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Advances in the design of self-supported ion-conducting membranes – New family of columnar liquid crystalline polyamines. Part 2: Ion transport characterisation and comparison to hybrid membranes

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ABSTRACT

An evaluation of ion transport in new biomimetic membranes, which are based on dendronised liquid crystalline polyamines is described. Two-step modification of starting polymer allowed preparation of self-supported membranes. Current-Voltage curves confirmed cation permselective nature of these new membranes and size-dependent preferential selectivity in following order: $H^+ > Na^+ > Ag^+ > K^+$. However, in case of chloride solutions, damage of the membranes was observed and was studied using SEM, TEM and ^1H NMR techniques. Selectivity of self-supported systems was compared with hybrid systems based on similar liquid crystalline polyamines and showed lower selectivity values in case of new membranes. Taking into account improved mechanical stability, extended liquid crystalline behaviour and higher clearing temperature values, these materials seem to address all disadvantages of hybrid systems, therefore are complementary in terms of practical application requiring selective ion transport.

1. Introduction

The interest in finding more sustainable methods of power generation has been increasing due to the awareness-raising about the climate change and the increasing demand for fossil fuels. Recently, artificial photosynthesis is one of the most studied systems, which is based on sunlight conversion into liquid hydrocarbons, which are further used to power the existing energy infrastructure [1]. Another green technology under development is fuel cells, which are able to transform chemical energy of a fuel into electrical energy [2].

Proton-conducting membranes are the element which contributes to the efficiency of artificial photosynthesis and fuel cells [3]; they have different functions like: charge carrier for protons, separation of the two compartments and electronic insulator since they do not let electrons pass through the membrane [4]. The efficiency of proton-exchange membranes depends mainly on their ability of rapid and selective transfer of proton ions; therefore, the study of these materials is essential for further development of green technologies [5,6].

Several materials have been developed in the last few decades in order to meet these requirements, while trying to reduce the cost of membranes [4]. Some of them, under development and very promising, are based on a biomimicking approach. The general idea is to develop artificial materials with exceptional properties similar to the ones observed in the natural systems. Biomimetics, studying the phenomena of ion transport in biological membranes, focuses on achieving high efficiency and selective systems for instance by incorporating biomolecules [7,8] or by implementing self-assembly technique as a tool [9,10].

In the literature many examples of promising materials that use self-assembly strategy can be found, like families of modified poly(epichlorohydrin) (PECH), polyglycidol (PG) and poly[2-(aziridin-1-yl)ethanol] (PAZE) with 3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoic acid (TAP) groups. The presence of dendritic groups allows their exo-recognition and forces the copolymer to adopt a

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columnar structure; the main chain forms a channel in the inner part of the columns, while the hydrophobic side-chain dendrons lie in the outer part [11]. These copolymers were synthesised for the first time with the objective to be used as non-ionomeric electrolyte membranes; this approach resulted successful in the case of self-supported PECH and PG-based membranes [11–13]. As for family of modified PAZE, all copolymers exhibit tendency to crystallise, which prevented preparation of self-supported membranes; hence, selected copolymers were used to prepare hybrid membranes containing anodised aluminium oxide (AAO) as support material [14]. It was reported that the inorganic support improves the mechanical properties; moreover, it induces formation of polymeric wires inside the pores. These wires, consisted of polymeric columns oriented in a homeotropical-like fashion, create conducting pathways. First in-depth studies of ion transport through biomimetic membranes were described for such hybrid membranes by means of current-voltage curves and impedance measurements. The results of those experiments put into evidence that, in the case of non-ionomeric membranes, more accurate characterisation can be obtained by linear sweep voltammetry [15].

To address the crystallisation issue and to enable the evaluation of ion transport properties of self-supported membranes based on dendronised polyamines, a two-step modification of PAZE was employed. The modification included grafting with dendritic TAP group and benzoyl units; the addition of benzoyl modifier aimed at disturbing the regularity of the structure and reducing number of free hydroxyl groups that can form hydrogen bonds. As reported in Part 1 of this paper [16], this approach successfully yielded a new family of liquid crystalline copolyamines and in most cases extended the liquid crystalline behaviour over a wider range of temperatures, as expected. Furthermore, those copolymers self-assembles into columnar structures. Ionic channels are formed by columns, consisting of the main chain as the central part, and the tapered side groups as the outer part. The presence of electron-donor atoms in main chain is expected to facilitate the cation transport through these channels; however, a homeotropical-like orientation of columns is essential for the transport and can be achieved by applying a thermal treatment at optimum conditions for each type of copolymer [16].

This work describes the evaluation of ion transport through biomimetic ionic channels in membranes prepared out of two selected liquid crystalline polyamines (Fig. 1), modified both with benzoyl groups and TAP in proportion 0.25:0.75 and 0.33:0.43 (PA3 and PA4 copolymers, respectively). These polymers are the closest analogues to the polymers used in hybrid system, in terms of modification degree with TAP (43% and 70% for PA4 and PA3, 40% and 72% for PAZE-40 and PAZE-72, respectively) and the total modification degree (76% and 72% for PA4 and PAZE-72, respectively). Current-voltage curves were used to study membrane selectivity as well as membrane resistance to the passing cations. In order to evaluate the performance of these new ion-conducting systems, a comparison with the hybrid systems based on PAZE modified with TAP only was done.

2. Experimental

2.1. Materials

1-(2-hydroxyethyl)aziridine (95%) and benzoyl chloride (99%) were supplied by Sigma Aldrich. 4-dimethylaminopyridine (DMAP, ≥98.0%) and *N,N'*-dicyclohexylcarbodiimide (DCC, ≥99.0%) were supplied by Fluka. Pyridine (99.99%) was supplied by Fisher Scientific and *N*-methyl-2-pyrrolidone (NMP, 99%) was supplied by Scharlab. All the solvents were purchased from Scharlab. Benzoyl chloride, DMAP and DCC were used as received. NMP and pyridine were purified prior to use. Anodised aluminum oxide (AAO) from Whatman™ with pore size 0.2 μm in a disc form and a diameter of 13 mm were used as received. All the acids (HCl and HNO_3) and all the salts (LiCl, NaCl, KCl, $NaNO_3$, KNO_3, $AgNO_3$) used in linear sweep voltammetry experiments were purchased from Sigma Aldrich (Purity ≥99.0%).

2.1.1. Synthesis of copolymers

The copolymers were obtained in two step reaction by grafting first with benzoyl chloride and then with the dendron 3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoic acid (TAP) according to the procedure described in Part 1 [16].

2.1.2. Membranes preparation

PA-based membranes were prepared according to the procedure described in Part 1 [16], while the hybrid membranes were prepared following procedure reported by Bogdanowicz et al. [15].

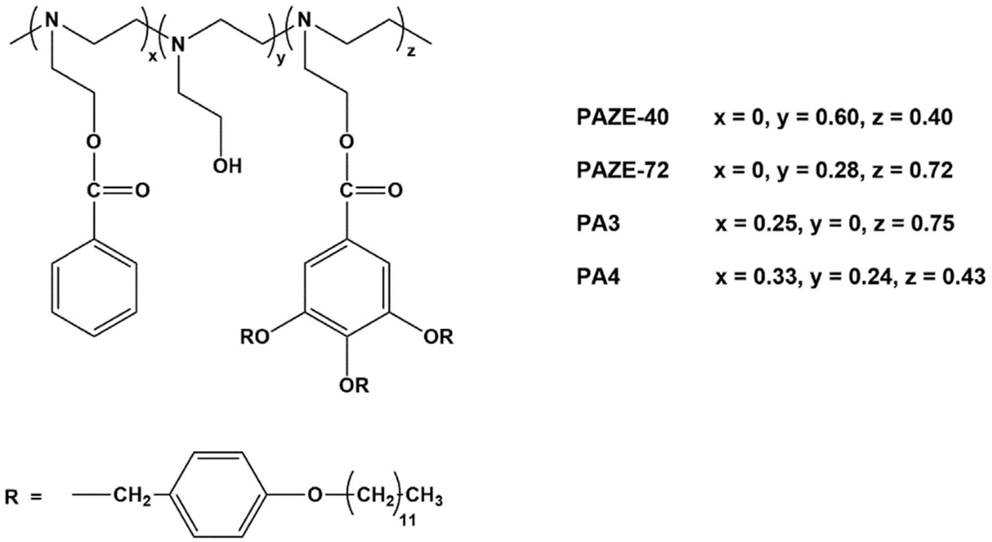

Fig. 1. General structure of the two polymeric families based on modified poly[2-(aziridin-1-yl)ethanol].