Nanostructured Materials through Orthogonal Self-Assembly in a Columnar Liquid Crystal

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This paper describes a system in which an acid functionalized discotic molecule and poly(propyleneimine) dendrimer self-assemble into a new type of oblique columnar liquid crystalline (LC) phase that displays a well-ordered superlattice. The orthogonal combination of hydrogen bonding in the columnar direction and ionic interaction in the plane perpendicular to the columns gives rise to a structure in which the dendrimer is confined to separate columnar domains. The structure of the mesophases formed in the mixed system has been elucidated by infrared spectroscopy and X-ray diffraction. Investigation by differential scanning calorimetry and polarizing optical microscopy has shown that the LC phase is most stable in an 8:1 molar mixture but remains stable over a wide temperature and composition range. In dendrimer enriched mixtures the lattice swells to take up more dendrimer, while discotic enriched mixtures show the appearance of lamellar phases with a columnar structure that is probably closely related to the oblique superlattice. Additionally, the structure of the oblique superlattice can be covalently stabilized at elevated temperature via amidation of the ionic carboxylic acid−amine complexes. The results show the potential of orthogonal self-assembly in columnar LC phases to obtain nanostructured materials with a periodicity of 2–10 nm.

1. Introduction

Liquid crystals (LCs) are self-assembled soft materials that possess orientational order without or with only low-dimensional positional order (less than 3D).[1,2] The combination of order and mobility found in LCs yields well-organized materials that are able to respond to external stimuli (e.g., electrical, chemical or mechanical).[3–5] This unique combination is also essential to achieve complex self-organized structures like those found in biological systems.[6] At the molecular level, LC behavior is directly related to structure and can be induced by a combination of structural factors that fall in three broad classes, namely, anisotropic shape of the molecules, microsegregation between incompatible molecular segments (at least one of which should be flexible), and specific interactions between individual molecules.[5,7] A number of recent fundamental studies have not only greatly aided in understanding the factors governing LC self-assembly, but have also shown that it is possible to design LC systems with intricate structures by carefully combining and balancing these factors.[8–10] The possibility to engineer complex structures in LC phases as well as their inherent properties make LCs extremely suitable to develop self-organized functional materials.[11]

Mesoporous structures (IUPAC definition: pore size 2–50 nm) are one of the many potential application areas for LC based functional materials. These porous materials currently attract much interest, because of the large surface area to volume ratio they provide and their possible applications in molecular separations.[12–14] Membranes with mesopores, also referred to as nanoporous membranes, are specifically well suited for the separation of proteins based on a difference in

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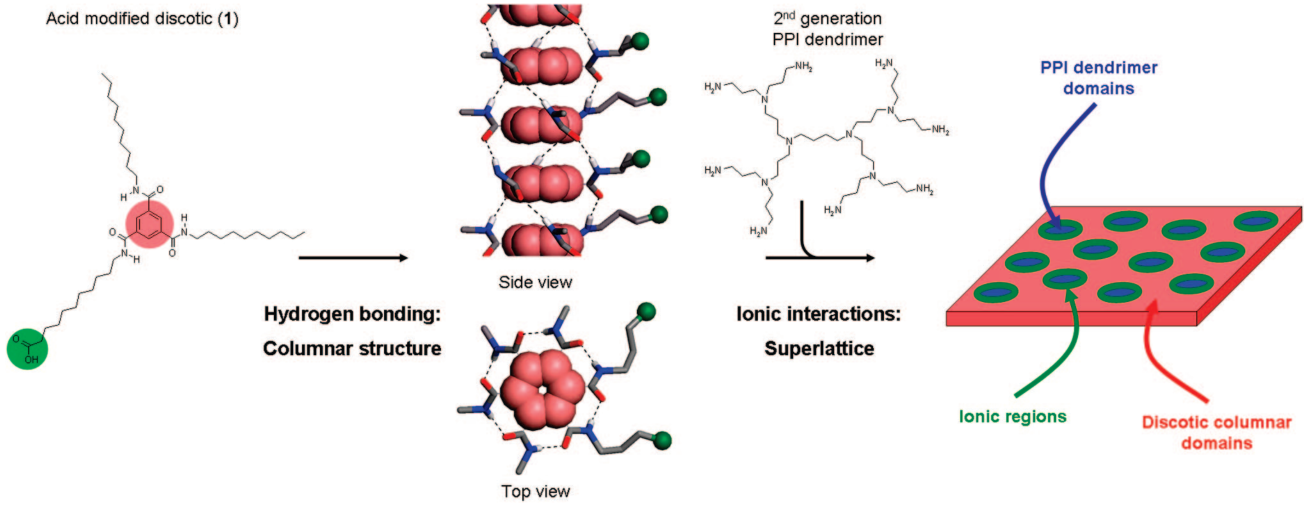
Scheme 1. Schematic Representation of the Approach Adopted in the Current Study and the Molecular Structures of the Acid-Modified Discotic (1) and PPI-dendr[27] [a]



[a] The three-dimensional structure of the hydrogen bonded stacks of **1** is depicted as follows: The benzene core is shown in red, atoms of the amide bonds are shown in stick rendering, and hydrogen bonds are indicated by black dashed lines. Only the acid-modified side chains are shown schematically, the green balls representing the carboxylic acid groups.

their hydrodynamic volume (typical range 5–25 nm).[15] Unfortunately, conventional polymer based nanoporous membranes generally have a high resistance to flow and display poorly defined pore features on the nanometer scale.[15,16] Alternatively, well-ordered nanostructured organic and inorganic films can be obtained from block-copolymers directly or by using amphiphilic block-copolymers as a template. Rendering such structures porous requires the selective removal of organic domains under relatively harsh conditions (high temperatures, reactive etching) which complicates their use in many applications.[17,18] In this context LC based systems that can be polymerized *in situ* are an attractive alternative. Such polymerizable LC assemblies with a well-defined porous structure were reported recently, most notably by Gin and his co-workers.[19–22] The pore size in the structures obtained by this elegant approach is 0.5–2.0 nm, which is around the lower limit of mesoporous materials.

In our research, we aim at developing functional materials based on columnar LCs formed by discotic benzene 1,3,5-tricarboxamide derivatives. These molecules are known to form hydrogen bonded columnar LCs in a wide temperature range. In addition, the strong macrodipoles present in these systems offer a handle for the alignment of the phase by an electric field.[23–25] Specifically, we want to target mixed LC phases in which the addition of a second, minor component gives rise to a well-ordered superlattice through reversible interactions orthogonal to the hydrogen bonding along the columns (see Scheme 1).[26] By using reversible interactions the minor component should easily be removed or substituted in a later stage to yield functional porous materials with pore sizes well within the mesoporous size range (2–10 nm).

In the present study we use ionic interactions between a carboxylic acid-modified discotic and a poly(propylene-imine) dendrimer (PPI-dendr). PPI-dendr is a well-defined and flexible molecule that has a large number of terminal amine groups.[28,29] As is well-known, covalent attachment of mesogenic units to PPI-dendr can lead to LC behavior.[30] The use of ionic interactions is an established method to prepare mixed LC materials and several ionic columnar LCs were reported recently.[31–34] For PPI-dendr, specifically, several self-assembled ionic LCs based on complexation with carboxylic acids were described by Serrano et al. and others.[35–37] Recently, Tschierske et al. showed that ionic

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Table 1. Phase Behavior of Pure 1 and 1/PPI-dendr Mixtures

composition (**1**:PPI-dendr)[a]	*T*, °C (Δ*H*, J/g)									
1:0	C	38	(15.1)[b]	Col_{hd}				116	(6.4)[c]	I
4:1				Col_{od}				123	(7.2)	I
5:1				Col_{od}				125	(9.6)	I
6:1	C	61	(1.2)	Col_{od}				135	(14.5)	I
7:1	C	66	(1.9)	Col_{od}				139	(16.0)	I
8:1	C	69	(2.7)	Col_{od}				141	(17.6)	I
10:1	C	70	(3.5)	Col[d]	114	(1.0)	Col_{od}	140	(16.2)[e]	I
12:1	C	62	(2.5)	Col	115	(3.2)	Col	137	(13.1)[e]	I
15:1	C	55	(2.1)	Col				133	(11.8)	I

[a] The composition of the samples is reported as mol **1**:mol PPI-dendr. [b] Corresponding to 10.1 kJ/mol. [c] Corresponding to 4.3 kJ/mol. [d] Designates a mixture of columnar phases or an unknown columnar phase. See the text for a detailed discussion of the nature of these phases. [e] The reported enthalpy is the combined energy of the Col-Col_{od} and Col_{od}-I transitions to allow for comparison across the mixture series.

interactions between PPI-dendr and acid functionalized facial amphiphiles give rise to a whole range of complex mesophases, some of which are columnar in nature.[38] None of these systems, however, displays the well-defined superlattice of dendrimer domains we aim for. Other examples of superlattices in columnar LC phases exist, but these were either induced by covalent coupling of the two components making up the superlattice or by combining free mesogenic units with a polymer that was functionalized with the same mesogenic groups.[39–42] Weakly ordered superlattice structures were also described for columnar LCs formed by molecules with incompatible molecular segments and were ascribed to microphase segregation.[43,44] In another study, Müllen and co-workers reported a columnar superlattice based on ionic interactions.[45] In this system a rigid alpha helical polymer and an acid-modified π-π stacked discotic self-assemble into a hexagonal superlattice.

In the following we report a system in which an acid functionalized discotic and PPI-dendr self-assemble through hydrogen bonding and ionic interaction that are mutually orthogonal. This leads to a new type of oblique columnar mesophase that displays a well-ordered superlattice. The LC phase behavior of the mixtures has been investigated by differential scanning calorimetry and polarizing optical microscopy. In addition, the structure of the mesophases formed in the mixed system has been elucidated by infrared spectroscopy and X-ray diffraction.

2. Results and Discussion

2.1. Synthesis of 1 and Preparation of the Mixtures. The acid-modified tri(decyl)benzene-tricarboxamide discotic (**1**, Scheme 1) was synthesized in a conventional manner by reacting benzene 1,3,5-tricarboxylic acid chloride with a mixture of the appropriate amines (decyl amine and amino undecanoic acid methylester). Saponification of the methylester and subsequent purification by column chromatography yielded **1** as a white solid. The structure and purity of **1** was confirmed by ^1H and ^{13}C NMR spectrometry, MALDI-TOF mass spectrometry and elemental analysis.[46]

Mixtures of **1** and the second generation PPI-dendr were prepared in various molar ratios by dissolving both components in methanol and evaporating the solvent. After drying under vacuum overnight, the mixtures appeared as waxy white solids up to a molar ratio of 5:1 (**1**:PPI-dendr) and as flakey white solids for mixtures with a higher content of the acid-modified discotic.

2.2. Liquid Crystallinity. The LC phase behavior of both pure **1** and the **1**/PPI-dendr mixtures was studied by Differential Scanning Calorimetry (DSC) and Polarizing Optical Microscopy (POM). The pure acid-modified discotic displays a single LC phase between 38 and 116 °C as determined by DSC (Table 1). Analysis by POM in the mesophase region after slow cooling from the isotropic melt showed a clearly birefringent texture (Figure 1a). This so-called pseudo focal conic fan-like texture is characteristic for columnar mesophases and similar to textures that were observed for other 1,3,5-tricarboxamide derivatives.[47–49]

Investigation by POM showed no birefringence for the 2:1 mixture, which points to a complete loss of liquid crystallinity at this mixing ratio. It was somewhat more complicated to investigate the phase behavior of the other mixtures because the two components react at temperatures well below the isotropization temperature of the mixtures. From recent work on supramolecular LCs based on ionic interactions between carboxylic acids and PPI-dendr, it is known that ionic acid–amine complexes are converted to covalent amide bonds above 100 °C.[35] Owing to this covalent linkage of the two components, it was impossible to obtain well-defined textures by slowly cooling from the isotropic melt. Therefore, we drop-cast the mixtures directly from a

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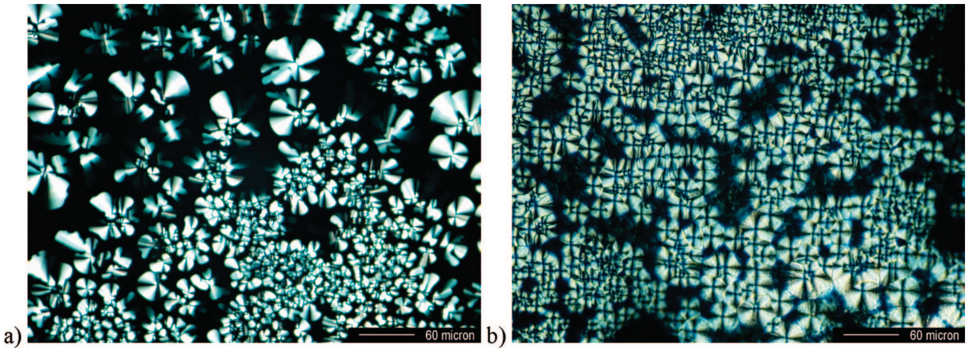

Figure 1. POM micrographs. (a) Pure **1** at 110 °C after slow cooling from the isotropic melt (2 °C/min). (b) The 8:1 molar mixture at 100 °C after slow evaporation of methanol.

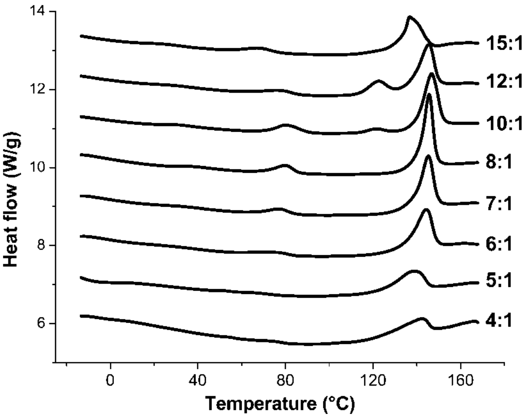

Figure 2. DSC traces for **1**/PPI-dendr mixtures (heating runs at 40 °C/min after annealing at 100 °C). The composition of the samples is indicated on the right side of the traces as mol **1**:mol PPI-dendr.

methanol solution, allowed the solvent to slowly evaporate at room temperature, and annealed at 100 °C. Samples prepared in this manner yielded POM textures with domains extending over several tenths of micrometers (Figure 1b). The brightly birefringent and mobile textures prove that the mixed phases are indeed liquid crystalline in nature. Moreover, the focal conic fan-like texture observed after annealing resembles the texture of pure **1** and is consistent with a columnar mesophase. DSC experiments on the **1**/PPI-dendr system showed a considerable depression of the phase transition temperatures as well as broadening of the corresponding peaks in subsequent heating and cooling cycles. These observations indicate that also during regular DSC experiments amidation occurs in the mixtures. Therefore, we decided to quantify the phase transitions of the mixtures based on DSC experiments in which the samples were first annealed at 100 °C for 15 min before performing a single cooling and heating cycle at a relatively high rate (40 °C/min).

The transition corresponding to isotropization as observed by POM is clearly seen in the DSC heating run for all mixtures with a **1**:PPI-dendr ratio of 4:1 or higher (Figure 2 and Table 1). The onset of isotropization ranges from 123 to 141 °C. Realizing that PPI-dendr is an isotropic liquid at room temperature and pure **1** is isotropic above 116 °C, these high isotropization temperatures for the mixtures are remarkable. Clearly, at least one new, mixed LC phase is formed that is thermally more stable than the columnar mesophase of the pure acid-modified discotic. The DSC data indicate that the 8:1 mixture has the highest clearing temperature, sharpest transition and highest transition enthalpy: hence it forms the most stable mixed mesophase. The stability of the 8:1 mixture can be explained by the fact that at this composition primary amines and carboxylic acid groups are present in a stoichiometric ratio. In this situation the complexation between the amines in the periphery of PPI-dendr and the acid-modified discotic is most effective. On the time scale of the DSC experiments crystallization only takes place at mixing ratios of 6:1 or higher, which gives rise to the crystal-mesophase transitions observed between 55 and 70 °C. Finally, all mixtures with a higher mixing ratio than 8:1 show a second melting peak around 115 °C, just below the isotropization temperature. This transition is probably due to melting of the lamellar phases that appear in the disk rich composition region (see section 2.3.4 below).

2.3. Mesophase Structure. We determined the mesophase structure of pure **1** and the structure of the mesophases formed in mixtures of **1** and PPI-dendr by Small and Wide Angle X-ray Scattering (SAXS and WAXS) and infrared (IR) spectroscopy, both at variable temperature. For clarity, the discussion of the mesophase structures will be divided in four parts. First, the mesophase structure for pure **1** is treated (2.3.1). Second, we discuss how orthogonal ionic and hydrogen bonding interactions direct the self-assembly of pure **1** and PPI-dendr into an oblique columnar superlattice in the most stable 8:1 mixture (2.3.2). Subsequently, we give a qualitative description of the phase behavior of the mixtures enriched in dendrimer (2.3.3) and acid-modified discotic (2.3.4), respectively, relative to the most stable composition.

2.3.1. Pure **1.** In many discotic LC molecules based on large aromatic cores (e.g., triphenylenes) π-π interactions between the cores play an important role.[50] This is less so for discotics with aliphatic chains coupled directly to a single benzene tricarboxamide core that mostly rely on hydrogen bonding interactions for their self-assembly into columnar mesophases.[51] Here the strong, 3-fold hydrogen bonding along the columnar axis in the mesophase leads to characteristic shifts in a number of amide related absorption bands in the IR spectrum when compared to the weaker hydrogen

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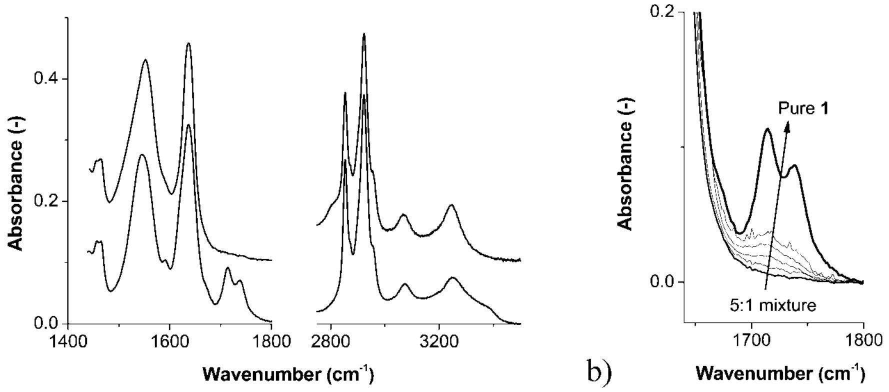

Figure 3. IR spectra at 100 °C. (a) Pure **1** (bottom) and the 8:1 mixture (**1**:PPI-dendr, top). The top spectrum is plotted with a vertical offset for clarity. (b) Magnification of the carboxylic acid absorption bands for pure **1** and the 5:1, 8:1, 10:1, 12:1, 15:1 mixtures. The spectra for the 5:1 mixture and pure **1** are plotted with a heavy line and the arrow indicates the observed trend with increasing content of **1**.

bonded isotropic state.[52,53] Therefore, IR spectroscopy is an ideal technique to probe the columnar structure of the mesophases formed in the present system.

The IR spectrum for pure **1** in the mesophase at 100 °C shows a strong amide C═O stretch absorption band at 1638 cm^{-1} and a relatively sharp amide N─H stretch band around 3247 cm^{-1} (Figure 3a). Both features are characteristic for strong hydrogen bonding between the individual discotics along the columnar axis.[51] More evidence for the regular columnar nature of the mesophase of **1** comes from the WAXS data recorded at the same temperature (Figure 4). Here we observe an intense and diffuse halo centered around a distance of ~0.47 nm and a weaker maximum at a higher q-value corresponding to a distance of 0.35 nm. The diffuse halo is commonly observed for discotic LCs in their mesophase and is attributed to the liquid-like order between the molten alkyl chains. The second maximum corresponds to the interdisk stacking distance along the columnar axis. From the width of this peak a correlation length of approximately 14 discotics can be estimated indicating a fairly disordered arrangement of the discotics along the columnar axis in the mesophase.[54,55] The stacking distance of 0.35 nm arises from the interplay between hydrogen bonding and π-π interactions between the benzene cores and was reported earlier for other benzene tricarboxamide derivatives, both in their crystalline and LC state.[56–58]

The two-dimensional arrangement of the columns in the plane perpendicular to the columnar axis has been investigated by SAXS. The neat acid-modified discotic displays a characteristic hexagonal diffraction pattern with three clear diffraction peaks spaced in q-space at relative positions $1{:}\sqrt{3}{:}2$ (Table 1). Therefore, we have indexed the SAXS data as a hexagonal lattice and, also based on the limited correlation length observed for the disk-disk stacking by WAXS, determined the mesophase type for pure **1** to be disordered hexagonal columnar (Col$_{hd}$).

2.3.2. 8:1 Mixture: An Oblique Columnar Superlattice. In the IR spectrum for the 8:1 mixture (Figure 3a) of the acid-modified disk and PPI-dendr, the bands that are indicative for hydrogen bonding of the amide group appear at approximately the same wavenumbers as in pure **1** (C═O stretch 1638 cm^{-1}, N─H stretch 3245 cm^{-1}). The corresponding regular columnar stacking in the mixed mesophase is confirmed by the practically constant interdisk distance as observed in the WAXS patterns of all the mixtures in the 8:1 composition range (Figure 4). In addition, the correlation lengths for the columnar stacking calculated from these patterns is comparable to that found for pure **1** (14–17 discotics). The formation of the ionic complex between the carboxylic acid and the amine in the mixed mesophase is demonstrated by the IR spectra as well. The absorption bands of the free and dimerized carboxylic acid at 1739 cm^{-1} and 1715 cm^{-1} respectively are completely absent in the IR spectrum of the 8:1 mixture, while the maximum of the broad absorption band in the amide II region shifts to a slightly higher wavenumber (1553 cm^{-1}) due to the contribution of the asymmetric stretching band of the carboxylate anion in this region.[35,61]

The combination of IR and WAXS data demonstrates the columnar stacking of the discotics in the mixed mesophase of the 8:1 mixture, while IR also clearly shows that both hydrogen bonding and ionic interactions are present. The presence of the ionic interactions does not change or weaken

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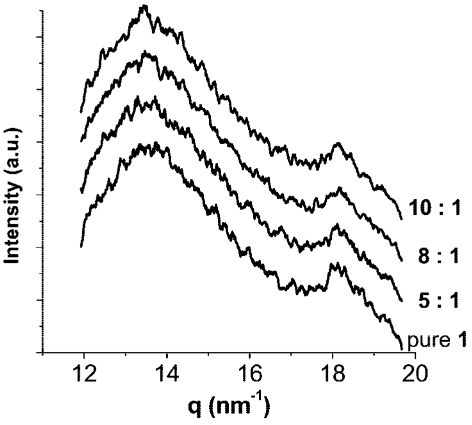

Figure 4. WAXS patterns for pure **1** and mixtures with different molar composition ratios (**1**:PPI-dendr) at 100 °C.

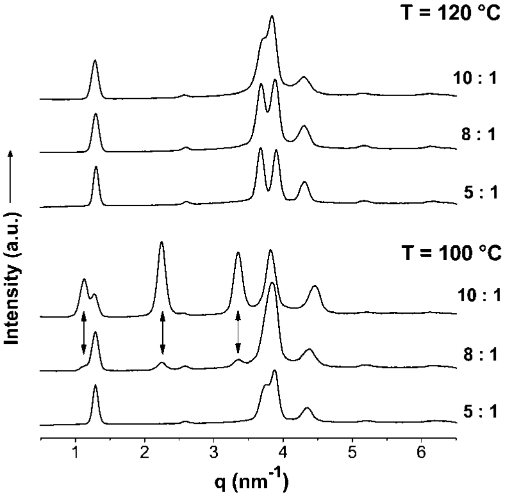

Figure 5. Integrated SAXS patterns for the 5:1, 8:1 and 10:1 mixture at 100 °C (bottom) and 120 °C (top).The double arrows in the patterns at 100 °C indicate the position of peaks that originate from a second, lamellar phase which coexists with the oblique columnar phase.

the hydrogen bonding interactions along the columnar axis of the acid-modified discotic to an appreciable extent, proving that the two interactions are indeed orthogonal in the present system.

The SAXS pattern of the 8:1 mixture turns out to be rather complicated (Figure 5). The most prominent features are the intense maximum in the low q-region (1–2 nm^{-1}) and the complete disappearance of reflections from the original hexagonal lattice of the acid-modified discotic. At 120 °C, the SAXS pattern shows one intense low-q maximum, two partly overlapping peaks with nearly equal intensity around 4 nm^{-1} and a number of weaker reflections. The SAXS pattern at 100 °C is qualitatively the same except for an additional set of three very weak peaks (indicated by the double arrows in Figure 5). This second set of peaks has in q-space a relative spacing of 1:2:3 attributed to the presence of a small amount of a coexisting lamellar phase (also see section 2.3.4).

The low-q maximum in the mixed mesophase originates from molecular order with a periodicity of about 5 nm, much larger than the diameter of the individual columns in the lattice of pure **1** (2 nm). Furthermore, two-dimensional SAXS of a weakly aligned sample of the mixtures in the LC state

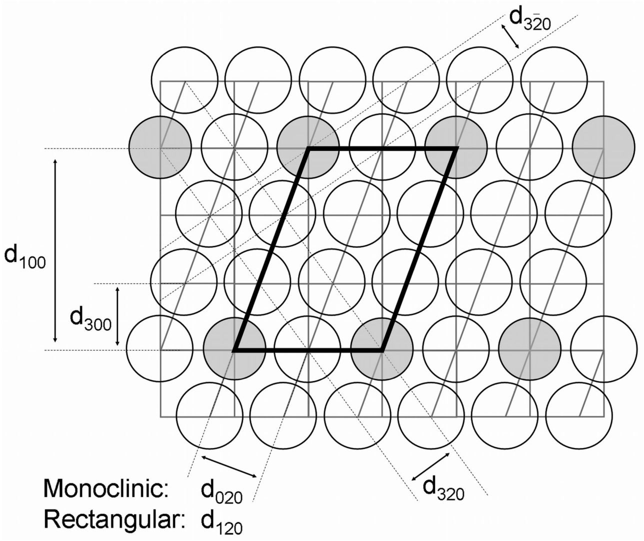

Figure 6. Structural model proposed for the oblique columnar mixed mesophase in the 8:1 composition range. Gray circles correspond to PPI-dendr domains and the white circles to the acid-modified disk columns. The light gray lines show the rectangular grid on which the model is based and the parallelogram in heavy black indicates the unit cell. The most important lattice planes are shown by the dotted lines and labeled by their *d*-spacing conform the monoclinic indexing (d_{hkl}) unless indicated otherwise.

prove that all observed diffraction peaks arise from order in[62] the same single plane. Evidently, addition of PPI-dendr to the acid-modified disk and the ionic interaction between the two components generate a completely new and well-developed columnar superlattice in the mixed LC phase.

To construct a two-dimensional structural model for the mixed mesophase that accounts for the observed diffraction pattern, we first consider the three strongest reflections. The low-q peak, which corresponds to the largest *d*-spacing, is attributed to an ordered arrangement of dendrimer domains in a columnar lattice of the acid-modified discotic and therefore taken to be the (100) reflection of the superlattice. In all SAXS patterns the positions of this first-order reflection and the second reflection of the pair of overlapping reflections around 4 nm^{-1} have exactly a relative ratio of 1:3. The combination of a high intensity of the third-order reflection and a very weak second-order one suggests an additional periodicity in the lattice in this direction that is exactly three times smaller than the first-order spacing. Comparing the SAXS patterns at different temperatures and compositions (Figure 5), it is clear that the position of the last intense reflection has no fixed ratio relative to that of the other two strong ones. Consequently, this reflection must originate from a set of lattice planes not parallel to the (100) and (300) planes. Ascribing a (120) index to the nonparallel reflection in a rectangular lattice we can accurately reproduce all observed *d*-spacings.

Starting from a simple rectangular lattice we have developed the more detailed structural model for the mixed mesophase depicted in Figure 6. The rectangular lattice is depicted by the light gray lines in Figure 6 and the planes are labeled using monoclinic indices, transforming the (120)

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(62) After shear alignment of the samples, all diffraction peaks split up in two opposing maxima that align in the same direction on the two-dimensional detector. See Supporting Information for details.

planes into (020) planes (see below). In this model, the discotic columns and dendrimer domains are located on the crossing points of a grid made up of the (100), (120) and (300) lattice planes in the rectangular lattice. This arrangement assures that the electron density is highest along these lattice planes and, thereby, accounts for the fact that these three sets of planes give rise to the most intense X-ray diffraction peaks. The PPI-dendr domains, which are responsible for the formation of the super structure, are only present in the (100) planes. The individual PPI-dendr domains are separated by a single column of the acid-modified discotic within the (100) plane and by a complete layer of discotic columns on each side in the perpendicular direction. Note that the dendrimer domains in subsequent (100) planes are shifted by one grid position in the direction along the plane. Since the periodicity of the dendrimer domains in this direction is two grid positions, this half-period shift explains why reflections from planes perpendicular to (100) are systematically absent in the SAXS patterns.

Although the structural model was constructed starting from a rectangular lattice, the smallest possible unit cell (enclosed by the heavy black lines in Figure 6) is actually a parallelogram with an angle of around 70°. In this way we are indeed able to index all the SAXS peaks using only (*hk*0) reflections in a monoclinic lattice (Table 2, monoclinic indices used in Figure 6). In short, based on the evidence from IR, SAXS and WAXS, the mixed LC phase formed in the 8:1 mixture can be characterized as a disordered columnar mesophase with an oblique superlattice ($\mathrm{Col_{od}}$).

The most important feature of the structural model is that in the mixed mesophase PPI-dendr is confined to separate columnar domains. Similar to the situation in a perfect hexagonal superlattice, each of the dendrimer domains is surrounded by six columns of the acid-modified discotic, thus allowing for efficient ionic complexation. However, not all discotic columns are equivalent in the present oblique superlattice: columns in the (100) lattice planes have two neighboring dendrimer domains and there are two distinct types of columns having one neighboring dendrimer domain (columns in the (010) planes on the unit cell edge are not equivalent to the columns enclosed by the unit cell). Consequently, the 6-fold symmetry is broken and the apparent stoichiometry of the superlattice is 5:1. In connection with the real stoichiometry of the superlattice, it is important to realize that PPI-dendr is a highly flexible molecule. Hence, the dendrimer domains are column-shaped continuums without any strict periodicity along the columnar axis. In case of the 8:1 mixture, a 0.35 nm thick slice (the interdisk distance) of the unit cell shown in Figure 6 contains 5/8 dendrimer molecules on average. Based on the structural model and these stoichiometric considerations the calculated density of the 8:1 mixture in the mesophase is 1.05 g/mL, somewhat higher than the densities of the separate components (pure **1** ~0.93 g/mL and PPI-dendr ~0.99 g/mL).[63] Since the mixed mesophase is partly ionic in nature, a slightly higher density is reasonable.[64,65]

We consider the structure of the oblique columnar superlattice as found in the 8:1 composition region quite astonishing and, to the best of our knowledge, unique in the literature so far. Starting out, we did not anticipate that mixing the isotropic PPI-dendr with a hexagonal columnar LC could give rise to a well-ordered nonhexagonal super structure. Deviations from the hexagonal symmetry as such are not unique in columnar LC phases. Numerous examples of rectangular and oblique columnar mesophases exist, which form because their columns have a certain degree of asymmetry.[60,66–68] The most common cause of such asymmetry is a uniform tilt of the individual discotics in the column with respect to the columnar axis.[69] Since in our system the columns of the acid-modified discotic are held together by three hydrogen bonds per discotic that should all have an equal length, tilt is very unlikely as a cause of dissymmetry in the columns. Another possible cause for asymmetric columns is a strongly anisotropic distribution of the volume occupied by the liquid-like alkyl chains around the discotic core.[66,70] Although the molecular structure of the acid-modified discotic is fairly symmetric, the mobility of the acid-modified side chains in the mixed mesophase is severely restricted by the strong ionic interactions with the dendrimer domains. The asymmetry imposed by this loss of free liquid-like volume is most probably the reason for the deviation from hexagonal symmetry in the mixed **1**/PPI-dendr system. Finally, note that two other strong and opposing driving forces direct the mesophase structure in the present system: (1) phase separation between the strongly hydrophilic PPI-dendr and the rather hydrophobic discotic and (2) favorable ionic interactions between the two components. The oblique columnar structure clearly combines microphase separated PPI-dendr domains with a high contact area allowing for ionic complexation. Considering these arguments, we can understand, at least on a qualitative level, that this unanticipated oblique columnar superlattice offers an optimal balance between the main driving forces and packing constraints acting in mixtures of the acid-modified discotic and PPI-dendr.

2.3.3. Dendrimer Enriched Mixtures: A Swollen Superlattice. The SAXS patterns of dendrimer enriched **1**/PPI-dendr mixtures all show the same general features as the patterns of the 8:1 mixture, even at a much lower

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(63) The density of pure **1** was calculated at 100 °C from the X-ray diffraction data. The value for PPI-dendr is the room temperature value reported by the supplier.

(64) Greaves, T. L.; Weerawardena, A.; Fong, C.; Krodkiewska, I.; Drummond, C. J. *J. Phys. Chem. B* **2006**, *110*, 22479–22487.

(65) For example, the density of a 1:1 molar mixture of propionic acid ($\rho = 0.993$ g/mL) and ethanamine ($\rho = 0.689$ g/mL) is 1.018 g/mL at 27 °C.

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Table 2. Summary and Indexing of the SAXS Data for Pure 1 and the 5:1, 8:1, and 10:1 Mixtures

composition (**1**:PPI-dendr)[a]	*T* (°C)	*hkl*	d_{obs} (nm)	d_{calc} (nm)	lattice type and parameters
1:0	100	100	1.73	1.73	type: $\mathrm{Col_{hd}}$ (p6 mm)[b]
		110	1.00	1.00	$a = 2.00$ nm
		200	0.88	0.87	$c = 0.35$ nm
		001	0.35		$\rho = 0.92$ g/mL
5:1	100	100	4.87	4.87	type: $\mathrm{Col_{od}}$ (p1 or p2)[c]
		200	2.43	2.44	$a = 5.19$ nm
		020	1.67	1.67	$b = 3.56$ nm
		300	1.62	1.62	$c = 0.35$ nm
		320	1.45	1.44	$\gamma = 69.9$ deg
		420	1.21	1.20	$\rho = 1.13$ g/mL[d]
		−320/520	1.01	1.00	
		001	0.35		
	120	100	4.84	4.84	type: $\mathrm{Col_{od}}$ (p1 or p2)
		200	2.41	2.42	$a = 5.18$ nm
		020	1.71	1.71	$b = 3.66$ nm
		300	1.61	1.61	$c = 0.35$ nm
		320	1.46	1.46	$\gamma = 69.3$ deg
		420	1.21	1.21	$\rho = 1.11$ g/mL
		−320/520	1.02	1.01	
		001	0.35		
8:1	100	100	4.88	4.88	type: $\mathrm{Col_{od}}$ (p1 or p2)
		200	2.43	2.44	$a = 5.19$ nm
		020	1.66	1.66	$b = 3.54$ nm
		300	1.63	1.63	$c = 0.35$ nm
		320	1.44	1.43	$\gamma = 70.1$ deg
		420	1.21	1.20	$\rho =$ N/A[e]
		−320/520	1.01	1.00	
		001	0.35		
	120	100	4.86	4.86	type: $\mathrm{Col_{od}}$ (p1 or p2)
		200	2.42	2.43	$a = 5.19$ nm
		020	1.71	1.71	$b = 3.64$ nm
		300	1.62	1.62	$c = 0.35$ nm
		320	1.46	1.46	$\gamma = 69.4$ deg
		420	1.22	1.21	$\rho = 1.05$ g/mL
		−320/520	1.02	1.01	
		001	0.35		
10:1	100	100	4.93	4.93	type: $\mathrm{Col_{od}}$ (p1 or p2)
		200	2.47	2.47	$a = 5.24$ nm
		020	1.65	1.65	$b = 3.50$ nm
		300	1.64	1.64	$c = 0.35$ nm
		320	1.41	1.43	$\gamma = 70.5$ deg
		420	1.21	1.20	$\rho =$ N/A
		−320/520	1.02	1.01	
		001	0.35		
	120	100	4.91	4.91	type: $\mathrm{Col_{od}}$ (p1 or p2)
		200	2.44	2.45	$a = 5.23$ nm
		020	1.69	1.69	$b = 3.60$ nm
		300	1.64	1.64	$c = 0.35$ nm
		320	1.46	1.45	$\gamma = 69.9$ deg
		420	1.22	1.21	$\rho = 1.01$ g/mL
		−320/520	1.03	1.01	
		001	0.35		

[a] The composition of the mixtures is reported as the molar ratio **1**/PPI-dendr. [b] The abbreviation of the mesophase type (following the conventions in refs 59 and 60) is given, followed by the plane group of the lattice between brackets. [c] Since the mesophase type is oblique, the plane group is either p1 or p2. The SAXS data did not allow us to discriminate between the two possibilities. [d] Calculated assuming a single phase is present with a uniform composition equal to the mixing ratio. See Supporting Information for a sample calculation. [e] No density was calculated because the SAXS pattern clearly shows the presence of multiple phases.

temperature (60 °C, see Figure 5 and 7). Accordingly, all the reflections have been indexed with the same oblique superlattice.[46] Evidently, the mixed mesophase can take up a much larger amount of dendrimer than in the most stable 8:1 composition by swelling the dendrimer domains in the oblique superlattice. In this swollen state, the oblique columnar mesophase does not crystallize out anymore upon cooling to 60 °C. The lack of any appreciable crystallization is in accordance with the DSC results and the waxy solid physical appearance of the dendrimer enriched mixtures at room temperature.

Swelling of the superlattice is immediately apparent when we compare the (100) spacings and *b* lattice parameters as calculated from the SAXS data (Figure 8). While the (100) spacing is constant within 0.1 nm over the complete composition range between 10:1 and 3:1, the cell parameter *b* increases about 0.2 nm for the dendrimer rich mixtures. As a consequence, the overall cell volume increases by

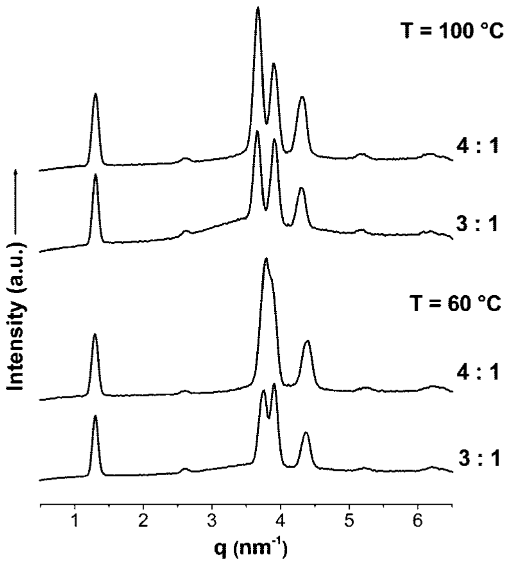

Figure 7. Integrated SAXS pattern for the 3:1 and 4:1 mixture at 60 °C (bottom) and 100 °C (top).

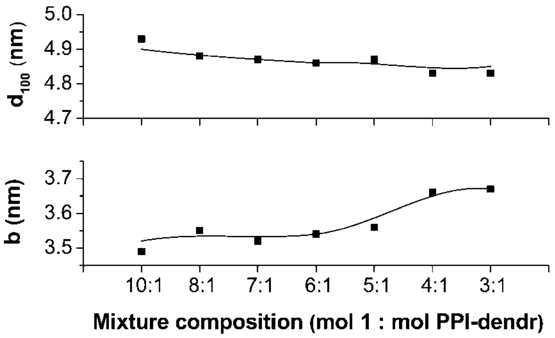

Figure 8. (100) spacing (top) and lattice parameter *b* (bottom) of the superlattice for the $\mathrm{Col_{od}}$ phase at 100 °C as a function of the mixture composition (**1**:PPI-dendr). The solid lines through the data points serve as a guide to the eye.

roughly 4%. Interestingly, the swelling of the lattice is anisotropic and most pronounced in the direction along the (100) planes. Figure 8 further indicates that the unit cell volume does not increase anymore when the **1**:PPI-dendr ratio decreases from 4:1 to 3:1. Apparently, the ability of the superlattice to incorporate more dendrimer reaches its limit in this composition range. Pushing the lattice beyond this limit leads to a two phase region in which the columnar phase coexists with an isotropic phase that probably contains mostly free dendrimer. Indeed, the diffraction peaks of the oblique superlattice in the SAXS pattern of the 3:1 mixture are superimposed on a broad diffuse halo which is centered around a q-value of ~3.5 $\mathrm{nm^{-1}}$ and belongs to the coexisting isotropic phase (see Figure 7).

2.3.4. Discotic Enriched Mixtures: Appearance of Lamellar Phases. The SAXS patterns for 12:1 and 15:1 mixtures of **1** and PPI-dendr are considerably different from those observed for the other mixtures (Figure 9). At 100 °C, there are three coexisting phases in both mixtures with strong reflections in the low q-range, one of which is the oblique columnar phase. However, there are no reflections that can be attributed to the original hexagonal lattice of the pure acid-modified discotic. The WAXS patterns for both the 12:1 and 15:1 mixtures clearly show the interdisk distance of 0.35 nm which strongly indicates that all coexisting phases are columnar.[46] The two unknown phases, arbitrarily denoted as $\mathrm{Col_l}$ and $\mathrm{Col_2}$, both have a characteristic lamellar diffraction pattern with clear multiple orders of reflection that are equally spaced along the q-axis. The *d*-spacings of 5.65 nm for $\mathrm{Col_l}$ and 6.46 nm for $\mathrm{Col_2}$ are larger than those found for the oblique columnar lattice (4.8–4.9 nm). At 120 °C, all peaks related to the lamellar phases have completely disappeared and the SAXS patterns closely resemble the patterns obtained for the oblique columnar phase. Although the *d*-spacing of the (100) reflection is the same, the high-q reflections except the (300) are weaker as well as broader than in the patterns measured at lower mixing ratios. These broader and less-defined peaks suggest a large degree of disorder in the packing of the columns in this composition range.

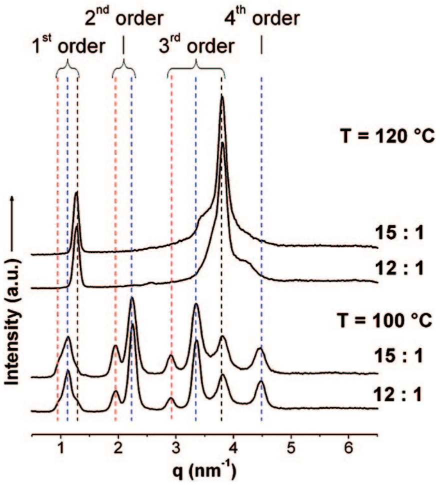

Figure 9. Integrated SAXS patterns for the 12:1 and 15:1 mixture at 100 °C (bottom) and 120 °C (top). The dashed lines indicate the position of the various orders of reflection for the three phases that coexist in this composition region: $\mathrm{Col_2}$ (red), $\mathrm{Col_l}$ (blue), and $\mathrm{Col_{od}}$ (black).

Let us now take a closer look at the possible structure of the unknown columnar lamellar phases $\mathrm{Col_l}$ and $\mathrm{Col_2}$. First of all, for various reasons a simple structure consisting of alternating continuous layers of PPI-dendr and the acid-modified discotic does not seem very likely. In that case, compared to the oblique lattice found in the 8:1 mixture, the dendrimer domains would be surrounded by a smaller number of discotics. Since the lamellar phases only appear in mixtures that contain a larger amount of discotic, there is no reason to assume a lower number of surrounding discotic columns that would lead to less efficient ionic complexation between the two components. Furthermore, we should take into account that the oblique columnar phase offers—as discussed before—the best possible balance between all the constraints and interactions involved in the current system (e.g., hydrogen bonding and ionic interactions, efficient packing of the columns, phase separation between **1** and PPI-dendr). A lamellar phase consisting of continuous layers is structurally completely different from this optimal arrangement and would also imply a large structural rearrangement between 100 and 120 °C when the $\mathrm{Col_l}$ and $\mathrm{Col_2}$ phases melt into a phase that closely resembles the oblique columnar phase. Such a major structural rearrangement would not be consistent with the rather low transition enthalpy observed by DSC in the 12:1 and 15:1 mixtures just below isotropization. In view of these arguments the structure of the lamellar phases should be closely related to that of the oblique columnar phase.

Taking the structural model of the oblique phase as a starting point, we can accommodate more columns of discotics by either inserting a complete layer of columns in the middle of the unit cell (in the (200) plane) or by putting additional columns in between de dendrimer domains along the original (100) plane. Furthermore, the overall density of the lamellar phases should be between that of the 8:1 mixture and that of the separate components: hence close to unity. In addition, the stoichiometry of the lamellar phases must exceed 12:1, because the lamellar phases coexist with the 8:1 phase in the 12:1 mixture. Based on these considerations and the lamellar spacings observed by SAXS, one can calculate that the average distance between two dendrimer domains along the (100) planes must be larger than in the original oblique lattice.[46] Therefore, we propose that the structure of the lamellar phases arises from the original oblique lattice by inserting both separate columns along the (100) plane and one or two complete layers of columns for the Col_1 and Col_2 phase respectively. Due to these additional layers of columns all correlation between the positions of the columns at both sides of the inserted layers is lost resulting in a lamellar structure without any mixed reflections in the SAXS pattern.

Although the direct experimental evidence to support our tentative structural model is limited, it does account for the strikingly high intensity of the second-order reflection in both lamellar phases when compared to the diffraction patterns of the oblique columnar mesophase. While the oblique columnar phase has a minimum in its electron density in the (200) plane, the inserted layers in the lamellar phases lead to a high electron density in this plane. Such modulations of the electron density within the layer will give rise to strong second-order lamellar reflections.[71] A similar argument might also explain why the Col_1 phase, which essentially consists of four layers of columns, even has a clearly detectable fourth-order reflection in contrast to the Col_2 phase.

According to the structure we propose for the lamellar phases, the columns in the inserted layers do not have neighboring dendrimer domains and, therefore, can not form any ionic complexes. Two lines of experimental evidence support this specific feature of the structural model. First, comparing the IR spectra for **1**/PPI-dendr mixtures with an increasing mixing ratio, the characteristic bands of the carboxylic acid start to come up at a composition of 10:1 where the lamellar phases first appear (Figure 3b). This observation proves that free and dimerized carboxylic acid groups are indeed present in the lamellar phases. Second, the DSC traces and SAXS patterns show that the lamellar phases melt at a temperature close to isotropization of pure **1**. Since the columns in the inserted layers are not stabilized by ionic bonds to the dendrimer, the local environment of these columns is similar to that in the mesophase of pure **1** and nearly equal melting temperatures can be expected. On the structural level, we assume that the inserted layers of uncomplexed columns melt while the layers of complexed columns remain intact during the phase transition to form a three-layered structure that is very similar to the oblique columnar lattice found in the 8:1 mixture. The disorder in the lattice of this high-temperature phase, which is revealed by the broad reflections in the SAXS patterns at 120 °C, could be explained by the presence of additional discotic columns along the (100) planes.

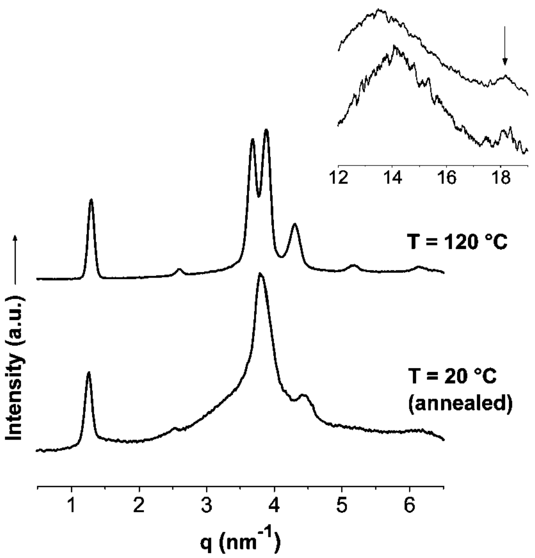

Figure 10. SAXS and WAXS (inset) patterns for the 8:1 mixture at 20 °C after annealing (bottom) and at 120 °C (top) for comparison. The arrow in the inset indicates the position of the reflections that correspond to the interdisk distance of 0.35 nm.

2.4. Covalent Stabilization of the Col_{od} Mesophase. A remarkable feature of the current system is that the mixed columnar mesophase found in the 8:1 mixture is stable in a temperature region where the ionic complexes that help stabilize the phase react to form covalent amide bonds (~100–130 °C). As noted before, the amidation of the ionic complexes complicates the characterization of the phase behavior of the system, but it also offers the interesting possibility to covalently stabilize the mesophase structure by simply annealing at a temperature between 100 °C and the isotropization temperature of the mixtures. To investigate if it is indeed possible to use the amidation process to our advantage and stabilize the structure of the Col_{od} mesophase, we annealed a 8:1 mixture for 16 h at 120 °C and studied the resulting structure at room temperature by SAXS and WAXS.

The physical appearance of the annealed mixture changes from the initial flakey solid to a somewhat brittle solid after the annealing procedure, thus indicating that amidation takes place. The formation of the amide bonds from the ionic complexes has also been confirmed by MALDI-TOF mass spectrometry.[46] The SAXS and WAXS patterns obtained for the annealed mixture at room temperature are comparable to the patterns obtained for the same mixture at the annealing temperature of 120 °C and do not show any signs of lamellar phases or crystallization (Figure 10). Accordingly, the SAXS pattern for the stabilized mixture can be indexed in a similar fashion as the Col_{od} mesophase.[46] The only difference

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(71) Francescangeli, O.; Rinaldi, D.; Laus, M.; Galli, G.; Gallot, B. *J. Phys. II* **1996**, *6*, 77–89.

between the two patterns in Figure 10 is the diffuse hallo in the q-region around ~3.5 nm^{-1} for the annealed mixture. The initial DSC experiments already showed that the amidation lowers the isotropization temperature of the mixed mesophase and, therefore, we attribute the diffuse halo to partial melting of the sample during the annealing period.

3. Conclusions

We have shown that a 8:1 molar mixture of an acid functionalized discotic and PPI-dendr self-assembles into a new type of oblique columnar mesophase that displays a well-ordered superlattice. The orthogonal combination of hydrogen bonding in the columnar direction and ionic interaction in the plane perpendicular to the columns gives rise to a structure in which PPI-dendr is confined to separate columnar domains. Moreover, the oblique superlattice found in the 8:1 mixture is stable over a wide temperature and composition range. In dendrimer enriched mixtures the lattice swells to take up more dendrimer, while discotic enriched mixtures show the appearance of lamellar phases with a columnar structure that is probably closely related to the oblique superlattice. Furthermore, we have demonstrated that the structure of the oblique superlattice can be covalently stabilized at elevated temperature by amidation of the ionic carboxylic acid-amine complexes.

The results obtained for this system clearly show the potential of our approach to obtain nanostructured materials with a periodicity of 2–10 nm. The current system also offers the straightforward possibility to tune the periodicity by varying the length of the alkyl chains in the tricarboxamide discotic. In terms of functionality, the system has potential to be used as a selective barrier due to the presence of the polar dendrimer channels in an apolar discotic matrix. Moreover, the design reported in this paper offers great promise to achieve more advanced functional materials if two important issues are addressed, namely the alignment of the columnar mesophase and the incorporation of polymerizable groups. Removal of the reversibly bound dendrimer from an analogous cross-linked system offers a direct route to highly ordered mesoporous films with sufficient mechanical integrity to be applied as membranes in size-selective separations. In addition, the superlattice can be used as template to obtain well-defined nanorods if the dendrimer domains can selectively be polymerized.

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Supporting Information Available: Experimental section, sample calculation for the density of the mixed mesophases, SAXS results for an aligned 5:1 mixture, complementary SAXS results and indexing, WAXS patterns for 12:1 and 15:1 mixtures, calculation of the average distance between two dendrimer domains in the lamellar phases, and MALDI-TOF MS data for the covalently stabilized 8:1 mixture (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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