

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.

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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 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-ionic 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

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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-ionic 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, $\geq 98.0\%$) and *N,N'*-dicyclohexylcarbodiimide (DCC, $\geq 99.0\%$) 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 $\geq 99.0\%$).

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].

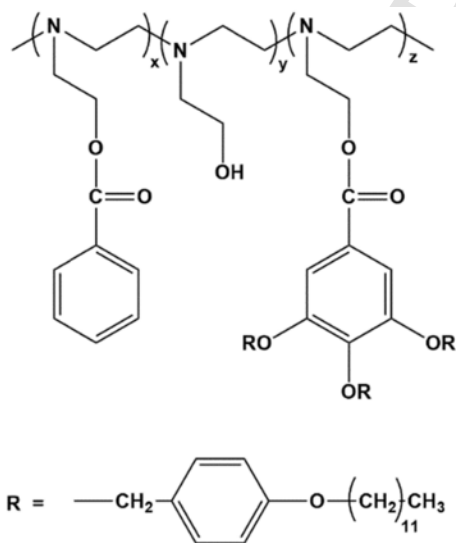
2.1.2. Membranes preparation

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]. In all cases membranes were prepared starting from polymers, which purity was confirmed by ^1H NMR.

2.2. Characterisation and measurements

2.2.1. Nuclear magnetic resonance (NMR) spectroscopy

Copolymers were characterised by ^1H NMR, which was performed using deuterated chloroform (CDCl_3) as deuterated solvent with a Varian Gemini 400 MHz spectrometer at room temperature with pulse delay time of 5 s. The central peak of the solvent was taken as the reference, and the chemical shifts were given in parts per



PAZE-40	$x = 0, y = 0.60, z = 0.40$
PAZE-72	$x = 0, y = 0.28, z = 0.72$
PA3	$x = 0.25, y = 0, z = 0.75$
PA4	$x = 0.33, y = 0.24, z = 0.43$

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

million from TMS (Tetramethylsilane) with the appropriate shift conversions.

2.2.2. X-ray diffraction (XRD)

For low 2θ range, XRD measurements were performed with a Bruker-AXS D8-Discover diffractometer equipped with parallel incident beam (Göbel mirror), vertical θ - θ goniometer, XYZ motorized stage and with a GADDS (General Area Detector Diffraction System). Samples were placed directly on to a low background Si(510) sample holder for reflection analysis. An X-ray collimator system close-to-the-sample allows to analyse areas of $500\ \mu\text{m}$. The X-ray diffractometer was operated at 40 kV and 40 mA to generate $\text{Cu}_{\text{K}\alpha}$ radiation. The GADDS detector was a HI-STAR (multiwire proportional counter of $30 \times 30\ \text{cm}$ with a 1024×1024 pixel) placed at 30 cm from the sample. The X-ray beam hit the sample at 0.5° of incidence. The collected frame (2D XRD pattern) covers a 2θ range from 0.9 up to 9.2° . The diffracted X-ray beam travels through a He beam path (SAXS attachment) to reduce the air scattering at low angles. The direct X-ray beam is stopped by a beam stop placed directly on the detector face. The exposition time was of 300 s per frame. The resulting frames were both gamma integrated to obtain a 2θ diffractogram and 2θ integrated to obtain a gamma diffractogram.

2.2.3. Linear sweep voltammetry (LSV)

Linear sweep voltammetry was performed using Autolab PGstat204 in potentiostatic mode with current ranging (automatic) from 100 mA to 100 μA , potential range from 0 V to 5 V, step 0.01 V and scan rate $0.01\ \text{V s}^{-1}$. The experimental set-up is presented in Fig. 2. The distance between the reference electrodes (Ag/AgCl) and membrane was 1 cm. The solution volume in each compartment was 200 mL. The measurements were performed at room temperature. Samples for these measurements were placed in Teflon frame with a window giving a total membrane area equal to $0.5\ \text{cm}^2$. The membranes were placed between two sheets of Teflon and pressed.

Hydrochloric acid and nitric acid both in concentrations of 0.1 M and 0.025 M were used to study the proton transport. Besides, a series of measurements with salts were performed in two concentra-

tions, 0.025 M and 0.1 M, in order to study the selectivity. Specifically, the following series of solutions were used: HCl, LiCl, NaCl and KCl; HNO_3 , NaNO_3 , AgNO_3 and KNO_3 . Silver nitrate was used only in series at 0.025 M electrolyte concentration. One series of measurements was applied to one membrane in the increasing order of cationic radius. An experiment for each specific cation includes five consecutive current-voltage measurements at different times: 0, 10, 20, 45 and 60 min. From one set of measurements, the last obtained curve (60 min) was used to calculate the ohmic resistance and limiting current densities for each cation.

The values of voltage for samples were calculated by subtracting the solution resistance without the membrane. Compensation was calculated according to equation:

$$U_{\text{comp}} = U_{\text{m}} - R_{\text{sol}} \cdot I_{\text{m}} \quad (1)$$

where U is the voltage, R is the resistance, I the current and the subscripts comp, m and sol refer to compensated value, measured value and solution alone, respectively.

2.2.4. Chronoamperometry

Chronoamperometry experiment was carried out using Autolab PGstat204 with constant potential of 4 V during 6 h in 0.1 M hydrochloric acid solution with two electrodes in cell similar to one used for linear sweep voltammetry.

2.2.5. Scanning electron microscopy (SEM)

SEM analysis was performed using a FEI Quanta 200 FEG (Eindhoven, The Netherlands) in high vacuum mode, using a secondary electron detector and an accelerating voltage ranging between 15 and 20 kV. The samples were cooled down with liquid nitrogen, and a brittle fracture was obtained. Before the analysis, samples were coated with a gold-palladium layer (about 15 nm thick) by means of an Emitech K575X sputter coater.

2.2.6. Transmission electron microscopy (TEM)

Samples of polymer membranes were embedded in a waterborne acrylic latex paint. Ultrathin membrane cross-section specimens (100 nm thick) were obtained using a Leica UC7 ultramicrotome system operating at 60°C . The sections were placed on copper grids and stained by immersion in an aqueous 1% phosphotungstic acid solution for 10 s, then observed in bright field mode on a FEI Tecnai G12 Spirit Twin TEM operating at 120 kV acceleration voltage.

2.2.7. Solution uptake test

Weighted membranes were immersed in Milli-Q water or methanol solutions (1 M, 2 M, 6 M and 12 M) at room temperature every 15 min during first 2 h and finally for 24 h to ensure the membranes were saturated. The liquid on the surface of the wet membranes was quickly removed with filter paper, and then the mass was measured. The mass of the dry membranes was obtained after the wet membranes were dried in air for 4 days at room temperature, until constant mass was reached. The water or methanol uptake can be calculated as follows:

$$\text{Water uptake (\%)} = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \cdot 100 \quad (2)$$

where W_{wet} and W_{dry} are the mass of wet and dry membrane samples, respectively.

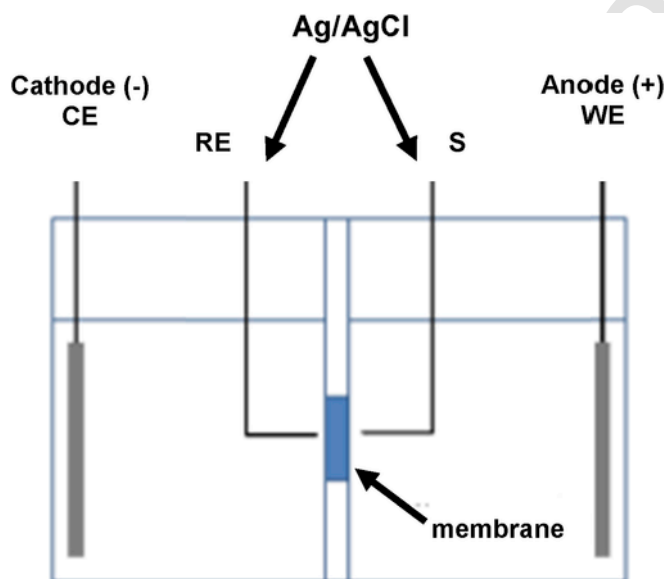


Fig. 2. The experimental set-up for lineal sweep voltammetry measurements. WE is working electrode, CE is counter electrode, RE is reference electrode and S is sensitive electrode.

3. Results and discussion

Part 1 of this article [16] presents an extensive description of synthesis and characterisation of a new family of liquid crystalline polyamines modified with both benzoyl and dendritic group 3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoic acid (TAP) in different molar ratios. Thanks to the dendritic moiety, copolymers tend to self-assemble forming columns, as confirmed by XRD analysis. Two of them, PA3 and PA4, were selected and used to successfully prepare self-supported membranes, which is a promising advantage over hybrid systems based on dendronised PAZE copolymer. A comparison between these systems will be done, presenting a number of strong and weak points of both of them in terms of future application as proton-conducting membranes.

3.1. Hybrid membranes vs. self-supported membranes: structural and morphological comparison

Bogdanowicz et al. described the development of liquid crystalline polymeric wires in anodised aluminium oxide (AAO) support by columnar mesophase growth of homeotropically-like oriented columns, inside the pores. As polymeric materials, two dendronised PAZEs with 40% (PAZE-40) and 72% (PAZE-72) modification degree were used. From the structural and the morphological point of view, both PAZE copolymers show almost identical features and behaviour in all studied aspects. The presence of the inorganic support does not affect the thermal properties of the polymer; furthermore, it strengthened the organisation of the columns in the satisfactory orientation and contributes to preserving the dimensional firmness of the membrane [14].

As described in Part 1 [16], the preparation of self-sustaining polyamine membranes was performed using two selected copolymers i.e. PA3 and PA4. The characteristics of the copolymers discussed in this paper are shown in Table 1.

Additional modification with benzoyl unit in PAn copolymers has a significant impact on the stability of the LC phase, displacing the clearing temperature towards higher values. This fact is an important point in terms of future application. As a matter of fact, it is desirable to use the membranes based on both copolymer families as polymer electrolyte membrane (PEM), for instance in direct methanol fuel cell (DMFC) devices, where the operating temperature usually may range between 23 °C and 80 °C [17]. If we compare, for instance, copolymers with very similar total modification degree, such as PAZE-72 and PA4 with clearing temperature at 44 °C and between 81 and 86 °C, respectively, it is evident that the replacement of approximately 30% of TAP by benzoyl units leads to an increase of mesophase stability. Therefore, PA4 could exhibit columnar organisation up to higher temperatures than PAZE-72, maintaining the alignment of columns, which is critical for ion-conductive properties; hence, it meets better the expectations set for PEM materials.

The study of columns orientation of these materials is very important, since it affects the correct formation of ion-conducting pathways. As indicators of columns orientation, we considered the posi-

tion of the maximum of the signal in the azimuthal scan on the reflection corresponding to d_{100} from XRD analysis, and its width at the half of the height (WHH). The first one represents the average angle of columns alignment with respect to membrane surface, while WHH gives information about the distribution of column orientation; it is desirable that the maximum is centred at 90° with distribution as sharp as possible. In general, membranes made of both polyamine families showed approximately perpendicular orientation of the columns to the membrane surface, although better results were observed in the case of non-supported PAn materials. As an example, in the hybrid system based on PAZE-72, the maximum intensity of d_{100} was centred at around 70° with WHH of 76° [14], while for PA4-based membrane the reflection d_{100} had a maximum centred at around 91° and WHH equal to 15° [16], as it can be observed in Fig. 3. This put into evidence that self-supported membranes achieve much better results in terms of homeotropical alignment and narrow orientation distribution. The arrangement of the columns in required fashion could be explained by increased mobility of polymeric columns in non-supported membrane during the thermal treatment, necessary for orientation.

Water uptake tests revealed low absorption, equal to $2.5 \pm 0.5\%$, reaching the saturation point after 20 min of immersion time, as it is presented in Fig. 4a. In the case of methanol uptake in 1 M solution, the test showed the same value as water. In concentrations above 1 M, low resistance of the copolymer to methanol was observed as negative values were noted during the experiment and mass decline of dry membrane after the experiment (Fig. 4b). The reason for such behaviour can be explained as a result of increased copolymer solubility with the increment of methanol concentration, as it could be reasonably expected. In case of supported membranes, the uptake values were found around $10 \pm 3\%$ both for water and methanol solutions, without noticing any mass loss after the experiments; in this case low solubility in methanol can be attributed to smaller copolymer-methanol contact area and inability to swell inside the rigid structure of AAO support.

3.2. Ionic transport

To characterise the ion transport, current-voltage measurements were performed using the proper set-up and applying the parameters described in the experimental section. A typical current-voltage curve can be generally divided into three regions. The first one, called ohmic region, gives information about resistance density of ion passing through the membrane. The following region can be presented as a *pseudo-plateau* characterised by a very slow variation of the current. From this region the limiting current density can be evaluated, that gives information about permselectivity, thickness of the diffusion boundary layer, diffusion coefficient and cation transport number in the membrane. Finally, a third region with increasing slope is called overlimiting current, which presence could be explained by electroconvection theory [12,13,18,19].

As it was presented by Bogdanowicz et al., linear sweep voltammetry is the most suitable technique to describe transport through non-ionomeric membranes. The experimental procedure includes set of measurements for different solutions using one membrane. The purpose of such design is to monitor ion transport in conditions where, in consecutive experiments, a membrane is exposed to more than one species passing through. This procedure could also give information about the stability of membrane after suffering several experiments. For sake of comparison, hybrid membranes were tested in the same conditions.

For membranes based on PA3 and PA4, it was impossible to perform a complete set of experiments using hydrochloric acid and its

Table 1

Total modification degree, TAP content and clearing temperatures in tested systems.

Copolymer	Total modification degree (%)	TAP modification degree (%)	T _c (°C)
PA3	100	75	100–104
PA4	76	43	81–86
PAZE-40	40	40	43
PAZE-72	72	72	44

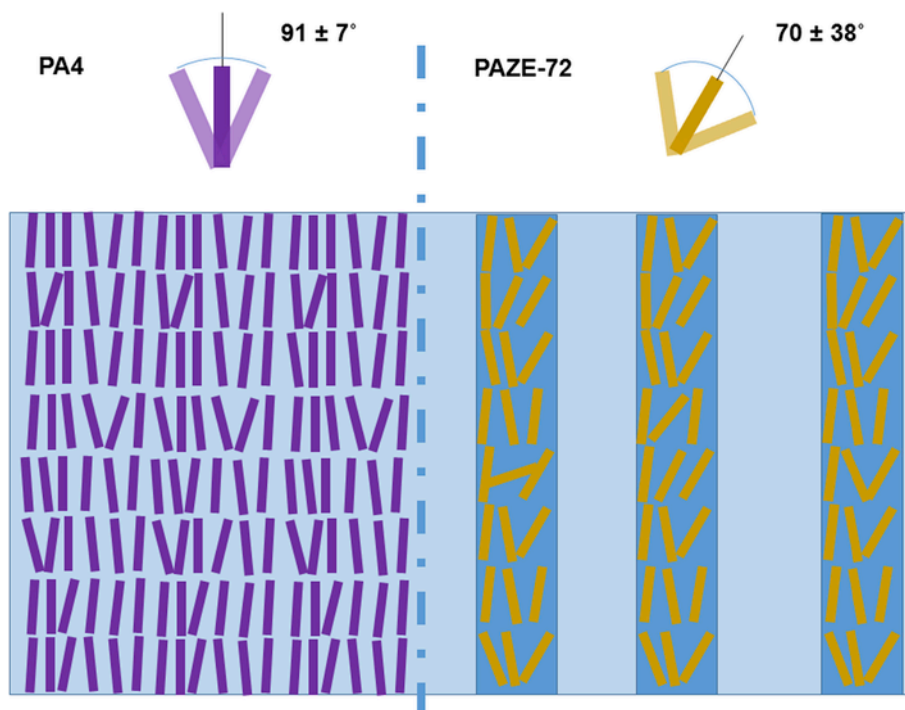


Fig. 3. Visualisation of polymeric column orientation inside a PA4 membrane (left) and PAZE-72 inside AAO support (right).

salts without damaging the membrane. At higher concentration (0.1 M), the current-voltage curves obtained for acid solution had linear trend, with the slope rising sharply, indicating consequently low resistance values, similar to the ones found in blank experiment performed for solution alone. For lower concentration (0.025 M) ion transport could be measured just for the hydrochloric acid solution: the resistance density values were in the range of 10^{-6} ($\Omega \text{ cm}^2$) and the limiting current density was $4.9 \cdot 10^{-7} \text{ A cm}^{-2}$. When the experiment was subsequently performed with 0.025 M lithium chloride solution on the same membrane, rapidly increasing slope for consecutive measurements, that is, decreasing resistance values, was found.

This is the opposite of expected behaviour, which might suggest physical damage of the membrane during the experiments with hydrochloric acid and chloride salts. It must be taken into account that throughout linear sweep voltammetry experiments electrolysis occurs; in the case of chloride anion, gaseous chlorine is formed in the anode side as a consequence of oxidation reactions. Chlorine is a strong oxidizing agent [20,21], which could interact with polymer structure at membrane surface, thus causing its degradation. To confirm this hypothesis further analyses were performed and are described in the following section. As for hybrid systems, no damages of the membrane were detected for experiments performed for different chloride solutions, as it was previously reported [15].

Therefore, in order to characterise the transport through PAn-based membranes, nitric acid and its salts were chosen to perform the experiments in two concentrations, 0.025 M and 0.1 M, since SEM analysis did not reveal any visible damage on the membrane surface and its cross section after LSV experiment. No limiting current region was observed in any of the cases; only the difference between ohmic and overlimiting regions was distinguishable just in the first scan, as it can be seen in Fig. 5 for PA4. The resistance for proton was generally lower than for the other cations, which implies that proton passes easier through the channels. For all experiments with nitrates, the limiting current was not observed, probably due to

inadequate setup configuration and experimental conditions (Tables 2 and 3). However, the cation permselective behaviour was confirmed in the experiments with hydrochloric acid at 0.025 M concentration, where limiting current was observed (Fig. 6).

In order to reproduce the exact conditions of ion transport and evaluate the performance similarly to PAn-based membranes, experiments for hybrid systems were performed in the same conditions of concentration and with the same type of electrolyte. Only current-voltage curves for PAZE-40 at concentrations 0.1 M did not evidence the limiting current region and displayed linear trend. In all other experiments on hybrid systems, it was possible to observe the limiting current region and the values of limiting current densities that are reported in Tables 2 and 3 along with specific ohmic resistance densities. As it was previously reported, hybrid membranes showed low resistance density values for proton in comparison to other tested monovalent cations when experiments were performed separately for each cation. Consecutive experiments performed on a single membrane revealed similar tendency, i.e. proton transport was favoured over other monovalent cations [15].

A direct comparison of resistances between hybrid system and PAn-based membranes cannot be done directly, due to the difference in the membrane thickness (Tables 2 and 3). However, some tendencies were observed, for instance: the cation resistance values increase with membrane thickness, as expected, and in the experiments performed with proton, resistance values decreased with progressive number of performed experiments. This latter evidence could be associated to the reorganisation of the ionic pathways that adapt their conformation after proton passage. An improvement of ion transport in subsequent experiments was also detected in permeability tests for other biomimetic membranes based on modified linear polyglycidol [22]. On the other hand, when subsequent experiments were performed with different cations, in order of increasing size, increasing resistance values were found (Tables 2 and 3).

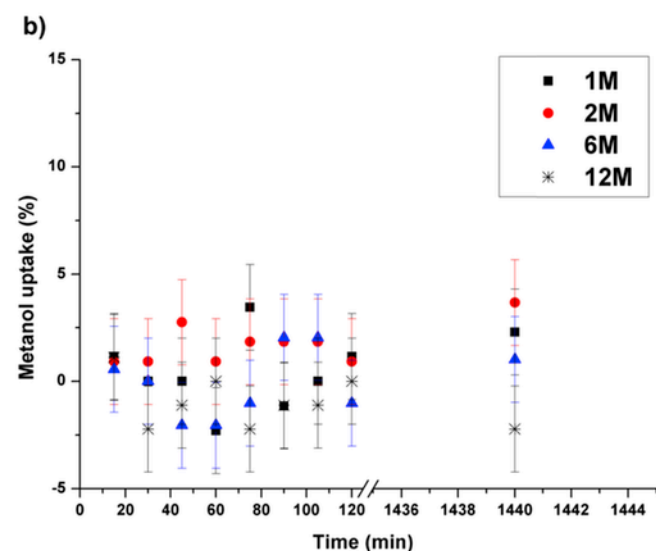
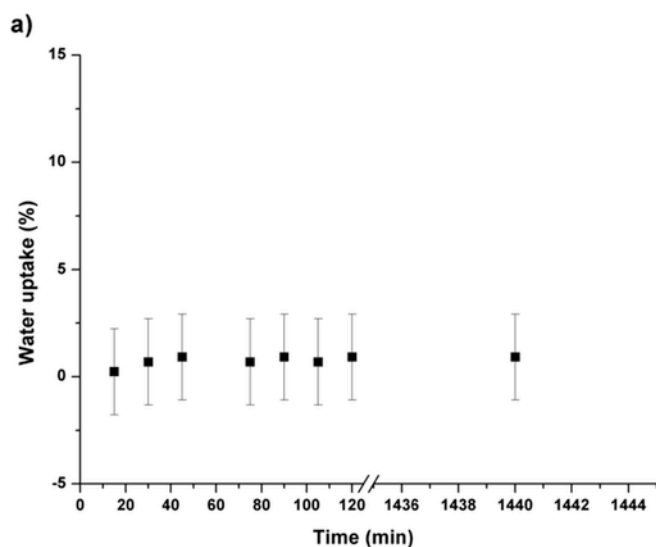


Fig. 4. Water (a) and methanol solutions (b) absorption for oriented PA4 membrane.

As an example, Fig. 7 shows the case of PAZE-40. The significant curve variation suggests a change in type of transported cations through the membrane. Further comparison of the last curve of one series, i.e. Na^+ , with the first curve of the new one, i.e. Ag^+ , showed relatively similar values of the resistance in spite of the difference in cationic radius (1.02 Å and 1.26 Å for sodium and silver, respec-

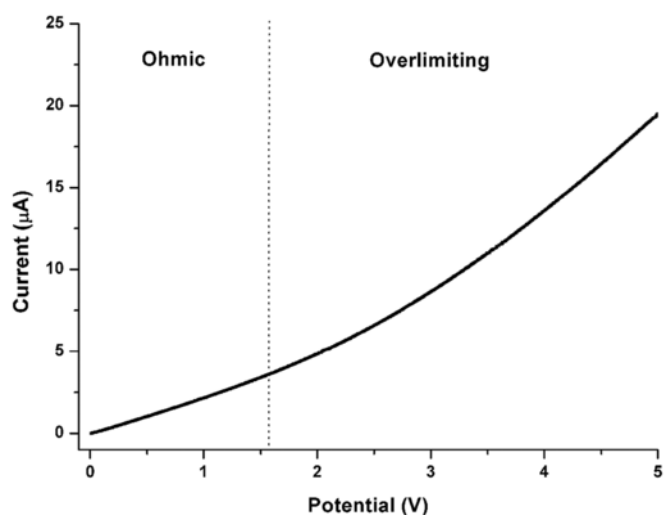


Fig. 5. PA4 current-voltage curve from the first scan in 0.1 M nitric acid.

tively). This suggests that the former test refers to a “mixed cations” transport: that is, at the beginning, current values are due to the passage of smaller cations, remaining in the membrane after the previous experiments; as experiments proceed further, these smaller cations are replaced in the structure by bigger ones, currently under analysis. Under this hypothesis, the first recorded curves therefore represent a mixed transport of cations remaining inside the membrane and of new ones provided by the new solution. Moreover, the concentration gradient phenomenon that is created between the cathode and anode compartments has its impact on ion transport. Cations in the anode side are forced to pass to cathode side by the applied potential; on the other hand, cations are accumulated in the cathode side in each measurement with the exception of proton that is reduced to hydrogen. As a result, during each subsequent measurement, cations need to overcome an increasing cation concentration gradient caused by previous experiments.

To express the membrane preferential selectivity, a ratio of conductance ($G_i = 1/R_i$) of alkali ion value over proton value ($G_{\text{ion}}/G_{\text{H}^+}$) was calculated and it is reported in Table 4. A direct comparison of conductance values between these two systems cannot be done due to the difference in the diffusion boundary layers and membrane thickness. However, it was possible to observe that membrane thickness generally improves selectivity. Besides, the tendency of preferential ion transport for most membranes, in decreasing order, was: proton, sodium, silver and potassium. PAn-based membranes revealed very similar performances despite different modification degrees and distinct ratios of benzoyl to TAP moieties. When compared with hybrid systems, non-supported membranes displayed lower selectivity. This

Table 2

The resistance density and limiting current density values for the experiments carried out with HNO_3 and NaNO_3 water solutions.

Copolymer	Thickness (μm)	HNO_3 (0.012 Å) ^a				NaNO_3 (1.02 Å) ^a			
		0.025 M		0.1 M		0.025 M		0.1 M	
		$R_{\text{ohm}} \times 10^{-2}$ ($\Omega \text{ cm}^2$)	$I_{\text{lim}} \times 10^3$ (A cm^{-2})	$R_{\text{ohm}} \times 10^{-2}$ ($\Omega \text{ cm}^2$)	$I_{\text{lim}} \times 10^3$ (A cm^{-2})	$R_{\text{ohm}} \times 10^{-2}$ ($\Omega \text{ cm}^2$)	$I_{\text{lim}} \times 10^3$ (A cm^{-2})	$R_{\text{ohm}} \times 10^{-2}$ ($\Omega \text{ cm}^2$)	$I_{\text{lim}} \times 10^3$ (A cm^{-2})
PA3	approx. 130	1215.9	—	181.2	—	1824.9	—	258.0	—
PA4	240–330	1697.4	—	851.9	—	2848.2	—	1201.9	—
PAZE-40	approx. 70	4.5	0.6	417.3	—	12.4	0.8	1365.7	—
PAZE-72	approx. 70	4.2	1.5	0.8	11.1	8.2	1.4	3.3	1.6

^a Cationic radius.

Table 3

The resistance density and limiting current density values for the experiments carried out with AgNO₃ and KNO₃ water solutions.

Copolymer	Thickness (μm)	AgNO ₃ (1.26 Å) ^a				KNO ₃ (1.38 Å) ^a			
		0.025 M		0.1 M		0.025 M		0.1 M	
		$R_{\text{ohm}} \times 10^{-2}$ ($\Omega \text{ cm}^2$)	$I_{\text{lim}} \times 10^3$ (A cm^{-2})	$R_{\text{ohm}} \times 10^{-2}$ ($\Omega \text{ cm}^2$)	$I_{\text{lim}} \times 10^3$ (A cm^{-2})	$R_{\text{ohm}} \times 10^{-2}$ ($\Omega \text{ cm}^2$)	$I_{\text{lim}} \times 10^3$ (A cm^{-2})	$R_{\text{ohm}} \times 10^{-2}$ ($\Omega \text{ cm}^2$)	$I_{\text{lim}} \times 10^3$ (A cm^{-2})
PA3	approx. 130	3005.0	—	—	—	4045.9	—	364.5	—
PA4	240–330	5033.1	—	—	—	5466.1	—	2112.9	—
PAZE-40	approx. 70	13.6	0.5	—	—	21.9	0.8	1607.2	—
PAZE-72	approx. 70	5.8	2.6	—	—	20.8	0.1	9.2	3.9

^a Cationic radius.

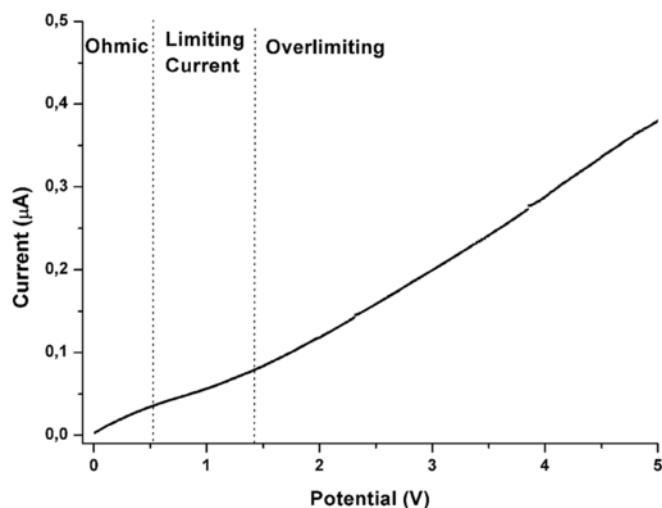


Fig. 6. Current-voltage curve obtained in 0.025 M hydrochloric acid for PA4.

could be explained by increased polymer mobility compared to supported membranes. In most cases size dependent transport was registered: the smaller the cation radius, the easier it passes through the membrane. Regarding the result for PAZE-72, surprisingly the higher achieved preferential selectivity was observed for silver ion. This phenomenon can be explained in terms of the different channel size and well-known affinity of silver to nitrogen atoms [23].

3.3. Degradation of PAN copolymers

In order to evaluate the extent of membrane degradation after LSV experiments in the presence of chloride anions, an electron scanning microscopy analysis was performed on the samples after applying linear sweep voltammetry (Fig. 8). The micrographs of PA4 membrane surface revealed a scaly-like texture (Fig. 8a), whereas the analysis of cross-section showed the presence of pores (Fig. 8b). These images put into evidence a physical damage caused by the oxidising conditions created during the ion transport experiment.

TEM analysis was performed on stained cross-section of PA4 membrane before and after LSV experiment in chloride solutions (Fig. 9). The analysis for sample before the LSV experiment demonstrated a striped-like cross-section surface. Measurement of the width of a single stripe gave approx. 60 nm and could correspond to columns agglomerates forming ionic pathways. The TEM image after LSV experiments disclosed morphological changes, presenting numerous dark lines and spots. This fact put into evidence that the oxi-

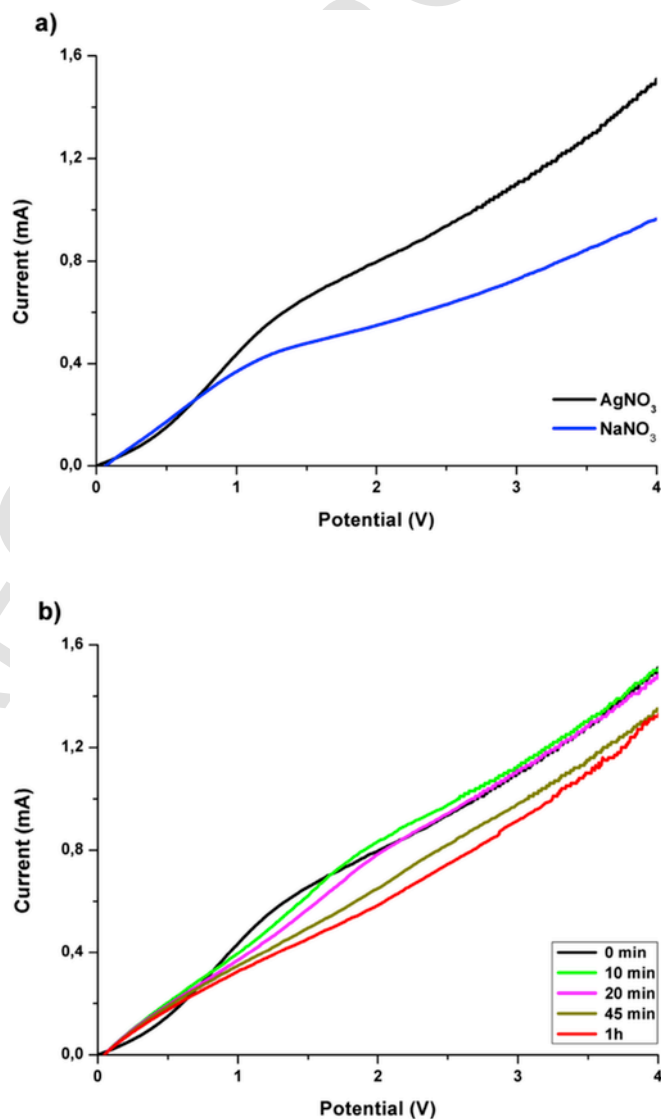


Fig. 7. Current-voltage curves for PAZE-40 at 0.025 M concentration: (a) last curve for Na⁺ and first of Ag⁺; (b) All five consecutive experiments for Ag⁺ at different time.

dising conditions during LSV experiment could cause chemical degradation of polymer.

In order to demonstrate chemical degradation of PAN-based membranes, NMR analysis was performed. Prior to nuclear resonance analysis, in order to increase the extent of degradation, the membrane

Table 4
Preferential selectivity of tested membranes for nitrate solutions.

Copolymer	G_{Na^+/H^+}		G_{Ag^+/H^+}		G_{K^+/H^+}	
	0.025 M	0.1 M	0.025 M	0.1 M	0.025 M	0.1 M
PA3	67%	70%	40%	–	30%	50%
PA4	60%	71%	34%	–	31%	40%
PAZE-40	36%	31%	33%	–	21%	26%
PAZE-72	51%	24%	73%	–	20%	8%

was exposed to long term oxidising conditions similar to those for LSV, according to the procedure described for chronoamperometry in the Experimental section. ^1H NMR quantitative spectra of the copolymer from the damaged membrane unveiled structural changes in the amount of modified lateral groups (Fig. 10). Generally, the spectra had qualitatively identical aspect to the starting polymeric material, showing all characteristic signals. From the integrated areas corresponding to benzoyl and TAP protons in the ranges: 0.8–2.0 ppm (aliphatic chains of TAP, 75 protons), 6.5–7.7 ppm (aromatic 14 protons of TAP and 3 protons of benzoyl) and 7.8–8.2 ppm (aromatic 2

protons of benzoyl) it was detected that the proportion of groups had changed from 0.33: 0.43 to 0.20: 0.43, for benzoyl and TAP respectively. The ratio of the integrals of TAP and main chain of copolymer maintained its starting proportion within the experimental error. These results evidenced that the most vulnerable part of the copolymer structure is the benzoyl group that can be detached in oxidising environment.

4. Conclusions

Self-supported biomimetic membranes based on liquid crystalline poly[2-(aziridin-1-yl)ethanol] modified both with benzoyl and TAP units in different proportion were prepared. Both copolymers self-assembled into homeotropically oriented columns, forming ionic channels. Evaluation of ion transport through the membrane confirmed cation permselective nature for all biomimetic membranes. Linear sweep voltammetry experiments in chloride solution revealed damage probably caused by the presence of gaseous chlorine, as confirmed by SEM, TEM and ^1H NMR analyses. A comparison of PAn-based membranes with their analogue hybrid systems put into

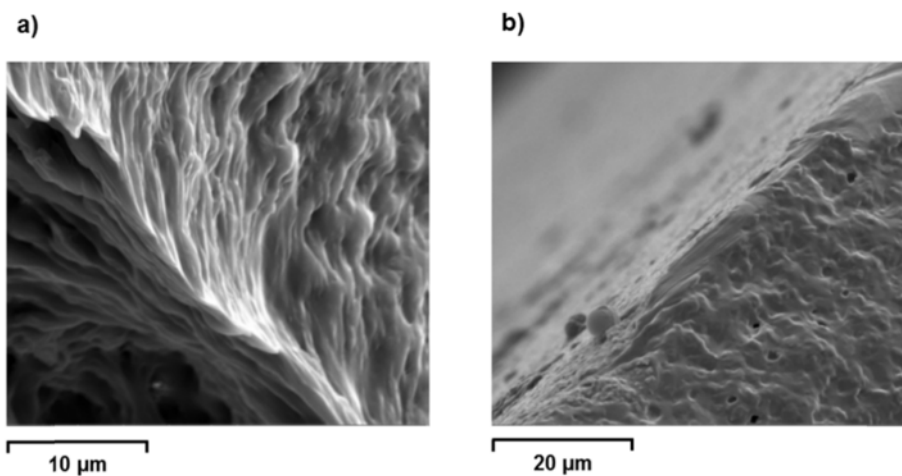


Fig. 8. SEM micrographs of surface (a) and cross-section (b) of membrane made of PA4.

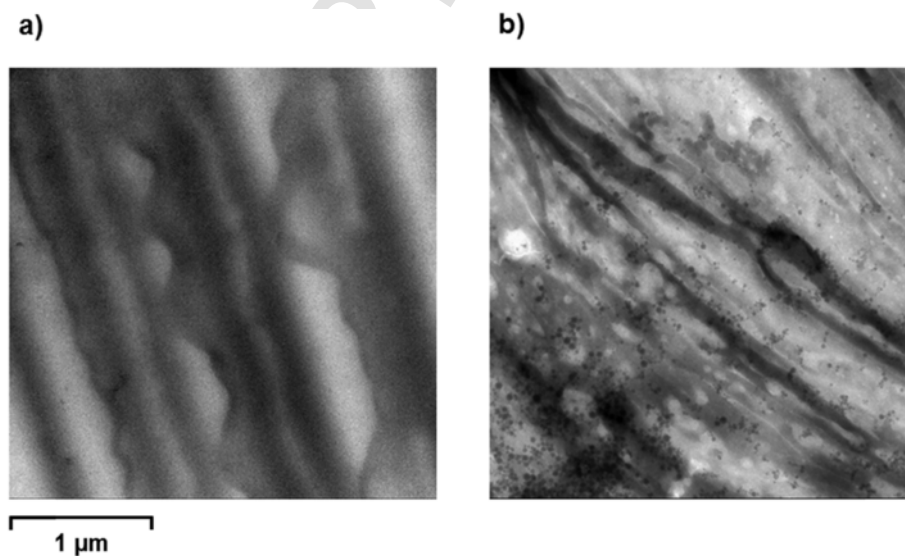


Fig. 9. TEM images of PA4 membrane cross-section before (a) and after (b) LSV experiment.

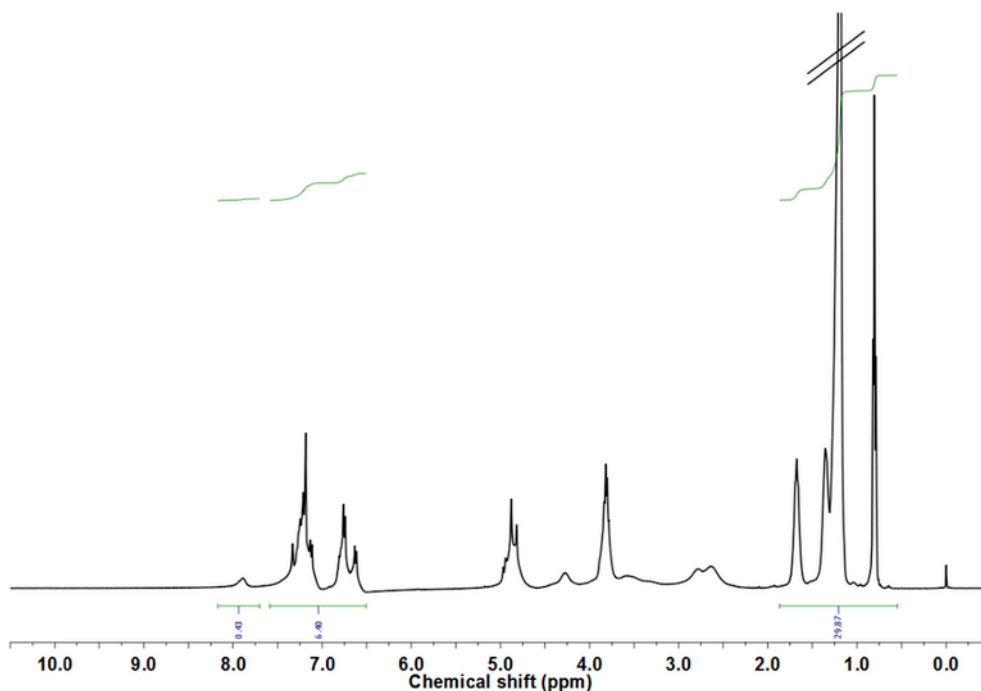


Fig. 10. Quantitative ^1H NMR spectrum of PA4 copolymer after the chronoamperometry experiment.

evidence better homeotropical orientation, higher values of clearing temperature and improved mechanical properties. However, some disadvantages like sensitivity to gaseous chlorine and lower selectivity were found. These novel biomimetic systems can be considered complementary to the hybrid membranes previously reported, since they exhibit worse performances as far as selectivity is concerned; on the other hand, membranes can be more easily prepared, are cheaper, possess higher thermal stability and are not brittle. Therefore, they could be used, for instance, in applications where higher temperature regimes are required.

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