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Liquid crystalline polyamines containing side dendrons: Toward the building of ion channels based on polyamines

Asta Šakalytė [a], José Antonio Reina [b], Marta Giamberini [a,*]

[a] Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans, 26, 43007 Tarragona, Spain
[b] Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, Carrer Marcel·lí Domingo s/n, 43007 Tarragona, Spain

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ABSTRACT

In this article, we modified poly[2-(aziridin-1-yl)ethanol] (PAZE) with the dendron 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoic acid, to obtain liquid crystalline columnar polyamines. The chemical modification reaction was first tuned on a model compound, *N,N*-dimethyl-2-hydroxyethylamine. The best results were obtained by the esterification method with N,N'-dicyclohexylcarbodiimide at room temperature, in the presence of 4-dimethylaminopyridine. The obtained copolymers showed higher char yield than starting PAZE. In all cases they exhibited small crystalline portions after annealing and columnar mesophases, as inferred by DSC, XRD and POM. The dimension of the unit cell resulted slightly narrower than in the case of the copolyethers bearing the same dendron. This is probably due to the presence of a longer spacer in PAZE, which allows better accommodating of the side tapered group.

1. Introduction

The design, synthesis, and study of supramolecular assemblies capable of transporting ions across membranes by the channel mechanism have been the subject of increasing interest [1–3]. A self-assembly event can be dominated by a single molecular recognition process based on directional and attractive forces such as hydrogen bonding, van der Waals, electrostatic, and hydrophobic interactions. However, these processes are cooperative, and their cooperative contribution could be equally important not only in the aggregation process but also particularly in the stabilization of a particular architecture.

Liquid crystals (LCs) present an attractive option to design functional materials with a well-ordered internal structure. Fitie and coworkers [4] reported the structure of mixed LC phases formed by orthogonal self-assembly between acid-modified discotic and various polyamines and demonstrated that the principle of orthogonal self-assembly can be applicable to create liquid crystalline superlattices of polyamines.

Percec and coworkers [5–9] have comprehensively investigated the self-organization of supramolecular monodendrons and styrene-, methacrylate-, or oxazoline-based polymers for the design of ion-active nanostructured supramolecular systems.

In our previous studies [10,11], we reported the chemical modification of poly(epichlorohydrin) (PECH) with tapered mesogenic groups to yield high-molecular-weight polyethers with different degrees of modification. Since we obtained good modification degrees and detected no dehydrochlorination side reactions in the chemical modification of PECH [12,13], we were encouraged to use the same strategy and reaction conditions also for poly(epichlorohydrin-co-ethylene oxide) [P(ECH-co-EO)]. In a very recent paper [14], we have reported the preparation of a new family of liquid crystalline columnar polyethers by chemically modifying P(ECH-co-EO) with the dendron 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoate under different conditions. Modification degrees ranged from 57 to 67%. 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 PECH modified with the same dendron, where proton permeability comparable to Nafion® 117 was found [15]. In those polymers, the polyether main chain forms a channel in the inner part of the columns, while the hydrophobic side-chain dendrons lie on the outer part. The presence of the polar ether linkages in the inner channel favors the interaction with proton and other cations, in the same way as crown ethers would do [16]. For this reason, the inner polyether chain can work as an ion channel. If this concept is transferred to a polyamine main chain, the occurrence of basic nitrogen atoms in the inner helical backbone structure will probably confer to these materials the capability to transport proton ions by the channel mechanism.

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* Corresponding author. Tel.: +34 977558174; fax: +34 977559621.
E-mail address: marta.giamberini@urv.net (M. Giamberini).

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Hydroxylated polymers can be regarded as powerful precursors in the preparation of new polymers through chemical modification, which can finally lead to properly functionalized macromolecules for specific applications. In our previous work [17] we tackled the polymerization of a hydroxylated aziridine, 2-(aziridin-1-yl) ethanol (AZE). In that study we deepened cationic polymerization of this monomer by using several initiators and reaction conditions in order to minimize the participation of the hydroxyl group and to get a polyamine with a structure as linear as possible and molecular weight suitable for future applications. This functionalized polymer (PAZE) resulted interesting as a versatile starting material for chemical modification reactions in order to obtain side-chain liquid crystalline polyamines. Nematic side-chain polyamines were obtained by chemical modification of polyethyleneimine (PEI) [18]. In this case, LC phases were obtained for modification degrees higher than 69%; however, polymers containing about 80% of mesogenic groups were crystalline. Moreover, the authors showed that ammonium quaternization occurred to some extent, which is undesirable in our case, since the presence of basic nitrogen atoms is crucial to determine proton transport. Therefore, in this article, we modified PAZE with the dendron 3,4,5-tris[4-(n-dodecan-1-yloxy) benzyloxy]benzoic acid, to obtain liquid crystalline columnar polyamines. To the best of our knowledge, this is the first example of LC columnar polyamine.

2. Experimental

2.1. Materials

Model compound *N*,*N*-dimethyl-2-hydroxyethylamine (DMHEA) (98%) was supplied from Aldrich and used as received (MW = 89.1 g/mol, $\rho = 0.89$ g/ml).

All organic and inorganic reagents were supplied by Fluka or Aldrich and used as received.

N,*N*-dimethylformamide (DMF) was purified according to the literature [19].

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

The synthesis of the polymer PAZE was reported in our previous paper [17]. The polymer used for modification reactions was obtained with 1 mol% ethylamine trifluoroborane ($BF_3 \cdot EtNH_2$) in the absence of solvent at 45 °C: in this case, a polymerization degree of about 44 monomeric units was found (as determined by size exclusion chromatography-multi-angle laser light scattering (SEC-MALLS)).

2.1.2. Synthesis of the tapered mesogenic compounds (1–3)

Methyl 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoate **(1)** was prepared as described elsewhere [10].

The synthesis of 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy] benzoic acid **(2)** was performed following a slight modification of a reported procedure [20] that involved easier workup and higher yield:

Potassium hydroxide (0.8 g, 14 mmol) in 5 ml of water was added to a solution of **1** (5 g, 5 mmol) in a mixture of 10 ml of tetrahydrofuran (THF) and 40 ml of ethanol. The reaction mixture was refluxed and monitored by thin layer chromatography (TLC) with toluene as an eluent and stopped after 30 min by pouring into 1 l of ice water. It was then acidified carefully with concentrated hydrochloric acid (HCl) (5 ml), refluxed for an additional 15 min period and the precipitate was filtered. The resulting solid was redissolved in chloroform and concentrated HCl was added. The organic layer was separated and washed several times with water, dried over anhydrous magnesium sulfate ($MgSO_4$) and filtered. The solvent was vacuum distilled and the obtained solid was recrystallized from isopropanol to yield 91% of the white product.

The synthesis of trifluoroacetic 3,4,5-tris[4-(n-dodecan-1-yloxy) benzyloxy]benzoic anhydride (**3**) was performed according to the following procedure: to a solution of 1 g (1 mmol) of **2** in 20 ml of chloroform, 0.2 g (1 mmol) trifluoracetic anhydride was added. The reaction mixture was stirred at room temperature and monitored by TLC with toluene as an eluent. After 15 min the solvent and excess of acid were vacuum distilled and the obtained product was recrystallized from hexane to yield of 66%.

^1H NMR [$CDCl_3$, TMS, δ, ppm]: 7.30 (s, 2H, ArH−COO−), 7.26 (d, 4H, ArH meta to $-CH_2-O-$ in lateral benzylic units), 7.18 (d, 2H, ArH meta to $-CH_2-O-$ in central benzylic units), 6.69 (m, 6H, ArH ortho to $-CH_2-O-$), 4.95 (m, 6H, $Ph-CH_2-O$ in lateral benzylic units), 3.86 (m, 6H, $-CH_2-O-Ph$), 1.66 (m, 6H, $-C\underline{H}_2-CH_2-OPh$), 1.37 (m, 6H, $-C\underline{H}_2(CH_2)_2-O-Ph$), 1.19 (m, 48H, $-(CH_2)_8-$), 0.81 (t, 9H, $-CH_3$).

^{13}C NMR ($CDCl_3$, TMS, δ, ppm): 167.3 ($\underline{C}OCF_3$), 159.2 (ArC para to $-CH_2-O-Ph$), 153.0 ($\underline{C}OOCOCF_3$), 152.7 (ArC meta to COO), 143.2 (ArC para to COO), 130.5 (ArC ipso to COO), 129.4 (ArC ortho to CH_2-O-Ph in central benzylic unit), 128.6 (ArC ortho to $-CH_2-O-Ph$ in lateral benzylic units), 125.6 (ArC ipso to $-CH_2$-O-Ph), 114.6 (ArC meta to $-CH_2$-O-Ph in lateral benzylic units), 114.3 (ArC meta to $-\underline{C}H_2-O-Ph$ in central benzylic unit), 114.2 ($\underline{C}F_3$), 109.7 (ArC ortho to COO), 74.8 ($Ph-CH_2-O-Ph$ in central benzylic unit), 71.1 ($Ph-CH_2-O-Ph$ in lateral benzylic units), 68.2 ($R-CH_2-O-Ph$), 32.4 ($-\underline{C}H_2CH_2CH_3$), 30.1–28.3 (C2 and C4 to C9 in aliphatic chains), 26.2 ($Ph-O-CH_2CH_2\underline{C}H_2-$), 22.8 ($-\underline{C}H_2CH_3$), 14.3 ($-CH_2\underline{C}H_3$).

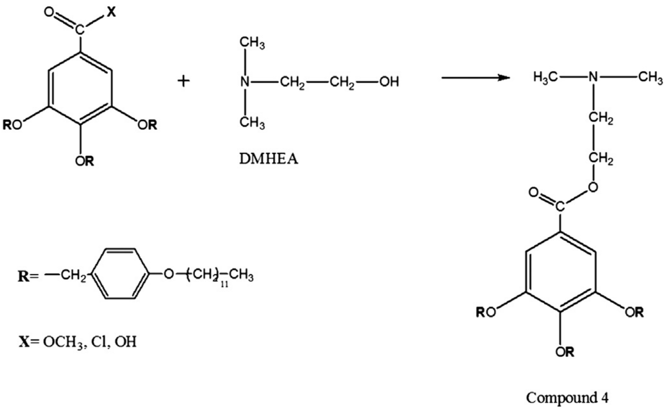
^{19}F NMR ($CDCl_3$, TMS, δ, ppm): −75.0 ($C\underline{F}_3$).

^{19}F NMR ($CDCl_3$, TMS, δ, ppm): −76.0 (trifluoracetic anhydride) [21].

2.1.3. Synthesis of 2-(dimethylamino)ethyl 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoate (4) (Scheme 1)

2.1.3.1. Method with thionyl chloride ($SOCl_2$) in the presence of DBU. To a solution of 1 g (1 mmol) of **2** in 20 ml of dry 1,2-dichloroethane, 0.3 g (2 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and few drops of DMF were added. The mixture was then cooled to 0 °C and 0.1 g (1 mmol) of $SOCl_2$ was subsequently added slowly. The reaction was monitored by TLC with toluene as an eluent. After 10 min 0.1 g (1 mmol) of the model compound N,N-dimethyl-2-hydroxyethylamine (DMHEA) was added and then the reaction mixture was stirred at room temperature for 20 h. The resulting solid was purified by column chromatography using toluene as an eluent to yield of 32%.

2.1.3.2. Method based on the Garegg–Samuelsson reaction [22]. To a solution of 2 g (8 mmol) I_2 in dry dichloromethane (30 ml), 2 g (8 mmol) triphenylphosphine (PPh_3) was added, giving a brown



Scheme 1. Reaction with the model compound.

yellow solution. Then, 1.2 g (20 mmol) imidazole was added, and the color changed to light yellow. Subsequently, 5 g (5 mmol) of **2** was added and the solution was stirred for 5 min at room temperature. Then 0.7 g (8 mmol) DMHEA was added. After 3 days the solvent was vacuum distilled and the resulting solid was purified by column chromatography using toluene as an eluent to yield of 47% of compound 4.

2.1.3.3. Transesterification reaction using sodium methoxide ($NaOCH_3$). To a solution of 1.5 g (1.5 mmol) of 1 and 0.3 g (3 mmol) of DMHEA in 20 ml of chloroform, 0.004 g (0.08 mmol) of $NaOCH_3$ was added. The mixture was then stirred for 5 days at 60 °C. The reaction was monitored by TLC with toluene as an eluent. Then the solvent was vacuum distilled and the obtained product was recrystallized twice from methanol to yield 58% of compound 4.

2.1.3.4. Esterification method with N,N′-dicyclohexylcarbodiimide (DCC)/DMAP. In a round-bottomed flask 0.2 g (2 mmol) of DMHEA and 0.1 g (0.8 mmol) of 4-dimethylaminopyridine (DMAP) were dissolved in chloroform (20 ml) by stirring for 15 min at 0 °C and then 0.4 g (2 mmol) of *N,N′*-dicyclohexylcarbodiimide (DCC) was added. After additional 15 min 1.7 g (2 mmol) of **2** was added slowly and the mixture was magnetically stirred at room temperature for 5 days. The reaction mixture was filtered in order to eliminate undesirable *N,N′*-dicyclohexylurea. The solvent was vacuum distilled and the obtained solid was purified by column chromatography using toluene as an eluent to yield 70% of the white product. Melting point: 43–45 °C.

^1H NMR [$CDCl_3$, tetramethylsilane (TMS), δ, ppm]: 7.30 (s, 2H, ArH–COO–), 7.26 (d, 4H, ArH meta to $-CH_2-O-$ in lateral benzylic units), 7.18 (d, 2H, ArH meta to $-CH_2-O-$ in central benzylic units), 6.69 (m, 6H, ArH ortho to $-CH_2-O-$), 4.94 (s, 4H, $Ph-CH_2-O$ in lateral benzylic units), 4.93 (s, 2H, $Ph-CH_2-O$ in central benzylic units), 4.30 (m, 2H, $-O-C\underline{H}_2-CH_2-N(CH_3)_2$), 3.85 (m, 6H, $-CH_2-O-Ph$), 2.62 (t, 2H, $-C\underline{H}_2-N(CH_3)_2$), 2.25 (s, 6H, $-N(C\underline{H}_3)_2$), 1.69 (m, 6H, $-C\underline{H}_2-CH_2-OPh$), 1.36 (m, 6H, $-C\underline{H}_2(CH_2)_2-O-Ph$), 1.19 (m, 48H, $-(CH_2)_8-$), 0.81 (t, 9H, $-CH_3$).

^{13}C NMR ($CDCl_3$, TMS, δ, ppm): 166.9 ($\underline{C}OO$), 159.6 (ArC para to $-CH_2-O-Ph$), 152.7 (ArC meta to COO), 142.4 (ArC para to COO), 130.4 (ArC ipso to COO), 129.4 (ArC ortho to CH_2-O-Ph in central benzylic unit), 128.8 (ArC ortho to $-CH_2-O-Ph$ in lateral benzylic units), 125.3 (ArC ipso to $-CH_2-O-Ph$), 114.7 (ArC meta to $-CH_2-O-Ph$ in lateral benzylic units), 114.2 (ArC meta to $-\underline{C}H_2-O-Ph$ in central benzylic unit), 109.3 (ArC ortho to COO), 74.7 ($Ph-CH_2-O-Ph$ in central benzylic unit), 71.3 ($Ph-CH_2-O-Ph$ in lateral benzylic units), 67.4 ($R-CH_2-O-Ph-$), 63.3 ($-O-\underline{C}H_2-CH_2-N(CH_3)_2$), 57.9 ($-\underline{C}H_2-N(CH_3)_2$), 46.2 ($-N(\underline{C}H_3)_2$), 32.1 ($-\underline{C}H_2CH_2CH_3$), 30.1–29.5 (C2 and C4 to C9 in aliphatic chains), 26.9 ($Ph-O-CH_2CH_2\underline{C}H_2-$), 22.9 ($-\underline{C}H_2CH_3$), 14.6 ($-CH_2\underline{C}H_3$).

IR (cm^{-1}): 2917–2850 (C–H aliphatic); 1721 (C=O); 1514 (C=C aromatic); 1334 (C–C aliphatic); 1244 (C–N).

2.1.4. Synthesis of copolymers PA1–PA6

In a round-bottomed flask 0.7 g (8 mmol) of polymer PAZE and 0.02 g (0.16 mmol) of DMAP were dissolved in 20 ml of chloroform by stirring for 15 min at 0 °C and then 0.3 g (1.5 mmol) of DCC was added. After additional 15 min, the necessary amount of **2** was added slowly and the mixture was magnetically stirred at different temperatures (25 °C or 60 °C) for 10 days. The reaction mixture was filtered in order to eliminate undesirable *N,N'*-dicyclohexylurea and precipitated twice from chloroform into methanol. The different modification conditions are reported in Table 1.

IR (cm^{-1}): 3364 (OH); 2920–2852 (C–H aliphatic); 1712 (C=O); 1513 (C=C aromatic); 1330 (C–C aliphatic); 1244 (C–N).

Table 1
Chemical modification conditions, resulting yields and modification degrees of copolymers PA1–PA6.

Copolymer	*T* (°C)	Polymer/COOH molar ratio	RCOOH (mmol)	Yield (%)	Modification degree (%)
PA1	25	1:0.2	1.5	79	16
PA2	25	1:0.4	2.7	77	39
PA3	25	1:0.5	2.3	70	46
PA4	60	1:1	2.2	58	55
PA5	25	1:0.7	2.4	69	67
PA6	25	1:1	2.2	62	100

2.2. Characterization 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 about 10 mg of sample in a nitrogen atmosphere (100 ml/min). The equipment was previously calibrated with indium (156.6 °C) and aluminum (660.3 °C) pearls.

2.2.2. Differential scanning calorimetry (DSC)

Calorimetric studies were performed in aluminum standard 40 μl crucibles without pin (ME-26763) with a Mettler DSC822e thermal analyzer 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 (419.58 °C) pearls.

2.2.3. Nuclear magnetic resonance (NMR) spectroscopy

Compounds were characterized by ^1H, ^{19}F and ^{13}C NMR spectra, which were recorded in deuterated chloroform ($CDCl_3$) with a Varian Gemini 400 MHz spectrometer (^1H – 400 MHz, TMS; ^{13}C – 100 MHz, TMS; ^{19}F – 377 – MHz) at room temperature using a pulse delay time of 5 s for ^1H NMR spectra.

2.2.4. Size exclusion chromatography (SEC)

Average molecular weights of PA1–PA6 were determined in tetrahydrofuran by SEC. Analyses were carried out in an Agilent 1200 series system with three serial columns (PLgel 3 μm MIXED-E, PLgel 5 μm MIXED-D and PLgel 20 μm MIXED-A), and equipped with an Agilent 1100 series refractive-index detector. Calibration curves were based on polystyrene standards with low polydispersities. THF was used as an eluent at a flow rate of 1.0 ml/min, the sample concentrations were 5–10 mg/ml, and injection volumes of 100 μL were used.

2.2.5. Polarized optical microscopy (POM)

Clearing temperatures were roughly estimated using polarized optical microscopy (POM); textures of the samples were observed with an Axiolab Zeiss optical microscope equipped with a Linkam TP92 hot stage.

2.2.6. Fourier transform infrared spectroscopy (IR)

Fourier transform 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 from the solid state pure compounds.

2.2.7. X-ray diffraction (XRD)

XRD patterns were recorded in a Bruker-AXS D8-Discover diffractometer equipped with parallel incident beam (Göbel mirror), vertical $\theta-\theta$ goniometer, and XYZ motorized stage. The GADDS (general area diffraction system) detector was an HI-STAR (multiwire proportional counter of 30×30 cm^2 with a 1024×1024 pixel). The X-ray diffractometer was operated at 40 kV and 40 mA to generate Cu Kα radiation. Samples were dissolved in THF and placed on the sample holder for transmission mode and then THF was left to evaporate. Two analytical conditions were used.

For low 2θ range: collimator, 100 μm; distance sample-detector, 30 cm; the collected frame (2D XRD pattern) covers a range from 0.9 up to 9.2° 2θ. The diffracted X-ray beam traveled through a He-filled chamber (SAXS attachment) to reduce the air scattering at low angles. The direct X-ray beam was stopped by a beam stop placed directly on the detector face. The exposition time was of 1800 s per frame and it was first chi-integrated to generate the conventional 2θ vs. intensity diffractogram and after it was 2θ-integrated to generate a Chi vs. intensity diffractogram.

For medium 2θ range: collimator, 500 μm; distance sample-detector, 9 cm; the collected frame (2D XRD pattern) covers a range from 3.0 up to 25.5^0 2θ. The direct X-ray beam was stopped by a beam stop placed behind the sample with an aperture of 4^0. The exposition time was of 300 s per frame and it was first chi-integrated to generate the conventional 2θ vs. intensity diffractogram and after it was 2θ-integrated to generate a Chi vs. intensity diffractogram.

For the recording of XRD patterns on oriented samples, the copolymers were mechanically oriented by shearing just below clearing temperature on a silicon single-crystal wafer surface cut parallel to the (510) plane. The exposition time was of 300 s per frame and it was first chi-integrated to generate the chi vs. intensity diffractograms. In this case XRD patterns were recorded in reflection mode.

3. Results and discussion

The aim of this work was to obtain polyamines bearing the tapered 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoate group in order to induce the formation of columnar mesophases.

3.1. Modification of model compound DMHEA and polymer PAZE

In order to choose the best reaction conditions to proceed with the chemical modification of PAZE, first we tested several esterification procedures with the commercially available model compound DMHEA, which was structurally very similar to our polymer (Scheme 1).

Thionyl chloride ($SOCl_2$) is probably the most attractive reagent for the chlorination of carboxylic acids. Thus, the chlorination of 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoic acid with $SOCl_2$ in the presence of a catalytic amount of DMF was tested. However, ^{1}H NMR spectrum showed that HCl induced cleavage of the highly reactive benzyl ether moieties also occurred. We also tried to use oxalyl chloride for the chlorination, but the same cleavage reaction was observed. We carried out the chlorination also with $SOCl_2$ in the presence of an excess of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), since Balagurusamy and coworkers [23] observed no cleavage products in the presence of an excess of a non-nucleophilic base scavenger. In our case, no cleavage products were observed, but compound 4 was obtained in low yield (32%) due to difficulties to eliminate excess of DBU.

Compound 4 can also be prepared directly from compound 1 by transesterification reactions. As we observed the cleavage of benzyl ether moieties in the presence of hydrogen chloride, we decided to try only base catalyst ($NaOCH_3$) for transesterification, different temperatures and solvents. In the reaction with the model compound we obtained compound 4 with 58% yield in the best case. However, when we applied this methodology to the chemical modification of PAZE, even using higher temperatures, longer reaction times and different solvents, we could not achieve modifications degrees higher than 20%.

Morcillo and coworkers [22] developed a method for the esterification/amidation of carboxylic acids based on the Garegg–Samuelsson reaction [24], which proposes the formation of an alkoxyphosphonium intermediate that suffers the nucleophilic attack to generate an iodo compound. In our case, by reaction with the model compound we were able to obtain compound 4 with 47% yield. However, when we performed the reaction with PAZE, modification degrees as low as 15% were obtained, probably due to the steric repulsion between the substituents of the phosphorous atom and the substituents of the alcohols, which prevented the nucleophilic attack.

Stacey and coworkers [25] suggested a method of esterification using trifluoroacetic anhydride. However, though we were able to obtain trifluoroacetic 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoic anhydride, some cleavage of the benzyl ether moieties was observed in ^{1}H NMR spectrum of compound 4.

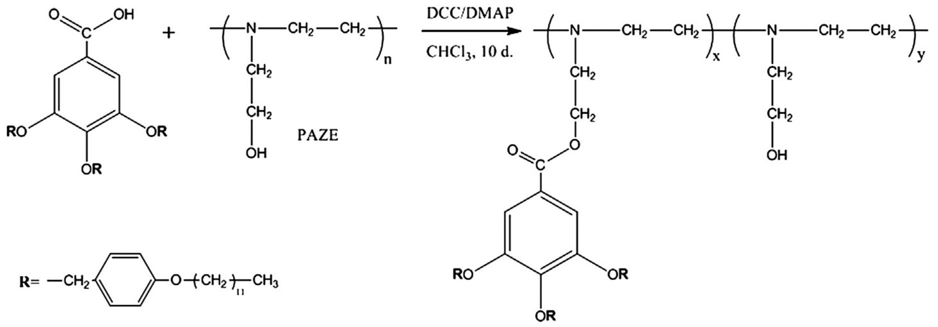
The use of *N,N'*-dicyclohexylcarbodiimide (DCC) as a promoter represents one of the most versatile esterification methods [26]. Although this reagent is irritant to skin and stoichiometric dosage or more is necessary, this procedure enjoys various advantages. The reaction usually proceeds at room temperature, and the conditions are so mild that substrates with various functional groups can be employed. The reaction is not sensitive to steric hindrance of the reactants, allowing production of esters of tertiary alcohols. As such, a wide range of applications have been achieved in the field of natural products, peptides, nucleotides, etc. however, 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 strong acids such as p-toluenesulfonic acid [27,28]. Alternatively, addition of a catalytic amount of p-aminopyridines is more effective [29,30].

To check the feasibility of this reaction with the model compound, we applied the esterification method using DCC and DMAP at room temperature. The reaction took place for 5 days and finally the desired compound 4 was obtained with 82% yield. This encouraged us to apply this reaction to the chemical modification of PAZE using a higher temperature and longer reaction time. However, high reaction temperatures gave poor results, since the degree of modification was low and we faced to the difficulties to eliminate unreacted acid. This could be explained by the occurrence of side reactions, for example, N–O intramolecular acyl migration reaction, which reduce the coupling yields, and also by the formation of acylureas, which usually exhibit very similar solubilities to the desired products, and therefore make their removal difficult to achieve. The amount of the side product is significantly affected by the experimental conditions: N-acylurea formation is less likely at lower temperatures and when solvents with low polarity are used [30]. So, when we performed the reaction with PAZE using DCC/DMAP at room temperature with chloroform as a solvent, good modification degrees were achieved and the final copolymers (PA1-PA6) were easy to purify (Scheme 2).

Chemical modification conditions, the resulting degrees of modification and yields are reported in Table 1.

The structure and composition of the copolymers were characterized by NMR spectroscopy. Fig. 1 reports the ^{1}H NMR spectrum of polyamine PA2 as an example.

All ^{1}H NMR spectra are characterized by broad signals in three regions. The aromatic region shows four partially overlapped signals at 7.3, 7.2, 6.8 and 6.7 ppm. Considering the relative integration



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

areas and by comparison with the spectrum of methyl 3,4,5-tris[4-(n-dodecan-1-yloxy)benzyloxy]benzoate, the signals at 7.3 and 7.2 ppm (8H) can be assigned to the protons of the benzoate group plus the benzyl aromatic protons *ortho* to the $-CH_2O-$. The signals at 6.8 and 6.7 ppm (4H + 2H) correspond to the benzyl aromatic protons *meta* to the $-CH_2O-$ of the lateral and central alkyloxybenzyloxy substituents respectively. The characteristic signals, corresponding to most protons of the long alkyl chains in the dendron, can be observed in the high-field region at 1.7, 1.4, 1.2 and 0.8 ppm. The most interesting region lies between 5 and 2.5 ppm in which five signals can be observed. The signal at 4.3 ppm corresponds to the methylenic protons d in the modified unit; the signal centered at 3.5 ppm corresponds to methylenic protons d' in the unmodified unit; the broad signal at 2.5 ppm corresponds to the methylenic protons a, b, c, a′, b′ and c′ in the modified and unmodified units. The signal at 3.9 ppm corresponds to the methylene attached to the oxygen in the long alkyl chains. Finally, the signal at 4.9 ppm can be assigned to the benzylic methylenes of the dodecyloxybenzyloxy substituent, which is overlapped with OH group.

Fig. 2 shows the ^{13}C NMR spectrum of the polyamine PA2 with the corresponding assignments. The aromatic and carbonyl carbons of the moiety introduced appear between 166 and 108 ppm, whereas carbons 2–12 of the long alkyl chains appear in the expected region at 32–14 ppm. The carbon 1 of the alkyl chains appears at 68.1 ppm. The chemical shifts of the benzylic methylenes depend on their relative position in the aromatic ring. Those in position 3 and 5 appear at 71.2 ppm, whereas the same carbon in position 4 appears downfield at 74.8 ppm. Similarly, aromatic signals II′ and III′ are also split. The carbons of the main chain appear at 50–60 ppm: the signals a, a′, b, b′ appear at 52.9 ppm; the signals c, c′ appear at 56.6 ppm. The methylenic carbons d and d′ of the modified and unmodified units appear resolved at 61.1 and 60.1 ppm, respectively.

The structures of copolymers were characterized and confirmed by FTIR-ATR technique. In the FTIR-ATR spectrum, a decrease of the −OH vibration band around 3360 cm^{-1}, coming from PAZE, was observed; we also detected the appearance of carbonyl group characteristic band around 1712 cm^{-1} (C=O) which confirms that polymer chemical modification occurred.

The modification degrees of copolymers were determined by NMR spectroscopy, since this methodology gave accurate results. Quantification was carried out from the ^{1}H NMR spectra by

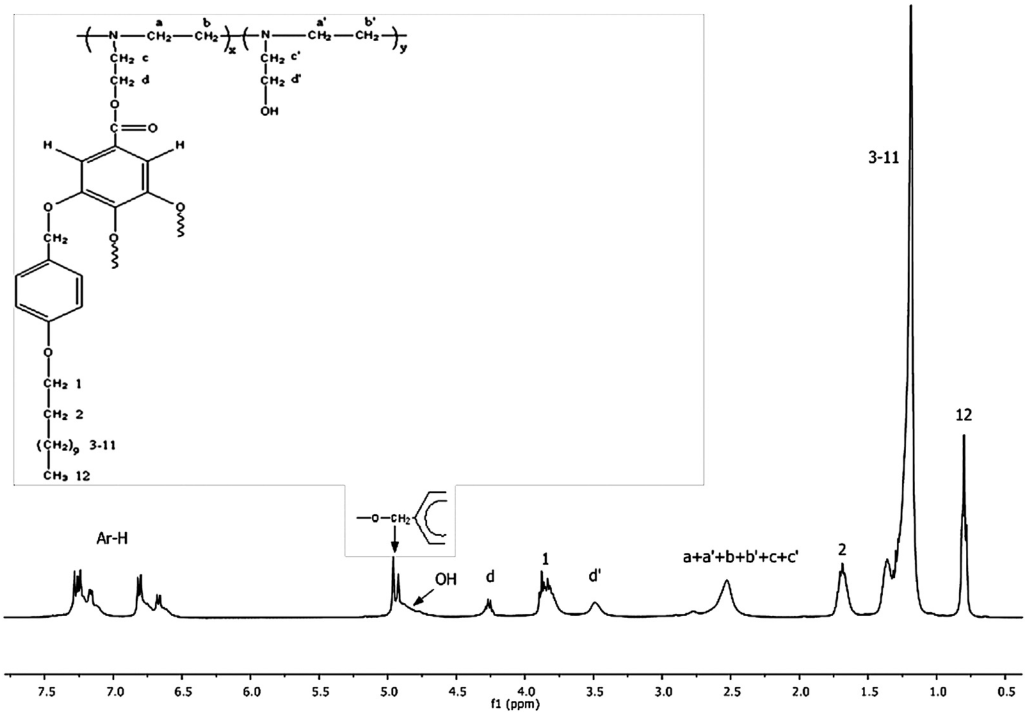


Fig. 1. ^{1}H NMR spectrum in $CDCl_3$ at room temperature of polyamine PA2.

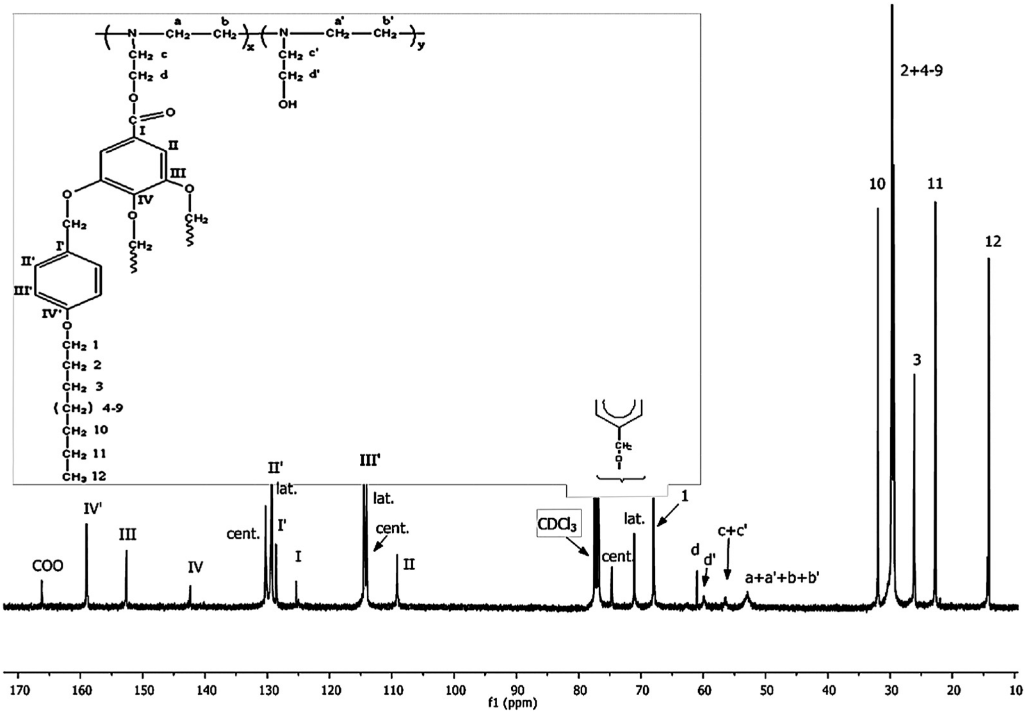


Fig. 2. ^{13}C NMR spectrum in $CDCl_3$ at room temperature of the polyamine PA2.

comparing the areas of the methylenic protons d in the modified unit at 4.3 ppm and the methylenic protons d' in the unmodified unit at 3.5 ppm.

Yields were calculated on the basis of the polymer recovery and the expected mass, considering the degree of modification achieved. PAZE was reacted with different ratios of acid (2). The degree of modification depended on the reaction conditions and ranged from 16 to 100%. The reactions performed at room temperature gave almost quantitative modification degrees and yields around 70%. On the other hand, the reaction performed at 60 °C with polymer/COOH molar ratio 1:1 gave 55% modification degree and 58% yield (copolymer PA4). As we mentioned before, the modification degree decrease found in this case could be explained by the formation of bigger amount of the side product *N*-acylurea, which reduce the coupling yields at higher temperatures.

All values of molecular weight and density are reported in Table 2.

The molecular weight of the starting polymer PAZE was determined by SEC-MALLS in N,N-dimethylacetamide as reported [17]. One might expect an increasing trend of the molecular weight with modification degree, since considerably heavy dendritic groups were introduced. Actually, it was not the case; however, one should keep in mind that molecular weight values were determined by SEC under the assumption that the copolymers behave like polystyrene in THF. For this reason, it is not easy to predict a trend of the molecular weights with the modification degree, since the introduction of the dendritic groups can lead to significant changes in copolymer conformation and greatly modify the hydrodynamic volume of the PA1–PA6 systems with respect to the starting polymer. Actually, the molecular weights of modified PA1–PA6 copolymers, which were obtained relatively to polystyrene in THF, were found considerably lower than the molecular weight of starting PAZE, determined by SEC-MALLS in N,N-dimethylacetamide. This suggests that a considerable change in copolymer conformation occurs as a consequence of the introduction of the bulky dendrons.

Table 2
Molecular weights and densities of PA1-PA6 copolymers determined by SEC in tetrahydrofuran.

Polymer	$M_n \cdot 10^{-3}$ (g mol^{-1})	$M_w \cdot 10^{-3}$ (g mol^{-1})	ρ (g cm^{-3})
PAZE[a]	3.80	7.70	–
PA1	1.61	1.76	1.09
PA2	1.74	1.88	1.10
PA3	1.83	2.10	1.14
PA4	1.41	1.44	1.02
PA5	1.79	2.02	1.12
PA6	1.54	1.57	1.02

[a] Molecular weight values determined by SEC-MALLS in N,N-dimethylacetamide [16].

3.2. Mesomorphic and thermal characterization of PA1–PA6

The mesomorphic characterization was performed on the basis of differential scanning calorimetry (DSC), optical microscopy between crossed polars (POM), and X-ray diffraction experiments (XRD). In most cases, the first calorimetric analysis showed a broad small endotherm at low temperature and a second sharper and bigger one centered at higher temperature. This suggested that these samples, due to their quite regular structure and relatively low molecular weight, tended to crystallize partially. Therefore, we annealed them for 2 h at temperatures located slightly below the first peak maximum and then we performed DSC analysis again. The first endotherm could be therefore related to a melting, while the second one was attributed to a clearing transition, as showed by POM. As a matter of example, Fig. 3 shows the liquid crystalline texture of PA3 at 32 °C and PA4 at 35 °C, respectively, observed by POM on cooling from the isotropic phase. These images show the typical dendritic growth aggregates of a discotic columnar mesophase.

Table 3 reports the melting and clearing temperatures, as well as the clearing enthalpies of PA1–PA6 samples.

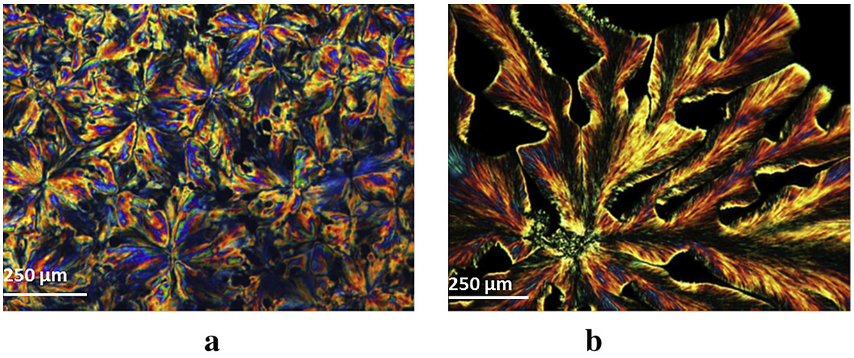


Fig. 3. Optical micrographies between crossed polars on cooling from the isotropic phase of (a) PA3 at 32 °C and (b) PA4 at 35 °C.

In the case of PA4 and PA5, DSC analysis just put into evidence one endotherm, which could be related to the clearing point. On increasing the modification degree, clearing points and enthalpies of the copolymers also increased, similarly to what was reported for columnar copolyethers obtained by modification of poly(epichlorohydrin) with the same Dendron [11]. As one could expect, the clearing enthalpies were found lower than in the case of similar low molecular weight dendrons [31]. On the other hand, clearing enthalpy values resulted considerably higher than in the case of the aforementioned copolyethers based on poly(epichlorohydrin) modified with the same dendron. This can be explained by the presence of the polyamine backbone which, due to its higher symmetry with respect to poly(epichlorohydrin), allowed better ordering of the dendritic side moieties.

XRD analysis was performed at different temperatures in order to confirm calorimetric features and to identify the copolymers mesophase. Prior to XRD analysis, copolymers PA1–PA3 and PA6 were annealed as previously described. Below T_m, XRD pattern of these samples showed the presence of very small diffraction peaks, which subsequently disappeared on heating above T_m. This confirmed the presence of crystalline portions in the annealed sample. These small diffraction peaks could be also foreseen in the XRD pattern of PA4 and PA5 recorded in the range 0°–20 °C, thus suggesting also in those cases the existence of crystalline domains, whose melting could not be seen by DSC.

In all cases, XRD analysis of the copolymers below T_c showed a sharp reflection, located around $2\theta = 2.3°$, and a broad halo at 2θ about 19.5°. This diffractogram is compatible with a columnar mesophase, the lower spacing corresponding to the average distance between dendrons, which is related to adjacent benzene rings and to the low ordered alkyl groups; the higher spacing corresponds to the lateral distance between columns. The former 2θ value corresponded to the d_{100} plane of a columnar phase and allowed to calculate the dimensions of the unit cell, while the latter could be referred to the distance between dendrons [11,32]. Table 4 reports the features of the X-ray patterns of PA1–PA6 copolymers below clearing temperature. The XRD patterns, recorded on samples oriented by shearing, showed that dendrons are perpendicular to the column axis in the whole copolymer series PA1–PA6.

Table 3
Calorimetric features of PA1-PA6 copolymers.

Copolymer	Modification degree (%)	T_m (°C)[a]	T_c (°C) [a]	ΔH_c [a] (kJ/mol)[d]	Mesophase
PA1	16	8	30–50[c]	5.6	Col
PA2	39	3	37	5.7	Col
PA3	46	8	39	11.8	Col
PA4	55	n.d.[b]	39	24.1	Col
PA5	67	n.d.[b]	43	24.9	Col
PA6	100	55	65	34.9	Col

[a] For PA1–PA3, melting temperature, clearing temperature and enthalpy determined after 2 h annealing in the range −10° to −5 °C; for PA6 after 2 h annealing at 45 °C.

[b] Not determined.

[c] Broad peak.

[d] Expressed per mol of repeat unit.

For a hexagonal columnar mesophase, and given the experimental densities ρ, one can calculate the number of repeat units of copolymer μ that are present in a hexagonal prism layer of height c from the following equation:

$$\rho = \frac{2\mu M}{\sqrt{3}N_A a^2 c} \tag{1}$$

where M is the average molecular weight of the repeat unit, N_A is Avogadro's number, $a = 2d_{100}/\sqrt{3}$ is the dimension of the hexagonal unit cell, and c is the prism height (distance between dendrons). By considering the experimental modification degree of the copolymer α, we can finally find the number of dendrons contained in a unit cell, $\delta = (\mu \times \alpha)/100$. We have not demonstrated a hexagonal columnar organization for PA1–PA6 copolymers. In spite of this, the same calculation can be applied to our samples in order to give a rough estimation of the number of dendrons, because geometrical considerations allow the assumption that in a columnar mesophase (such as shown by PA1–PA6) the columns self-assemble in a compact hexagonal packing where statistical fluctuations in the column positions do not produce any of the additional reflections that are expected in a Col_h phase: that is, the instantaneous positions of the columns fit a hexagonal organization even if the average positions do not [10].

In all cases the dimension of the unit cell ranged around 45 Å, that is, was slightly narrower than in the case of the copolyethers bearing the same dendron [14]. This is probably due to the shorter spacer linking the backbone and dendron on copolyethers derivatives, which forced the backbone to adopt a broader helical

Table 4
X-ray diffraction patterns of PA1–PA6 copolymers below clearing temperature.

Copolymer	Spacings[a] (Å)	a (Å)[b]	μ[c]	δ[d]
PA1	4.5 (b), 40 (s)	46	21.9	3.5
PA2	4.5 (b), 38 (s)	44	10.5	4.1
PA3	4.5 (b), 38 (s)	44	9.6	4.4
PA4	4.5 (b), 41 (s)	47	8.5	4.7
PA5	4.5 (b), 40 (s)	46	7.5	5.0
PA6	4.5 (b), 39 (s)	45	4.6	4.6

[a] b = broad halo; s = sharp reflection.

[b] Dimension of the hexagonal unit cell.

[c] Number of repeat units contained in a unit cell.

[d] Number of dendrons contained in a unit cell.

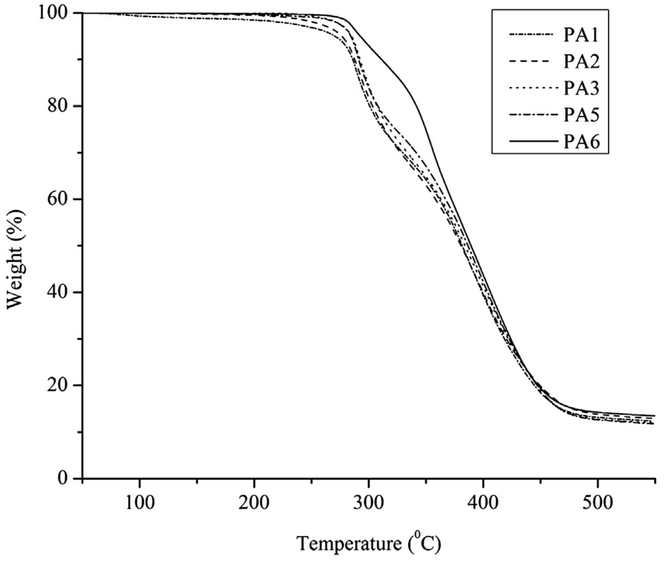


Fig. 4. TGA thermograms of selected copolymers recorded at a heating rate of 10 °C/min.

conformation to successfully accommodate the dendrons. It must be noted that in PECH derivatives, dendrons are not perpendicular to the column axis, but tilted; this can also be explained on the basis of its shorter spacer. In the case of PA1–PA6, the number of dendrons contained in a unit cell is roughly independent (3–5) on the degree of modification, and consequently the number of repeat units μ decreases as the degree of modification increases.

The thermal stability of the polymers was studied using TGA. As an example, TGA scans of selected samples are reported in Fig. 4.

The onset of thermal decomposition (determined as the temperature corresponding to 5% mass loss) ranged between 270 and 300 °C. The onset of thermal decomposition increased on increasing the copolymers modification degree, probably due to higher amount of mesogenic groups introduced in the structure. Copolymer PA6 behaved the best in this respect, exhibiting a mass loss onset temperature of 293 °C. As far as char yield is concerned, in the case of starting PAZE it was only 1.4% at 600 °C [17], while all the copolymers showed more than 10% char yield at 800 °C. Again, PA6 behaved the best in this respect, exhibiting a char yield of 11.8%.

4. Conclusions

A family of copolyamines bearing the tapered 3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoate group was synthesized by chemical modification of poly[2-(aziridin-1-yl)ethanol] (PAZE). The chemical modification was tackled by different procedures on the model compound *N*,*N*-dimethyl-2-hydroxyethylamine, and we finally found that the esterification method with N,N′-dicyclohexylcarbodiimide at room temperature, in the presence of 4-dimethylaminopyridine, gave the highest yield. In the case of PAZE, the reactions performed at room temperature gave almost quantitative modification degrees and yields around 70%. The resulting copolymers showed higher char yield than starting PAZE. Moreover, all of them exhibited small crystalline portions after annealing, as well as columnar mesophases, as inferred by DSC, XRD and POM. The dimension of the unit cell resulted slightly narrower than in the case of the copolyethers bearing the same dendron, probably due to the longer spacer present in PAZE, which allows better accommodating of the side tapered group. This first example of LC columnar polyamine can represent a potential candidate for preparing proton-transport membranes by the channel mechanism, due to the presence of basic nitrogen atoms in the inner helical backbone structure.

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