



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



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ARTICLE INFO

Article history:

Received 10 May 2013

Received in revised form

4 July 2013

Accepted 9 July 2013

Available online 15 July 2013

Keywords:

Chemical modification

Liquid crystalline polymers

Columnar mesophase

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.

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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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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 ($\text{BF}_3 \cdot \text{EtNH}_2$) in the absence of solvent at 45 °C: in this case, a polymerization degree of about 44 monomeric units 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) trifluoroacetic 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 $-\text{CH}_2-\text{O}-$ in lateral benzylic units), 7.18 (d, 2H, ArH meta to $-\text{CH}_2-\text{O}-$ in central benzylic units), 6.69 (m, 6H, ArH ortho to $-\text{CH}_2-\text{O}-$), 4.95 (m, 6H, Ph– CH_2-O in lateral benzylic units), 3.86 (m, 6H, $-\text{CH}_2-\text{O}-\text{Ph}$), 1.66 (m, 6H, $-\text{CH}_2-\text{CH}_2-\text{O}-\text{Ph}$), 1.37 (m, 6H, $-\text{CH}_2(\text{CH}_2)_2-\text{O}-\text{Ph}$), 1.19 (m, 48H, $-(\text{CH}_2)_8-$), 0.81 (t, 9H, $-\text{CH}_3$).

^{13}C NMR (CDCl_3 , TMS, δ , ppm): 167.3 (COCF_3), 159.2 (ArC para to $-\text{CH}_2-\text{O}-\text{Ph}$), 153.0 (COOCOCF_3), 152.7 (ArC meta to COO), 143.2 (ArC para to COO), 130.5 (ArC ipso to COO), 129.4 (ArC ortho to $\text{CH}_2-\text{O}-\text{Ph}$ in central benzylic unit), 128.6 (ArC ortho to $-\text{CH}_2-\text{O}-\text{Ph}$ in lateral benzylic units), 125.6 (ArC ipso to $-\text{CH}_2-\text{O}-\text{Ph}$ in lateral benzylic units), 114.3 (ArC meta to $-\text{CH}_2-\text{O}-\text{Ph}$ in central benzylic unit), 114.2 (CF_3), 109.7 (ArC ortho to COO), 74.8 (Ph– $\text{CH}_2-\text{O}-\text{Ph}$ in central benzylic unit), 71.1 (Ph– $\text{CH}_2-\text{O}-\text{Ph}$ in lateral benzylic units), 68.2 (R– $\text{CH}_2-\text{O}-\text{Ph}$), 32.4 ($-\text{CH}_2\text{CH}_2\text{CH}_3$), 30.1–28.3 (C2 and C4 to C9 in aliphatic chains), 26.2 (Ph– $\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-$), 22.8 ($-\text{CH}_2\text{CH}_3$), 14.3 ($-\text{CH}_2\text{CH}_3$).

^{19}F NMR (CDCl_3 , TMS, δ , ppm): -75.0 (CF_3).

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

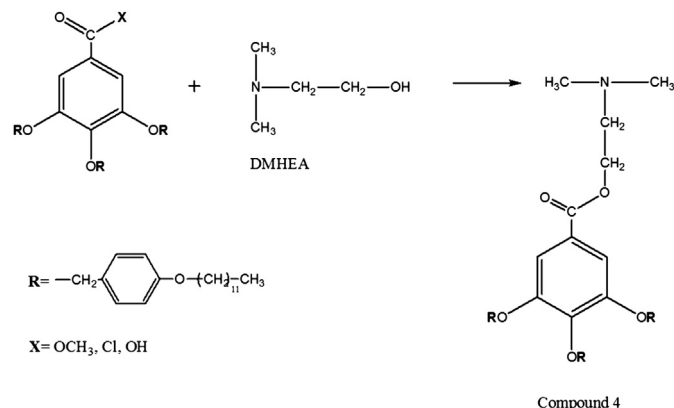
2.1.3. Synthesis of 2-(dimethylamino)ethyl 3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoate (**4**) (Scheme 1)

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.

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