

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 2θ 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[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[®] 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

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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 ($\text{BF}_3 \cdot \text{EtNH}_2$) 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 10/1) 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)

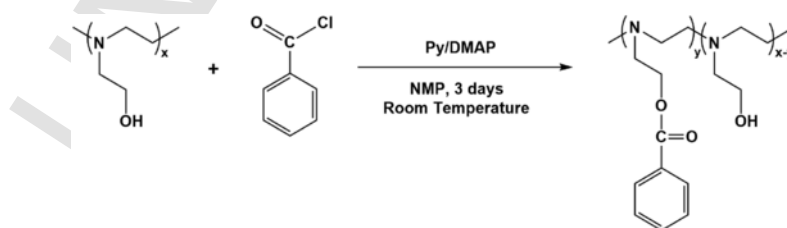
In a round-bottomed flask 1.7428 g (20 mmol) of PAZE was dissolved in 10 mL of dry NMP by stirring for 30 min at 0 °C and then the stoichiometric amount of dry pyridine to benzoyl chloride and 0.1222 g (1 mmol) of DMAP were added giving a pale green solution. After additional 15 min, the required amount 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 Saucá 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

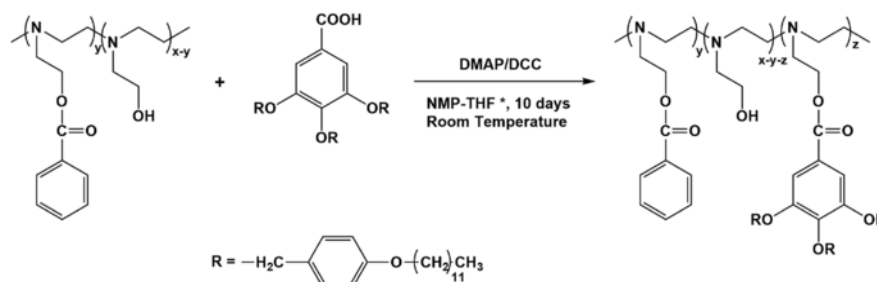
In a round-bottomed flask 0.7509 g (1.66 mmol) of PAZE-Bn and the stoichiometric amount of DMAP to TAP were dissolved in 10 mL of NMP (or in CHCl_3 in case of PA1.1) by stirring for 30 min at 0 °C. Subsequently, the stoichiometric amount of DCC to TAP was added. After additional 15 min, the necessary 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 precipitation bath, while the non-solvent (water) diffused into the cast



Scheme 1. Chemical modification of PAZE with benzoyl chloride.



Scheme 2. Modification reaction of copolymers PAZE-Bn with 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoic acid (TAP) using esterification method with DMAP/DCC.

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 each polymer. The temperature of isothermal step was always selected slightly below the clearing temperature based on POM microscopy observation, in order to allow a slow growing of the mesophase. The same thermal procedure was repeated on a bigger scale using a Hewlett Packard 5890 Series II Gas Chromatograph oven. After the baking process, the membrane was kept at room temperature for approximately 1 h and then it was separated from the FEP sheet and obtained as an intact, uniform membrane with thickness between 200 and 400 μm . The thickness of the membranes was measured using a micrometer with a sensitivity of 5 μm . The measurements were carried out at various points, and the membranes were found to have constant thickness.

2.2. Characterisation and measurements

2.2.1. Thermogravimetric analysis (TGA)

Thermal stability studies were carried out in ALU OXIDE crucibles of 70 μL (ME-24123) with a Mettler TGA/SDTA851e/LF/1100 device at temperatures ranging from 30 to 600 °C with a heating rate of 10 °C/min using around 10 mg of sample in a nitrogen atmosphere (100 mL/min). The equipment was previously calibrated with indium (156.6 °C) and aluminium (660.3 °C) pearls.

2.2.2. Differential scanning calorimetry (DSC)

Calorimetric studies were performed in aluminium standard 40 μL crucibles without pin (ME-26763) with a Mettler DSC822e thermal analyser at the heating rate of 10 °C/min using about 5 mg of sample, nitrogen as a purge gas (100 mL/min) and liquid nitrogen for the cooling system. The equipment was previously calibrated with indium (156.6 °C) and zinc (418.6 °C) pearls.

2.2.3. Nuclear magnetic resonance (NMR) spectroscopy

^1H NMR and ^{13}C NMR spectra were recorded at 400 and 100.4 MHz, respectively, on a Varian Gemini 400 spectrometer with proton noise decoupling for ^{13}C NMR. The ^{13}C NMR spectra of the polymers were recorded at 30 °C, with a flip angle of 45°, and the number of transients ranged from 20,000 to 40,000 with 10–20% (w/v) sample solutions in deuterated chloroform (CDCl_3) or deuterated dimethyl sulfoxide ($\text{DMSO-}d_6$). A pulse delay time of 5 s for the ^1H NMR spectrum was used. The chemical shifts were given in parts per million from TMS (Tetramethylsilane) in ^1H NMR spectra, while the

central peak of the solvent was taken as the reference in the case of ^{13}C NMR spectra.

Quantitative ^{13}C NMR spectra were performed using deuterated chloroform (CHCl_3) or deuterated dimethyl sulfoxide ($\text{DMSO-}d_6$) at 30 °C with a pulse delay time of 5 s. Delay time was selected on the basis of the relaxation times determined for the monomer 1-(2-hydroxyethyl)aziridine.

2.2.4. Polarised optical microscopy (POM)

Clearing temperatures and LC mesophases were investigated by polarised optical microscopy (POM); textures of the samples were observed with an Axiolab Zeiss optical microscope equipped with a Linkam TP92 hot stage.

2.2.5. Fourier-transformed infrared spectroscopy (FT-IR)

Fourier-transformed infrared spectra were recorded on an FTIR-ATR 680 PLUS spectrophotometer from JASCO with a resolution of 4 cm^{-1} in the absorbance mode. This device is equipped with an attenuated total reflection accessory (ATR) with thermal control and a diamond crystal (Golden Gate heated single reflection diamond ATR from Specac-Teknokroma). The spectra were recorded at room temperature and at 150 °C for pure compounds.

2.2.6. X-ray diffraction (XRD)

For X-ray experiments, two different diffractometers were used depending on the 2θ range investigated:

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 μm . The X-ray diffractometer was operated at 40 kV and 40 mA to generate $\text{Cu}_{K\alpha}$ radiation. The GADDS detector was a HI-STAR (multiwire proportional counter of 30 \times 30 cm with a 1024 \times 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 an azimuthal intensity plot. In the case of membranes, XRD experiments were performed on both sides and no differences could be detected.

For medium 2θ range, XRD measurements were performed with a Siemens D5000 diffractometer (Bragg-Brentano parafocusing geometry and vertical θ - θ goniometer) fitted with a curved graphite dif-

fracted-beam monochromator, incident and diffracted-beam Soller slits, a 0.06° receiving slit and scintillation counter as a detector. Samples were placed directly on to a low background Si(510) sample holder for reflection analysis. The X-ray diffractometer was operated at 40 kV and 30 mA to generate $\text{Cu}_{K\alpha}$ radiation. The angular 2θ diffraction range was between 1 and 40° . The data were collected with an angular step of 0.03° at 6 s per step.

2.2.7. 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 fractured by impact after cooling them with liquid nitrogen. In the resulting specimens 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.

3. Results and discussion

In a previous paper our group reported the chemical modification of PAZE with a dendritic group in order to induce the formation of columnar mesophases and to get a material which could be used in the preparation of proton transport membranes [16]. However, the obtained LC side-chain polyamines evidenced a strong tendency to crystallise, to the detriment of columnar phase stability and the mechanical properties of final membranes. To explain the crystallisation process, considering the low molecular weight of the starting polymer, the regularity of the structure increases on increasing the modification degree with TAP; in the same way, the presence of free hydroxyl groups can contribute to the crystallinity through hydrogen bonds formation. In order to overcome this drawback, another side group could be grafted in addition to TAP to suppress some of the free hydroxyl groups of PAZE: thus, some irregularities in the structure are introduced. The chosen group was a benzoyl because it is a small group that should not affect the self-assembling process of the resulting polymer. The first way that we chose to introduce the benzoyl units was by the reaction with benzoic acid. Thus, the reaction of PAZE polymer with both dendritic group and benzoic acid was tested in one pot using the same conditions as in previous studies performed with TAP only [16]. However, this attempt was unsuccessful, probably due to the poor solubility of benzoic acid in chloroform. Therefore, we tackled the reaction in two steps, the former by nucleophilic substitution with benzoyl chloride and the second by Steglich esterification with TAP, respectively.

3.1. Chemical modification of PAZE using benzoyl chloride (synthesis of copolymers PAZE-Bn)

Scheme 1 shows the first step of the chosen pathway to modify the PAZE polymer. Chemical modification conditions, the resulting degrees of modification and product yields are reported in Table 1.

The structure of the copolymers was characterized by NMR spectroscopy. As we can see in Table 1, benzoyl moieties always are grafted to PAZE quantitatively. Table 2 reports ^1H NMR spectrum data in $\text{DMSO-}d_6$ of modified PAZE-B5 as an example.

All ^1H NMR spectra are characterized by broad signals in two regions. The aromatic region shows 4 partially overlapped signals at 8.0 , 7.6 , 7.5 and 7.4 ppm. Considering the relative integration, the signal at 8.0 ppm was assigned to the protons of the benzoyl group plus the benzyl aromatic protons *ortho* to the carbonyl group. The signals between 7.6 and 7.4 ppm ($2\text{H} + 1\text{H}$) correspond to the benzyl aromatic protons *meta* and *para* to the carbonyl group, respectively.

Table 1

Chemical modification conditions, modification degrees, resulting yields and thermal characterisation of PAZE-Bn copolymers.

Polymer	T (°C)	Polymer/COCl molar ratio	Modification degree (%) ^a	Yield (%) ^b	T _g (°C)	Onset TGA curve (5% mass loss) (°C)
PAZE	RT ^c	–	0	75	–35	217
PAZE-B1	RT	1:0.1	9	54	–16	185
PAZE-B2	RT	1:0.20	19	48	–1	184
PAZE-B3	RT	1:0.25	25	56	4	195
PAZE-B4	RT	1:0.35	33	73	20	211
PAZE-B5	RT	1:0.5	48	74	29	220
PAZE-B6	RT	1:0.75	75	50	43	228

^a Modification degree determined by using ^{13}C NMR.

^b Calculated from the degree of modification.

^c RT = 25 ± 5 °C.

Table 2

NMR data and structure of the PAZE-B5 copolymer in $\text{DMSO-}d_6$.

^1H -NMR		^{13}C -NMR	
Signal (ppm)	Assignment	Signal (ppm)	Assignment
b, b'	3.2–3.4	a, a'	47.9–48.3; 56.0
c'	3.5	b, b'	54.8
a, a'	3.6–3.9	c'	58.5
c	4.5	c	61.3
d'	5.3	I-III	128.1–129.4
f, g	7.4–7.6	IV	133.1
e	8.0	COO	165.5

The protons of the main chain and the protons assigned to the signals *b*, *b'* and *c'* appear overlapped between 3 and 4 ppm. The signal at 4.5 ppm corresponds to the methylenic protons *c* in the modified unit and a broad signal at 5.3 ppm corresponds to the —OH group.

Table 2 shows the ^{13}C NMR data of the polyamine PAZE-B5 with the corresponding assignments. The aromatic and carbonyl carbons of the introduced moiety appear between 165.5 and 128.1 ppm. The carbons of the main chain are observed between 47.9 and 48.3 and 56.0 ppm, while the signals assigned as *b*, *b'* appear at 54.8 ppm. The methylenic carbons *c'* and *c* of the unmodified and modified units appear resolved at 58.5 and 61.3 ppm, respectively.

The structures of copolymers were also characterized and confirmed by FT-IR technique. In the FT-IR spectrum, we could observe the decrease of the —OH vibration band around 3290 cm^{-1} , coming from PAZE. Furthermore, the ester carbonyl group characteristic band around 1715 cm^{-1} (C=O) appears, which confirms that polymer chemical modification occurred.

The results of thermal characterisations shown in Table 1 indicate that the T_g of the resulting copolymers increased on increasing the modification degree as expected on the basis of the higher amount of side bulky aromatic groups contained. Moreover, the thermal stability was moderately improved as shown by higher values of temperature of 5 wt% mass loss by increasing the modification degree with benzoyl, which reduces the number of free hydroxyl groups responsible for thermal dehydration. In the case of starting PAZE, partial crystallinity is responsible for higher thermal stability than the expected one.

3.2. Chemical modification of PAZE-Bn with TAP

The second step of the modification of PAZE polymer consists of the modification of the PAZE-Bn copolymers with TAP by Steglich esterification (Scheme 2).

The use of *N,N*-dicyclohexylcarbodiimide (DCC) as a promoter represents one of the most versatile esterification methods [22]. Although stoichiometric dosage of this reagent or even a small excess is necessary, this procedure demonstrates its various advantages over other esterification reactions. The reaction usually proceeds at room temperature, and the conditions are mild. Unfortunately, this procedure has some drawbacks: yields are not always high, and undesirable *N*-acylureas are occasionally formed. These drawbacks can be overcome by addition of a catalytic amount of *p*-aminopyridines [23,24].

In the case of the previously synthesized PAZE-Bn copolymers, we studied this chemical modification under different reaction conditions, which are given in Table 3 with their corresponding degree of modification and product yields.

In all cases this esterification was carried out at room temperature, since the side product *N*-acylurea formation is less likely at lower temperatures; in other words, high temperatures favour the formation of side products and are therefore expected to reduce modification degrees correspondingly. In these conditions, the FT-IR spectrum of the resulting copolymers showed the decrease of the —OH vibration band around 3290 cm^{-1} , attributed to the remaining hydroxyl groups.

As we can see in Table 3, when we increase the modification degree with benzoyl chloride, the expected modification with the TAP dendron decreases probably due to conformational inaccessibility of the remaining free hydroxyl groups of the copolymers PAZE-Bn. As a matter of fact, of the entire family of copolyamines, only in one case, i.e. polymer PA3, we succeeded in quantitatively modifying free hydroxyl groups of the starting PAZE polymer. Furthermore, in the case of samples PA1.1 and PA3.1 a total modification degree around 90% was reached. On the opposite side, when the degree of modification with benzoyl units was 75%, the reaction with TAP groups did not occur.

Surprisingly, we found an exception that breaks the observed tendency. PAZE-B1 had the highest amount of free hydroxyl groups before carrying the Steglich esterification. When the second step was performed, the grafted amount of TAP into the copolymer structure was smaller than expected (only 29% of the 91% possible amount of the dendron was introduced). The copolymer, modified only with 9% by benzoyl moieties, exhibited poor solubility in the used mixture of solvents (*N*-methyl-2-pyrrolidone and THF). Therefore, the behaviour of PAZE-B1 can be justified in terms of its solubility. It was observed that this copolymer showed a similar behaviour to the starting PAZE polymer. For this reason, as we did in previous studies, when we modified PAZE polymer with TAP alone [16], we replaced the mixture of solvents (*N*-methyl-2-pyrrolidone and THF) by chloro-

form and the chemical modification with TAP was improved considerably from 29 to 85%.

For the sample PA5, the modification degree with TAP was not quantitative. To improve the modification of this step, we changed the molar ratio between the free hydroxyl groups of the polymer and the acid groups of the dendron. Nevertheless, as we could observe in the case of copolymer PA5.1, an excess of 20% mol of the mesogen only increases the TAP modification from 21 to 31%, still far away from the maximum 50% expected.

As it can be observed in Table 3, the samples: PA3, PA3.1 and PA3.2, have the same modification degree with benzoyl units (25%), nonetheless the amount of introduced TAP dendrons is different. These changes could be justified by the usage of different batches of starting PAZE polymer that differ in the number of repetitive units of starting PAZE polymer batches (44 for PA3, and 60 for both PA3.1 and PA3.2, respectively), as well as in the inherent viscosity (η_{inh}) values. Due to the use of the same batch of PAZE for the synthesis of PA3.1 and PA3.2, these two copolymers present both a modification degree of TAP around 60%. In the case of PA3, the modification with TAP differs from the other samples (i.e. a modification degree with TAP equal to 75% was achieved).

The structure of the copolymers was characterized by NMR spectroscopy. Table 4 reports the ^1H NMR spectrum data in CDCl_3 of modified PA4 as an example (Fig. S1).

All ^1H NMR spectra are characterized by broad signals in three regions. The aromatic region shows 4 partially overlapped signals at 7.9, 7.2, 6.7 and 6.6 ppm. Considering the relative areas, the signal at 7.9 ppm can be assigned to the protons of the benzoyl unit in *ortho* to the carbonyl group. In comparison with the spectrum of 3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoic acid, the signals between 7.0 and 7.4 ppm can be assigned to the protons of TAP group in *ortho* to the $\text{—CH}_2\text{OPh—}$. Also the two protons in *ortho* position to the carbonyl group of the inner aromatic ring of TAP can be found between 7.0 and 7.4 ppm. The rest of the signals of the protons of the benzoyl units added previously appear overlapped with the signals between 7.0 and 7.4 ppm. The signals at 6.7 and 6.6 ppm (4H + 2H) correspond to the benzyl aromatic protons *meta* to the $\text{—CH}_2\text{OPh—}$ of the lateral and central alkyloxybenzyloxy substituents of TAP, respectively. The characteristic signals of the protons which correspond to the long alkyl chains in TAP can be observed in the upfield region at 1.7, 1.3, 1.1 and 0.8 ppm. The most interesting region lies between 5 and 2 ppm in which 4 signals can be observed. First of all, a signal at 4.7 ppm can be assigned to the benzylic methylenes of the dodecyloxybenzyloxy substituent. The signal at 4.3 ppm corresponds to the methylenic protons c, c' in the modified monomeric units with

Table 3
Chemical modification conditions, modification degrees and resulting yields of PA1-PA6 copolymers.

Copolymer	Solvent	PAZE-Bn/COOH molar ratio	Benzoyl modification degree (%) ^a	TAP modification degree (%) ^a	Total modification degree (%) ^a	Yield (%) ^b
PA1	THF/NMP	1:1	9	29	38	56
PA1.1	CHCl_3	1:1	9	85	94	28
PA2	THF/NMP	1:1	19	55	74	40
PA3 ^c	THF/NMP	1:1	25	75	100	39
PA3.1 ^c	THF/NMP	1:1	25	62	87	34
PA3.2 ^c	THF/NMP	1:1	25	57	82	71
PA4	THF/NMP	1:1	33	43	76	79
PA5	THF/NMP	1:1	48	21	69	27
PA5.1	THF/NMP	1:1.2	48	31	79	51
PA6	THF/NMP	1:1	75	–	75	–

^a Modification degree determined by using ^{13}C NMR.

^b Calculated from the degree of modification.

^c PA3 copolymer was prepared using a batch of PAZE polymer with an inherent viscosity (η_{inh}) equal to 0.013 dL/g, whereas PA3.1 and PA3.2 copolymers were prepared using a different batch of PAZE polymer with $\eta_{\text{inh}} = 0.023$ dL/g.

Table 4
NMR data and structure of the PA4 copolymer in CDCl₃.

¹ H NMR		¹³ C NMR	
Signal (ppm)	Assignment	Signal (ppm)	Assignment
12	0–8	12	14.0
3–11	1.2–1.4	11	22.6
2	1.7	3	26.0
a, a', a'', b, b', b''	2.5–2.8	2, 4–9	29.1–29.6
c'	3.6	10	31.8
1	3.8	a, a', a'', b, b', b''	52.0–57.0
c, c''	4.3	c'	59.3
e''	4.8	c, c''	62.3
Ar	6.5–7.9	1	67.8
		e'' lateral	70.8
		e'' central	74.6
		II'	108.8
		VII'	114.0
		I'	124.8
		I–IV, V', VI'	128.3–133.0
		IV'	142.4
		III'	152.5
		VIII'	158.6
		COO	165.9–166.2

benzoyl and TAP, whereas the signal at 3.8 ppm corresponds to the methylene attached to the oxygen in the long alkyl chains. Hidden behind the last peak and centred at 3.6 ppm, the signal of the methylenic protons c' of the unmodified units appears. Finally, a broad signal centred at 2.7 ppm is observed, which corresponds to the carbons a, a', a'', b, b', b'' of the modified and unmodified units.

Table 4 shows the ¹³C NMR data of the polyamine PA4 with the corresponding assignments (Fig. S2). The carbonyl carbons of benzoyl group and TAP introduced appear between 165.9 and 166.2 ppm. The aromatic carbons appear between 108.8 and 158.6 ppm, whereas carbons 2–12 of the long alkyl chains appear in the expected region at 14.0–31.8 ppm. The carbon assigned as 1 of the alkyl chains appears at 67.8 ppm. The chemical shifts of the benzylic methylenes depend on their relative position in the aromatic ring: the ones in position 3 and 5 appear at 70.8 ppm, whereas the one in position 4 appears downfield at 74.6 ppm. The carbons of the main chain appear in the range within 52.0 and 57.0 ppm. By last, the methylenic units assigned as c' of the non-modified monomeric units appear resolved at 59.3 ppm and the methylenic carbons c, c'' of the modified units appear upfield at 62.3 ppm.

3.3. Mesomorphic characterisation of modified LC polyamines

The mesomorphic characterisation was performed on the basis of differential scanning calorimetry (DSC), optical microscopy between crossed polars (POM) and X-ray diffraction experiments (XRD). Table 5 shows calorimetric data of the whole PAn copolymers while Table 6 presents the obtained XRD results of this family of copolyamines.

In all cases, the DSC analysis reveals the presence of two endotherms. For the samples PA1 and PA2 to PA5.1, the first endotherm could be related to the melting and the second one to the clearing point. On increasing the modification degree with the mesogenic group, the clearing points and enthalpies of the copolymers also increased, similarly to what was reported for columnar copolyethers and copolyamines modified only with TAP [13,16]. Besides, the clearing enthalpy values were of a similar order like in the case of the previously mentioned copolyethers. In addition, another tendency regarding enthalpy and benzoyl content can be observed: on increasing the modification degree with benzoyl units, the polymers exhibit a decrease of the clearing enthalpy values. An exception could be also

Table 5
Calorimetric features of modified copolyamines.

Copolymer	Total modification degree (%)	T _m (°C) ^a	T _c (°C) ^a	Onset TGA curve (5% mass loss) (°C)	ΔH _c (kJ/mol) ^{b,c}
PA1	38	–14	92–96	272	1.1
PA1.1	94	62	48 ^d	291	–
PA2	74	–7	82–86	273	1.6
PA3	100	–13	100–104	285	1.7
PA3.1	87	–14	102–105	276	1.5
PA3.2	80	–10	93–97	278	1.4
PA4	76	–14	81–86	266	0.9
PA5	69	–17	88–91	235	0.5
PA5.1	79	–19	86–89	261	0.8

^a Determined by DSC second heating scan and POM.

^b Expressed per mol of TAP group.

^c Error: ± 3%.

^d Monotropic liquid crystal.

Table 6
X-ray diffraction data of modified copolyamines at room temperature.

Copolymer	Total modification degree (%)	d ₁₀₀ (Å)	d ₁₁₀ (Å)	d ₂₀₀ (Å)	d ₀₀₁ (Å)	a (Å) ^a	Mesophase ^b
PA1	38	45.1	26.9	23.0	4.4	52.1	Col _h
PA1.1	94	41.3	28.8	–	–	41.3	Col _r ^k
PA2	74	45.1	26.7	23.1	4.4	52.1	Col _h
PA3	100	41.9	24.3	21.3	4.5	48.4	Col _h
PA3.1	87	42.5	24.7	21.6	4.5	49.1	Col _h
PA3.2	80	46.5	26.9	23.5	4.5	53.7	Col _h
PA4	76	45.8	27.0	23.3	4.6	52.9	Col _h
PA5	69	43.1	25.5	–	4.5	49.8	Col _h
PA5.1	79	49.6	28.8	25.1	4.5	57.3	Col _h

^a Dimension of the hexagonal unit cell.

^b Col_r^k: crystalline rectangular columnar, Col_h: hexagonal columnar mesophase.

found in the less modified copolymer (PA1), which demonstrates different behaviour as a consequence of low modification degree, as expected.

In the obtained family of copolyamines, except for PA1.1, benzoyl small side group was introduced in order to enhance the stability of the LC mesophase with respect to the previously reported columnar copolyamines modified only with TAP [16]. Considering PA2 to PA5.1 copolymers, as we can observe in Table 5, the highest clearing temperatures were found when the introduced amount of benzoyl is 25% and also the dendron content is higher than 62%. (PA3 and PA3.1 copolymers). For these two copolymers the amount of free hydroxyl groups, which unfavourably affects the LC mesophase, is the smallest found in the whole group of copolymers (except for PA1.1). On the other hand, a decrease in the TAP content leads to a decrease of the clearing temperature as we expected. Related to the benzoyl, a higher amount than 25% of this side group induces a diminution of the clearing temperature.

On the contrary, the sample PA1.1 has a similar behaviour to the previously reported copolyamines modified only with TAP [16]. For this sample, two endotherms appear overlapped in the second calorimetric analysis: the first one showed a sharp and big endotherm at 46 °C and a second one broader and smaller with maximum at 61 °C. This suggested that this sample, due to its quite regular structure and relatively low molecular weight, tended to crystallise partially. To confirm the hypothesis and to have better visualisation of both endotherms, prior to DSC analysis the sample was annealed for 2 h at temperature slightly below the first peak maximum (39–42 °C) and cooled to –100 °C. Due to the pre-treatment, two sharp endotherms were obtained, one at 48 °C and another at 62 °C. The first transition

could be related to the melting of crystalline part, whereas the second one can be attributed to the clearing of a monotropic LC mesophase that grew during the annealing.

Liquid-crystalline mesophase of PA1.1 was observed under POM microscope between crossed polars and exemplary micrographs are shown in Fig. 1. The liquid-crystalline texture was obtained after performing the annealing at 40 °C, evident as a typical dendritic aggregates growth. After subsequent cooling the same sample to 30 °C, the appearance of crystals, combined with the remaining small domains of the LC mesophase was noticed, thus confirming the monotropic nature of the columnar mesophase.

The liquid-crystalline textures of other LC polyamines were observed by POM after annealing samples between 2 and 16 h at a temperature slightly lower than their respective clearing temperatures, in order to favour the growth of the liquid-crystalline domains.

POM images in Fig. 2 revealed a broken fan-shaped texture in case of PA3 and PA3.1 sample, whose modification degree of benzoyl is 25% and the degree of modification with TAP is 75 and 61% respectively. Differently, PA4 exhibited a texture which resembled smectic bâtonnets.

In order to confirm assignation of their mesophases, the synthesized LC polyamines were studied by XRD. The analysis was performed at different temperatures in order to confirm calorimetric features and to identify the copolymers mesophase.

For all copolymers except PA1.1, the XRD analysis below T_c showed three quite sharp reflections located in ranges of 2θ angles 1.8° – 2.1° , 2.9° – 3.6° and 3.1° – 4.2° , corresponding to d-spacings between $d = 41.9 \text{ \AA}$ – 49.6 \AA , 24.3 \AA – 30.6 \AA and 21.3 \AA – 25.0 \AA , respectively; also a presence of a broad halo centred around $2\theta = 19.4^\circ$ – 20.1° , giving $d = 4.4$ – 4.6 \AA was identified (Fig. S3 and S4

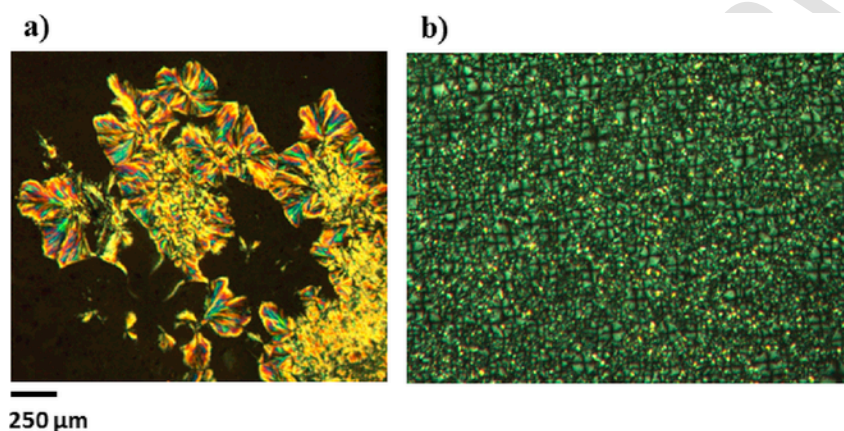


Fig. 1. Optical micrographics between crossed polars on cooling from the isotropic phase of PA1.1 at: a) 40 °C; b) 30 °C.

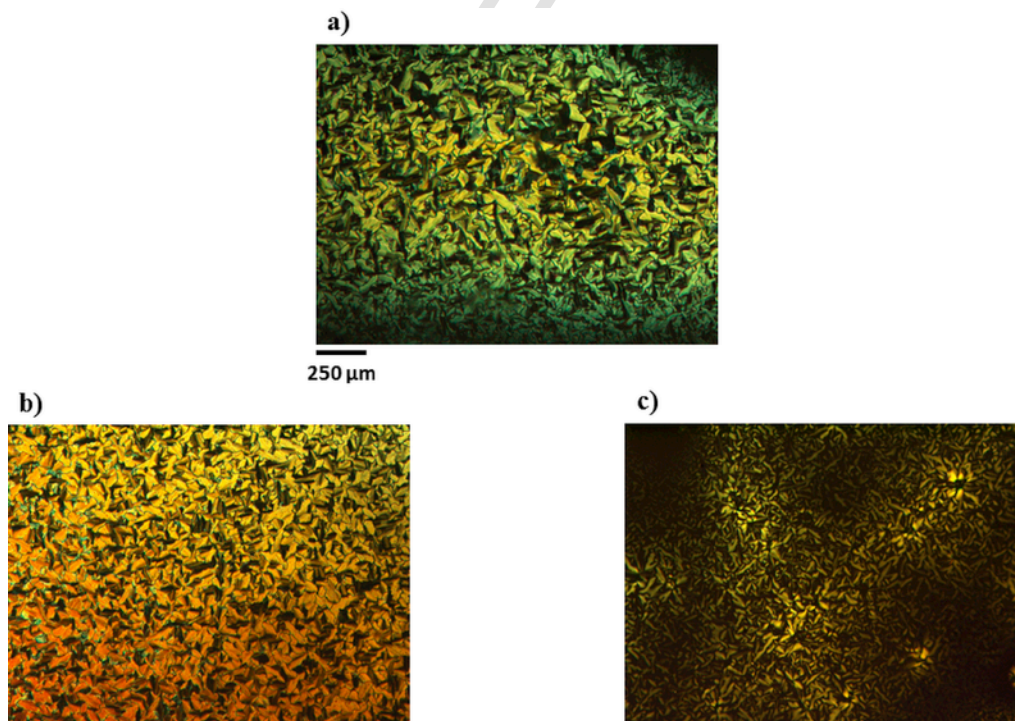


Fig. 2. Optical micrographics between crossed polars on cooling from the isotropic phase of: (sample, test temperature) a) PA3, 80 °C; b) PA3.1, 80 °C; c) PA4, 80 °C.

XRD pattern of PA3 and PA4). This diffraction pattern, which exhibited d-spacings of the sharper reflections in the ratio $1:1/\sqrt{3}:1/2$ and a diffuse halo at higher angles, confirmed the presence of a hexagonal columnar mesophase (Col_h), where the first three sharp reflections correspond to the planes (100), (110) and (200), respectively, while the broad halo is related to the plane (001).

Differently, the X-ray diffraction pattern of polymer PA1.1 suggested a rectangular columnar crystalline phase (Col_r^k), as evident from the high number of sharp reflections (Fig. S5). As a matter of fact, the reflections located at $2\theta = 2.1^\circ$ and 3.1° , corresponding to $d = 41.3 \text{ \AA}$ and 28.8 \AA , exhibited d-spacings in the ratio $1:1/\sqrt{2}$ and could be assigned to (100) and (110) planes, respectively. Unfortunately, due to the insufficient number of indexed signals, we could not univocally assign the spatial group for this copolymer.

In all cases, the organisation of the copolymers into columns can indicate a possible formation of biomimetic ion channels, where the polyamine main chain arranges in the inner part of the column.

The thermal stability of the polymers was studied using TGA. As an example, TGA scans of selected samples are reported in Fig. 3. The onset of thermal decomposition (determined as the temperature corresponding to 5% mass loss) ranged between 235 and 291 °C. The onset of thermal decomposition increased on increasing the copolymers modification degree with TAP, probably due to higher amount of mesogenic groups introduced in the structure. Copolymer PA1.1 behaved the best in this respect, exhibiting a mass loss onset temperature of 291 °C. Moreover, as far as char yield is concerned, the obtained copolymers have a similar behaviour to the copolymers modified with the mesogenic TAP group only [16]. In this case, the char yield at 600 °C ranged from 9 to 14%.

3.4. Membrane preparation and characterisation

As described in the experimental part, all membranes were prepared by immersion precipitation process. In previous studies, we proved the positive influence of the thermal treatment on the improvement of the homeotropic alignment of columns formed by liquid crystal polyglycidols, polyethers and polyamines containing TAP groups as side dendrons [15,25,26]. In these cases, to obtain the required alignment of the columns, the membrane was heated above the clearing temperature; next, it was kept at a temperature slightly below the clearing point for a proper time and then cooled slowly to room temperature. This process is characteristic for each polymer and al-

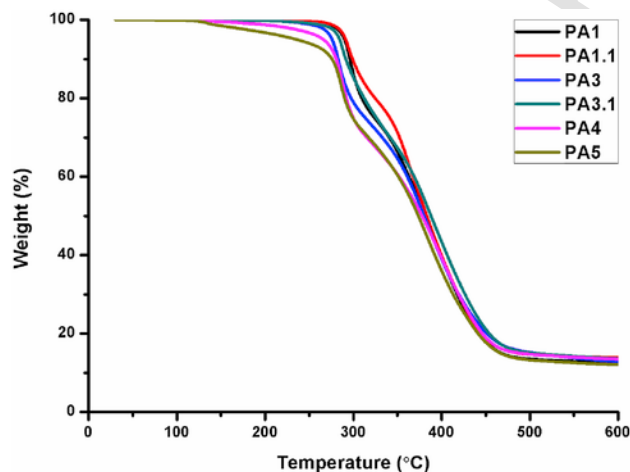


Fig. 3. TGA thermograms of selected copolymers recorded at a heating rate of 10 °C/min.

lows orientation of the columns in the expected direction for the observed columnar mesophases.

With the described baking process we obtained homeotropically oriented membranes. To ensure the growth of the columnar mesophase for these kind of LC copolymers, the baking process was carried out during overnight at their respective temperatures. PA3 and PA4 were selected as two representative examples because they present different modification degrees of benzoyl, TAP mesogenic groups and free hydroxyl groups in the resulting copolymer structure. As shown in Fig. 4, homogeneous and mechanically stable membranes were obtained with a thickness between 200 and 400 μm .

To assess the orientation of the columns, the membranes were analysed by X-ray diffraction. As an example, Fig. 5 shows the XRD diffractogram of two membranes, one prepared with the copolyamine PA3 and another one using the copolyamine PA4.

In the case of the membrane obtained with the copolymer PA3, at low 2θ angles three sharp reflections can be observed at 2.1° , 3.7° and 4.3° , corresponding to $d = 41.1 \text{ \AA}$, 23.9 \AA and 20.7 \AA respectively (Fig. 5a). These d-spacings give the ratio $1:1/\sqrt{3}:1/2$, which is characteristic for hexagonal columnar mesophase (Col_h), and thus confirm its presence in the tested material. Moreover, a narrowing of the signal at $\phi = 92^\circ$ in the azimuthal scan for the reflection d_{100} demonstrates orientation of the columns in the equatorial plane with calculated width at half height (WHH) of the peak equal to 35.8° . This confirms that in this membrane most of the columns are quite uniformly oriented perpendicularly to the membrane surface.

Similar to PA3, the XRD diffractogram of the membrane prepared with the copolyamine PA4 shows three sharp reflections corresponding to $d = 45.9 \text{ \AA}$, 26.7 \AA and 23.0 \AA respectively (Fig. 5b). The d-spacings correspond also to the (100), (110) and (200) planes of the hexagonal columnar mesophase. Referring to the alignment of the columns, for this membrane the azimuthal scan shows a narrowing of the signal centred at $\phi = 91^\circ$ for the reflection attributed to the spacing d_{100} , which confirms that also in this membrane most of the columns are homeotropically oriented. Moreover, the width at half height (WHH) of the peak is 15.2° .

Figs. 6 and 7 present some micrographs of membranes prepared with PA3 and PA4 copolymers, respectively obtained by SEM microscopy. In Fig. 6a we can observe the cross-section of an unoriented membrane of PA3 copolymer while the surface of an unoriented membrane prepared with the PA4 copolymer is appreciated in Fig. 7a. In both pictures, we can observe the presence of pores in the material resulting from the fast precipitation of the copolymer during the phase inversion process. On the other hand, Figs. 6b and 7b show a micrograph of the same membranes after applying the thermal treatment. It is possible to observe that, after this treatment, the homogeneity of the membranes was clearly improved. Two changes were detected, which evidenced this fact: the removal of the membrane

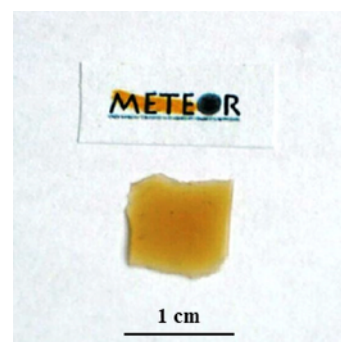


Fig. 4. Oriented membrane of polymer PA4 obtained after the baking process.

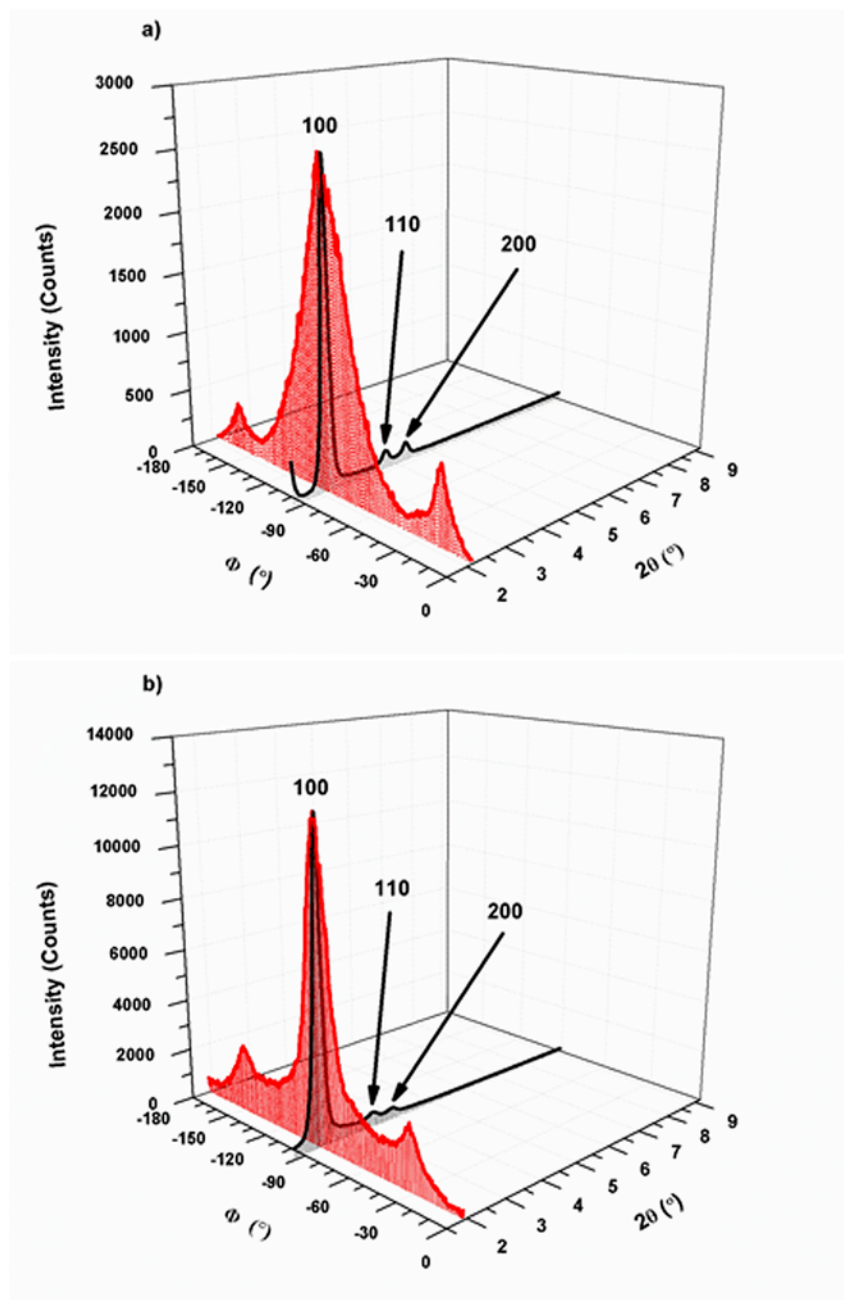


Fig. 5. Comparison of 2-theta in the range 1.5° – 9.0° and azimuthal scan at room temperature of baked membranes obtained from different copolymers after annealing: a) PA3, at 99°C and b) PA4 at 75°C , respectively.

pores and the presence of a smoother fracture surface in the case of the unoriented membranes.

Thus, the introduction of a small side group to the PAZE polymer before modifying with TAP allows to obtain LC copolymers with a higher range of the LC mesophase, as predicted. Furthermore, a successful preparation of homeotropically oriented self-supported membranes based on these side-chain liquid-crystalline polymers (SCLCP) shows a great potential in terms of further applications.

4. Conclusions

We prepared a family of self-assembling LC polyamines by chemical modification of PAZE with different amounts of benzoyl chloride and the dendron 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoic acid (TAP). To achieve this goal, PAZE was first modified with benzoyl chloride by using a nucleophilic substitution and afterward the resulting polymer was modified with the dendritic group by using carbodiimide mediated Steglich esterification. In all cases, the modification of PAZE polymer with benzoyl chloride took place quantitatively. On the other hand, the quantity of introduced TAP depends on

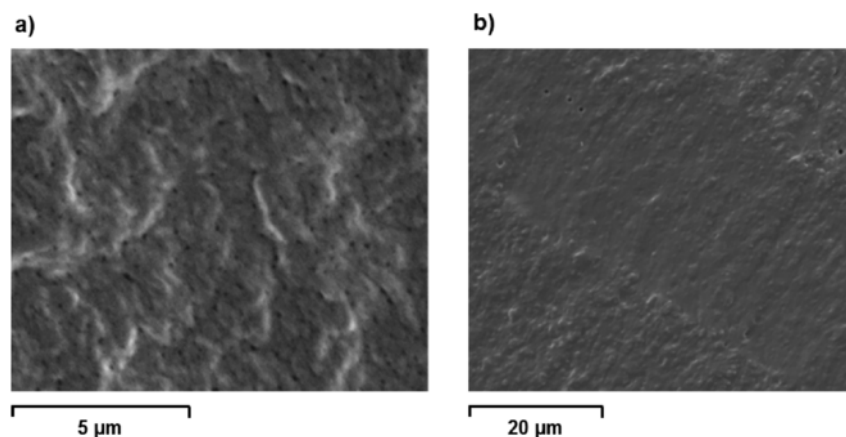


Fig. 6. SEM micrographs showing the morphology of the cryofractured cross-section of a membrane prepared with the PA3 copolymer: a) unoriented and b) oriented membrane.

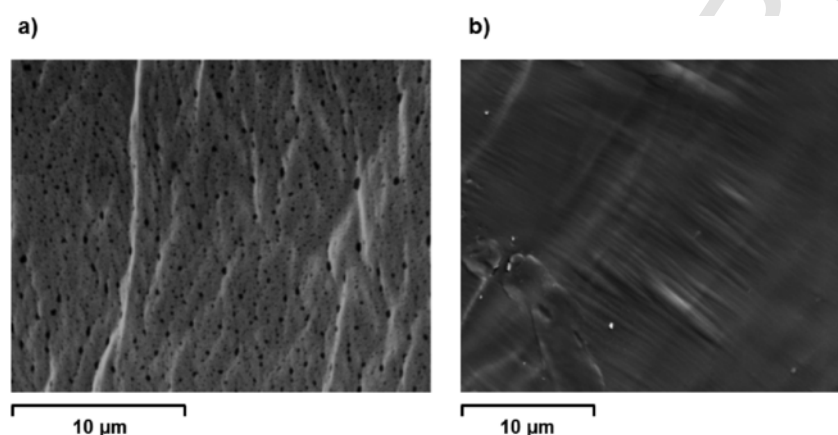


Fig. 7. SEM micrographs showing the morphology of the cryofractured surface of a membrane prepared with the PA4 copolymer: a) unoriented and b) oriented membrane.

the amount of remaining free hydroxyl groups and also of the amount of benzoyl units introduced in the first step, causing additional steric effect reducing in some cases the possibility of complete modification. In the case of modification degree with benzoyl chloride higher than 25%, the modification with TAP groups was not quantitative, probably due to conformational inaccessibility of free hydroxyl groups. Despite of this, in all cases the obtained copolymers exhibited a LC columnar mesophase. Moreover, they are not crystalline at room temperature 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.

Finally, oriented membranes based on selected LC polyamines were prepared. An orientation of the copolymer columns perpendicular to the membrane surface was accomplished using a thermal treatment and confirmed by XRD.

Furthermore, ionic transport across the oriented membranes will be the subject of extensive studies presented in the second part of this article.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2016.10.047>.

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