



The importance of orientation in proton transport of a polymer film based on an oriented self-organized columnar liquid-crystalline polyether

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ABSTRACT

We prepared membranes based on a liquid-crystalline side-chain polyether obtained by chemical modification of commercial poly(epichlorohydrin) (PECH) with dendrons. This polymer exhibited a columnar structure, which could form an ion channel in the inner part. The columns were successfully oriented by taking advantage of surface interactions between the polymer and hydrophilic substrates, as confirmed by X-ray diffraction analysis (XRD), environmental scanning electron microscopy (ESEM) and optical microscopy between crossed polars (POM). Column orientation was found to be crucial for effective transport: the oriented membranes exhibited proton transport comparable to that of Nafion® N117 and no water uptake. An increase in sodium ion concentration in the feed phase suggested a proton/cation antiport. On the contrary, no proton transport was detected on unoriented membranes based on the same liquid-crystalline side-chain polyether or on unmodified PECH.

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1. Introduction

Nature was the first to take advantage of proton transport: most biochemical reactions are very sensitive to pH changes, and proton transport plays a crucial role in cell pH stabilization [1]. In biological systems, information can be transferred via alkaline metal ions in some cases. Nevertheless, all processes that imply energy conversion from one form to another involve protonation and deprotonation reactions mediated by proton conductivity: this is the case, for instance, in ATP formation during photosynthesis [2]. Proton conductivity also plays a key role in the production of electricity in hydrogen fuel cells [3,4]. As a consequence, proton transport and transfer phenomena have been the object of extensive research from rather different points of view by materials scientists, chemists, physicists and biologists [5,6]. In the late 1960s, the need for cation-conducting separator materials for industrial chlorine-alkali electrolysis encouraged the development of chemically resistant cation-exchange membranes, which also exhibited good proton transport properties in their hydrated protonic form. Over the past three decades, most research in the field of proton conductivity has been undertaken by the materials science community, mainly for the development of new proton-conducting materials to be used in electrochemical cells (e.g. fuel cells, batteries, sensors). Perfluorosulfonic acid (PFSA) membranes,

such as Nafion® (marketed by DuPont), have aroused great interest in recent years for their proton-conducting properties [7]. The achievement of optimum performance for these materials requires detailed knowledge of chemical microstructure and nanoscale morphology. In particular, it is essential to control properties such as proton conductivity, water management, relative affinity of methanol and water in direct methanol fuel cells (DMFCs), mechanical, thermal and oxidative stability, etc. This is a challenge for Nafion® materials, in which the possible chemical variations are quite limited; furthermore, PFSA membranes are expensive. Another serious drawback of membranes of this sort is their environmental inadaptability. New types of membranes based on different concepts are therefore being developed, but Nafion® remains the benchmark material against which most results are compared. In recent years, more than 200 patents and papers have been published on the preparation of new proton-conducting membranes [8–12]. An alternative approach is to design materials containing ion transport channels, in which the channels localize the permeation path and simultaneously protect the transport process against the environment, like an ion-transporting molecular cable [13,14]. Very recently, two types of one-dimensional ion-conductive polymer films containing ion nanochannels were prepared by means of photo-polymerization of the aligned columnar liquid crystals of a fan-shaped imidazolium salt with acrylate groups at the periphery [15]. In this columnar structure, the ionic portion self-assembles in the inner part of the column; anisotropic ionic conductivities were observed for the oriented films fixed by photo-polymerization. Very recently, an approach based on

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an inverse-ion-conducting cable was reported [16]. In this paper, an oriented columnar hexaphenylbenzene-based material, containing phosphonic acid groups at the periphery, was synthesized and proved to have good proton conductivity, independent of temperature. This columnar structure contains a proton-conducting periphery and an insulating core; in this case, proton conductivity is not a water-based diffusion process, as in common amorphous polymers used to date.

In this study, we prepared membranes capable of transporting protons based on a side-chain liquid-crystalline polyether, which we synthesized ourselves. As we reported in a previous paper [17], this polymer self-assembles into a columnar structure (Fig. 1), due to an exo-recognition of the side-chain dendrons. In the resulting structure, the polyether main chain forms a channel in the inner part of the columns, while the hydrophobic side-chain dendrons lie on the outer part. The presence of the polar ether linkages in the inner channel favors the interaction with proton and other cations, in the same way as crown ethers would do [18]. For this reason, the inner polyether chain could work as an ion channel. The orientation of the columns, which is crucial to getting efficient transport, was achieved by means of a very simple procedure: casting the polymeric chloroform solution in the presence of water. The prepared membranes exhibited a proton permeability comparable to that of Nafion® due to the presence of the oriented channels.

2. Experimental

2.1. Characterizations

X-ray diffraction (XRD) measurements were made using a Bruker-AXS D8-Discover diffractometer equipped with parallel incident

beam (Göbel Mirror), vertical θ - θ goniometer, XYZ motorized stage and general area diffraction detector system (GADDS). Samples were placed directly or mounted on MYLAR film. An X-ray beam was collimated with a 100 μm collimator for optimum resolution in transmission mode. The X-ray diffractometer was operated at 40 kV and 40 mA to generate $\text{CuK}\alpha$ radiation. The GADDS detector was 30 \times 30 cm^2 with a 1024 \times 1024 pixel CCD sensor. The detector was equipped with a small-angle X-ray scattering (SAXS) attachment that encloses the secondary beam in an He atmosphere to minimize air scattering at low angles. We collected one frame (2D XRD pattern) per sample covering 0.5–9.5° 2θ at a distance of 30 cm from the sample to the detector. The exposure time was 1800 s per frame and the frame was χ -integrated to generate the conventional 2θ versus intensity diffractogram.

The thickness of the membranes was measured using a micrometer with a sensitivity of 2 μm . The measurements were carried out at various points, and the membranes were found to have constant thickness.

The cross-sections and surface morphologies of the polymeric membranes were characterized by environmental scanning electron microscopy (ESEM) (Quanta 600, FEI). Cross-sections were prepared by fracturing the membranes in liquid nitrogen. When SEM experiments were performed in high vacuum, samples were coated with a gold layer before observation.

Optical microscopy between crossed polars was performed at room temperature with an Axiolab Zeiss optical microscope.

The surface morphology of the oriented membranes was detected by atomic force microscopy (AFM) (Pico+, 5500, Agilent Technologies). The surface area of the topographical images was 2 \times 2 μm .

Thermogravimetric analyses (TGA) on polymer A membranes were carried out between 25 and 600 °C on a Mettler Toledo TGA/

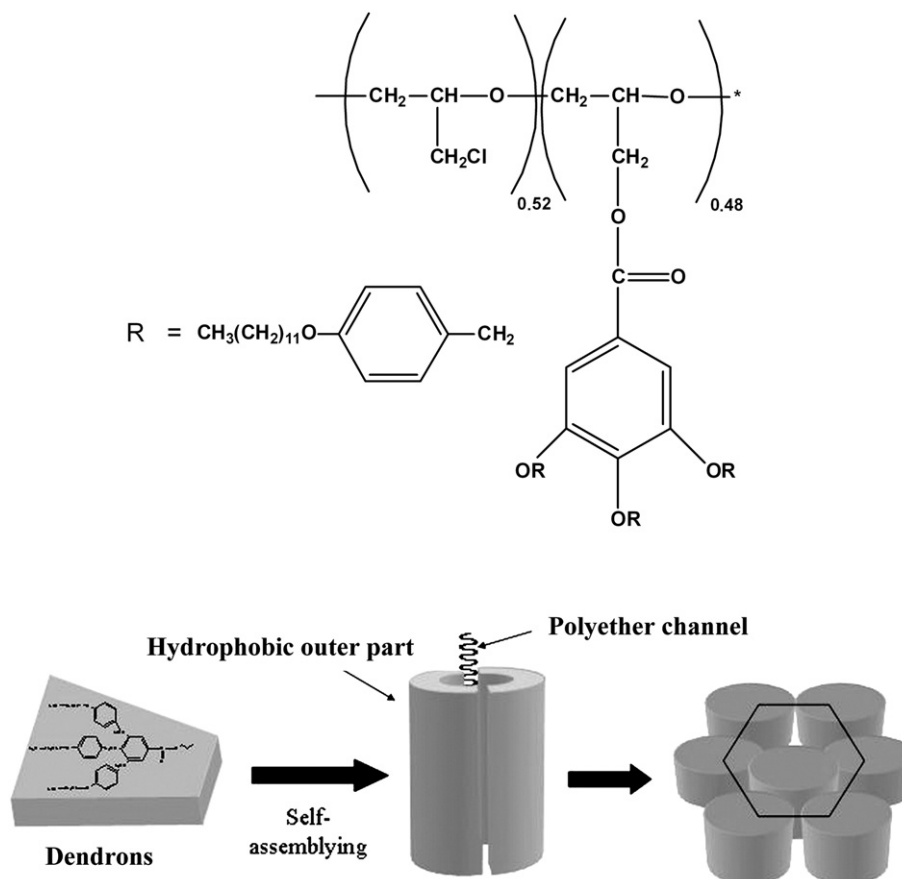


Fig. 1. Structure of polymer A and its self-assembly into columnar structure.

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