent and monomer (styrene) at low temperature (-76 ° C). After irradiation the bottle was heated (60°C) to the reaction of grafting occurred following the basic requirements of a methodology for pre-irradiation. The radiation-induced grafting process was followed by sulfonation reaction. Membranes with degree of grafting around 40% were obtained. The thermal behavior of the membranes was also investigated using thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC).

The scattering curve of the pristine ETFE film with crystallinity around 35% presents a long period peak around 17nm⁻¹ characterizing the contrast between the crystalline and the amorphous phases of the pristine film. After the grafting process, an increase in the absolute scattering intensity was observed. With the knowledge that the styrene shows lower electron density than the fluorinated polymeric matrix, this behavior is consistent with the fact that the grafting of styrene increases the contrast of electronic density between the crystalline and amorphous phases, increasing the scattering intensity. The grafting also shifted the long period peak to lower angle (25nm⁻¹) indicating an increase in the long period. Sulfonation of the grafted polystyrene did not shift significantly the long period peak (26nm⁻¹), but caused a decrease in absolute scattering intensity. These suggest that the groups SO₃⁺ diffuse to the vacancies in the amorphous phase, increasing its electronic density. Effectively, this reduces the electronic density contrast between the amorphous and crystalline phases in the membrane, decreasing the overall small angle scattering intensity.

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