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Supramolecular architecture of a functionalized hexabenzocoronene and its complex with polyethyleneimine

Andreas F. Thünemann,*[a] Dirk Ruppelt,[a] Shunji Ito[b] and Klaus Müllen[b]

[a]*Max Planck Institute of Colloids and Interfaces, Kantstraße 55, 14513 Teltow, Germany. E-mail: andreas@terra.mpikg-teltow.mpg.de; Tel. 03328–46–271, Fax. 03328–46–272*
[b]*Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany*

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A hexabenzocoronene, functionalized with a carboxylic acid group, was complexed with a hydrophobic modified polyethyleneimine and the thermotropic columnar liquid-crystalline-like complex was investigated by X-ray scattering and dynamic–mechanical analysis.

The construction of disc-like molecules with large π-conjugated cores opens a way to new supramolecular aggregates,[1,2] which are interesting because of their electronic and optoelectronic properties.[3] It has been observed, for instance that *peri*-condensed hexabenzocoronenes show diode-like current–voltage signals for single molecules[4] and a rapid charge transport along self-assembled columns with high carrier mobilities. For an oriented layer with a thickness of 1 μm and an applied potential of 1 V the drift time of charges across such a layer was calculated to be less than one microsecond.[5] The one-dimensional nature of the charge transport makes these molecules promising as nanowires in molecular electronic devices or as building blocks for transport layers in electrocopying or electrophotography. A decisive aspect is to take advantage of their self-organizing capability particularly with respect to the control of the spatial orientation of molecular wires, as formed *e.g.* by hexakis(tetradecyl)hexa-*peri*-hexabenzocoronenes.[5] The first step in this direction is the functionalization of such sheet-like molecules by an anchor group, which may, in principle, allow the immobilization of supramolecular aggregates. The binding of molecular columns to polyelectrolytes is a possibility to enhance their long-range order and stability. In this article we describe the phase behavior and mechanical properties of a hexabenzocoronene (**b**) which is functionalized by a carboxylic acid group and that of its complex with hydrophobic modified polyethyleneimine (**a**). The structures of the compounds are shown in Fig. 1. The synthesis of (**b**) will be described elsewhere.[6]

In the last few years, it has been shown that the complexation of polyelectrolytes with surfactants in water results in a number of new solid materials,[7,8] *e.g.* with interesting optical[9] and surface-energy lowering properties.[10–12] Analogously to polyelectrolyte–surfactant complexes we treated (**b**) as an amphiphile and used (**a**) as a polyelectrolyte. Due to the insolubility of (**b**) in water, the complexation with (**a**) was carried out in chloroform using an equimolar amount of (**a**) with respect to amino and carboxylate functions. The resulting complex (**c**) was solvent-cast as films and analyzed by IR spectroscopy, differential scanning calorimetry (DSC), X-ray scattering and dynamic–mechanical measurements. Comparison of the IR spectra of (**b**) and (**c**) shows that the carboxylic acid vibration found for (**a**) at 1710 cm^{-1} is absent for (**c**) (see Fig. 2). Instead of the sharp carboxylic acid band in the spectrum of (**b**) a broad diffuse band between 1500 and 1760 cm^{-1} is present in (**c**) resulting from ionic ammonium carboxylate structures. In the two spectra both the C=C stretch vibrations at 1610 cm^{-1} and the CH$_2$ bending vibrations at 1466 and 1456 cm^{-1} are identical. From this we conclude that within the experimental error all of the carboxylic acid functions of (**b**) form acid–base pairs with the amino functions of (**a**), resulting in a stoichiometric complex (**c**). In the wide-angle X-ray diagram of (**a**) at 20 °C, sharp reflections were found at a scattering vector of $s = 2.39$ nm^{-1} and 2.63 nm^{-1}. This is attributed to a side-chain crystallinity of (**a**), in which the docosyl chains crystallize. For determination of the lattice parameters we compare the data with that found for orthorhombic polyethylene[13] with lattice constants of $a = 0.7417$ nm, $b = 0.4945$ nm and $c = 0.2547$ nm. Assuming the same lattice for (**a**), the indexing of the upper reflections is (110) and (200) giving lattice constants $a = 0.76$ nm and $b = 0.50$ nm. In the unit cell the alkyl chains are oriented perpendicular to the *a*–*b*

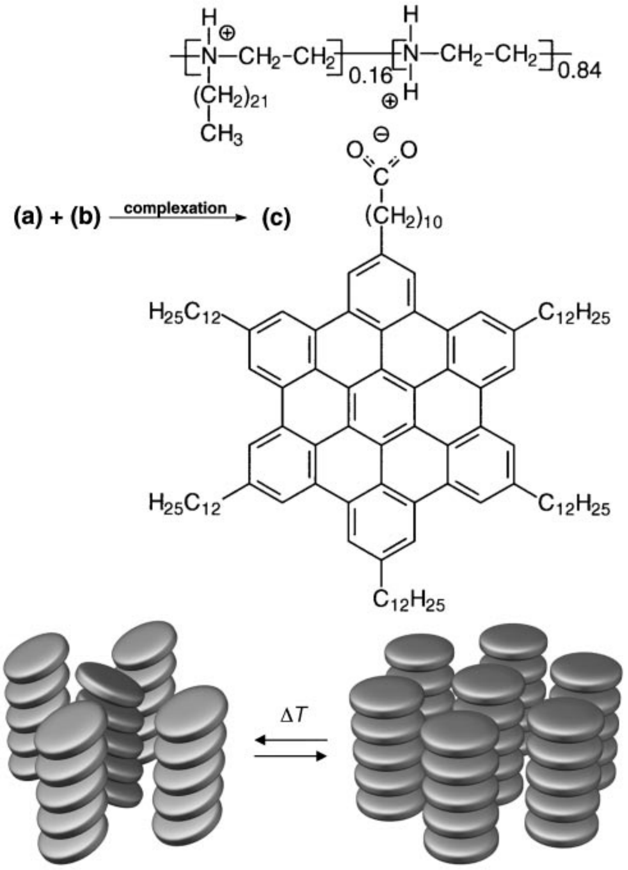

Fig. 1 The molecular structure of an ionically bound complex (**c**), formed by a hydrophobic modified polyethyleneimine (**a**) and a hexabenzocoronene (**b**). (**a**) and (**b**) are not drawn. 16% of the amino functions of (**a**) are alkylated by *n*-docosyl chains, (**b**) is functionalized by a carboxylic acid function which serves as anchor group. The sketch at the bottom illustrates the columnar mesophases formed by (**b**) and (**c**). For clarity only the aromatic cores of (**a**) are drawn. At room temperature a rectangular centered lattice is found for both. The aromatic cores are tilted with respect to the column axis. At higher temperatures the columns are oriented in a hexagonal columnar mesophase.

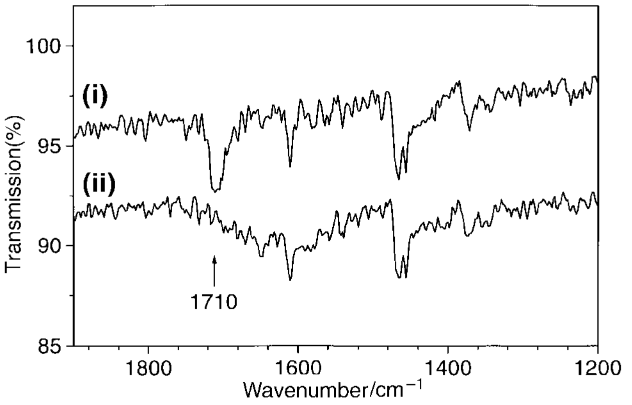

Fig. 2 FTIR-spectrum of (**b**) (curve i) and that of complex (**c**) (curve ii). In the spectrum of (**b**) an intense carboxylic acid band at a wave number of 1710 cm^{-1} is found resulting from the C=O stretch vibration. This band is absent in the spectrum of (**c**) indicating a stoichiometric 1 : 1 complexation.

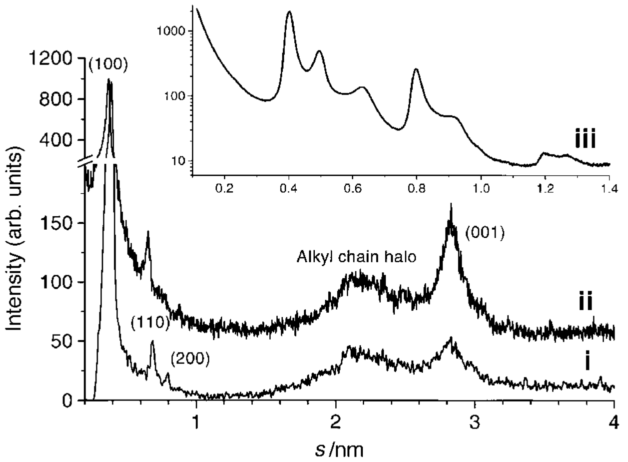

Fig. 3 The X-ray diffraction of (**b**) (curve i) and that of complex (**c**) (curve ii) in the hexagonal mesophase at 110 °C. The (001)-reflection of (**c**) is more intense than that of (**b**) indicating a higher stacking order of aromatic cores for (**c**) than that of (**b**). The insert shows the small-angle X-ray scattering of compound (**b**) at 20 °C (curve iii), which is due to a rectangular centered columnar phase (see Table 1).

Table 1 Small-angle X-ray data of (**b**). Reflex positions and Miller indices are given for the two-dimensional ordered lattices at 20 and 110 °C. The scattering vector is defined as $s=2/\lambda \sin\theta$

(hkl)	s_{observed}/nm^{-1}	$s_{\text{calculated}}$/nm^{-1}
Rectangular discotic structure, $T=20$ °C		
(110)	0.401	0.400
(200)	0.495	0.495
(020)	0.629	0.629
(220)	0.787	0.800
(310)	—	0.806
(130)	0.910	0.975
(330)	1.194	1.201
(040)	1.262	1.257
(510)	—	1.277
Hexagonal discotic structure, $T=110$ °C		
(100)	0.389	0.389
(110)	0.679	0.674
(200)	0.790	0.778

plane and the average area per chain is 0.19 nm^2, which is slightly larger than that for polyethylene (0.183 nm^2). Neither (**b**) nor the complex (**c**) show sharp reflections in the wide-angle region of the scattering curves, proving the absence of crystallinity in the structures. The disappearance of crystallinity in (**c**) is also indicative of a stoichiometric complex. The DSC curve of (**a**) shows a melting peak at 59 °C with an enthalpy of 73 J g^{-1}. Under the usual assumptions made for the calculation of crystallinity,[14] the amount of crystalline side-chains of (**a**) can be determined to be in the range of 40 to 50%. In the DSC trace of (**b**) an endothermic transition was found at 93 °C for heating and at 62 °C for cooling. For (**c**) an endothermic transition is found at 70 °C for heating and at 52 °C upon cooling. The different values found for the hysteresis, 18 °C (**c**) and 31 °C (**b**), may be interpreted as a consequence of a faster relaxation to an equilibrium state of (**c**). Considering the absence of crystalline reflections in the X-ray diagrams of (**b**) and (**c**), the exothermic transitions could be assigned to liquid-crystalline phase transitions. This assumption was proven by optical polarization microscopy and by small-angle X-ray scattering. Both compounds show strong birefringence when observed between crossed polarizers and a texture change at transition temperatures found by DSC. Unfortunately, the textures do not allow an unambiguous determination of the liquid-crystalline phases. Therefore, small-angle X-ray scattering diagrams were recorded at 20 and 110 °C. As shown in Fig. 3, at 20 °C seven reflections were found in the small-angle scattering curve of (**b**). This pattern can be interpreted as a columnar structure with a two-dimensional centered superstructure (see Fig. 1). The columns are aligned parallel, where the aromatic cores of (**b**) form stacks and are tilted with respect to the column axis. The indices of the reflections and the observed and calculated reflex positions are listed in Table 1. On the basis of these values the lattice parameters are determined to be 4.04 nm and 3.18 nm, giving an inter-columnar distance of 2.71 nm. A tilt angle between the plane normal to the aromatic cores aligned and the column direction is calculated to be about 38°. The SAXS diagram of complex (**c**) shows a reflection pattern very similar to that of (**b**), but with broader reflections. We conclude that both materials have the same liquid-crystalline rectangular columnar structure at room temperature, although differing in the lateral packing of the columns, which appears to be better in (**b**) compared to (**c**). At a temperature of 110 °C, in the small angle X-ray region of (**b**) and (**c**) three reflections were found with relative positions of $1:\sqrt{3}:2$. This can be interpreted as an ordered columnar structure with a hexagonal superstructure as was already found for alkylated non-functionalized hexa-*peri*-benzocoronenes.[1] From the reflex positions, inter-columnar distances of 3.00 nm (**b**) and 3.12 nm (**c**) were determined. Again, the small-angle reflections observed for (**c**) are broader than for (**b**), but the (001) reflection located in the wide-angle region is significantly smaller for the complex than for the free acid (see Fig. 3). The inter-columnar distances, derived from the (001) reflection for both are the same ($d_{\text{intra}}=0.354$ nm). This value is nearly the same as found earlier for non-functionalized hexa-*peri*-benzocoronene[1] and indicates an effective π–π-overlap of adjacent cores.[5] For quantification of the difference between the inter-columnar ordering and intra-columnar ordering of (**b**) and (**c**), the correlation lengths were calculated from the widths of the (100) and the (001) reflections. The correlation lengths of (**b**) are 45 nm and 3.7 nm for the inter- and intra-columnar long-range ordering, respectively. For (**c**) the corresponding values are 33 nm and 5.7 nm. Thus, the inter-columnar order in the pure compound is higher than in the complex, whereas the intra-columnar long-range order of the pure substance is lower than in the complex. For the desired rapid charge transport along the columns, the π–π-overlap and the intra-columnar long-range ordering are critical values. Since the π–π-overlap of (**b**) and (**c**) is equal, but the intra-columnar long-range order of (**c**) is better, a higher charge transport may be expected for (**c**) than for (**b**).

In addition to the control of the mesomorphic structure, the mechanical properties play a key role in estimating the potential of (**b**) and (**c**) as promising materials. For many polyelectrolyte–surfactant complexes it is known that the mechanical properties were significantly improved due to the polymeric compound.[15] Hence we expect such an improvement for the complexation of (**b**), too. The shear modulus *G* of

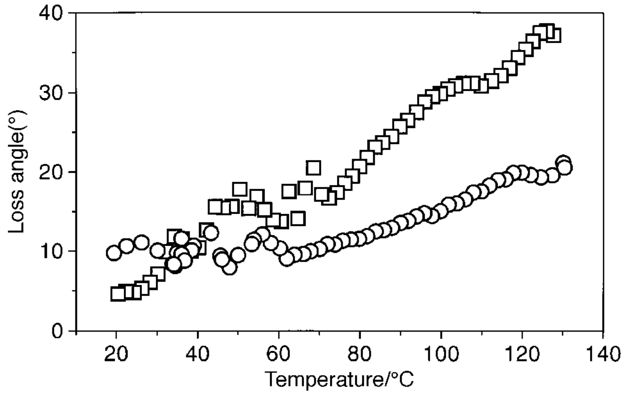

Fig. 4 Temperature dependent loss-angle determined by dynamic–mechanical measurements of (**b**) (squares) and of (**c**) (circles). The shear rate was 0.1 s^{-1}.

films, prepared by solvent casting of (**b**) and (**c**), was determined by temperature-dependent dynamic–mechanical measurements. It was found for the pure substance and the complex that the shear modulus of the rectangular columnar phase is one order of magnitude higher than that of the hexagonal columnar phase. Below the phase transition, values of G in the range from 1 MPa to 10 MPa were measured for (**b**) and (**c**). Above the phase transition, G is about 0.1 MPa. Characteristic is the different behavior of loss-angle δ as shown in Fig. 4. It can be seen that δ increases from about 5 to 40° in the range from 20 to 130 °C for (**b**), whereas δ increases only from 10 to 20° in the same temperature range for (**c**). This means that (**b**) is more elastic at room temperature and viscous at higher temperature. On the other hand (**c**) shows an approximately constant elasticity over the whole temperature range. This may be explained by considering (**a**) as a kind of cross-linker, which forms a flexible three-dimensional network bound ionically to (**b**).

In conclusion it was found that the carboxylic acid functionalized hexabenzocoronene (**b**) forms two columnar liquid-crystalline structures. At room temperature a rectangular centered symmetry is found, which changes to a hexagonal ordered columnar structure at temperatures higher than 93 °C. Furthermore, the complexation of (**b**) in chloroform with a hydrophobic modified polyethyleneimine gives a stoichiometric complex similar to solid waterborne polyelectrolyte–surfactant complexes. For the stoichiometric complex of (**a**) and (**b**) resulting in (**c**), the same columnar liquid-crystalline phases are present, but with a lower phase-transition temperature (70 °C *vs.* 93 °C) and a lower hysteresis (18 °C *vs.* 31 °C), observed for the phase-transition temperature between heating and cooling. Furthermore, the intra-columnar order of the complex is higher than that of the non-complexed specimen, whereas the inter-columnar order is lower. From the temperature dependence of the loss-angle it was concluded, that the elasticity of (**b**) could be improved by complexation, probably without the danger of reducing high carrier mobilities.

The hydrophobic modification of polyethyleneimine (Polymin G100®, BASF, $M_w = 5.000\text{–}7000\ \mathrm{g\ mol^{-1}}$) with docosyl bromide (Aldrich, 97%) was carried out by a procedure described by Nöding and Heitz.[16] The degree of alkylation, as determined by ^{1}H-NMR spectroscopy, was 16 mol%. Synthesis and characterization of the functionalized hexabenzocoronene (**b**) (see Fig. 1) are described in detail elsewhere.[6] For complexation 6.5×10^{-2} mmol (100 mg) of the hydrophobically modified polyethyleneimine, dissolved in 10 mL chloroform (HPLC grade), was added slowly to an equimolar amount of (**b**) dissolved in 25 mL chloroform (HPLC grade). The complex precipitated as a fine yellow powder and was removed by centrifugation, washed three times with 10 mL chloroform and dried under vacuum. The yield was about 95%. The complex is soluble in warm dimethylformamide and tetrahydrofuran. Wide-angle X-ray scattering measurements were carried out with a Nonius PDS 120 powder diffractometer in transmission geometry. A FR590 generator was used as the source of Cu-Kα radiation; monochromatization of the primary beam was achieved by means of a curved Ge crystal. The scattered radiation was measured with a CPS120 position sensitive detector. The resolution of this detector is better than 0.018°. Small-angle X-ray scattering measurements were recorded with an X-ray vacuum camera with pinhole collimation (Anton Paar, Austria; model A-8054) equipped with image plates (type BAS III, Fuji, Japan). The image plates were read out with a MACScience Dip-Scanner IPR-420 and IP reader DIPR-420 (Japan). Differential scanning calorimetry (DSC) measurements were performed on a Netsch DSC 200 (Germany). The samples were examined at a scanning rate of 10 K $\mathrm{min^{-1}}$ by applying one cooling and two heating scans. The phase transition temperatures were determined as onset points. Polarized light optical microscopic observations of the films were performed with a Zeiss DMRB microscope (Germany). A Bohlin CVO-50 rheometer with a plate-plate geometry (20 mm diameter) was used for dynamical–mechanical measurements. The substances (**b**) and (**c**) were cast from a 0.2% (w/w) dimethylformamide solution to give a homogeneous film on the lower plate. Measurements were carried out at a temperature range from 20 to 130 °C with a cooling and heating rate of 2 K $\mathrm{min^{-1}}$ at a shear rate of 0.1 s^{-1}, loading with a constant shear stress of 50 Pa.

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