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Mesomorphism from Bent-Core Based Ionic Dendritic Macromolecules

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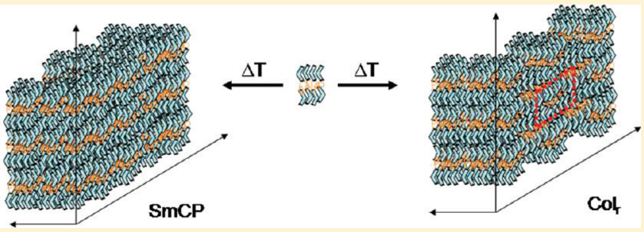
S *Supporting Information*



ABSTRACT: A wide variety of ionic dendritic macromolecules based on bent-shaped structures have been synthesized and fully characterized. Regular polypropyleneimine dendrimers (PPI) of different generations and a random hyperbranched polymer (PEI) were selected as dendritic cores. Different bent-core structures derived from the 3,4′-biphenyl angular core with 5 or 6 aromatic rings as well as short and long terminal chains and spacers have been used for this study. The bent-core structure acts as strong driving force for the supramolecular arrangement of this type of macromolecules. All of the ionic dendritic polymers prepared show mesogenic behavior over broad temperature ranges, even if the carboxylic acid precursors were not mesomorphous. An extensive chemical structure-supramolecular organization relationship has been proposed for first time for this kind of bent-core dendrimer. Two types of supramolecular packing with lamellar and columnar order have been proposed on the basis of polarizing optical microscopy, differential scanning calorimetry, and X-ray diffraction. Additionally, fibers that present anisotropic optical behavior can be drawn from the materials. These results open new and stimulating possibilities for both bent-core based and dendritic supramolecular systems, with interest in basic and applied supramolecular chemistry and materials science scenarios.

KEYWORDS: supramolecular chemistry, ionic dendrimers, dendritic polymers, bent-shaped molecules, liquid crystals

INTRODUCTION

Liquid crystal dendrimers, also known as dendromesogens,[1] constitute a significant and original type of matter in the field of Supramolecular Chemistry. Indeed, it is possible to obtain dendritic architectures that display liquid crystalline arrangements by the introduction of rod-like or disk-like mesogenic units at the periphery of a dendritic core, thus forming a mesomorphic shell around the central dendritic nucleus. This strategy has been employed to obtain a variety of calamitic or columnar mesophases that add control of the supramolecular organization to the exciting characteristics of dendrimers.

Interestingly, in the field of liquid crystals (LC), the so-called *bent-core liquid crystals* (BCLC) have become a topic of increasing interest since Niori et al.[2] reported them for the first time in 1996. Due to the particular bent shape of their molecules, these materials are able to organize in such a way that their rotational freedom in the mesosphase is significantly restricted. As a result of this compact arrangement a polar order occurs that gives rise to a wide variety of new columnar and lamellar mesophases,[3] which provide very attractive characteristics in bulk. The examples range from academic curiosities, i.e., supramolecular chirality and its control, to application interests involving ferroelectric or antiferroelectric switching under electric fields, optical biaxiality or highly efficient NLO, and piezoelectric responses—despite the fact that achiral molecules are used.[3,4] However, a major drawback of the majority of these compounds is that such appealing liquid crystal packing is generally achieved far from room temperature, thus limiting both the possibilities for studying them and, more importantly, to process them for application purposes. In this respect, new strategies to stabilize these supramolecular arrangements at lower temperatures have been evaluated and several of them have focused on the design and processing of macromolecules bearing bent-shaped structures.[5]

The first BCLC dendrimer was reported by Tschierske et al. in 2002.[6] In this work, a first generation carbosilane-type dendrimer was functionalized with bent-core moieties. The same group later prepared the third generation of the same carbosilane dendrimer functionalized with bent-core mesogenic units in the periphery.[7] All of these materials showed microsegregation of the carbosilane core and the bent-shaped structures, leading to ferroelectric and antiferroelectric SmCP organizations.[8] Dendrimers based on silicon, polyhedral oligomeric silesquioxanes (POSS),[9] and oligosiloxanes[10] have also been functionalized with bent-core promesogens.

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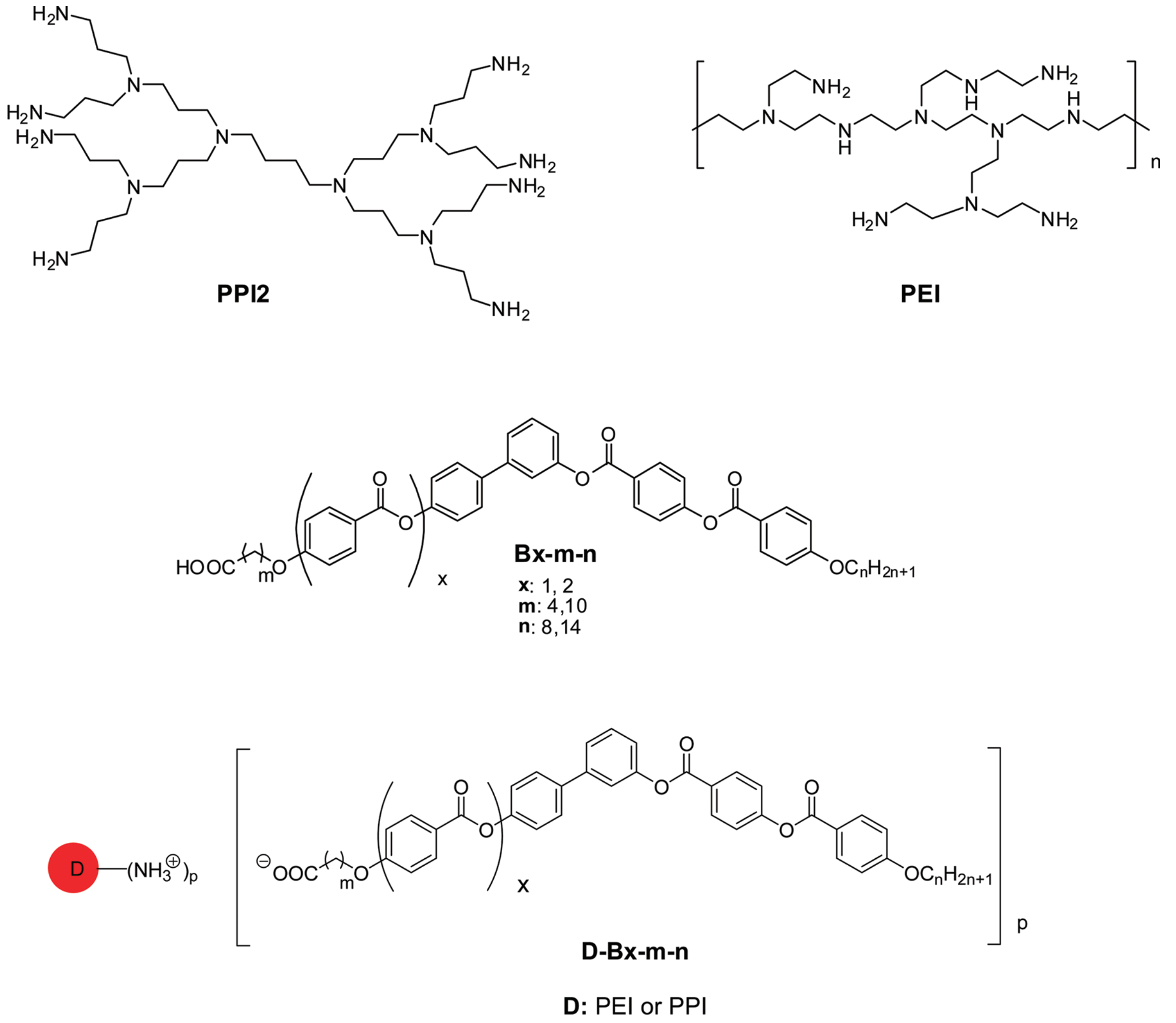


Figure 1. Structure of the 2nd generation polypropyleneimine dendrimer (**PPI2**), the polyethyleneimine hyperbranched polymer (**PEI**), the acid-ended bent-shaped molecules (**Bx-m-n**) used as promesogenic structures, and the general chemical structure of bent-core based ionic polymers studied (**D-Bx-m-n**).

In 2005 a few covalent dendrimers that incorporated bent-core units in the first and second generation of a PPI dendrimer were also described by Tschierske's group[11] and, interestingly, these materials exhibit either lamellar or columnar bent-core mesophases.

In spite of this relevant research, a systematic study on the chemical structure—liquid crystalline properties of BCLC dendrimers is lacking, mainly due to the acknowledged synthetic difficulties. Unfortunately, this drawback has seriously limited the potential of this kind of macromolecule in the target of achieving size-controlled macromolecules with the ability to organize through supramolecular packing.

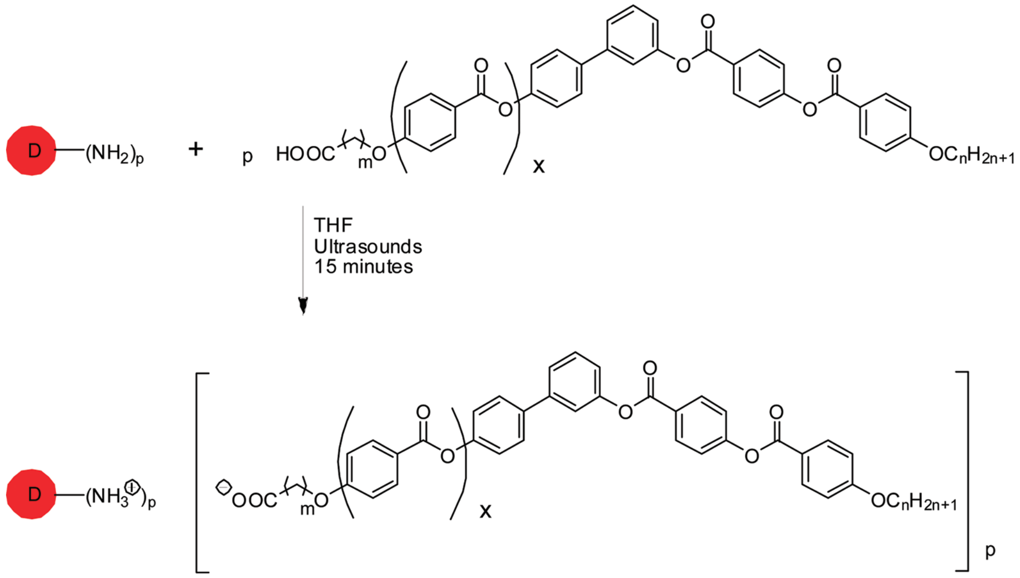
Ionic dendrimers have emerged as a desirable type of dendromesogen. These macromolecules, in which the promesogenic units are attached to the dendritic system by electrostatic interactions, have attracted great interest in traditional LC due to two main aspects, their easy preparation and the fact that they can be considered as valid alternatives to covalent analogs for a number of purposes. The majority of ionic dendromesogens are based on PPI and PAMAM systems and, depending on the promesogenic structures used, calamitic, columnar, and even cubic mesophases have been described.[12]

Herein, we report the first extensive systematic study on BCLC dendritic macromolecules and several series of ionic polymers incorporating bent-core units that have been synthesized and fully characterized. The ionic dendrimers derived from several polypropyleneimine (PPI) dendrimer generations, namely the first (**PPI1**), second (**PPI2**), third (**PPI3**) and fifth (**PPI5**), as well from a random hyperbranched polymer of polyethyleneimine [(**PEI**) (M_n = 10 000)] have been prepared by the spontaneous assembly of their amine groups in the periphery with different acid-ended bent-shaped structures (**Bx-m-n**) (Figure 1).

Ionic polymers are denoted by the dendritic nucleus type followed by the nomenclature of the acid-ended bent-shaped molecule used. As an example, **PPI1-B1-10-14** represents the ionic dendrimer formed from the first generation of PPI (**PPI1**) and the acid-ended bent-shaped compound with 5 aromatic rings (**B1**), and **10** and **14** carbon atoms at the inner and outer flexible tail, respectively.

It should be mentioned that the congested bent-core based dendrimers (up to 64 promesogenic units) and hyperbranched polymers (with a high number of amino groups on the dendritic surface, ~75 amino groups on average) that have very attractive possibilities,[13] have been prepared for the first time.

Scheme 1. Synthesis of Ionic Polymers



The liquid crystalline properties of these new ionic dendrimers have been thoroughly investigated by means of polarizing microscope (POM), differential scanning calorimetry (DSC), thermal analysis (TGA), and X-ray diffraction (XRD). On the basis of the results obtained, relevant conclusions concerning the chemical structure—supramolecular organization of BCLC macromolecules are proposed. In particular, the way in which structural changes brought about by changing the size of the dendrimer by using different generations of PPI or the regularity of branching (using hyperbranched PEI) affect the liquid crystal behavior of this kind of macromolecule is analyzed. Furthermore, a number of variations were made to the promesogenic core. In this respect, the effect on the mesomorphic properties of the ionic macromolecules of the length of the flexible chains in the inner (m: 4, 10) or the outer (n: 8, 14) tails of the promesogenic unit, as well as the number of aromatic rings (x: 1, 2) in the bent-rigid structures, have been explored.

RESULTS AND DISCUSSION

1. Synthesis of the Compounds. The general synthetic procedures to prepare all the bent-shaped acids are outlined in Schemes S1 and S2 of the Supporting Information (SI). It should be pointed out that a new and alternative synthetic procedure for the acid-ended 3,4′-bipyphenyl molecules, which differs from the approaches used previously,[10,14] is reported here.

The ionic complexes were prepared according to the method reported by Crooks.[15] A solution of the commercial amine-terminated PPI dendrimer or random hyperbranched PEI polymer in dry THF was added to a solution of acid in the same solvent (1:1 stoichiometry between the acid and each of the N-terminal amine groups present in the dendrimer or hyperbranched polymer) (Scheme 1). The mixture was sonicated for 15 min and then the solvent was evaporated. The ionic polymers were dried under vacuum. Further experimental details of all these synthetic processes are available as Supporting Information.

2. Spectroscopic Studies. The proton transfer from the carboxylic acid to the amine group, which gives rise to the ionic macromolecules, was studied by NMR and FT-IR spectroscopy (see SI).

NMR Studies. ***(a).*** ***^{1}H NMR Studies in Solution.*** NMR spectra of all the compounds were obtained in $CDCl_3$ at 25 or 50 °C depending on the solubility of the complexes. The chemical structures of the ionic polymers were confirmed by one-dimensional ^{1}H and ^{13}C NMR spectroscopy and by two-dimensional ^{1}H−^{1}H COSY, ^{1}H−^{13}C HSQC, and ^{1}H−^{13}C HMBC experiments (see SI).

Interestingly, two different sets of peaks can be observed for these complexes by ^{1}H NMR, a phenomenon that has not been reported previously for ionic dendrimers.[12a,b,f,g] In these spectra a set of well-resolved signals was observed along with several broad peaks (Figure 2b.)

Analysis of the well-resolved peaks shows a clear shift of the signals corresponding to H_α of both the amine and carboxylic acid moieties of the single components in comparison to the dendrimeric ones. This change is consistent with the formation of ionic interactions and hence the presence of the ionic bent-core based dendrimers (Figure 2). A downfield shift (from 2.6−2.7 ppm for the PPI to 2.9−3.0 in the complexes) was observed for H_α of the $-NH_2/-NH_3^+$ groups on the dendritic part [CH_2(z)]. These peaks are correlated through HSQC with the ^{13}C shifts associated with the corresponding ^{13}C shifts from 38.6−39.9 ppm for the PPI to 40.2−40.7 ppm in the complexes (see also SI Figure S6). In contrast, an upfield shift (from 2.48−2.30 ppm in the acids to 2.38−2.20 ppm in the complexes) is observed for H_α of the carboxylic acid on the bent-core moiety [CH_2(1)] due to the ionic formation process; this change correlated to ^{13}C shifts from 33 to 35−37 ppm. These results are in good agreement with those reported for other ionic dendrimers.[12a,b]

Additionally, significant upfield shifts corresponding to the resonance of the aromatic protons and OCH_2 (4) on the carboxylic chain also occurred. This shift was noticeable for all aromatic protons, but the shifts observed for H_{a1} and H_{a2} close to the carboxylic chain are remarkable at almost 80 Hz. The shift is more marked the lower the number of aromatic rings on the bent

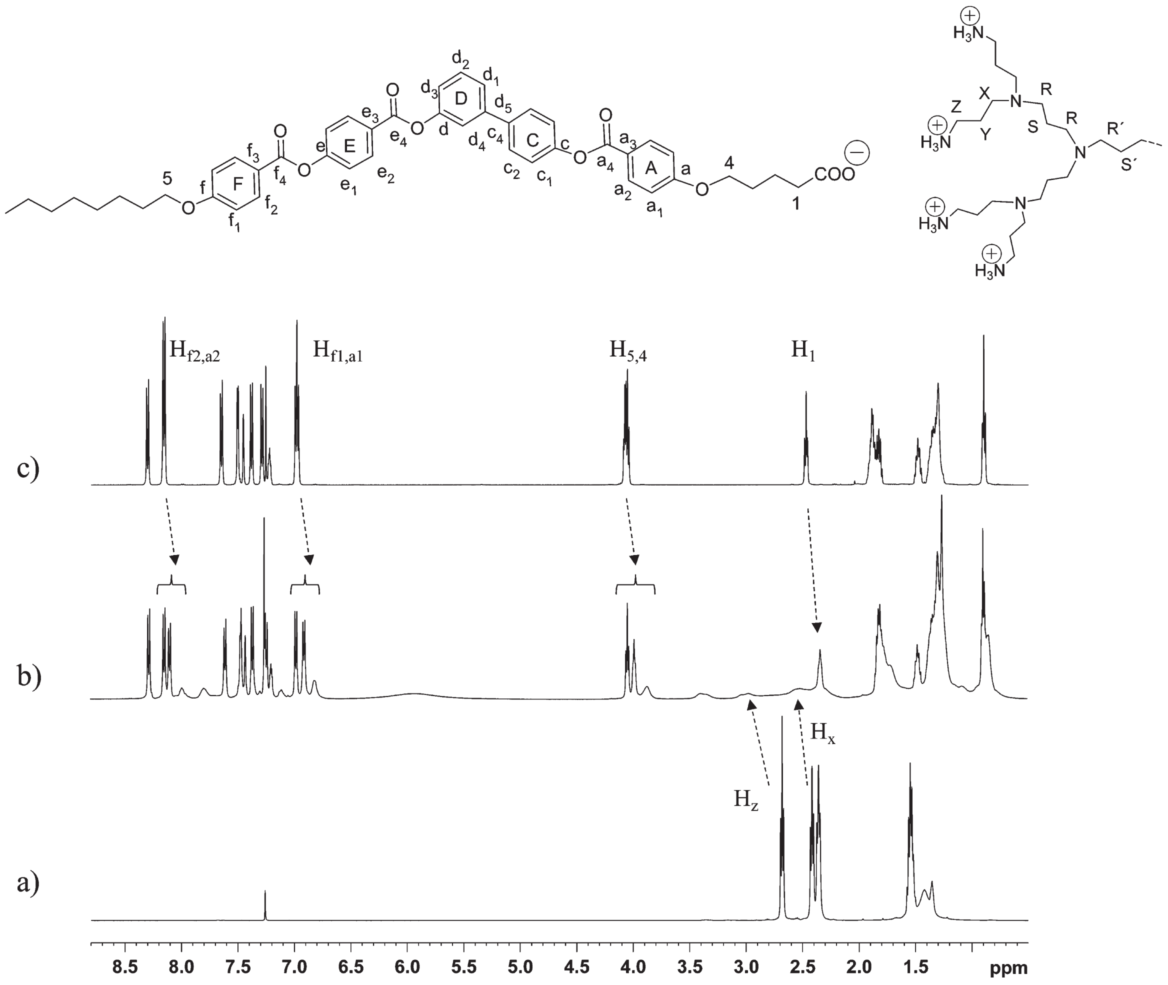


Figure 2. ^1H NMR spectra in $CDCl_3$ at 25 °C of (a) the dendrimer **PPI2**, (b) complex **PPI2-B1-4-8**, and (c) the acid **B1-4-8**.

core (series B1), the shorter the flexible spacer (m:4), and the higher the PPI generations. This trend could be due to the proximity of bent-core moieties forced by the dendritic structure (see Figure 2 and also SI Figure S13).

To determine the origin of the broad signals detected in the NMR spectra of these complexes, different studies were carried out for regular and random hyperbranched macromolecules:

1. NOESY experiments provided information about $^1H-^1H$ proximity. Interestingly, the broad aromatic signals show cross-peaks with the H_α atoms on the carboxylic spacers [$-CH_2$ (1)] as well as with the dendritic branch chains (see SI, Figure S14).
2. DOSY experiments (diffusion ordered spectroscopy) revealed two different diffusion coefficients: one related to the well-resolved peaks and the other related to the broad signals (see SI, Figure S15). From these data the presence of two species in solution could be inferred. Furthermore, the species with the lowest diffusion coefficient (around 20% lower), and therefore with the largest size or volume, is responsible for the broad peaks. Furthermore, both of these species are different from the bent-shaped or the PPI (or PEI) components used to generate the ionic complex, but they do consist of both the bent-core moiety and the polyamine dendritic structure (see SI, Figure S11).

Based on these results and those of additional studies gathered in the SI, we propose that these macromolecules in solution show some kind of aggregation in an equilibrium that is slow on the NMR time scale. Such peculiarity could be connected with the diblock character of these molecules, origin of the aggregation-capacity reported in the literature for some ionic amine terminated polymers.[15,16] However, taking into account that such results have not been observed for ionic calamitic dendrimers (see SI Figure S10), we could reasonably attribute the effect to the bent-shaped moieties. It is feasible that the characteristic compact packing of this kind of bent-structure occurs to some extent in solution to promote self-assembled species with a lower mobility. Additional research is currently in progress, with the aim to explore the ability of these kinked molecules to prop up size- and morphology-controlled aggregates in solution, a hot-topic on the route to self-assembling and self-organizing functional materials.

b). ^{13}C NMR Studies in Bulk. To assess the formation of the ionic complexes in bulk, ^{13}C−CPMAS NMR experiments were performed. Furthermore, to investigate the presence of free acid in these samples, the synthesis of one of the dendrimers (**PPI2-B1-4-8**) with 20% excess acid was carried out. The ^{13}C−CPMAS NMR spectra of a carboxylic acid (**B1-4-8**) and several ionic compounds are shown in Figure 3, along with the spectra of the 1/1 ionic dendrimer, the 1.2/1 dendrimer prepared with excess

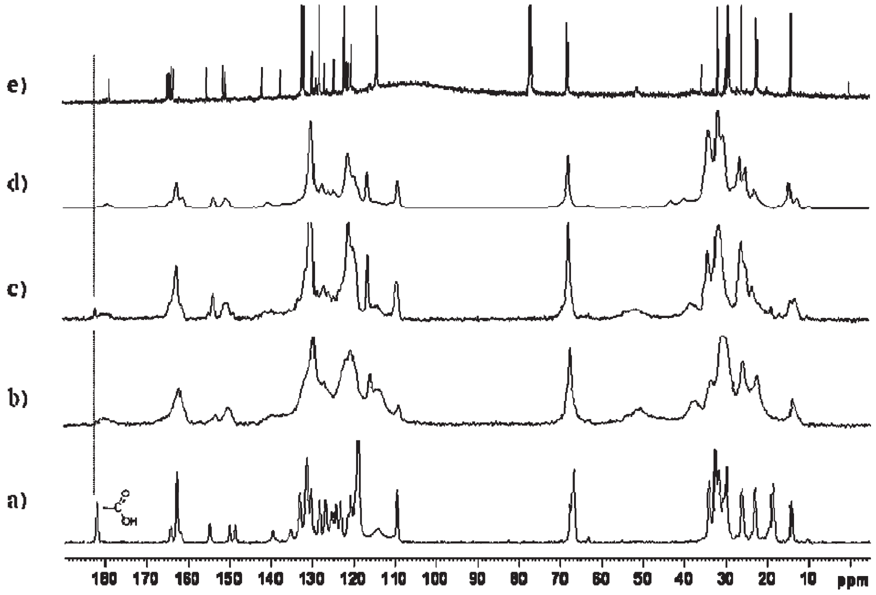


Figure 3. ^{13}C−CPMAS NMR spectra of (a) acid **B1-4-8**, (b) complex **PPI2-B1-4-8**, (c) complex **PPI2-B1-4-8** with 20% excess acid **B1-4-8**, (d) ammonium salt (**A-B1-4-8**), and (e) ^{13}C NMR spectrum in $CDCl_3$ of complex **PPI2-B1-4-8**.

Table 1. Transition Temperatures and Enthalpies As Determined by DSC for the Ionic Polymers

	compound	phase transition temperature [°C] and enthalpy [kJ mol^{-1}]^{a,b}	$\Delta H_{\text{M-I/m.u.}}$[kJ mol^{-1}]^{c}
1	**PPI1-B2-10-14**	Cr 91 [181.8] SmCP 169 [90.0] I	22.5
2	**PPI2-B2-10-14**	Cr 93 [335.1] SmCP 171 [149.6] I	18.7
3	**PPI3-B2-10-14**	Cr 99 [203.3] SmCP 163 [321.3] I	20.1
4	**PPI5-B2-10-14**	Cr 96 [1059.1] SmCP 164 [1044.5] I	16.3
5	**PPI1-B1-10-14**	Cr 104 [123.3] SmCP 156 [26.5] I	6.6
6	**PPI2-B1-10-14**	Cr 100 [408.0] SmCP 151 [65.8] I	8.2
7	**PPI2-B1-4-14**	Cr 94 [157.0] SmCP 144 [37.6] I	4.7
8	**PPI2-B1-10-8**	Cr 82 [94.2] Col$_r$ 161 [50.0] I	6.3
9	**PPI2-B1-4-8**	Cr 76 [48.2] Col$_r$ 138 [35.2] I	4.4
10	**PPI5-B1-4-8**	Cr 75 [1256.5] Col$_r$ 139 [299.9] I	4.7
11	**PEI-B2-10-14**	Cr 87 [830.6] SmCP 162 [670.8] I	8.9
12	**PEI-B1-10-14**	Cr 93 [849.6] SmCP 141 [26.5] I	2.9
13	**PEI-B1-4-14**	Cr 90 [1286.2] SmCP 135 [295.8] I	3.9
14	**PEI-B1-10-8**	Cr 82 [279.1] Col 112 [282.6] I	3.8
15	**PEI-B1-4-8**	Cr 80 [267.1] Col$_r$ 139 [574.2] I	7.6

[a] Data determined in the first scans at a scanning rate of 10 °C/min. Maxima of a broad peak for the clearing points. [b] Cr: crystal; SmCP: Polar smectic C mesophase. Colr: rectangular columnar mesosphase, Col: columnar mesophase. I: isotropic liquid. [c] Enthalpy of the mesophase-to-isotropic transition per promesogenic unit.

acid, and the salt **A-B1-4-8** (*n*-pentyl ammonium salt of **B1-4-8**, see SI).

Two main points can be highlighted from these studies. First, the presence of free carboxylic acid can be detected in the bulk if it exists, although this is apparently not the case for the dendritic macromolecules reported here. Thus, proton transfer appears to be the origin of the ionic polymers studied. In contrast, experiments in solution were not suitable to determine the presence of free acid. Second, in the bulk a significant upfield shift of the ^{13}C aromatic resonances can be observed with respect to the solution spectra in $CDCl_3$, suggesting a dense packing of bent-core molecules in the bulk.

3. Thermal Characterization. *Thermal Stability Studies.* Thermal studies of the ionic materials were carried out by thermogravimetric analysis (TGA) (see SI, Figure S4). The heating rate was 10 °C/min and the weight losses against temperature were recorded. In general, the first weight loss occurred up to 220 °C. Likewise, lower generation ionic dendrimers (weight losses around 240 °C for PPI1 and PPI2 dendrimers) are more stable than the higher generation materials (weight losses at 225 and 180 °C for PPI3 and PPI5 dendrimers, respectively). Random hyperbranched ionic complexes (PEI) can be compared with those of the higher generation PPI dendrimers (weight losses at 225 °C). However, the number of rings or the length of the terminal chains of the bent-core units did not have any appreciable effect on the thermal stability.

Liquid Crystal Properties. The bent-core intermediates and the ionic polymers were investigated by polarized light optical microscopy (POM) on a hot stage, by differential scanning calorimetry (DSC), and by variable temperature X-ray diffraction (XRD) studies.

Mesomorphic Properties of the Bent-Shaped Intermediates. The phase transitions of all the bent-shaped carboxylic acids and their corresponding benzyl esters were studied (see SI compounds **17**−**21**). The thermal properties of benzyl esters **20** and **21** and the carboxylic acids **B1-10-14** and **B2-10-14** have already been described[11,14] and their properties are in good agreement with those reported previously.

Short benzyl esters reported here (**17**−**20**) do not form mesophases, and lamellar mesomorphism was only detected for benzyl ester **21**, which has 6 aromatic rings and the longest flexible tails. In the case of the carboxylic acids, only compounds containing a long *n*-tetradecyloxy chain as the terminal tail (namely, **B1-4-14**, **B1-10-14**, and **B2-10-14**) show a monotropic mesophase, regardless of the number of aromatic rings present in the rigid core of the molecule and the length of the HOOC−$(CH_2)_m$− chain. A slight increase in the transition temperatures can be observed on increasing the number of aromatic rings in the structure, as expected. Unfortunately, a conclusive assignment of these monotropic mesophases could not be made due to crystallization of the samples during the X-ray diffraction experiments. However, observation of the textures under polarized optical microscope pointed toward a SmCP-like mesophase because a *schlieren* texture with some Maltese crosses, as reported previously for this mesophase, were observed on cooling the isotropic liquid (see SI, Figure S5a).

*Mesomorphic Properties of the Ionic Polymers. (**D-Bx-m-n**).* Transition temperatures and enthalpy changes for the ionic materials are gathered in Table 1. These data correspond to the first heating scans at 10 °C/min as the sample decomposed in the isotropic liquid, as reported for numerous ionic dendromesogens.[12b] However, all materials appeared to be stable far from their clearing transition. Thus, they showed reproducible melting transitions if temperatures of 30−50 °C above the melting point were reached in all cycles. These dendritic macromolecules appear as pristine semicrystalline materials, and in the cooling process they show a slow crystallization. Interestingly, none of the ionic polymers showed a crystallization peak but a glass transition at around 40−50 °C, when the samples are fast cooled to room temperature from the mesophase (see SI, Figure S3).

As can be seen, even though the PPI, PEI, and the carboxylic acid were not mesogenic, all of the ionic macromolecules reported here showed enantiotropic mesophases over broad temperature ranges, as confirmed by XRD (Table 2). Even though the mesomorphic character of the ionic materials was confirmed by POM, the type of mesophase could not be assigned as the textures obtained were not conclusive (see SI, Figure S4). For example, in some of the PPI dendrimers a *schlieren* texture with small defects was observed, indicating a lamellar nature for the mesophase. However, the PEI analogs did not show a defined texture and homeotropic regions were observed that showed birefringence upon shearing.

X-ray diffraction studies were necessary to confirm the type of mesophase exhibited by each compound. As mentioned before, these ionic complexes start to decompose when they reach the isotropic state, although X-ray diffraction studies could be carried out in all cases in the cooling process. The samples were heated to the clearing temperature but immediately cooled to prevent decomposition and to allow at room temperature freezing the order of the mesophase in a glassy state. The data obtained at room temperature are gathered in Table 2.

Table 2. X-ray Diffraction Data for the Mesophases of the Ionic Polymers

	compound	phase	d_{obs} (Å)	Miller indexes *hkl*	lattice parameter (Å)[a]
1	**PPI1-B2-10-14**	SmCP	49.3	0 0 2	c:98.7
			32.9	0 0 3	
			19.8	0 0 5	
			16.5	0 0 6	
2	**PPI2-B2-10-14**	SmCP	98.6	0 0 1	c:98.6
			49.3	0 0 2	
			32.8	0 0 3	
			19.7	0 0 5	
			16.5	0 0 6	
3	**PPI3-B2-10-14**	SmCP	52.8	0 0 2	c:103.4
			33.6	0 0 3	
			26.0	0 0 4	
4	**PPI5-B2-10-14**	SmCP	105.8	0 0 1	c:104.0
			51.1	0 0 2	
5	**PPI1-B1-10-14**	SmCP	87.0	0 0 1	c:87.3
			43.8	0 0 2	
6	**PPI2-B1-10-14**	SmCP	89.6	0 0 1	c:89.0
			44.4	0 0 2	
			29.5	0 0 3	
7	**PPI2-B1- 4-14**	SmCP	44.8	0 0 2	c:88.6
			29.6	0 0 3	
8	**PPI2-B1-10-8**	Col_r	42.7	1 1 0	a: 61.6
			30.8	2 0 0	b: 58
			17.9	1 3 0	
9	**PPI2-B1-4-8**	Col_r	58.4	1 0 0	a:58.4
			29.2	2 0 0	b:57
			25.8	2 1 0	
			20.2	2 2 0	
			15.9	2 3 0	
10	**PPI5-B1-4-8**	Col_r	79.2	1 0 0	a:79.0
			34.7	2 1 0	b:72.0
			24.5	3 1 0	
			19.8	4 0 0	
11	**PEI-B2-10-14**	SmCP	53.3	0 0 2	c:106.6
			26.7	0 0 4	
12	**PEI-B1-10-14**	SmCP	51.9	0 0 2	c:103.8
			37.0	0 0 3	
13	**PEI-B1-4-14**	SmCP	89.6	0 0 1	c:89.5
			44.4	0 0 2	
			22.5	0 0 4	
14	**PEI-B1-10-8**	Col[b]			
15	**PEI-B1-4-8**	Col_r	79.2	1 0 0	a:79.0
			34.7	2 1 0	b:73.7
			27.1	2 2 0	
			19.8	4 0 0	

[a] a, b: rectangular lattice constants; c: layer spacing. [b] Columnar mesophase. Lattice parameters not assigned due to low number of reflections.

All of the X-ray patterns recorded in these conditions showed a diffuse halo in the wide-angle region (*ca.* 4.4 Å). This scattering is

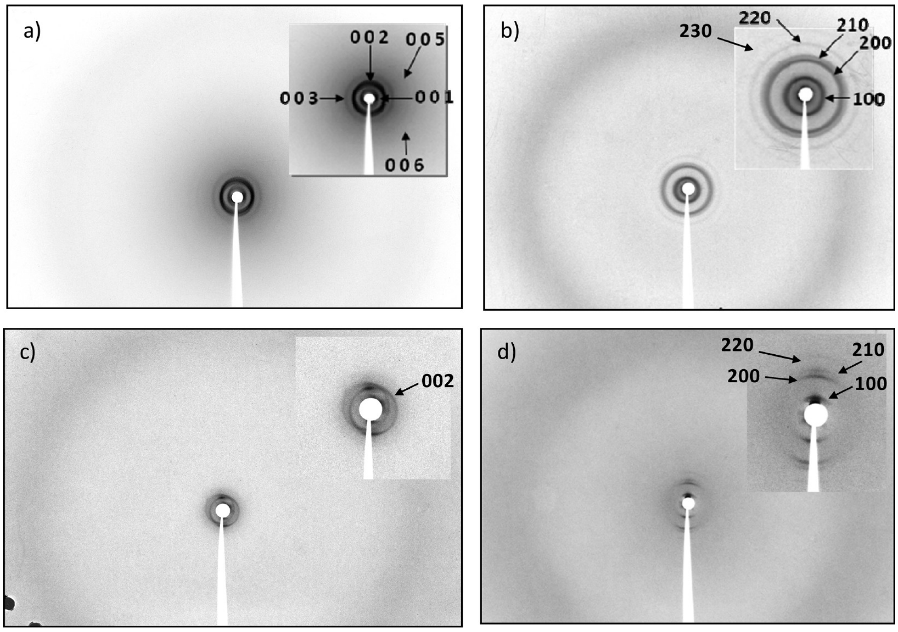


Figure 4. X-ray diffractograms of different dendrimers at room temperature after thermal treatment: (a) **PPI2-B2-10-14**, SmCP phase; (b) **PPI2-B1-4-8**, Col$_r$ phase; (c) aligned fibers of **PPI2-B2-10-14**, glassy SmCP-like order; and (d) fiber of **PPI2-B1-4-8**, glassy Col$_r$-like order. In (c) and (d) the fiber axis is horizontal. The measured spacing and indexation for all the reflections are detailed in Figure S16, SI.

associated with the melting of the flexible tails, and the absence of other scattering in this region confirms the presence of a glassy mesophase (Figure 4).

For a significant number of ionic dendrimers, particularly when the terminal chain and the flexible spacer are long (n = 14 and m = 10), up to four X-ray reflections appeared in the small angle region. These maxima are the successive reflection orders (in some cases until the sixth order) of a layer organization, and this confirms the lamellar character of these mesophases. The switching response of these compounds under an electric field at the mesophase could not be evaluated so the potential polar character of this supramolecular organization cannot be elucidated. However, the textures observed by POM and the high number of reflection orders observed by XRD suggest for these compounds a SmCP-like mesophase arrangement. Interestingly, XRD confirmed that this lamellar organization can be frozen on cooling the samples to room temperature.

From the small-angle maxima it is possible to deduce the layer spacing parameters gathered in Table 2. Comparison of these experimental data and the theoretical length of the promesogenic units and the size of the dendritic core allow us to propose an elongated conformation for these molecules—a situation in fair agreement with the model found for other covalent[17] and ionic[12b] liquid crystal dendrimers. The ionic-dendritic part is located in the middle and the bent-shaped structures are arranged above and below the dendritic core parallel to each other in a segregated and ordered manner, thus defining the layers through a compact packing. The proposed model is represented schematically in Figure 5.

When the outer terminal chain is shortened (n = 8), the X-ray results point to a different supramolecular arrangement. This situation is observed for compounds **PPI2-B1-10-8** (**8**), **PPI2-B1-4-8** (**9**), **PPI5-B1-4-8** (**10**), **PEI-B1-10-8** (**14**), and **PEI-B1-4-8** (**15**). In these cases, the X-ray patterns cannot be interpreted in terms of a layered structure, but the reflections can be indexed to a two-dimensional rectangular lattice (Table 2). This phase can be considered either a rectangular columnar mesophase or a smectic-frustrated structure with a two-dimensional modulation, in agreement with some bent-core mesophases reported for low molecular weight compounds.[3] The lattice constants a and b measured for **PPI5-B1-4-8** (**10**) and **PEI-B1-4-8** (**15**) (around 75 Å) compared to **PPI2-B1-10-8** (**8**) and **PPI2-B1-4-8** (**9**) (around 58 Å) are consistent with the significant difference in the number of bent-shaped units and the molecular size. Further discussion on the assignment of these parameters is gathered in the Supporting Information.

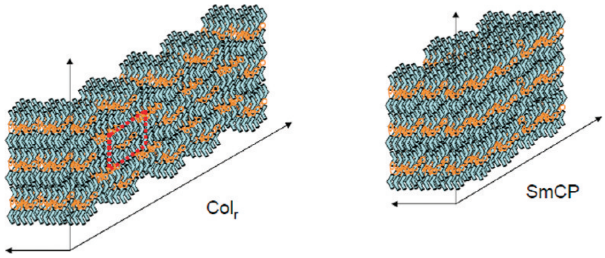


Figure 5. Schematic representation of the models proposed for the ionic polymers at the Col$_r$ and SmCP mesophase. The dendritic part is located in the middle of an elongated conformation of the dendritic macromolecule and the bent-shaped structures are arranged above and below the dendritic core, parallel to each other in an ordered manner with the layers defined through a compact packing. The red rectangle represents the 2D rectangular unit cell of the Col$_r$ mesophase. The direction of the columns is perpendicular to the 2D lattice.

4. Chemical Structure–Liquid Crystal Properties Relationships. Chemical structure–supramolecular organization relationships for bent-core based polymers are scarce. Based on our results, interesting comparative conclusions on the influence of the dendritic core (the generation number in case of the PPI and the structure) and the size of the promesogenic unit on

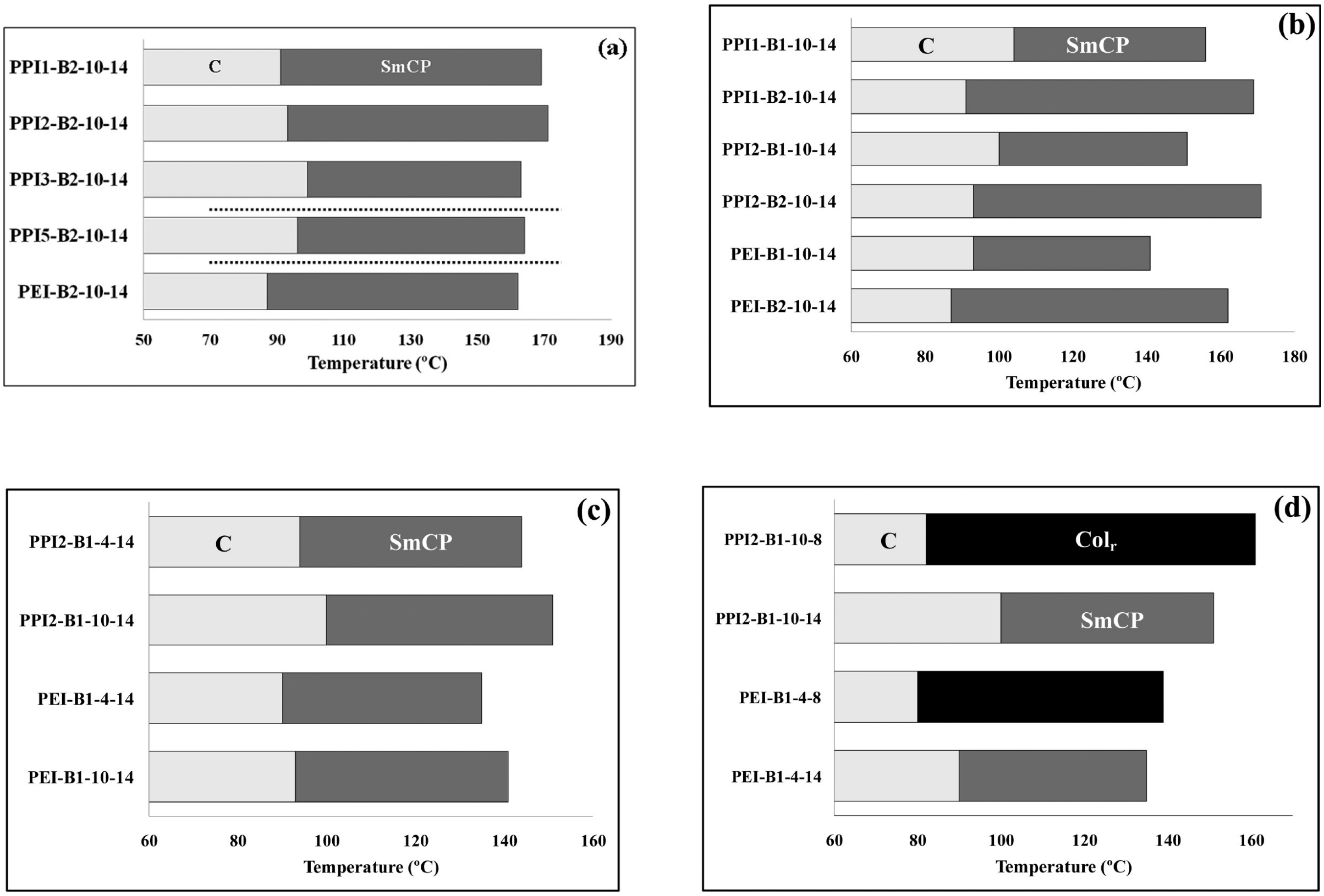


Figure 6. Graphical representation of the transition temperatures in the heating processes of ionic materials. C: Crystal phase, SmCP: polar SmC mesophase, Col$_r$: rectangular columnar mesophase. (a) Effect of the dendrimer generation and structure (**PPI1** vs **PPI2** vs **PPI3** vs **PPI5** vs **PEI** dendrimers). (b) Effect of the bent-core structure (**B1** vs **B2** structures). (c) Influence of the inner spacer (**4** methylenic units vs **10** methylenic units). (d) Influence of the outer terminal chain (**8** carbon atoms vs **14** carbon atoms in the terminal chain).

the supramolecular order of this sort of macromolecule can be discussed. For the sake of simplicity, bar graphs have been included in order to facilitate comparisons (Figure 6).

a). Effect of the Dendritic Core. As can be seen from Table 1 and Figure 6a, the dendrimer generation (i.e., the number of bent-shaped moieties in the periphery of the ionic dendrimer) does not have a marked influence on the type of mesophase and the transition temperatures, melting points, or the clearing temperatures. It should be pointed out that in all cases broad mesophase ranges (more than 50 °C) were observed for the dendritic molecules—in contrast to the nonmesomorphic character of the bent-core acid used in the synthesis of these dendrimers. On the other hand, no remarkable effect is either observed in the analogous hyperbranched PEI structure (**PEI-B2-10-14**), confirming the strong influence of the bent-core structure on the mesomorphic behavior of these dendritic macromolecules. Indeed, it can be said that in most cases ionic hyperbranched PEI dendrimers afford supramolecular packing very similar to those promoted by regular PPI structures of the higher generations.

In general terms, the enthalpy change at the mesophase—isotropic transition per mesogenic unit is about the same order of magnitude for the different generations (from around 20 kJmol^{-1} for bent-core unit), showing a constant contribution of each bent-core unit to the total enthalpy amount as it has been previously reported for other mesogenic dendrimers based on poly(propyleneimine).[18]

On the other hand, only a slight increase of the layer spacing going from lower to higher generation number is observed (from 98.6 Å for the first generations to 104 Å in the fifth, Table 2). This can be ascribed to the flexibility of the dendritic part of the complex, which is able to expand mainly in the plane of the layer in order to accommodate the increasing number of promesogenic units on the higher generations, as it has been proposed for ionic dendrimers with calamitic units.[12]

b). Effect of the Promesogenic Unit. The influence of the bent-shaped structure on the mesomorphic properties is significant and represents a useful tool to modulate the supramolecular behavior of dendritic molecules (see Table 1 and Figure 6b, c, and d). Three main aspects can be outstanding:

i. Influence of the Rigid Bent-Core Structure. The long 6-aromatic ring structure induces wider mesophase ranges and leads to stabilization of the liquid crystalline order when compared with the 5-ring system, both in the PPI and PEI ionic materials (Figure 6b) but no effect on the mesophase arrangement can be observed.

ii. Influence of the Inner Spacer. Allowing to the same type of mesophase, a shorter inner spacer (m:4) lowers the melting points and slightly destabilizes the liquid crystal order, resulting in similar mesophase ranges when compared to the longer inner spacer (m:10) (Figure 6c).

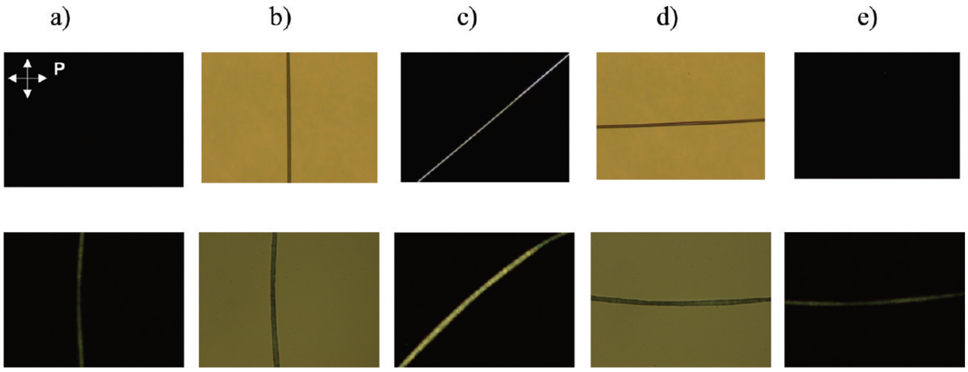


Figure 7. Microphotographs of the fibers extruded from the SmCP phase of **PPI2-B2-10-14** (top) and from the Col$_r$ mesophase of **PPI2-B1-4-8** (bottom) seen by POM: (a) fiber oriented at 0° with respect to the polarizers, (b) fiber oriented at 0° without polarized light; (c) fiber rotated 45° with respect to the polarizer with polarized light; (d) fiber rotated 90°, without polarized light; (e) fiber rotated 90°, with polarized light.

iii. Influence of the Outer Terminal Chain. This part of the molecules has proved to be the main tool to modulate the supramolecular arrangement of the macromolecules in the mesophase. In particular, shortening the outer terminal chains (from n:14 to n:8) leads to columnar packing over broad temperature ranges (>60 °C) instead of the more common lamellar packing observed for the longer terminal chain (Figure 6d). This effect is also present when a congested dendritic structure is used. Thus, both **PPI5-B1-4-8** and **PEI-B1-4-8** promote a columnar arrangement of the bent-core units.

This behavior is in good agreement with results concerning low molecular weight BCLC, i.e., that short terminal chains allow a balance to be achieved between the intermolecular interactions of flexible/rigid parts and their microsegregation, which results in interdigitated block packing (columnar phases) or lamellar arrangements depending on this balance.[3] Furthermore, in dendritic systems the mesogenic units, while extending approximately perpendicular to the mean plane of the dendritic nucleus, are expected to arrange themselves more radially in the columnar phase than in the SmCP mesophase, where the macromolecule adopts a more compact elongated structure. A more radial or “open” arrangement makes interdigitation possible and this can account for the dramatic decrease in the rectangular lattice parameters in Col mesophase compared to the layer spacing of SmCP packing (see Table 2 and S7).

Apart from these differences, layers spacing for 6-rings dendrimers are approximately 10 Å larger than those measured for the 5-rings ones (Table 2), which can be attributed to the extra aromatic ring (the theoretical length of one aromatic ring is 5 Å). For the random hyperbranched polymers (**PEI-B1-10-14** vs **PEI-B2-10-14**), this effect is not so neat probably due to the lesser regularity of this structure.

On the other hand, it is worth also mentioning that there is no remarkable difference of the layer spacing for random branched (PEI) or regular (PPI) derivatives. Thus, all these dendritic cores, regardless of their size and regularity, allows accommodating the rigid bent-core units through the microsegregation through a rather similar way.

5. Processing of the Materials. Due to the high molecular weights of the materials and the compact arrangement of the molecules within these mesophases, it was possible to extrude fibers from most of these macromolecules. To draw fibers, a sample of the material was heated at 20−30 °C above the melting point and the temperature was maintained for a few minutes to stabilize the temperature and allow mesophase formation. A needle was used to draw fibers with a diameter of around 50 μm from the soft sample. Observation of these fibers at room temperature by POM showed that they were birefringent (Figure 7). Birefringence was not observed in fibers from the lamellar melt (for example **PPI2-B2-10-14**) when the fiber was aligned parallel to one of the polarizers (0° and 90°, Figure 7a and e). However, birefringence was maximum when the fiber was aligned at 45° to the polarizers (Figure 7c). On the other hand, fibers that did show birefringence at any rotation angle when fibers were drawn from the columnar liquid crystal phases of **PPI2-B1-4-8** and of the highly congested system **PPI5-B1-4-8**.

These fibers were also studied by X-ray diffraction and the patterns showed that the fibers were not crystalline and indeed retained the supramolecular arrangement characteristic of the mesophase. For example, in the case of **PPI2-B2-10-14**, a diffuse halo in the wide angle region and a single reflection in the low angle region can be observed in the X-ray diffractogram (Figure 4c and d). The intensity of these scattering maxima is reinforced in the meridian and equator, indicating that the sample is aligned and that the fiber retains the order of the mesophase in a frozen state. The rest of the reflections recorded in the powder patterns cannot be observed in the oriented patterns due to the small diameter of the fibers, which dramatically reduces the intensity of the scattering.

Similar conclusions for the alignment and retention of the Col$_r$ mesophase order apply to the fiber of **PPI2-B1-4-8** (Figure 4d). However a higher number of reflections are recorded in this case.

6. CONCLUSIONS

Through an easy synthesis, the preparation and characterization of an extensive series of ionic PPI- and PEI-based dendritic polymers bearing bent-core functional structures (up to 64 or 75 repetitive units) have allowed the systematic study of the supramolecular arrangement of this type of macromolecules for which very few references are available.

In summary, the bent-core structure acts as a strong driving force for the mesogenic supramolecular arrangement of ionic polymers. All of these macromolecules form bent-core liquid crystalline phases over large temperature ranges in contrast to the nonmesomorphic ability of the bent-shaped carboxylic monomers used. Interestingly, these intermolecular interactions are present also in solution as NMR studies have shown, opening interesting additional research on their aggregation ability.

Concerning the structure−liquid crystal properties relationship of this type of macromolecules, several conclusions should be pointed out. Both regular and random branched dendritic structures seem to favor and stabilize lamellar and columnar organizations with a neat segregation of the flexible dendritic structure and the bent-rigid cores. Additionally, dendrimers of low generations or congested dendritic structures render very similar bent-core-like supramolecular organizations. Nevertheless, in bent-core based dendrimers the length of the inner flexible spacer and the number of aromatic rings are the main parameters to modulate the transition temperatures of lamellar organizations. Alternatively, the use of short outer terminal chains will afford columnar order.

These results could provide the starting point for other targeted designs and studies on new functional bent-core based dendritic molecules. Amusingly, ionic bent-core based dendrimers could allow transfer of the attractive properties reported for bent-core mesophases—or the exploration of new phenomena—in size-controlled macromolecules that have thus far scarcely been investigated. Otherwise, selection of the appropriate dendritic-core from the broad range now available would enable suitable and exciting combinations of flexibility and hydrophobic/hydrophilic character, for example, with the polar and compact packing of bent-core moieties. To sum up, new and very stimulating possibilities for bent-core based dendritic systems are open, an area that is of interest in basic and applied supramolecular chemistry and materials science scenarios.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Additional text and graphics as noted in the text. This information is available free of charge via the Internet at http://pubs.acs.org/.

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