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α -Helical-*within*-Discotic Columnar Structures of a Complex between Poly(ethylene oxide)-*block*-poly(L-lysine) and a Hexa-*peri*-hexabenzocoronene

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Abstract: Poly(ethylene oxide)-*block*-poly(L-lysine) (PEO-PLL) was complexed with an amphiphilic hexa-*peri*-hexabenzocoronene (HBC). This produced a thermotropic liquid crystalline material (PEO-PLL-HBC), which was investigated by FTIR spectroscopy and differential scanning calorimetry as well as by wide- and small-angle X-ray scattering. It was found that the poly(L-lysine) blocks form an α -helical secondary structure. Each helix is surrounded symmetrically by six discotic columns of HBC, which gives an α -helical-*within*-discotic column structural entity. The dense packing of these entities produces hexagonal sublattices (formed by the columns) in the frame of a two-dimensional hexagonal lattice (formed by the helices). An order-order transition from a columnar structure Col₁ to Col₂ was found at 54 °C. The unit cell constants are 5.75 nm (Col₁) and 6.60 nm (Col₂). The larger unit cell size of Col₂ was explained by a higher intracolumnar order of the latter in which the packing distance of the disklike HBC cores is well-defined (0.353 nm). PEO-PLL-HBC combines essential features of liquid crystals with a basic structural element of proteins into a single material.

Introduction

The complexation of block copolymers with amphiphiles is a new strategy for the formation of self-organized supramolecular polymeric materials, as was introduced and developed by ten Brinke et al.^{1,2} and recently reviewed.³ They have shown, for example, that a combination of covalent block copolymers, proton transfer, and hydrogen bonding yields a hierarchy of two different length scales (4.8 and 35.0 nm),⁴ which was termed a lamellar-*within*-lamellar structure. Further known hydrogen bonded structure-*within*-structure morphologies are lamellar-*within*-spherical, lamellar-*within*-cylindrical, cylindrical-*within*-lamellar, and spherical-*within*-lamellar structures.⁵ Diblock copolymers with one block that can be complexed via a certain interaction and a second block which cannot be used for this purpose. Poly[ethylene oxide]-*block*-poly[L-lysine] (PEO-PLL) is such a type of polymer, and it is a typical representative of the so-called double hydrophilic block copolymers.⁶

The poly(L-lysine) block is transformed from neutral to cationic via protonation of its amino functions, and the resulting ammonium side groups can be complexed by anionic species. For example, complexes of PEO-PLL and DNA (the anionic species) are used to explore the feasibility of polymeric complexes as novel vector systems for genes and oligonucleotides.⁷⁻⁹ When PEO-PLL is complexed with anionic amphiphiles, like retinoic acid, the PLL block becomes water insoluble and forms smectic A-like structures in the solid state and core-shell micelles in aqueous solution.¹⁰ In recent studies, we have shown that a carboxylic acid functionalized hexa-*peri*-hexabenzocoronene (HBC) functions successfully as the proton donor/anionic amphiphile in similar schemes involving polymers with amino groups such as poly(ethylene imine) and an amino functionalized poly(siloxane).^{11,12} The essential features of these complexes are their columnar discotic structures with long-range order and improved mechanical properties when compared with the noncomplexed HBC.

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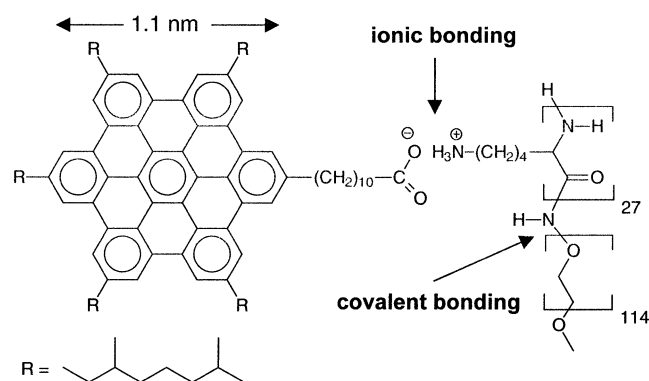


Figure 1. Molecular structure of a complex between poly(ethylene oxide)-block-poly(L-lysine) and hexa-*peri*-hexabenzocoronene (PEO-PLL-HBC).

In this study, we combine the discotic-columnar phase forming feature of HBC, with the capability of PLL to form well-defined secondary structures for the generation of new supramolecular arrangements. PEO-PLL was chosen because it was shown clearly by Kataoka et al. that the copolymerization of PLL with PEO has a strong stabilizing effect on the α -helical conformation of PLL.¹³ Especially the fact that PLL can adopt an α -helical state already for a low degree of polymerization makes PEO-PLL an attractive candidate for the combination of columnar discotic and helical structures. It is furthermore essential, for the formation of highly ordered complexes, that the amino-functional polymer and the amphiphile are soluble in the same solvent. This excludes the use of a PLL homopolymer, for example, while the PEO-PLL and the HBC are both well soluble in chloroform. The chemical structure of the polymeric complex that is formed upon proton transfer from the HBC to the PEO-PLL is shown in Figure 1. In the following, we focus on the secondary and the supramolecular structure of the PEO-PLL-HBC. An important design principle invoked here is that the repeating distance between the complexing sites along the polymer chain matches closely the repeating (stacking) element within HBC columns. We want to combine liquid crystallinity, as a basic property of many smart materials, with the well-defined conformation of a poly(amino acid), which is essential for biological function. Such may be useful in the development of new bioinspired materials.¹⁴

Experimental Section

Materials. The PEO-PLL block copolymer was synthesized and characterized by Kukula as described in an earlier study.¹⁰ This polymer has a poly(L-lysine) block with a length of 27 monomers and a PEO block with 114 monomers (PEO; $M_w = 5000$, $M_w/M_n = 1.10$). The 2-(10-carboxy-undecyl)-5,8,11,14,17-(3,7-dimethyloctanyl)hexa-*peri*-hexabenzocoronene, an amphiphilic HBC, was synthesized by a slight modification of a published procedure¹⁵ starting from 2-(bromo)-5,8,11,14,17-(3,7-dimethyloctanyl)hexa-*peri*-hexabenzocoronene.¹⁶

Complex Formation. For complex formation, 142.5 mg (0.102 mmol) of HBC and 31.2 mg (3.773×10^{-6} mol) of PEO-PLL (which contains 0.102 mmol of amino groups) were each dissolved in 25 mL of chloroform. The ratio of carboxylate to amino functions was 1:1.

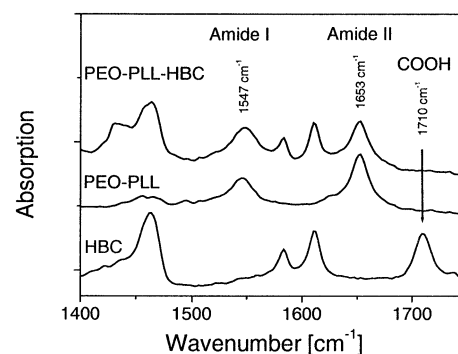


Figure 2. IR spectrum of the HBC (lower curve), the PEO-PLL (middle curve), and the complex PEO-PLL-HBC (upper curve). The arrow indicates the position of the carboxylic acid vibration band, which is present only in the spectrum of uncomplexed HBC.

Both solutions were heated to 60 °C, and the solution of HBC was added dropwise to the PEO-PLL solution while being stirred. The resultant yellow-brownish solution was slowly evaporated and the remaining PEO-PLL-HBC complex (a brownish soft matter) was dried for 12 h in a vacuum oven at 50 °C at a pressure of 10^{-3} mbar.

Methods. IR spectroscopy was performed on a Bio Rad 6000 FTIR spectrometer. Differential scanning calorimetry (DSC) measurements were performed on a Netsch DSC 200. The samples were examined at a scanning rate of 10 K/min by applying one cooling and two heating scans. Wide-angle X-ray scattering (WAXS) measurements were carried out with a Nonius PDS120 powder diffractometer in transmission geometry. An FR590 generator was used as the source for Cu K α radiation, monochromatization of the primary beam was achieved by means of a curved Ge crystal, and the scattered radiation was measured with a Nonius CPS120 position sensitive detector. The resolution of this detector in 2θ is 0.018°. The scattering vector is defined as $s = 2/\lambda \sin \theta$ with the scattering angle 2θ and the wavelength λ . Small-angle X-ray scattering (SAXS) measurements were carried out with an X-ray vacuum camera with pinhole collimation (Anton Paar, Austria, Model A-8054) equipped with image plates (type BAS III, Fuji). The image plates were read with a MAC Science Dip-Scanner IPR-420 and IP reader DIPR-420. The diffraction patterns were calculated using a simple approximation of the 2D unit cell in terms of circular disks of appropriate densities (cf. Figure 6), resulting in the correct lattice factor (peak positions) and a reasonable approximation for the structure factor (peak intensities), plotted using Cauchy peak profiles with empirical peak widths. Details concerning the procedure used for simulating scattering curves have been recently described.¹⁷

Results and Discussion

The PEO-PLL-HBC complex was first investigated by IR spectroscopy in order to determine the degree of complexation and the secondary structure of the PLL block. Figure 2 shows the IR spectra of HBC, PEO-PLL, and PEO-PLL-HBC. It appears that an intense carboxylic acid vibration band is present in the spectrum of HBC at 1710 cm^{-1} , while it is absent in the spectrum of PEO-PLL-HBC. From this, we conclude that, within the experimental error, all of the carboxylic acid functions of HBC form acid-base pairs with the amino functions of PEO-PLL, resulting in a stoichiometric complex PEO-PLL-HBC. Therefore, 27 HBC molecules are linked ionically to each PLL block. This finding is within our expectation because we observed stoichiometric complexes of HBC with amino functionalized random copolymers in earlier studies.^{11,12} The vibrations of the aromatic rings of HBC at 1584 and 1611 cm^{-1} , the

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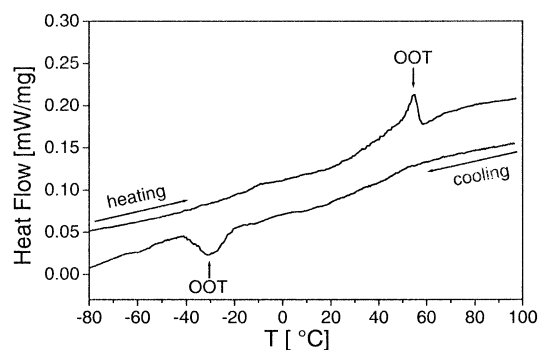


Figure 3. DSC traces of PEO-PLL-HBC while heating and cooling. The exothermic transition at 54 °C in the heating scan and the endothermic transition at -30 °C indicate a reversible order-order transition from a columnar phase Col₁ to a columnar phase Col₂.

symmetric and asymmetric CH₂ deformation vibrations, and those of the CH₃ groups at 1464 cm⁻¹ are also visible in the PEO-PLL-HBC spectrum.

Secondary Structure. The secondary structure of the PLL block could principally contain random coil, α -helical, and β -sheet motifs. Because of the α -helix stabilizing effect of the PEO block,^{10,13} a well-defined conformation of the PLL chains can be assumed. We confirmed that the poly(L-lysine) block adopts an α -helical conformation in the solid-state form of the complexed and noncomplexed PEO-PLL, as shown by the positions¹⁸ of the amide I and amide II vibrations (Figure 2). The amide I vibrations of PEO-PLL and of PEO-PLL-HBC are represented by a band at 1653 cm⁻¹. The amide II vibration band of both is located at 1547 cm⁻¹, and no significant amount of β -sheet was detected (amide II vibration band at 1534 cm⁻¹).¹⁹ This finding is similar to a PEO-PLL retinoate complex, which shows a highly stable α -helix.¹⁰ Tirrell et al. reported on the structure of poly(L-lysine) complexes with alkyl sulfates which instead form lamellar structures.¹⁹ They found that the α -helical and β -sheet portions of the poly(L-lysine) chains in their complexes depend largely on the conditions used for the preparation of the complexes, from solution to the solid state. The exact reason for the existence of the different chain conformation is not clear, but we assume that the formation of interchain hydrogen bridges, which favors the β -sheet formation, is strongly suppressed for the PEO-PLL-HBC complex but not for the complexes of poly(L-lysine) with alkyl sulfates. But the possibility of β -sheet formation in PEO-PLL-HBC, however, cannot be excluded should different complex forming conditions be used (e.g., different temperatures, other solvents).

Thermal Properties. In our earlier studies, we have shown by X-ray and differential scanning calorimetry (DSC) that the complexes of amphiphilic HBC undergo thermotropic liquid crystalline transitions between interesting columnar phases.^{11,12} Typical DSC traces for heating and cooling scans of the PEO-PLL-HBC, measured at a heating range of 10 K min⁻¹, are given in Figure 3. An endothermic transition with a maximum at 54 °C and an enthalpy of 4 J/g was found upon heating. As PEO-PLL-HBC was cooling, the transition was also found with an enthalpy of 4 J/g but with a maximum at -30 °C. The large hysteresis of the transition (84 °C) indicates that the bulky aromatic cores are involved in the transition, as their reorienta-

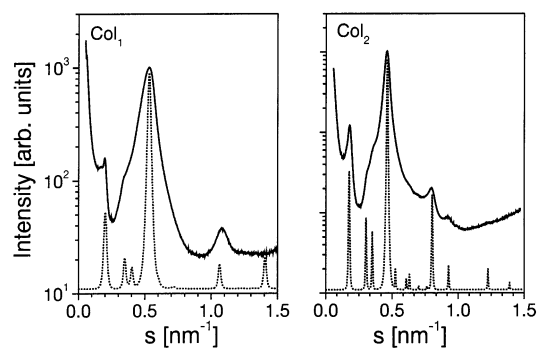


Figure 4. Small-angle X-ray scattering curves of the PEO-PLL-HBC complex in the Col₁ phase at 20 °C (left-hand figure) and in the Col₂ phase at 80 °C (right-hand figure). The solid lines are the measured intensities, and the dashed lines are the calculated scattering curves. Both phases are two-dimensional hexagonal phases. Therein, each α -helix is surrounded by six columns of HBC stacks. The lattice parameters are 5.75 nm in Col₁ and 6.60 nm in Col₂. Each column has a diameter of 1.32 nm. The (1,1) peak does not show up for the Col₁ phase, since it is near a minimum of the structure factor.

tion is known to show slow kinetics.^{11,12} We tentatively assign this finding to a reversible liquid crystalline transition between two columnar phases Col₁ and Col₂.

Discotic Columnar Structures. The α -helix is a rigid structural element in PEO-PLL-HBC, in contrast to the highly flexible amino polymers used as building blocks of HBC complexes described earlier, that is, poly(ethylene imine)¹¹ and poly(siloxane).¹² This difference should have a significant influence on the supramolecular structures adopted by the complexes, and this was confirmed by temperature-dependent small-angle X-ray scattering. As expected, and as shown in Figure 4, a number of reflections are present in the scattering curves of PEO-PLL-HBC in the Col₁ phase (20 °C) and also the Col₂ phase (80 °C). It can be seen that an intense peak at a value of the scattering vector $s = 0.531 \text{ nm}^{-1}$ dominates the pattern of the Col₁ phase ($1/s = \text{Bragg distance}$). A peak at 0.458 nm^{-1} represents that of the Col₂ phase. Taking the typical phase behavior of polyampholyte complexes of HBC into account,^{11,12} we tentatively attribute these peaks to the lateral ordering of columns of HBC. Assuming a two-dimensional hexagonal packing of columns for Col₁, we preliminarily indexed the peaks at 0.531 nm^{-1} as (1,0) and as (2,0) at 1.078 nm^{-1} . The peaks of Col₂ can be indexed as a (1,0) reflection at 0.458 nm^{-1} , (1,1) reflection at 0.796 nm^{-1} , and (2,0) at 0.926 nm^{-1} .

If a two-dimensional structure is present in both phases, however, we have to explain how the sharp reflections at 0.197 nm^{-1} (Col₁) and 0.177 nm^{-1} (Col₂) are produced. Also, the shoulders present on the lower side of the dominating reflections must be explained. The solution is surprisingly simple. It is a two-dimensional hexagonal superstructure whose lattice constant is a factor of $\sqrt{7}$ times larger than the lattice constant of the column packing. Models of the structure are displayed in Figure 5 (3D, side view) and Figure 6 (2D, top view). The columns are displayed in red, the interstitial volume filled by alkyl chains is green, and the PLL-PEO backbones are blue. It can be seen that each column, which is formed by the HBC cores, has exactly one backbone chain as its nearest neighbor. HBC and PLL are bound to each other ionically via the ammonium carboxylate moiety (cf. Figure 1). The α -helix is rigid, stretched, and confined in a cylinder, which is in agreement with the

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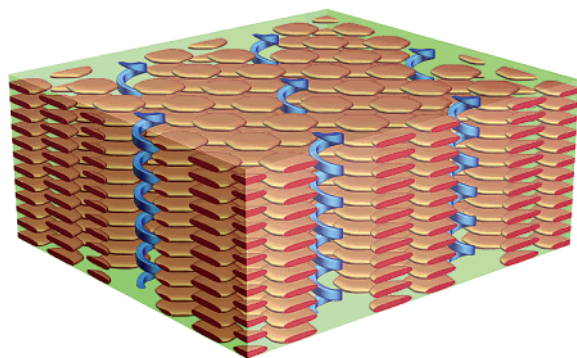


Figure 5. Model of PEO–PLL–HBC with its α -helical-within-discotic columnar structure. Each PLL chain, which adopts an α -helical secondary structure, is surrounded symmetrically by six columns of HBC (aromatic cores are plotted as disks). The helices and columns are separated by a matrix of alkyl chains. Col₁ and Col₂ phases have the same symmetry but differ in the size of their unit cells and the intracolumnar order.

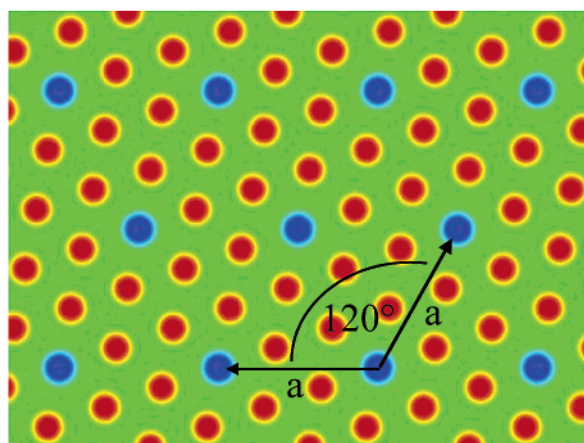


Figure 6. Density profiles of the PEO–PLL–HBC complexes perpendicular to the PLL helices (blue) and HBC columns (red and yellow). The alkyl chains form a matrix in which helices and columns are embedded. The helices form a two-dimensional hexagonal lattice with a lattice constant of $a = 5.75$ nm (Col₁ at 20 °C) and $a = 6.60$ nm (Col₂ at 80 °C).

chemical structure. A backbone chain surrounded by six columns forms the α -helical-within-discotic columnar subunit of the hexagonal lattice. The center-to-center distance between two adjacent columns within a subunit is exactly the same as the distance between two adjacent columns of two neighboring subunits. This produces the ratio $\sqrt{7}$ between the most intense reflection and the first reflection. The indexing of the reflections is changed to fit this superlattice model, as listed in Table 1.

It is noteworthy that we need only a single parameter, namely the hexagonal lattice constant a , to define the reflex positions (the angle γ is 120°). This makes the result rather significant, even though there are some uncertainties about some of the shoulders of the reflections present in the experimental curve (cf. Figure 4, solid curves). Simulations¹⁷ of the scattering patterns with approximated intensities were carried out using a fixed column diameter of 1.32 nm, which is slightly larger than the van der Waals diameter of a single HBC core (1.25 nm).²⁰ The resulting calculated scattering curves with lattice constants of 5.75 nm (Col₁) and 6.60 nm (Col₂) are displayed in Figure 4 (dashed curves). The reciprocal widths of the first reflections (empirical data) were taken as estimations of the in-plane

Table 1. Small-Angle X-ray Data of PEO–PLL–HBC^a

(<i>h</i> <i>k</i>)	<i>S</i> _{subst} [nm ^{−1}]	<i>S</i> _{calcd} [nm ^{−1}]
lower-temperature phase, Col ₁ , <i>T</i> = 20 °C		
(0,1)(1,1)(1,0)(1,0)(1,1)(0,1)	0.197 (<i>d</i> = 5.07 nm)	0.201
(1,2)(1,1)(2,1)(2,1)(1,1)(1,2)	0.348	0.348
(0,2)(2,2)(2,0)(2,0)(2,2)(0,2)		0.402
(1,3)(2,3)(1,2)(3,2)(2,1)(3,1)	0.531	0.531
(3,1)(2,1)(3,2)(1,2)(2,3)(1,3)		
(2,6)(4,6)(2,4)(6,4)(4,2)(6,2)	1.078	1.063
(6,2)(4,2)(6,4)(2,4)(4,6)(2,6)		
(3,8)(5,8)(0,7)(7,7)(3,5)(8,5)		1.406
(5,3)(8,3)(7,0)(7,0)(8,3)(5,3)		
(8,5)(3,5)(7,7)(0,7)(5,8)(3,8)		
higher-temperature phase, Col ₂ , <i>T</i> = 80 °C		
(0,1)(1,1)(1,0)(1,0)(1,1)(0,1)	0.177 (<i>d</i> = 5.65 nm)	0.175
(0,2)(1,1)(2,1)(2,1)(1,1)(1,2)	shoulder	0.303
(0,2)(2,2)(2,0)(2,0)(2,2)(0,2)	shoulder	0.350
(1,3)(2,3)(1,2)(3,2)(2,1)(3,1)	0.458	0.463
(3,1)(2,1)(3,2)(1,2)(2,3)(1,3)		
(0,3)(3,3)(3,0)(3,0)(3,3)(0,3)		0.525
(2,4)(2,2)(4,2)(4,2)(2,2)(2,4)		0.606
(1,4)(3,4)(1,3)(4,3)(3,1)(4,1)		0.631
(4,1)(3,1)(4,3)(1,3)(3,4)(1,4)		
(1,5)(4,5)(1,4)(5,4)(4,1)(5,1)	0.796	0.802
(5,1)(4,1)(5,4)(1,4)(4,5)(1,5)		
(2,6)(4,6)(2,4)(6,4)(4,2)(6,2)	0.926	0.926
(6,2)(4,2)(6,4)(2,4)(4,6)(2,6)		
(3,8)(5,8)(0,7)(7,7)(3,5)(8,5)	shoulder	1.225
(5,3)(8,3)(7,0)(7,0)(8,3)(5,3)		
(8,5)(3,5)(7,7)(0,7)(5,8)(3,8)		
(3,9)(6,9)(3,6)(9,6)(6,3)(9,3)		1.389
(9,3)(6,3)(7,6)(3,6)(6,9)(3,9)		

^a Reflex positions and Miller indices are given for the Col₁ and Col₂ phase at 20 °C and 80 °C. The scattering vector is defined as $s = 2/\lambda \sin \theta$. The Bragg-distance is $d = 1/s$.

correlation lengths, which are about 40 nm for both phases. This means that about six to seven of the α -helical-within-discotic columnar structural entities scatter coherently.

It must be mentioned that the difference in electron densities between the PEO and alkyl chains are not sufficient to produce a significant intensity contribution. Therefore, it seems unclear whether the PEO chains reside within the embedding matrix (displayed in green in Figure 6) or the cylinders that contain the PLL chains (displayed in blue in Figure 6).

The next questions are why is the lattice constant of the Col₁ phase smaller than that of Col₂ and how might this relate to apparent differences in their intracolumnar ordering. This was investigated by wide-angle X-ray scattering, and examples of the scattering profiles are presented in Figure 7. The fluidlike packing of the alkyl chains is represented by the broad halos in the wide-angle diagrams. The maxima correspond to Bragg spacings of 0.463 nm (Col₁, 20 °C) and 0.478 nm (Col₂, 80 °C). Therefore, the side chains are in an amorphous state in both phases, as expected because of their branching, and slightly less densely packed at higher temperatures because of increased thermal motions.

It can be seen there that Col₂ gives rise to a distinct reflection at $s = 2.83$ nm^{−1}, while there is only a broad reflection at this position in the curve of Col₁. We attribute these wide-angle reflections to the typical intracolumnar distance of ~ 0.35 nm, separating face-to-face HBC cores. The intracolumnar order is obviously better in the Col₂ phase than in the Col₁ phase. It is striking that the intracolumnar order is better in the higher temperature phase than in the lower temperature phase. Such

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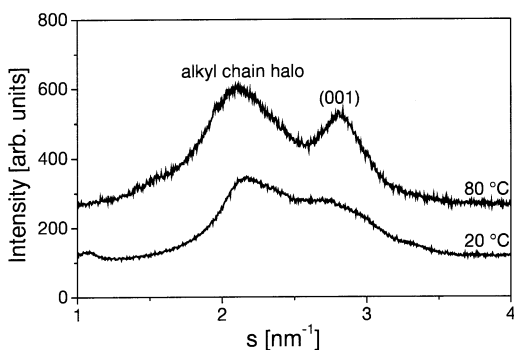


Figure 7. Wide-angle X-ray scattering of the PEO–PLL–HBC complex in the Col₁ phase at 20 °C (lower curve) and in the Col₂ phase at 80 °C (upper curve). The (001) reflection corresponds to a disc-to-disc distance of the HBC cores of 0.353 nm in the Col₂ phase. The disc-to-disc packing is of the long-range order in the Col₂ phase, while it is of short-range order in the Col₁.

examples, however, have been found earlier,^{11,12} and this feature might be characteristic for polyelectrolyte complexes of HBC. A possible explanation is that packing constraints are responsible for the unexpected lower intracolumnar order of Col₁. That is, contraction of the unit cell at lower temperatures is compensated by deformation of the columns. Another possibility is that the HBC cores are tilted with respect to the column axis in the Col₁ but not in the Col₂ phase similar to other HBC complexes.^{11,12}

Conclusion

In this study, we have found that a complex of poly(ethylene oxide)-*block*-poly(L-lysine) with HBC forms a thermotropic

liquid crystal with two novel columnar structures Col₁ and Col₂. Both structures are defined by cylinders containing poly(L-lysine) blocks which adopt an α -helical secondary structure. Each α -helix is surrounded symmetrically by six columns of HBC cores and produces an α -helical-*within*-discotic columnar entity. These structural entities are tightly packed in two-dimensional hexagonal lattices. The Col₂ displays a larger unit cell (6.60 nm) than Col₁ (5.75 nm) and a better intracolumnar packing of the HBC disks. The complex presented here is the first example for a bioinspired material that combines the structural properties of liquid crystals with an element of the well-ordered structure of proteins. Such materials may have superior physical properties such as high one-dimensional conductivity, which result from the binding of the columns to a rigid molecule as an anchor. The macroscopic orientation of the PEO–PLL–HBC super-structure, for example, in thin films, and their application in electronic devices are challenging tasks for future investigations.

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