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Hydrolytic degradation of sulfonated polyimide membranes for fuel cells

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ABSTRACT

The hydrolytic degradation mechanism of sulfonated polyimide (sPI) membranes was determined through the study of model compounds and validated with a fully sulfonated polymer. Two model compounds characteristic of the ionic sequence and of the junction between ionic and neutral sequences in block copolymers were synthesized and aged in water at different temperatures. Liquid chromatography was used to separate and identify the degradation products by means of various spectroscopies (IR, UV, NMR). It is shown that the hydrolysis of the naphthalenic imide rings is an equilibrated reaction and that the imide rings are more stable when located between ionic substituted monomer than in the hydrophilic–hydrophobic junctions. It is concluded that block copolymers with long ionic sequences or blends of sulfonated and non sulfonated homopolymers should be more stable than random copolymers. This conclusion is confirmed by the study of the hydrolytic degradation of fully sulfonated polyimide.

1. Introduction

Proton exchange membrane fuel cells (PEMFC) considered as the most promising power source for automotive and portable applications [1] are mainly based on the Nafion® type membranes (a perfluorosulfonated ionomer produced by DuPont). However, these membranes suffer from a prohibitive cost and a limited resistance to operation under cycling conditions. Moreover, their main properties such as the ionic conductivity or the mechanical resistance highly depend on the water content which involves a complex water management and a restricted range of operating temperatures. Alternative low cost membranes with improved properties are thus needed. In order to increase the operating temperature, different series of new membranes based on the aromatic thermostable polymers have been developed since fifteen years [2–5]. Initially prepared by post-sulfonation of commercial polymers like polysulfones [6] or polyaryletherketones [7], direct polymerization using sulfonated aromatic monomers was then preferred in order to control both the architecture and the ion distribution along the polymer chains [4,8]. However, these polymers exhibit some major drawbacks: (i) the ionic conductivity is significantly lower compared to Nafion at the same ion content [5], (ii) the membranes are often very brittle on dry state and (iii) the chemical stability under fuel cell conditions is far from being satisfactory [9]. The ionic conductivity was improved increasing the ion content. However, the enhancement of the fuel cell performance was obtained at the expense of the mechanical properties on the swollen state due to an excessive swelling when immersed in water at elevated temperatures. New monomers were then synthesized with the objective to introduce some flexibility and to increase the hydrophobic character of the polymer chain enhancing the phase separation between the ionic domains and the hydrophobic backbone [4]. Surprisingly, only scarce data concerning both the microstructure and the stability of these new materials have been published. The membrane stability under fuel cell conditions rarely exceeds one thousand hours of operation even under stationary conditions [10]. Among new proposed polymers, sulfonated polyimides (sPIs) have been extensively studied during the last ten years [8,11–16]. Phthalic sPIs composed of 5-membered imide rings were first synthesized but they were shown to be highly sensitive to hydrolysis and their lifetime in fuel cell was about few tenths of hours even at moderate temperature [11]. The sPI membrane stability was significantly improved (up to 3000 h of operation at 60 °C) using naphthalenic monomers containing 6-membered imide rings [11,17].

A second improvement of the membrane stability was proposed synthesizing multiblock copolymers with long ionic sequences [8,13,18]. The former sPIs were prepared using commercial monomers [11] to minimize production costs but the hydrolytic stability was not sufficient with regard to the required specifications. Chemically modified monomers were then used to enhance

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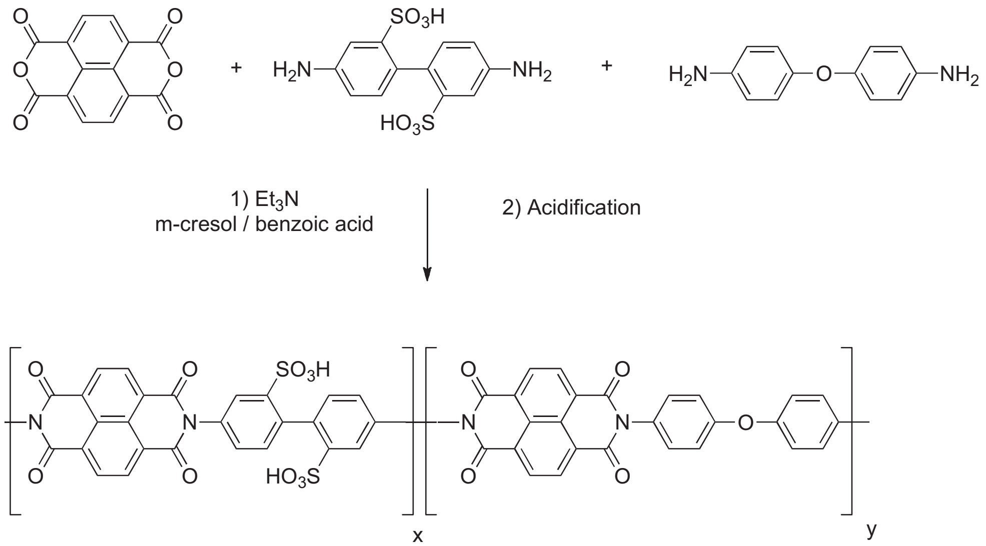

Fig. 1. Synthesis of sulfonated polyimide block copolymers.

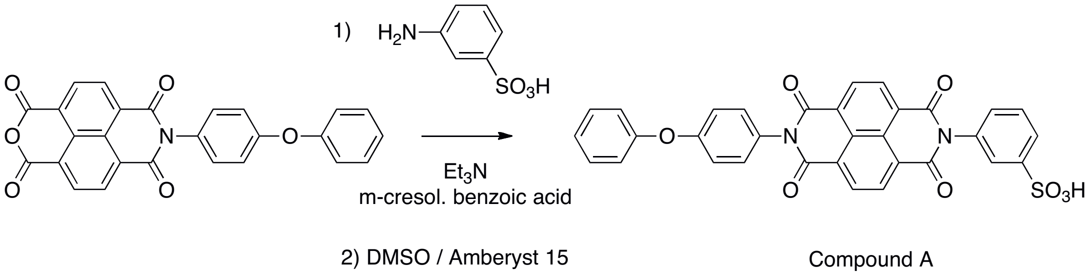

Fig. 2. Synthesis of model compound A.

the stability against hydrolytic and oxidative attacks [19,20]. The first attempt was the modification of the monomers in the neutral sequence increasing the polymer solubility in usual organic solvents but with no actual improvement of the ionic conductivity and stability [18]. A more successful attempt was the modification of the monomer bearing the sulfonated groups introducing spacers between the ionic groups and the imide rings [21]. This extensive research on new monomers has lead to a significant improvement of the polymer stability and a fuel cell was operated over 5000 h at 80 °C [22] which fulfills the required specifications in terms of durability and operating temperature. It is according to our knowledge the longest test ever performed with non perfluorinated membranes. Indeed, previous studies have clearly demonstrated that the main degradation process is the imide ring opening due to hydrolysis favored by the presence of the sulfonic acid group [23]. The membrane stability is usually estimated through the loss of the mechanical properties when immersed at elevated temperature (80 °C) either in pure water or in more or less concentrated hydrogen peroxide solutions (Fenton reactants). The lifetime evaluation is often restricted to the determination of the immersion time until membrane dissolution or membrane breaking when lightly bent [24]. This procedure strongly depends on the experimental conditions and does not reveal any information about the degradation mechanism [25,26]. Moreover, the loss of mechanical properties consecutive to polymer chain scissions highly depends on the initial molecular weight which can hardly be determined with such poorly soluble polymers. In more recent works, the hydrolytic stability was studied in both fuel cells and *ex situ* conditions [9,23]. Spectroscopic techniques were used to estimate the decrease of the number of both imide and sulfonic acid functions as degradation time increases. A plateau was observed for long time and moderate temperatures ($T = 80\,°C$) which suggests that the degradation

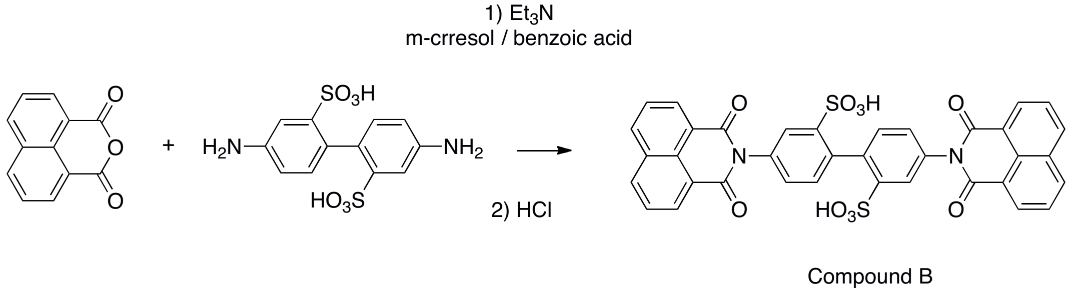

Fig. 3. Synthesis of model compound B.