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Liquid crystalline semifluorinated ionic dendrimers

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Poly(propyleneimine) [PPI-$(NH_2)_n$] and poly(amidoamine) [PAMAM-$(NH_2)_n$] dendrimers with n=4, 8, 16, 32 and 64, have been functionalized with a semifluorinated carboxylic acid [$CF_3(CF_2)_7CH_2CH_2COOH$] on the surface. The thermal and liquid crystal properties of the resulting ionic dendrimers have been studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). All dendrimers show a smectic A (SmA) mesophase, except that derived from the fifth generation of PPI, which displays a columnar mesophase. The mesomorphic behaviour of the dendrimers is attributed to the formation of ionic bonds and to the microsegregation of the dendritic branches and the fluorinated peripheral chains.

1. Introduction

Dendrimers are monodisperse, hyperbranched polymers with a dense concentration of surface functional groups for high generations [1, 2]. The chemistry of these end groups has been one of the most studied areas in dendrimer research. Indeed, many different ways of end-group modification have been reported on several dendritic polymers [3, 4]. In the case of poly(propyleneimine) (PPI)-derived dendrimers, a wide range of modification reactions have been performed leading to new materials such a "dendritic box" [5], liquid crystals [6–8], dye-extraction agents [9], chiral dendrimers and dendrimers with catalytic sites [10, 11]. We have employed PPI and PAMAM dendrimers for the attachment of (pro)mesogenic units, i.e. those derived from salicylaldehydes. These materials exhibit thermotropic liquid crystal behaviour (nematic, lamellar or columnar) depending on the length or the number of terminal chains of the (pro)mesogenic units [7]. Most of the liquid crystal dendrimers described to date are constituted by covalent neutral molecules. Recently, we have reported on the synthesis and properties of ionic thermotropic liquid crystal dendrimers [12, 13]. Semifluorinated and perfluorinated molecules have had a significant impact in the field of chemistry and their use has provided new strategies in organic, biomolecular and supramolecular synthesis [14]. It is well established that perfluoroalkanes are stiffer and less miscible than the corresponding perhydrogenated alkanes (fluorophobic effect) [15, 16]. Percec *et al.* [14] replaced some hydrogen atoms with fluorine atoms at the end tail of a dendron and found an unexpected change in the structural motif and assembly behaviour: the non-fluorinated dendron has a conical shape which leads to spherical assemblies that self-organize into a cubic lattice, whereas the partly fluorinated dendron has a crown-like shape and gives rise to columnar assemblies that self-organize into a hexagonal liquid crystal lattice. Few dendrimers with perfluoroalkyl groups on the surface have been reported to date. In 1997, Frey and co-workers [17–19] presented the synthesis and characterization of a series of four carbosilane dendrimers bearing 4, 12, 36 and 108 C_6F_{13} end groups which exhibited liquid crystal properties depending on the dendrimer generation. Fluorination affords some typical properties to dendrimers such as hydrophobicity and very good thermal stabilities [17, 18].

The formation of supramolecular complexes using ionic interactions, called by Faul ionic self assembly (ISA) [20–23], was recently shown to be a feasible route for the production of self-organizing nanostructured materials. In 2003, Faul *et al.* [24] described the synthesis and liquid crystal properties of PAMAM–fluorosurfactant complexes, which change their structure from planar to spherical with generation number (from G=0 to G=4). (See Thünemann [25] for a review focusing largely on the fluoro-complexes).

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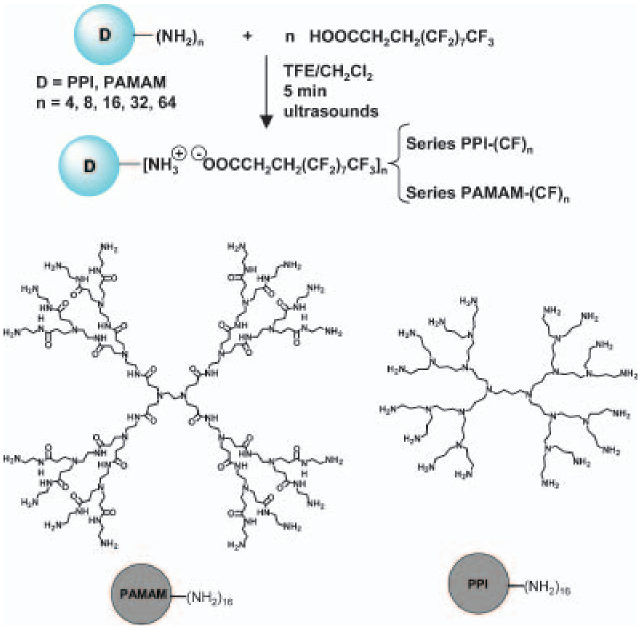
In order to compare the properties of the ionic dendrimers with either perhydrogenated or semifluorinated alkanoate chains in their structures, we have synthesized and characterized two series of PPI and PAMAM dendrimers bearing 4, 8, 16, 32 and 64 $CF_3(CF_2)_7(CH_2)_2COO^-$ groups (scheme 1). In this paper, we present the liquid crystal behaviour of these dendrimers, studied by polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD), as well as a study of the influence of the stiffness and interactions of the alkyl chains in the mesomorphic properties of the ionic dendrimer materials.

2. Experimental

2.1. *Techniques*

Infrared spectra were obtained with a Perkin-Elmer 1600 (FTIR) spectrophotometer in the 400–4000 cm^{-1} spectral range. All samples were recorded in KBr discs. The optical textures of the mesophases were studied with a Nikon polarising microscope equipped with a Linkam THMS 600 hot stage and a Linkam TMS 91 central processor. The transition temperatures and enthalpies were measured by differential scanning calorimetry with a Perkin-Elmer DSC-7 instrument operated at a scanning rate of 10°C min^{-1} on heating and cooling. The apparatus was calibrated with indium (156.6°C; 28.4 J g^{-1}) as the standard.



Scheme 1. Synthetic route to ionic dendrimers PPI-$(CF)_n$ and PAMAM-$(CF)_n$.

The XRD patterns were obtained with a pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu-Kα beam. The sample was held in Lindemann glass capillaries (1 mm diameter). The capillary axis is perpendicular to the X-ray beam and the pattern is collected on a flat photographic film perpendicular to the beam. Spacings were obtained via Bragg's law.

Solid-state NMR experiments were performed on a Bruker Avance 400 spectrometer, operating at frequency of 400.13 MHz for ^1H and 100.61 MHz for ^{13}C. Data were acquired at 296 K and chemical shifts are referenced to TMS. A double resonance (1H-X) probe with 4 mm rotor diameter was used and the spinning frequency was set to 5 kHz. The ^1H and ^{13}C 90° pulse length were of 3.6 and 9.4 µs respectively and the CP contact time of 1.5 ms. The recycle delay was 5 s. The pulse sequence employed consisted of ramped cross-polarization with TPPM decoupling and with TOSS to eliminate the spinning sidebands.

2.2. *Materials*

Semifluorinated carboxylic acid $CF_3(CF_2)_7(CH_2)_2COOH$ was synthesized as previously described [26]. PPI and PAMAM dendrimers and trifluoroethanol (TFE) were purchased from Aldrich Chemical Co. All substances were used without further purification. Dry dichloromethane (refluxed over calcium hydride, distilled and stored over molecular sieves 4 Å) was used as a reaction cosolvent.

2.3. *Synthesis*

The semifluorinated dendrimers were synthesized following a previously described procedure [24], as shown in scheme 1. 2 mmol of 2,2,3,3-tetrahydrogenoperfluoroundecanoic acid was dissolved in TFE (5 ml). A molar equivalent amount of PPI-$(NH_2)_n$ or PAMAM-$(NH_2)_n$ dendrimers (n=4, 8, 16, 32 and 64) was dissolved in dichloromethane. Both solutions were mixed, stirred and sonicated for 5 min. The resulting solution was then slowly evaporated at 35°C and the solid obtained was vacuum dried at 25°C for 2 days.

3. Results and discussion

3.1. *Synthesis and characterization*

The protonation of the amino groups on the periphery of PPI and PAMAM dendrimers by the semifluorinated acid has the advantage that can ensure a 1:1 complexation due to the very strong acidity. The occurrence of proton transfer was checked for all the materials by IR spectroscopy. In figure 1, the IR spectra of the starting carboxylic acid and final materials are shown. The band

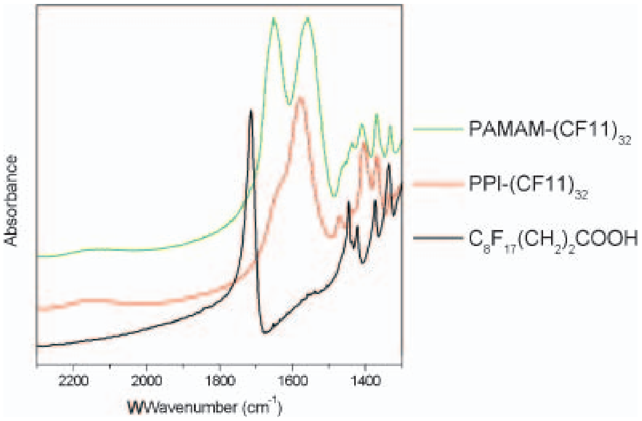


Figure 1. FTIR of the semifluorinated carboxylic acid and the PPI and PAMAM ionic dendrimers.

corresponding to the stretching of the carbonyl bond of the acid disappears in the ionic dendrimers. The weak and broad band around 2100 cm^{-1} is characteristic of these systems and also appears for the zwitterionic form of the amino acids [27].

^{1}H and ^{13}C NMR in solution could not be carried out due to the insolubility of the ionic dendrimers. For this reason, CPMAS experiments were performed in the solid state. For both dendrimers series, PAMAM and PPI, the deprotonation of the acid was confirmed by the presence of the signal corresponding to the carbon of the carboxylate group at 178.9 ppm (PPI) and 179.9 ppm (PAMAM).

3.2. *Thermal properties*

In general, amphiphiles with lipophilic and perfluoroalkyl segments tend to self-organize into layered superstructures due to the immiscibility of perfluoroalkyl chains with alkyl groups and their stiffness. In addition, the differences in the cross-section of the $(CF_2)_\alpha$ chains compared to that of hydrocarbon chains favour the formation of mesophases [14]. The phase behaviour of the semifluorinated dendrimers was analysed by a combination of techniques including polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The transition temperatures and the corresponding enthalpy changes that were obtained from the first heating scan are listed in tables 1 and 2.

The assignment of the liquid crystal phase is done on the basis of the POM observations. The SmA mesophase was clearly identified by the fan-shaped and homeotropic textures (figure 2).

DSC studies have revealed that in the first heating scan, the semifluorinated materials exhibit a liquid crystal behaviour up to decomposition and suffer a decrease of the transition temperatures in subsequent scans, as was also observed for the perhydrogenated homologues due to the formation of amide bonds and to the migration of the alkanoate chains to the inner tertiary amino groups of the dendrimer scaffold [12]. For this reason, further DSC experiments were performed in which the highest temperature reached was set well below the clearing point. In this case, the successive heating and cooling cycles are reproducible.

Table 1. Transition temperatures and enthalpies as determined by DSC of PPI ionic dendrimers (1st scan) (C=crystal, SmA=smectic A mesophase, Col$_r$=rectangular columnar mesophase, I=isotropic liquid).

	Transitions/°C, (ΔH/J g^{-1})
Dendrimer	Heating process
PPI-$(CF)_4$	C 78 (17.3) SmA 171 (4.6) I
PPI-$(CF)_8$	C 98 (21.2) SmA 171 (5.6) I
PPI-$(CF)_{16}$	C 49 (20.0) SmA 181 (4.5) I
PPI-$(CF)_{32}$	C 47 (2.3) SmA 149 (1.3) I
PPI-$(CF)_{64}$	C 117 (2.7) Col$_r$ 152 (3.8) I

When comparing the mesomorphic thermal ranges and transition temperatures of the semifluorinated ionic dendrimers with those of their perhydrogenated homologues [12], the following conclusions can be drawn: first, the mesophase to isotropic liquid transition temperature is significantly higher for the semifluorinated dendrimers. Second, the mesomorphic ranges are similar in both cases, although some exception can be found, as for example the range of the columnar mesophase for the fifth generation of PPI-dendrimers, which is significantly narrower for the semifluorinated material.

3.3. *X-ray diffraction*

Measurements were carried out on samples of all the materials. The data obtained with this technique are gathered in tables 3 and 4.

Table 2. Transition temperatures and enthalpies as determined by DSC of PAMAM ionic dendrimers (1st scan) (C=crystal, SmA=smectic A mesophase, I=isotropic liquid).

	Transitions/°C, (ΔH/J g^{-1})
Dendrimer	Heating process
PAMAM-$(CF)_4$	SmA 184 (3.0) I
PAMAM-$(CF)_8$	SmA 164 (10.5) I
PAMAM-$(CF)_{16}$	C 30 (7.5) SmA 185 (3.7) I
PAMAM-$(CF)_{32}$	C 79 (5.5) SmA 161 (1.6) I
PAMAM-$(CF)_{64}$	C 80 (4.8) SmA 165 (2.8) I

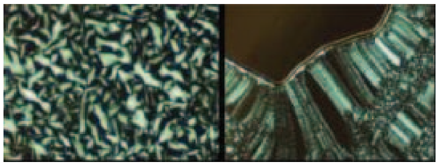

(*a*) (*b*)

Figure 2. (a) Fan-shaped texture of the SmA mesophase of PAMAM-$(CF)_{32}$ at 137°C (1st heating scan). (b) Oily streak texture of the SmA mesophase of PPI-$(CF)_{16}$ at 147°C (1st heating scan).

The smectic nature of the mesophase, previously established by POM observations, was confirmed by XRD.

The ideal model proposed for the dendrimer supermolecule consists in a cylinder in which the three different molecular regions are segregated (figure 3). The model for the molecular organization in the SmA mesophase is shown in figure 3 as well. As it can be seen, a layered structure with fluorophilic, lipophilic and hydrophilic alternating layers is proposed.

The layer thickness of the ionic dendrimers can be calculated from the XRD results, as well as the diameter of the ideal cylinder which represents the supermolecules. We can compare the results obtained with those found for the homologous PPI ionic dendrimer with perhydrogenated alkyl peripheral chains, i.e. PPI–undecanoic acid complex, PPI-$(C)_n$. As shown in figure 4a, all the generations of the lamellar PPI dendrimers exhibit similar layer thickness within the same series. When increasing the stiffness of the carboxylic acid chain, this is when introducing semi-fluorinated chains instead of perhydrogenated alkyl chains, a significant increase of the layer thickness is observed. PAMAM-$(CF)_n$ dendrimers show even a more pronounced increase of the layer thickness due to the larger size of the dendritic scaffold. This phenomenon is easily understood because of the flexible nature of the molten perhydrogenated alkyl chains, which may adopt a curly conformation with the result of a decrease of the layer thickness in the model proposed for the dendrimer molecule and for the supramolecular organization in the mesophase.

Table 3. Structural data of the mesophases of the ionic PPI dendrimers with fluorinated chains measured by X-ray diffraction. The columns list, respectively, the compound name, the mesophase type, the temperature of the experiment (T), the observed spacings (d_{obs}), the proposed indexation ($h\ k\ l$: Miller indexes) and the deduced layer thickness (d) or rectangular lattice constants (a and b).

Dendrimer	Mesophase	T/°C	d_{obs}/Å	$h\ k\ l$	Parameters/Å
PPI-$(CF)_4$	SmA	110	27.4	0 0 1	d=27.3
			13.6	0 0 2	
			9.1	0 0 3	
			5.4[a]		
PPI-$(CF)_8$	SmA	110	27.2	0 0 1	d=27.2
			13.5	0 0 2	
			9.1	0 0 3	
			5.4[a]		
PPI-$(CF)_{16}$	SmA	110	28.7	0 0 1	d=28.5
			14.2	0 0 2	
			5.4[a]		
PPI-$(CF)_{32}$	SmA	110	27.1	0 0 1	d=27.1
			13.6	0 0 2	
			5.4[a]		
PPI-$(CF)_{64}$	Col_r	RT	33.0	1 1 0	a=40.5
			28.7	0 2 0	b=57.0
			17.1	1 3 0	
			14.2	0 4 0	
			5.4[a]		

[a] Diffuse maximum.

Table 4. Structural data of the mesophases of the ionic PAMAM dendrimers with fluorinated chains measured by X-ray diffraction. The columns list, respectively, the compound name, the mesophase type, the temperature of the experiment (T), the observed spacings (d_{obs}), the proposed indexation ($h\ k\ l$: Miller indexes) and the deduced layer thickness (d).

Dendrimer	Mesophase	T/°C	d_{obs}/ Å	$h\ k\ l$	Parameters/ Å
PAMAM-$(CF)_4$	SmA	108	30.4	0 0 1	d=30.2
			15.0	0 0 2	
			5.4[a]		
PAMAM-$(CF)_8$	SmA	108	31.4	0 0 1	d=31.4
			5.4[a]		
PAMAM-$(CF)_{16}$	SmA	108	30.8	0 0 1	d=30.9
			15.5	0 0 2	
			5.4[a]		
PAMAM-$(CF)_{32}$	SmA	108	34.8	0 0 1	d=34.8
			5.4[a]		
PAMAM-$(CF)_{64}$	SmA	108	34.3	0 0 1	d=34.3
			5.4[a]		

[a] Diffuse maximum.

A clear increase of the diameter of the supermolecular cylinder is observed as the generation number increases (figure 4b).

Figure 5 shows the XRD pattern at room temperature of a mechanically aligned sample obtained for dendrimer

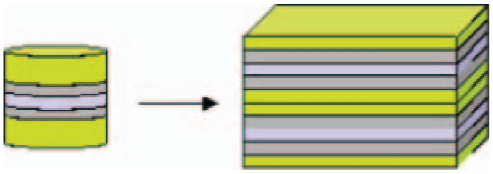


Figure 3. Schematic representation of dendrimer supermolecule as a cylinder and of the layered model for the SmA mesophase [green: fluorophilic layer $F(CF_2)_8$; grey: lipophilic layer $(CH_2)_2$; blue: hydrophilic layer (dendrimer-$NH_3^{+-}OOC$)].

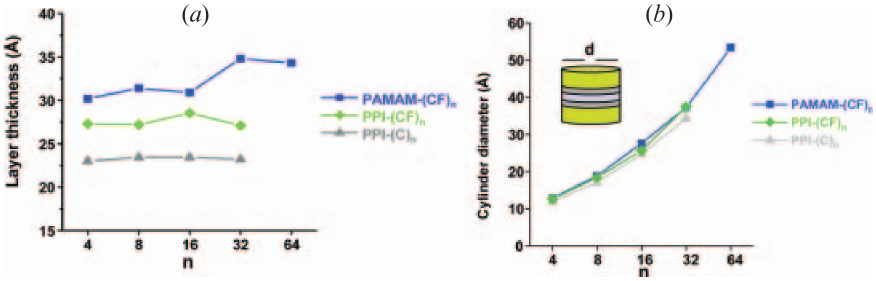


Figure 4. (a) Graphical representation of the layer thickness of three different ionic dendrimers as a function of the generation number. (b) Evolution of the supermolecular cylinder diameter with the generation number (calculated from XRD results, assuming a density d=0.7 g cm^{-3} for the hydrocarbon chain and d=1.4 g cm^{-3} for the fluorinated moiety).

PPI-(CF)$_{64}$ and the corresponding indexing scheme, which can be assigned to a columnar mesophase with a rectangular lattice symmetry. As it was previously found for ionic dendrimers with alkanoate moieties, the surface-functionalised fifth generation of PPI dendrimer affords materials with a columnar mesomorphism [12, 13]. The occurrence of this type of mesomorphism can be explained by the surface congestion of the peripheral amino groups in the fifth generation of the PPI dendrimer. In contrast, PAMAM dendrimers show no columnar mesomorphism, due to the larger volume of the PAMAM dendritic architecture with respect to the PPI one, which prevents the steric hindrance of the primary amino groups on the surface.

This fact evidences the flexibility and plasticity of the dendrimeric core, which adopts the most appropriate conformation to favour the interaction of the units responsible of the mesomorphic organization. In this case, the molecular model consists of a cylinder with the dendrimer matrix occupying a central sub-cylinder and the semifluorinated chains radially arranged, as shown in figure 6.

The supramolecular organizations obtained, both lamellar and columnar, and the chemical nature of the segregated areas, as well as the ability of these dendrimer materials to afford oriented films and fibres, allow us to envisage the possibility of obtaining interesting physical properties, such as ionic conductivity. The preparation of oriented samples and their physical characterisation is currently in progress and the results will be reported elsewhere.

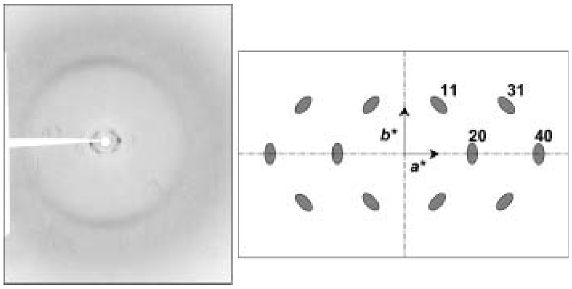


Figure 5. (a) XRD pattern at room temperature of an aligned sample of PPI-(CF)$_{64}$. (b) Schematic drawing and indexing of the SAXS pattern.

4. Conclusions

We have shown that the attachment of a linear semifluorinated alkanoic acid to commercial PPI-(NH$_2$)$_n$ and PAMAM-(NH$_2$)$_n$ dendrimers yields an ionic lamellar mesophase in all cases and a columnar mesophase is also observed for the dendrimer PPI-(CF)$_{64}$. Microsegregation acts as a driving force capable to organize these block supermolecules within ordered structures showing mesomorphic behaviour. The fluoroalkyl chains lead to a more pronounced microphase separation, which is expected to drive to the formation of liquid crystal phases. The mesomorphic behaviour (mesophase type) of the semifluorinated ionic dendrimers is similar to that observed for the corresponding perhydrogenated homologues.

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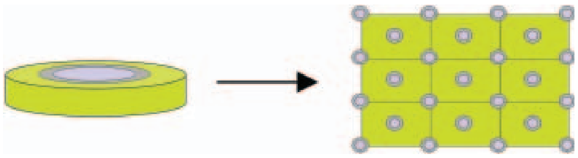

Figure 6. Schematic representation of dendrimer supermolecule as a disk and of the model for the rectangular columnar mesophase [green: fluorophilic layer F(CF$_2$)$_8$; grey: lipophilic layer (CH$_2$)$_2$; blue: hydrophilic layer (dendrimer-NH$_3{}^{+-}$OOC)].

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