



# Advances in the design of self-supported ion-conducting membranes—new family of columnar liquid crystalline polyamines. Part 1: Copolymer synthesis and membrane preparation



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## ABSTRACT

Poly[2-(aziridin-1-yl)ethanol] (PAZE) is a suitable polyamine candidate which can be dendronised with 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoic acid (TAP) in order to obtain liquid crystalline columnar polyamines, as previously reported. However, the resulting copolymers evidenced a strong tendency to crystallise which leads to the detriment of columnar phase stability and the mechanical properties of the resulting polymeric membranes. In order to overcome this drawback, we successfully prepared LC columnar polyamines based on poly[2-(aziridin-1-yl)ethanol] modified with both TAP and benzoyl chloride at different extents. The presence of the dendron group induces self-assembling into a columnar structure, due to an exo-recognition of the side-chain dendrons, while the benzoyl group is expected to inhibit polymer crystallinity. All copolymers, except one, have lower melting points and exhibit higher clearing temperatures ( $T_c$ ), when compared to the LC polyamines obtained by modification of PAZE with TAP only, reported in previous studies. In all cases they exhibited LC columnar mesophases after annealing, as inferred by DSC, XRD and POM.

When casted as membranes, these columnar copolyamines can be homeotropically oriented under thermal treatment at optimal conditions, as was confirmed by X-ray diffraction studies at low  $2\theta$  angles. Additionally, SEM microscopy was used in order to evaluate the morphology of the prepared membranes.

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## 1. Introduction

In natural systems proton transport conductivity occurs with high selectivity and efficiency. For this reason, in the last thirty years, most research in the field of proton conductivity has been devoted to 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) [1,2]. Liquid crystals (LCs) are interesting materials because of their unique properties: they combine molecular order and mobility. This unique combination leads to the formation of chemical species that

present a well-ordered internal structures [3]. Thus, the design of LCs as new functional materials can be an attractive option for various applications such as ion [4,5] or charge [6,7] transport, separation membranes [8,9], and catalysis [10,11]. Up to now, the Percec group carried out an extensive investigation on the synthesis and posterior self-assembly process of supramolecular dendrons, dendrimers and dendronised polymers into liquid-crystalline mesophases [12].

In our group we design dendronised polyethers and polyamines that form ion transport channels by self-assembling, in which the channels localise the permeation path and simultaneously protect the transport process against the environment, like an ion-transporting molecular cable [13–16]. As it was described previously, we tackled the chemical modification of polymer poly[2-(aziridin-1-yl)ethanol] (PAZE) with the mesogenic group 3,4,5-tris

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[4-(n-dodecan-1-yloxy)benzyloxy]benzoic acid (TAP) in order to obtain side-chain liquid-crystalline polyamines [16]. In that study we prepared a family of copolyamines with different degrees of modification of TAP groups. These copolymers can be used to prepare oriented membranes for small cation transport, in agreement with the results that we obtained on oriented membranes based on poly(epichlorohydrin) (PECH) modified with the same dendron, where proton permeability comparable to Nafion<sup>®</sup> 117 was found [17]. As we reported before, these polymers self-assemble into a columnar structure, due to an exo-recognition of the side-chain dendrons. In the resulting structure, the polyamine main chain forms a channel in the inner part of the columns, while the hydrophobic side-chain dendrons lie in the outer part. The presence of the polar linkages in the inner channel favours the interaction with proton and other cations, in the same way as crown ethers would do [18]. For this reason, the inner polyamine main chain could work as an ion channel, while the hydrophobic side-chain dendrons lie on the outer part. However, the resulting copolyamines evidenced a strong tendency to crystallise.

In this work, to suppress the crystallisation process of the obtained copolymers and give more stability to the LC mesophases, we successfully modified PAZE using different amounts of both TAP and benzoyl chloride units. The presence of the TAP group induces self-assembling into a columnar structure, due to an exo-recognition of the side-chain dendrons, while the benzoyl group is expected to inhibit polymer crystallinity. Finally, we prepared oriented and stable membranes based on selected copolymers, having two different modification degrees. Membrane orientation was achieved by means of a simple and reproducible thermal treatment on fluorinated ethylene propylene (FEP) sheet support.

## 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. NMP was first dried by removing water as benzene azeotrope (Dean-Stark apparatus) and then fractionally distilled, collecting the desired fraction (78–79°C/12 mmHg) over Linde type 4 Å molecular sieves. Pyridine was first predried over KOH pellets and then fractionally distilled from sodium hydride over Linde type 5 Å molecular sieves [19]. Linde type 4 Å and 5 Å molecular sieves were previously activated by heating them in an oven at 220 °C for 48 h, and then left to cool and kept under argon atmosphere in a well-dried flask.

3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoic acid (TAP) was synthesized as previously reported [16]. Yield: 93%.

#### 2.1.1. Synthesis of the poly[2-(aziridin-1-yl)ethanol] (PAZE)

The synthesis of the PAZE polymer was reported in our previous study [20]. The polymer used for modification reactions was obtained with 1 mol% boron trifluoride ethylamine (BF<sub>3</sub>·EtNH<sub>2</sub>) in the absence of solvent at 45 °C. In this case, a polymerization degree of about 44 monomeric units and an inherent viscosity of 0.013 dL/g was generally used except in the synthesis of PA3.1 and PA3.2 copolymers, in which a different batch of PAZE with a degree of polymerization equal to 60 and inherent viscosity of 0.023 dL/g was used.

The inherent viscosity of PAZE starting batches was measured

on a viscosimeter Ubbelohde (DIN 510 10/I) connected to an automatic mater Schott Geräte AVS310 equipped with a thermostatic bath Schott Geräte CT 050/1 and one extern cryoscopic unit Selecta 6000382. Measurements were carried out from a capillary viscosimeter Schott Geräte type 50110/I at 30 °C using sample of 2 g/l diluted in dimethyl sulfoxide (DMSO).

Absolute molecular weights of PAZE were determined by SEC-MALLS. SEC measurements were performed using PolarGel-M column (Polymer Labs, UK), Agilent isocratic pump Series 1200 (Agilent Tech, USA), differential refractive index (RI) detector K2301 (Knauer, DE) and a MiniDAWN MALLS Detector (Wyatt Tech, USA). The eluent was *N,N*-dimethylacetamide (DMAc) with 3 g/L LiCl and a flow rate of 1.0 mL/min. The dn/dc value was calculated from the measurements as 0.134 dL/g. The molecular weights were calculated using the Astra 4.9 software as well as Corona software (Wyatt Tech, USA). The samples were measured at room temperature. In order to prevent aggregation, pretreatment of the solutions at 60 °C for 24 h was carried out.

#### 2.1.2. Chemical modification of PAZE using benzoyl chloride (synthesis of copolymers PA-Bn)

In a round-bottomed flask 1.7428 g (20 mmol) of PAZE was dissolved in 10 mL of dry NMP by stirring for 30 min at 0 °C and then the stoichiometric amount of dry pyridine to benzoyl chloride and 0.1222 g (1 mmol) of DMAP were added giving a pale green solution. After additional 15 min, the required amount of benzoyl chloride was added dropwise and the solution colour changed to a bright yellow. The mixture was magnetically stirred under argon atmosphere at room temperature (Scheme 1). After 3 days the reaction mixture was precipitated in THF according to Saucă et al. [21]. The precipitated product was dissolved in methanol and reprecipitated in THF twice. Finally, the modified polymer was collected and dried at 40 °C *in vacuo* for 48 h.

#### 2.1.3. Chemical modification of PAZE-Bn with TAP

In a round-bottomed flask 0.7509 g (1.66 mmol) of PAZE-Bn and the stoichiometric amount of DMAP to TAP were dissolved in 10 mL of NMP (or in CHCl<sub>3</sub> in case of PA1.1) by stirring for 30 min at 0 °C. Subsequently, the stoichiometric amount of DCC to TAP was added. After additional 15 min, the necessary amount of TAP dissolved in 6 mL of THF was added dropwise and the mixture was magnetically stirred for 10 days at room temperature according to Šakalytė et al. (Scheme 2) [16]. The reaction mixture was filtered in order to eliminate undesirable *N,N'*-dicyclohexylurea and precipitated into cold ethanol. The precipitated product was dissolved in chloroform and precipitated twice in methanol or cold ethanol, depending on the modification degree. Finally, the modified polymer was collected and dried at 40 °C *in vacuo* for 48 h.

#### 2.1.4. Membranes preparation

Membranes were prepared by immersion precipitation process, in which a homogeneous polymer solution in THF (30% w/w) was cast on a FEP (fluorinated ethylene propylene) sheet support and immersed in a bath of Milli-Q water. The solvent diffused into the cast film. After a time, in which the solvent and the non-solvent were exchanged, the polymer solution (wet film) became thermodynamically unstable and demixing took place. Finally, a solid polymer membrane was formed with an asymmetric structure. Afterward, the membrane was dried overnight at room temperature and subsequently used for baking process. The polymer membrane along with FEP sheet was mounted on a hot stage (Linkam TP92) and it was heated above the clearing temperature; then it was allowed to cool slowly (0.5 °C/min) to room temperature, including an isothermal step at temperature characteristic for

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