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Philic and Phobic Segregation in Liquid-Crystal Ionic Dendrimers: An Enthalpy–Entropy Competition**

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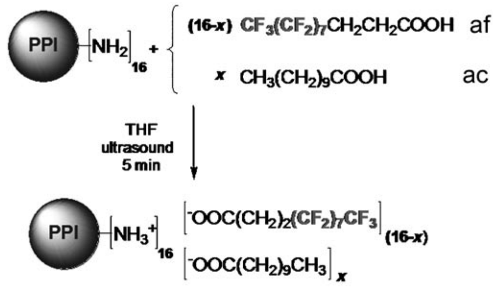
In recent years, dendrimers have been considered one of the most thriving lines of polymer research.[1] Nowadays, they appear as indispensable tools in diverse fields, such as biomedical[2] and material sciences.[3] One of the most remarkable features is their structural characteristics, which allow their core and surface to be functionalized by simple modifications, a fact that has promoted the great development focused on these molecules.[4]

Since the beginnings of dendrimer research, liquid-crystal (LC) dendrimers, commonly known as dendromesogens, have been reported. Initial efforts involved the covalent linkage of the promesogenic units either constituting the core or at the periphery. This work has been excellent scaffold for the structure–mesogenic-activity relationship.[5] Especially interesting are LC co-dendrimers, because by the mixing of different terminal units, a wide variety of phases have been obtained.[6]

Ionic interactions have emerged as a simple and original way to create LC dendrimers.[7] In these compounds, classical promesogenic units, which are constituted by a rigid moiety and flexible terminal chains, are replaced by carboxylic acid derivatives, generating electrostatic attraction instead of the conventional interaction of the promesogens joined by covalent bonds. Thus, by modifying the kind of acids introduced to commercially available poly(amido amine) (PAMAM) and poly(propylene imine) (PPI) dendrimers, it is possible to obtain different types of mesophases.[8,7a] For this reason, the microsegregation effect plays a determinant role in most LC compounds.[9] Generally speaking, molecules with a certain grade of conformational freedom tend to organize themselves to adopt the most favorable thermodynamic conformation by locating together compatible moieties (philic contribution) and at the same time placing incompatible moieties (phobic contribution) as far away as possible. However, LC co-dendrimers produce more complicated behavior because incompatible moieties are often forced to stay close in the space and they must search for alternate strategies, other than microsegregation, to reach the higher stability of the system, leading to outstanding properties.

Herein we present a significant advance in the study of this phenomena by joining incompatible terminal acids in the same molecule. Mesomorphic, structural, and surface properties of ionic co-dendrimers constituted by third-generation PPI (Supporting Information, Figure S1) functionalized with 2*H*,2*H*,3*H*,3*H*-perfluoroundecanoic acid (af) and undecanoic acid (ac) in different proportions are reported. The choice of a semifluorinated acid arises not only because of its ability to produce the segregation effect,[10] but also because of its similar reactivity when comparing with the other chosen unit (undecanoic acid) to achieve the attachment to the dendrimer in the selected proportion.

Ionic co-dendrimers were synthesized following a modification of the method described by R. M. Crooks et al. (Scheme 1).[11] IR and NMR spectroscopy, together with elemental analysis, reveal the correct formation of the



PPI-(ac)$_x$-(af)$_{16-x}$[a]	ac%[b]	ac%[c]
PPI-(ac)$_{16}$	100.0	100.0
PPI-(ac)$_{14}$-(af)$_2$	87.5	88.0
PPI-(ac)$_{12}$-(af)$_4$	75.0	72.0
PPI-(ac)$_{10}$-(af)$_6$	62.5	65.6
PPI-(ac)$_8$-(af)$_8$	50.0	50.0
PPI-(ac)$_6$-(af)$_{10}$	37.5	40.6
PPI-(ac)$_4$-(af)$_{12}$	25.0	[e]
PPI-(ac)$_2$-(af)$_{14}$	12.5	[e]
PPI-(af)$_{16}$[d]	0.0	[e]

Scheme 1. Synthetic route of ionic dendrimers. [a] ac = undecanoic acid, af = 2*H*,2*H*,3*H*,3*H*-perfluoroundecanoic acid, PPI = poly(propylene imine). [b] Percentage of ac groups introduced in the reaction. [c] Percentage of the ac groups detected by ^{1}H NMR spectroscopy (see Supporting Information). [d] This compound has been previously reported.[8a] [e] Data not available because of the broadness and low intensity of the signals.

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compounds. The disappearance of the bands in the IR spectrum at about 1700 cm^{-1} corresponding to carbonyl groups in the carboxylic acids and the presence of the bands around 1560 and 1400 cm^{-1} corresponding to the asymmetric and symmetric stretching modes of the carboxylate group observed indicated the formation of the complexes. The same conclusion is drawn by ^1H NMR, because of the appearance of the signal at circa $\delta = 2.95$ ppm that corresponds to $CH_2NH_3^+$ and the absence of signal at $\delta = 2.70$ ppm related to CH_2NH_2 of PPI.[8d,12]

NMR studies also allow the proportion of the perhydrogenated and the semifluorinated chains in the co-dendrimers to be studied (see Scheme 1 and the Supporting Information). The ratio of the integrals corresponding to the protons of the methylene groups linked to the carboxylate group of the ac moiety, $CH_3(CH_2)_8CH_2COO^-$, that appear at $\delta = 2.15$ ppm and the protons of the methylene groups linked to the ammonium group coming from the terminal protonated amine groups of the PPI dendrimer, $NCH_2CH_2CH_2NH_3^+$, at $\delta = 3.00$ ppm confirmed the correspondence between the theoretical and experimental composition of the ac moiety in each co-dendrimer.

The mesomorphic behavior of these dendrimers was analyzed by combining different techniques, including polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). Despite the fact that neither the acids nor commercial dendrimer are mesogens, the ionic interaction forces the phase segregation responsible of the mesomorphism of these compounds. All of them were liquid crystals at room temperature, except for the fully semifluorinated dendrimer[8a] [PPI-$(af)_{16}$], which has a melting point at 47 °C (Figure 1).

Upon observation by POM, textures characteristic of the smectic A mesophase were detected. Fluorinated chains stabilize liquid crystal behavior in the molecules;[13] therefore, these materials show a tendency to increase the isotropization temperature as the percentage of semifluorinated moiety increases. Surprisingly, X-ray results indicated some more complicated phase behavior, because despite the fan-shaped texture observed by POM, two SmA phases with different spacing layers were detected. Both homo-dendrimers present a SmA mesophase, but the layer thicknesses are different (see Table 1). The layer spacing of the homodendrimer PPI-$(ac)_{16}$ (SmA_H, 24.3 Å) is significatly lower than the analogous totally semifluorinated PPI-$(af)_{16}$ (SmA_F, 28.5 Å). This difference is because the perhydrogenated chains possess more flexibility and may adopt a curly conformation,[14] whereas the stiffness arising from fluorinated chains produces a more elongated conformation of the molecule. The layer spacing slightly increases by 0.4 Å in PPI-$(ac)_{14}$-$(af)_2$ (24.7 Å) relative to the homodendrimer PPI-$(ac)_{16}$ owing to the introduction of two semifluorinated units. PPI-$(ac)_2$-$(af)_{14}$, PPI-$(ac)_4$-$(af)_{12}$, and PPI-$(ac)_6$-$(af)_{10}$ present a SmA phase with a similar layer spacing, indicating the predominance of the semifluorinated chains.

Table 1: Phases and X-ray data of the ionic compounds.

Co-dendrimer	Phase[a]	T [°C][b]	Layer spacing [Å][c]
PPI-$(ac)_{16}$	SmA_H	RT	24.3
PPI-$(ac)_{14}$-$(af)_2$	SmA_H	RT	24.7
PPI-$(ac)_{12}$-$(af)_4$	SmA_H/SmA_F	RT	23.5[d]/27.4[e]
PPI-$(ac)_{12}$-$(af)_4$	SmA^+	50	–
PPI-$(ac)_{10}$-$(af)_6$	SmA^+	RT	–
PPI-$(ac)_8$-$(af)_8$	SmA^+	RT	–
PPI-$(ac)_6$-$(af)_{10}$	SmA_F	RT	27.4
PPI-$(ac)_4$-$(af)_{12}$	SmA_F	RT	27.7
PPI-$(ac)_2$-$(af)_{14}$	SmA_F	RT	27.6
PPI-$(af)_{16}$	SmA_F	110	28.5

[a] Mesophases exhibited by the compounds. [b] Temperature of the X-ray study of these mesophases. [c] Layer spacing of the smectic phase determined by X-ray diffraction. [d,e] Layer spacings of the two coexisting smectic phases obtained for PPI-$(ac)_{12}$-$(af)_4$.

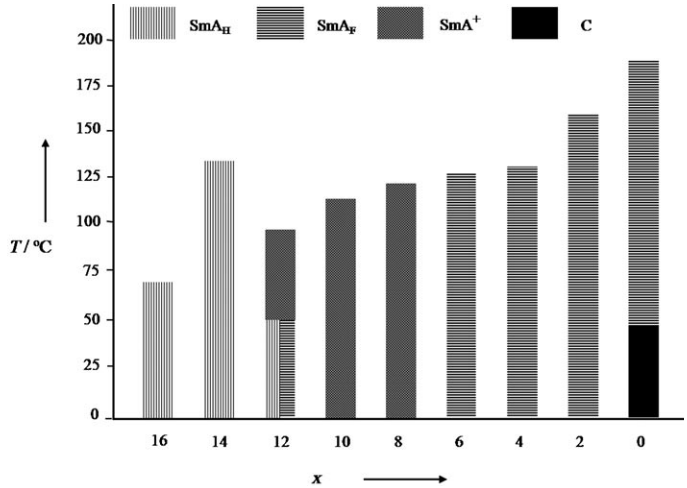

Figure 1. Mesomorphic behavior. SmA^+ = frustrated smectic A phase; SmA_H = smectic A phase with dimensions similar to those for PPI-$(ac)_{16}$; SmA_F = smectic A phase with dimensions similar to those for PPI-$(af)_{16}$; C = crystalline behavior. x = average number of undecanoic acid units that contain the dendrimer.

PPI-$(ac)_8$-$(af)_8$, PPI-$(ac)_{10}$-$(af)_6$, and PPI-$(ac)_{12}$-$(af)_4$ present textures observed by POM typical of a SmA mesophase, but they exhibit a singular X-ray behavior, because only diffuse scattering in the small-angle region appeared, which suggests the existence of a frustrated smectic A phase (SmA^+).[15] Furthermore, in case of PPI-$(ac)_{12}$-$(af)_4$ the coexistence of two SmA phases with different parameters (23.5 Å and 27.4 Å) is detected at room temperature. These values agree with those coming from dendrimers with only perhydrogenated acids (SmA_H, 23.5 Å) and only semifluorinated acids (SmA_F, 27.4 Å).

The composition necessary to avoid the less-organized SmA^+ phase is clearly dominated by semifluorinated moieties, because SmA_F phase is maintained even with six ac moieties; in contrast, a SmA_H phase is only obtained when the content of ac is higher than twelve. The most plausible explanation of this phenomenon is the different nature and geometry of the semifluorinated and perhydrogenated chains. Taking into account the cross-sectional area that each chain takes up[16] (0.28 nm^2 and 0.18 nm^2 respectively), the relative percentage that each moiety occupies in the global sectional area of the dendrimer was calculated (see Supporting Information). If the content of each moiety is higher than about 70 %, incompatibility effects are avoided and chains can mix regularly over the surface of the dendrimer (Figure 2 a). In this case, the dendrimer can adopt an approximately cylindrical shape and arranges in a lamellar phase (Figure 2 b) as it has been demonstrated previously.[8] However, when the content of the moieties comprises 30 to 70 %, incompatibility effects dominate the packing behavior of the chains, and they segregate in nanodomains to try to join those of the same nature (Figure 2 c), thus generating a SmA^+ structure (Figure 2 d) because of the disruption of the layers in domains too small to be detected by X-rays.

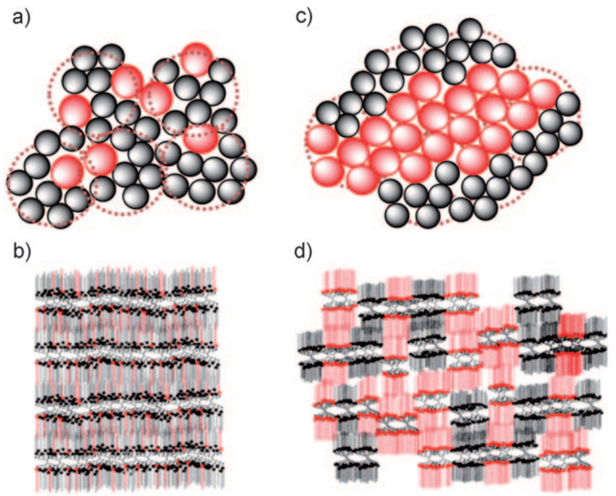

Figure 2. Proposed molecular organization in a,b) the SmA_H phase PPI-(ac)$_{14}$-(af)$_2$ and c,d) the SmA^+ phase PPI-(ac)$_{10}$-(af)$_6$. a,c) Upper views, b,d) side views relative to the alkyl chain orientation. Perhydrogenated chains are shown in black and semifluorinated chains in red.

To corroborate that SmA^+ phase apparition comes from the mobility of the terminal groups in the mesomorphic state, some analogous covalent co-dendrimers were prepared. All of them present a SmA phase, which was unambiguously identified by X-ray diffraction at room temperature, and their clearing point and layer spacing increase as the quantity of semifluorinated units grows (Table 2). Covalent bonds force the acids to be in fixed positions in the scaffold of the co-dendrimer and, therefore, the frustrated SmA phase does not appear in any case.

Table 2: Phases and X-ray data of the covalent compounds.

Co-dendrimer	Phase[a]	Lattice constants [Å][b]	Clearing *T* [°C]
PPI-(ac)$_{12}$-(af)$_4$-cov	SmA	28.0	80
PPI-(ac)$_8$-(af)$_8$-cov	SmA	28.2	100
PPI-(ac)$_4$-(af)$_{12}$-cov	SmA	32.9	125

[a] Mesophases exhibited for the covalent compounds at room temperature. [b] Layer spacing of the smectic phase determined by X-ray diffraction at room temperature.

To improve our knowledge of the microsegregation phenomenon and the molecular arrangement, AFM studies were performed. Samples were prepared by drop-casting deposition on mica (see the Supporting Information). Perhydrogenated homodendrimer organize in a monolayered surface with a thickness of 3.3 ± 0.1 nm (Figure 3 a). If we assume both the negative charge of the mica surface[17] and the flexibility of the dendrimer core, we can propose a mixed-molecular model to explain this value. The positive dendrimer core part interacts with mica surface, whereas carboxylic chains are oriented perpendicular to the substrate towards the air phase. A second layer, with molecules adopting a cylinder shape (as it has been described in bulk state)[8] is placed over the first one, thus attaining a total thickness of 3.6 nm, and resembling 1.5 layers in reference to XRD. The small difference (0.3 nm) could be attributed to an interdigitation process or a slightly curled arrangement of the chains of the layer in contact with the air phase.[18] To the best of our knowledge, it is the first time that such a good flat self-assembly is observed by simple drop-casting for these compounds.[19]

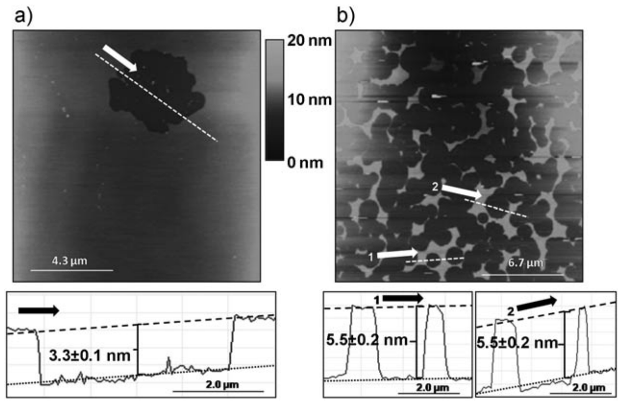

Figure 3. AFM topographic images and cross-sections of a) PPI-(ac)$_{16}$ and b) PPI-(af)$_{16}$ at room temperature. Lighter areas correspond to the dendrimeric material.

In contrast, semifluorinated homodendrimer adopts a disrupted bulky arrangement (Figure 3 b). In fact, SPFM[20] studies reveal the segregation towards the air phase of the semifluorinated chains, which causes thicker layers, probably owing to the electrostatic repulsion with mica surface[21] (see the Supporting Information). All the bulky arrangements show a similar height of 5.5 ± 0.2 nm. A similar arrangement model to PPI-(ac)$_{16}$ can be proposed but taking into account that the stiffer nature of the semifluorinated chains[14] makes their interdigitation more difficult and therefore the total thickness is approximately twice the molecular layer (according to XRD data).

Especially relevant are results in case of PPI-(ac)$_{12}$-(af)$_4$ at room temperature, because two phases are detected, namely the stiffer phase with a height of 3.4 ± 0.1 nm and the softer phase with a height 2.1 ± 0.1 nm (Figure 4 a,b). These data resemble the two layer spacings (SmA_F and SmA_H) observed

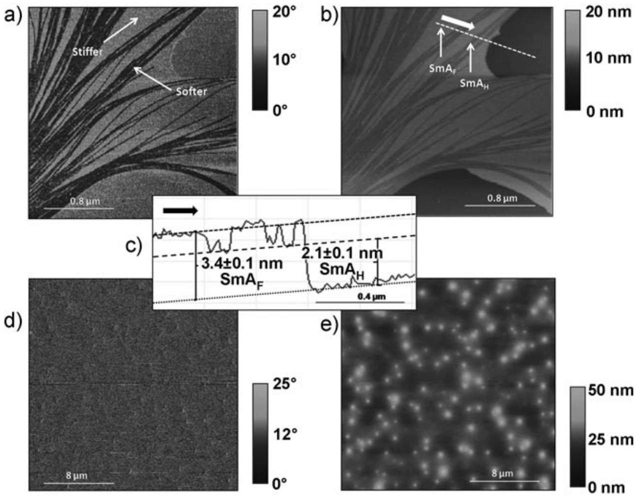

Figure 4. AFM images of PPI-$(ac)_{12}(af)_4$: a) phase, b) topographic, c) cross-section at room temperature; d) phase and e) topographic at 50 °C.

by X-rays (Figure 4 b,c). This phase evolves to a single phase (SmA^+) at 50 °C, as shown its phase image (Figure 4 d,e).

Surprisingly, PPI-$(ac)_8$-$(af)_8$, which exhibits the SmA^+ mesophase from room temperature, adopts a terraced disposition with different thickness layers (Figure 5). Thus, these compounds show a huge tendency to arrange in a lamellar organization when they are disposed on mica, in contrast to the lack of such a long-order lamellar arrangement exhibited in the bulk state, as XRD data indicates.

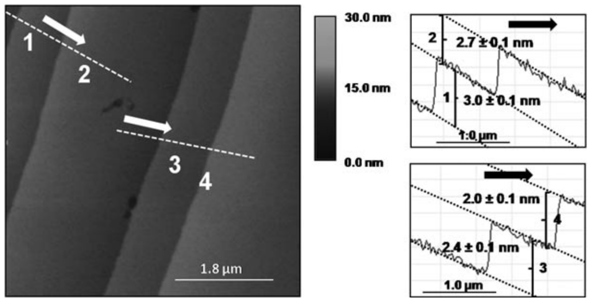

Figure 5. AFM topographic image and cross-section of PPI-$(ac)_8$-$(af)_8$ at room temperature.

Additional studies by XPS (see Supporting Information) show that, at least in a microscopic level, the semifluorinated chains appear regularly distributed in the surface, indicating that segregated chains domains only appear at nanoscopic level.

In summary, the ionic nature of these mesophases is crucial to determine the nanoscopic molecular arrangement in these materials, both in bulk and disposed on a surface. The moieties can flow to produce a more stable system, thus overriding steric incompatibility and forming smectic or frustrated smectic phases. Incompatible ionic terminal groups tend to segregate (phobias) whereas similar ones tend to be together (philias). The prevalence of a majority group obscures the minority group effect. Therefore, despite the elevated molecular entropy (minority groups remain almost isolated from their homologous in a random molecular distribution), enthalpic forces dominate and conventional lamellar phases appear owing to the long-order organization of the molecules. Therefore, the philias of the majority microdomains overcome terminal-group phobias.

By contrast, when the quantity of both groups are similar, enthalpic factors that would force the identical chains to be together is dominated by the entropic factor, and therefore the nanodomains of homologous molecules are prevented from joining in a long-range order, and conventional lamellar mesophases are not detected by X-rays. In this case, phobias of the microdomains is the most important effect and overcomes the philia of the terminal groups.

Topographic and phase AFM images agree with the results obtained by XRD. Futhermore, these compounds have a high tendency to self-assemble in a layered structure, which is probably caused by electrostatic interactions with the substrate.

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