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Mimicking nature: Biomimetic ionic channels

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ABSTRACT

Membranes with a high but remarkably humidity-independent proton conductivity were prepared. Side-chain liquid crystalline polyethers (SCLCPs), based on poly(epichlorohydrin) (PECH) and poly(epichlorohydrin-co-ethylene oxide) (P(ECH-co-EO)), dendronized with potassium 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoate were specially designed for this purpose. When cast as membranes, these tailored polymers self-assembled into columns, driven by exo-recognition. They thus mimic the highly specific supramolecular organization observed in nature and present the first biomimetic material for proton transport out of which stable, oriented and self-sustained membranes could be prepared. As revealed by combined X-ray diffraction, Atomic Force Microscopy and Transmission Electron Microscopy, polymeric column formation was obtained in the cast membranes following a thermally induced homeotropical orientation. Two unique and highly desired properties were found in the resulting membranes. While conventional proton conducting membranes exploit an "acidic group-based" transport mechanism, the current columns pillaring across the membranes formed ionic paths, giving rise to a remarkable size-dependent antiport transport mechanism. It resulted in conductivity values in the range of 10^{-2}–10^{-3} S/cm, comparable to current state-of-the-art Nafion membranes, but, most importantly, with a complete independency from relative humidity. Reported membranes thus open excellent opportunities for further fine-tuning of their properties, wider exploitation of the exceptional transport mechanism, and final applications in fuel cells and related fields.

1. Introduction

The increasing world population with higher levels of development has entailed a constantly increasing demand on fossil fuel. Climate change and energy instability have turned attention towards alternative energy production. Artificial photosynthesis and membrane fuel cells seem appealing alternatives, offering clean, efficient and reliable power generation [1–3]. Those green technologies are able to convert solar or chemical energy into electric current, with extremely high efficiency not limited by the Carnot cycle. Key elements in such systems are the proton conducting membranes [4]. The most frequently used ionomeric membranes are based on perfluorinated polymers containing proton conducting groups, such as Nafion® (DuPont), which exhibit high proton conductivity, good mechanical strength and chemical stability [5]. However, they are difficult to recycle at the end-of-life; moreover, they require a certain degree of hydration since proton transport occurs by Grotthus mechanism and electroosmotic drag [6]. This entails several drawbacks, like loss of mechanical properties at high water contents, low selectivity and a dramatic decrease in performance at elevated temperature caused by water evaporation [7]. Therefore, the design of alternative materials that contain ion transport channels, in which the channels localize the permeation path and simultaneously protect the transport process against the environment, is still a topic of great interest.

Biological systems often show proton transport in a highly selective way, sometimes even in absence of water. Ion transport through cell membranes frequently uses proteic channels. Even though highly effective in cell membranes, they are inadequate for technological applications, due to difficult purification and complex chemical modification. Different approaches were investigated dealing with polyether-based structures, [8] or with channels formed by stacked crown ethers [9] and oligo(tetrahydrofuran)s [10]. Nonetheless, complications were observed, related to the main chain random-coil conformation of polyethers, the energy barrier of discontinuous transport between piled crown ethers and a demanding multistep oligo(tetrahydrofuran)

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synthesis. On the other hand, a way of forcing a polymer chain to adopt a helical conformation could be found by the aid of supramolecular chemistry. In this sense, for instance dendritic polymers have been proposed as building blocks for various bioinspired functions [11]. A sophisticated example found in nature is the Tobacco Mosaic Virus (TMV), which self-assembles upon mixing of its individual components, leading to a cylindrical structure in which the proteins organize in a helical array by the exo-recognition of the specific protein shape.

In 1991, a first synthetic example of arrangement by exo-recognition of a polymer was reported [12]. Tapered mini-dendritic side groups on the polymer backbone assembled into ionic channels, enhancing conductivity along these ion-passages. The ion-channel cores were formed by crown-ethers and oligo(ethylene oxide) which were organized in a hexagonal columnar bi-dimensional lattice [13,14]. The shape of the supramolecular architecture depended on the molecular taper angle and an increased ionic conductivity was disclosed in other liquid crystalline states [15].

Recently, two types of one-dimensional ion-conductive polymer films containing ion channels were reported, based on the photopolymerization of aligned columnar liquid-crystals [16]. In the columnar structure, the ionic section self-assembles into the inner part of the column.

In present work, polymers were designed to self-assemble into columns, which were subsequently aligned perpendicularly to a substrate by applying a thermal treatment. Side-chain liquid crystalline polyethers (SCLCPs) were dendronized for this purpose with potassium 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy] benzoate. Oriented and stable membranes were prepared out of these dendronized polyethers. Proton conductivity as a function of temperature and humidity of the membrane was measured and compared with Nafion®. After detailed polymer characterization, the ion transport mechanism was studied in aqueous solution.

2. Experimental section

2.1. Materials

Inorganic and organic compounds were provided by Sigma-Aldrich and Fisher Scientifics and used as received. For all experiments that required water or aqueous solutions, Mili-Q water was used.

2.2. Potassium 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoate

Potassium 3,4,5-tris[4-(n-dodecan-1-yloxy)bezyloxy]benzoate was synthesized according to procedure reported by Bhosale et al. [17].

2.3. Polymers

The polymers were obtained via the modification of poly(epichlorohydrin) (PECH) and poly(epichlorohydrin-co-ethylene oxide) (P(ECH-co-EO)) (50:50) by the dendron potassium 3,4,5-tris [4-(n-dodecan-1-yloxy)benzyloxy]benzoate, in order to obtain columnar mesophases. Anhydrous THF as a solvent, stoichiometric amounts of TBAB, the reaction duration of 8 days and 65 °C were selected in all cases. In order to obtain a higher degree of modification, the concentration of PECH in the solution was increased from 0.083 M to 0.1 M and also the amount of the tapered group was increased by 4, as compared to the previous report [18]. Moreover, the temperature was increased from 60 to 65 °C.

The microstructure and real composition of the copolymers were characterized by NMR spectroscopy. Fig. S1 reports the ^{1}H NMR spectrum of CP1 copolymer as an example. The copolymer composition was calculated by NMR spectroscopy because this methodology gave accurate results (as compared with elemental chlorine analysis) in previous studies [17,18]. Quantification was carried out from the ^{1}H NMR spectra by comparing the areas of the aromatic peaks between 7.4 and 6.8 ppm, the benzylic proton signal at 4.8 ppm, and the methylenic protons **c'** at 4.4 ppm with the broad signal between 4.0 and 3.5 ppm (Fig. S1). The results agreed with those of the comparative elemental analysis.

2.4. Membrane preparation

2.4.1. Supports

A teflon support, with a thickness 0.2 mm, was purchased from Servicio Estación S.A. (Barcelona). The support was washed with acetone and air-dried before being used.

The glass plates were immersed in a piranha solution (3:7 v/v of 30% H_2O_2 and H_2SO_4) for 5 min. Next, the substrate was washed, in the following exact order, with water, acetone and methanol, and dried. The hydrophilicity of the treated glass was confirmed by contact angle (CA) measurements (CA before treatment: 49.1°; after treatment: 38.1°).

2.4.2. Immersion precipitation

A 30% solution (w/w) of polymer in THF was prepared and spread with a casting machine (K paint applicator, RK Paintcoat Instruments Ltd., United Kingdom) onto a treated glass surface or a teflon sheet with a controlled thickness (gap size 300 μm). Later, the support with a wet film on top was immersed in a bath of Milli-Q water. After which, a polymer dense membrane with a thickness of approximately 200 μm was formed and peeled off from the support.

2.4.3. Vapor precipitation

A polymeric solution, similar to the immersion precipitation, was placed onto a treated glass support. Afterwards, the wet film was placed in a chamber with stable conditions of 20 °C and 95% humidity. The sample was kept inside until the full precipitation of polymer occurred.

2.4.4. Thermal treatment (baking process)

A teflon-supported membrane was prepared by immersion precipitation as described above. Then placed on a Linkam TP92 hot stage and heated above the polymer clearing temperature, after that being slowly cooled (0.5 °C/min) to room temperature. Subsequently, the membrane was kept at room temperature for approximately 1 h and then separated from the teflon sheet. An intact and uniform membrane was obtained as is shown in Fig. S2. This process was tested on a hydrophilic substrate that is treated glass, with the same results.

2.4.5. Shearing process

HP1 was mechanically oriented by shearing at temperatures slightly below its clearing temperature on a silicon single crystal wafer surface cut parallel to the plane (510). The direction of shearing was in the xy plane.

2.5. Characterization

2.5.1. Transmission electron microscopy (TEM)

The samples were cooled with liquid nitrogen to the cutting temperature of −60 °C to prevent deformation of the original microstructure. A cutting speed of 0.1 mm/s was used to obtain samples with thickness of 50 nm. The samples were placed on carbon coated-copper grids.

The ultramicrotomized samples were then stained dark by exposure to the ruthenium tetroxide vapors for 5 min to