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Long-range ordered columns of a hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene–polysiloxane complex: towards molecular nanowires

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The complexation of a carboxylate functionalized hexabenzocoronene with an amino functionalized polysiloxane results in a polymeric complex, which forms two highly ordered discotic columnar liquid crystalline structures Col_1 and Col_2. By using small-angle X-ray scattering it was shown that four columns per unit cell are two-dimensionally ordered in oblique lattices. An order–order transition from Col_1 to Col_2 was detected at about 90 °C. The lattice constants of Col_1 are $a=b=5.0$ nm and $\gamma=112°$, that of Col_2 are $a=b=5.5$ nm and $\gamma=108°$. As a structural consequence to the complexation the heights of the columns within these phases are remarkably large. The heights were estimated using electron microscopy to be in the range of at least 200 nm which is more than 100 times their diameter (1.4 nm). The disc-like aromatic cores are arranged tilted with respect to the column axis in Col_1 and with low intracolumnar ordering. By contrast the cores are oriented perpendicular to the column axis in the Col_2 phase. Here a sharp intracolumnar reflection is present which results from a well-defined disc distance of 0.35 nm with strong π–π interactions. The mechanical properties of the highly flexible complex material were investigated using dynamic mechanical analysis and its thermal properties using differential calorimetry. Such polymeric complex nanostructures, which contain a hierarchy of three incompatible elements (aromatic cores are embedded in a matrix of alkyl chains which itself is embedded in a matrix of polysiloxane), could be useful for the fabrication of molecular nanowires.

Introduction

There is currently much interest in polycyclic aromatic materials with strong π–π interactions and which form columnar mesophases.[1–5] Apart from the beauty of their structures, potential applications such as vectorial charge transport layers in xerography, electrophotography and molecular electronic devices are under discussion. It was observed, *e.g.*, that *peri*-condensed hexabenzocoronenes show diode-like current–voltage signals for single molecules[6] 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.[7] The one-dimensional nature of the charge transport makes these molecular structures promising as nanowires in molecular electronic devices. Recently we reported on a hexabenzocoronene, functionalized with a carboxylic acid group, which was complexed with a hydrophobically modified polyethyleneimine.[8] In comparison to the non-complexed discotic material the complex was found to be more elastic over a wide range of temperatures. The intracolumnar ordering of the complex, which is an essential characteristic for a one-dimensional conductivity, was better than in the pristine hexabenzocoronene. Further, an important general property of mesophases formed by polyelectrolyte–surfactant (ionic amphiphile) complexes compared with typical liquid crystalline phases is the absence or reduction of sharp dislocations in their optical textures.[9,10] This indicates the presence of smoother domain boundaries in their complex mesophases than those present in their amphiphile liquid crystalline phases. We expect that highly extended columns in a polymer complex of an amphiphilic hexabenzocoronene could be useful molecular nanowires. Therefore in this contribution we report on a complex which is formed by an alkylated, *peri*-condensed hexabenzocoronene (functionalized by a carboxylic acid group), and an amino-functionalized polysiloxane.

Experimental

Materials and preparation

The aminoethylaminopropyl functionalized polysiloxane is a commercial product from Wacker Chemie GmbH (Burghausen, Germany). Its content of functionalized monomers is 6.4 mol% and the degree of polymerization P_n is about 1000 (information by the supplier). The synthesis and characterization of the carboxylic acid functionalized hexabenzocoronene has been described elsewhere.[11] For complexation 180 mg (0.116 mmol) hexabenzocoronene and 154 mg (0.116 mmol functionalized moieties) polysiloxane were dissolved, each in 40 ml tetrahydrofuran (HPLC grade, Aldrich). Both solutions were heated to 60 °C and the polymer solution was added slowly to the solution of the hexabenzocoronene. The complex was obtained as a yellow to brownish precipitate, separated by centrifugation and dried by slow evaporation of the solvent in a vacuum oven.

Measurements

The FTIR spectra were recorded on a Nicolet Impact 400 spectrometer. Differential scanning calorimetry (DSC) measurements were performed on a Netsch DSC 200 (Germany). The samples were examined at a scanning rate of 10 K min^{-1} with one cooling and two heating scans. For determination of the complex shear modulus $G'+iG''$, dynamic mechanical measurements were carried out using a Netzsch DMA 242 in sandwich geometry at a heating rate of 2 K min^{-1}. The

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frequency used was 1 Hz. Wide-angle X-ray scattering (WAXS) measurements were carried out with a Nonius PDS120 powder diffractometer in transmission geometry. A FR590 generator was used as the source of CuKα 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 with a resolution in 2θ of 0.018°. The 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 by a MACScience Dip-Scanner IPR-420 and IP reader DIPR-420 (Japan). The scattering vector s is defined as $s = 2/\lambda \sin \theta$, where 2θ is the angle between the primary beam and the scattered beam. Standard transmission electron microscopy (TEM) was performed on thin sections of the complex using a Zeiss EM 912 Omega TEM.

Results and discussion

The complexation of the aminoethylaminopropyl functionalized polysiloxane **a** with the hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene **b** to complex **c** is schematically shown in Fig. 1 and has been monitored by IR-spectroscopy. It can be seen in Fig. 2 that a carboxylic acid vibration band at 1710 cm^{-1} is present in the sum of the FTIR spectra of **a** and **b** (curve i) while it is absent in the spectrum of **c** (curve ii). The other vibrations of both spectra are identical and identified as the C=C stretch vibration around 1600 cm^{-1}, the CH_2 symmetric (scissors) and the CH_3 asymmetric deformation vibrations at 1460 cm^{-1}. Further the CH_3 symmetric (umbrella) deformation is seen at 1260 cm^{-1}. 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** in the complex.

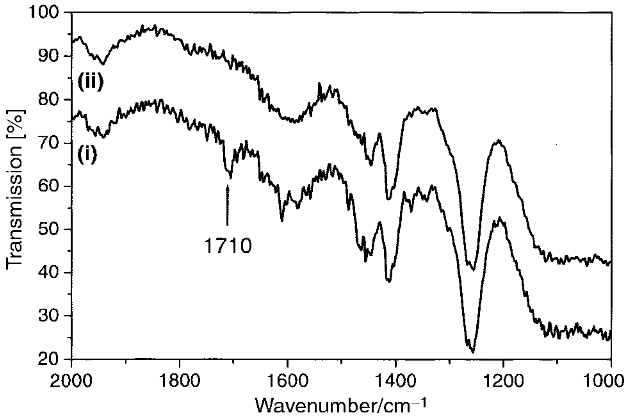

Fig. 2 FTIR-spectrum of **b** (curve i) and that of complex **c** (curve ii). In the spectrum of **b** an intense carboxylic acid band at 1710 cm^{-1} is found resulting from the C=O stretch vibration. This band is absent in the spectrum of **c** indicating a stoichiometric 1 : 1 complexation.

Molecular and supramolecular order

ten Brinke *et al.* reported on lamellar structures of comb copolymer-like systems obtained by hydrogen bonding between polymers containing basic moieties and amphiphiles.[12] Their complexes are similar to **c** with respect to their molecular interactions. Recently, we have shown that the **b** units form columnar polymer complexes, which contain about 9% (w/w) of a hydrophobically modified polyethyleneimine.[8] Here the polymer content of **c** is much higher (46% (w/w)). Therefore we expect new columnar morphologies of **c** compared to that of the earlier complex. Temperature dependent small-angle X-ray diffraction was used to investigate its supramolecular ordering. As expected, a number of reflections were present in the scattering curves (Fig. 3 and 4, solid lines) but it was surprising that more and sharper reflections were found at 120 °C (Fig. 4) than at 20 °C (Fig. 3). Obviously a hexagonal columnar phase, which is typical for hexabenzocoronene compounds[13] can be excluded. The most simple models which explain the reflection positions and their relative intensities are two-dimensional oblique lattices of columnar phases: Col_1 which is stable at room temperature and Col_2 which is stable at higher temperature. For the lattice constants we calculated $a = b = 5.0$ nm and $\gamma = 112°$ for Col_1 and $a = b = 5.5$ nm and $\gamma = 108°$ for Col_2. The areas of the unit cells are 23.2 nm^2 (Col_1) and 28.8 nm^2 (Col_2). It is striking that the scattering intensity of the reflections at lower scattering vectors (around 0.2 nm^{-1}) is lower than that of the group of reflections around 0.4 nm^{-1}. This can be explained by an arrangement of four columns per unit cell which group around the center of the unit cell (see inserts of Fig. 3 and 4; the corresponding analytical scattering curves are shown as dashed lines). Lists of the measured and calculated reflex positions and Miller indices are given in Table 1. The normals of the aromatic planes within Col_1 are tilted with respect to the column axes. The tilt angle is about 45° which gives an axis ratio of 1 : 0.7 for the in-plane

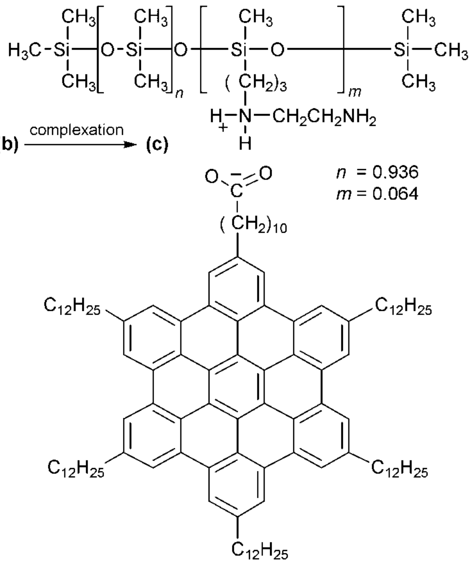

Fig. 1 The molecular structure of an ionically bound complex (**c**), formed by an aminoethylaminopropyl functionalized polysiloxane (**a**) and a hexabenzocoronene (**b**). (**a** and **b** are not drawn.) **b** is functionalized by a carboxylic acid function which serves as an anchor group.

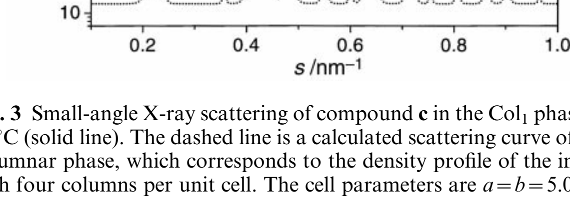

Fig. 3 Small-angle X-ray scattering of compound **c** in the Col_1 phase at 20 °C (solid line). The dashed line is a calculated scattering curve of the columnar phase, which corresponds to the density profile of the insert with four columns per unit cell. The cell parameters are $a = b = 5.0$ nm and $\gamma = 112°$. The discs have a tilt angle of about 45° with respect to the column axis.

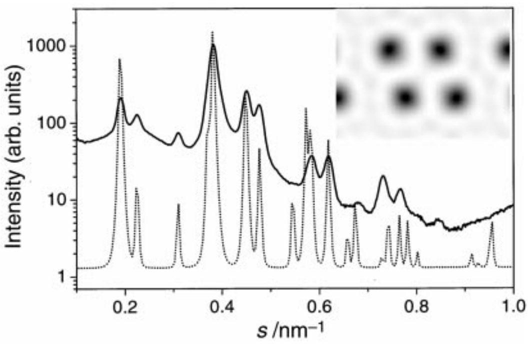

Fig. 4 Small-angle X-ray scattering of compound **c** in the Col_2 phase at 120 °C (solid line). The dashed line is a calculated scattering curve of the phase, which corresponds to the density profile of the insert with four columns per unit cell. The cell parameter are $a=b=5.5$ nm and $\gamma=108°$. The discs are not tilted.

projection. Within the Col_2 phase the normals of the column axis are aligned parallel to the column axis. It has been observed, for the complex of **b** with a polyethyleneimine, that the normals of the aromatic cores are tilted at lower temperatures and are parallel at higher temperatures.[8] Explanations for the reduced symmetry of Col_2 and Col_2 compared to the expected hexagonal and rectangular structures may be packing constraints, because the carboxylic acid function is linked ionically to the polysiloxane and it reduces the molecular symmetry from D_{6h} to C_{2v}. Further the alkylated chains and the siloxane chains are not miscible and therefore, together with the aromatic cores, the complex contains three incompatible elements, which lead to micro-segregation. The situation may be considered similar to that of triblock copolymers where the formation of mesomorphous structures is controlled by the relative incompatibilities of the three polymeric components of the block copolymers.[14] It is surprising that, from the widths of the reflex positions, the supramolecular order of Col_2 is better than in Col_1. From the width of the most intensive reflection (index 200) the in-plane correlation length of Col_1 is about 50 nm (20 °C) and that of Col_2 is about 150 nm (120 °C). Due to the thermal energy, the reverse situation was expected. The reason for the better order within the higher temperature phase than in the lower temperature phase may be that the intracolumnar stacking order of the tilted arrangement is not as good as it is for the non-tilted one. In order to prove this assumption the molecular order was investigated using wide-angle X-ray scattering. It can be seen in Fig. 5 (curve b) that, in addition to two broad reflections at $s=1.32\ \mathrm{nm}^{-1}$ and $2.30\ \mathrm{nm}^{-1}$, a relatively sharp reflection is present at $s=2.86\ \mathrm{nm}^{-1}$ in the diagram of Col_2 at 120 °C (curve c) (Bragg distances are 0.76 nm, 0.46 nm and 0.35 nm). The first reflection can be attributed to the short-range order of the siloxane segments. For clarity, the wide-angle scattering of the pristine siloxane is shown in Fig. 5 (curve a). It can be seen there that in the scattering curve of the siloxane only one reflection is present at about the same position ($1.32\ \mathrm{nm}^{-1}$) as the first wide-angle reflection of Col_1. The reflection at $d=0.46$ nm can be attributed to the scattering of the alkyl chains which is found typically in polyelectrolyte–surfactant complexes with a mesomorphous structure, such as the complexes of polystyrenesulfonate with alkyltrimethylammonium surfactants described by Antonietti *et al.*[15] The relatively sharp reflection with $d=0.35$ nm defines the intracolumnar distance. This value is about the same as that of graphite (0.335 nm) and indicates a strong π–π overlapping of adjacent hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene discs in the Col_2 phase, which is consistent with the supramolecular model derived from the small-angle scattering data. In the wide-angle diagram of Col_1 two broad reflections are found at about the same position ($1.35\ \mathrm{nm}^{-1}$, $2.33\ \mathrm{nm}^{-1}$) and with the same width as for Col_2 (Fig. 5, curve b). Therefore Col_1 and Col_2 are very similar in the molecular order of their siloxane and alkyl chains, which is only of short range. But in contrast to Col_2 only a weak reflection is present in the region around $3\ \mathrm{nm}^{-1}$ which is characteristic for an intracolumnar ordering. Therefore it can be concluded that the intracolumnar order within Col_1 is much weaker than within Col_2. From a curve fitting of Lorentzian profiles onto the scattering curves (not shown) the intracolumnar correlation length of Col_1 was estimated to be 2 nm, whereas that of Col_2 is 8 nm. This agrees with the structure model of Col_1 with tilted discs (Fig. 3, insert) which show a lower π–π-overlapping than within the columns of Col_2.

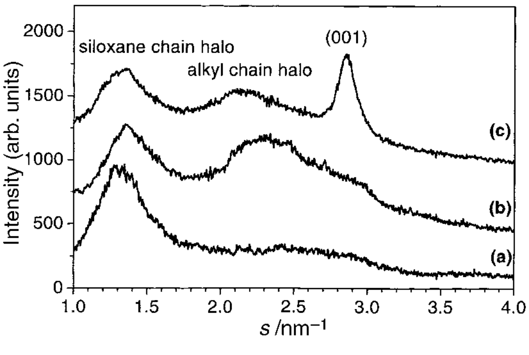

Fig. 5 Wide-angle X-ray scattering of the polysiloxane (curve a), the Col_1 phase at 20 °C (curve b) and the Col_2 phase at 120 °C (curve c).

Table 1 Small-angle X-ray data of **b**. Reflex positions and Miller indices are given for the Col_1 and Col_2 phase at 20 °C and 120 °C. The scattering vector is defined as $s=2/\lambda \sin\theta$

(hk)	$s_{\mathrm{observed}}/\mathrm{nm}^{-1}$	$s_{\mathrm{calculated}}/\mathrm{nm}^{-1}$
Lower-temperature phase, Col_1, $T=20$ °C		
$(0,\bar{1})(\bar{1},0)(1,0)(0,1)$	0.225	0.216
$(1,\bar{1})(\bar{1},1)$		0.241
$(\bar{1},\bar{1})(1,1)$		0.358
$(1,\bar{2})(\bar{2},1)(2,\bar{1})(\bar{1},2)$		0.404
$(0,\bar{2})(\bar{2},0)(2,0)(0,2)$	0.424	0.431
$(2,\bar{2})(\bar{2},2)$	0.478	0.483
$(\bar{1},\bar{2})(\bar{2},\bar{1})(2,1)(1,2)$	0.561	0.550
$(1,\bar{3})(\bar{3},1)(3,\bar{1})(\bar{1},3)$		0.600
$(2,\bar{3})(\bar{3},2)(3,\bar{2})(\bar{2},3)$		0.629
$(0,\bar{3})(\bar{3},0)(3,0)(0,3)$		0.647
$(\bar{2},\bar{2})(2,2)$	0.700	0.715
$(\bar{1},\bar{3})(\bar{3},\bar{1})(3,1)(1,3)$		0.755
$(1,\bar{4})(\bar{4},1)(4,\bar{1})(\bar{1},4)$		0.807
$(2,\bar{4})(\bar{4},2)(4,\bar{2})(\bar{2},4)$		
$(0,\bar{4})(\bar{4},0)(4,0)(0,4)$	0.853	0.863
$(\bar{2},\bar{3})(\bar{3},\bar{2})(3,2)(2,3)$	0.900	0.902
$(\bar{1},\bar{4})(\bar{4},\bar{1})(4,1)(1,4)$		0.965
$(4,\bar{4})(\bar{4},4)$		
Higher-temperature phase, Col_2, $T=120$ °C		
$(0,\bar{1})(\bar{1},0)(1,0)(0,1)$	0.192	0.191
$(1,\bar{1})(\bar{1},1)$	0.225	0.225
$(\bar{1},\bar{1})(1,1)$	0.310	0.309
$(1,\bar{2})(\bar{2},1)(2,\bar{1})(\bar{1},2)$		0.371
$(0,\bar{2})(\bar{2},0)(2,0)(0,2)$	0.383	0.382
$(2,\bar{2})(\bar{2},2)$	0.451	0.450
$(\bar{1},\bar{2})(\bar{2},\bar{1})(2,1)(1,2)$	0.478	0.477
$(1,\bar{3})(\bar{3},1)(3,\bar{1})(\bar{1},3)$		0.546
$(0,\bar{3})(\bar{3},0)(3,0)(0,3)$		0.574
$(2,\bar{3})(\bar{3},2)(3,\bar{2})(\bar{2},3)$	0.584	0.583
$(\bar{2},\bar{2})(2,2)$	0.619	0.619
$(\bar{1},\bar{3})(\bar{3},\bar{1})(3,1)(1,3)$		0.658
$(3,\bar{3})(\bar{3},3)$	0.681	0.674
$(1,\bar{4})(\bar{4},1)(4,\bar{1})(\bar{1},4)$		0.729
$(2,\bar{4})(\bar{4},2)(4,\bar{2})(\bar{2},4)$	0.731	0.742
$(0,\bar{4})(\bar{4},0)(4,0)(0,4)$	0.767	0.765
$(\bar{2},\bar{3})(\bar{3},\bar{2})(3,2)(2,3)$		0.781
$(3,\bar{4})(\bar{4},3)(4,\bar{3})(\bar{3},4)$	0.804	0.802
$(\bar{1},\bar{4})(\bar{4},\bar{1})(4,1)(1,4)$	0.846	0.844
$(2,\bar{5})(\bar{5},2)(5,\bar{2})(\bar{2},5)$		0.913
$(0,\bar{5})(\bar{5},0)(5,0)(0,5)$		0.956

In order to confirm the proposed model of extended columns, the structure was visualized by electron microscopy. Patterns of dark and bright stripes are found in samples prepared in thin sections. An example is shown in Fig. 6. The average distance of equal stripes is about 2.3 nm. We attribute the bright lines to columns of hexabenzocoronene and the dark ones to their surrounding matrix of polysiloxane, which has a higher electron density. The cut along the columns can be explained by the assumption that these are the directions with the lowest mechanical strength and that these are preferred because the siloxane matrix remains soft even at lower temperatures. To our surprise, as a consequence of the complexation, the patterns are almost free of dislocations. From the length of the stripes the average column height was estimated to be at least 200 nm. This is more than 100 times the column diameter (1.4 nm). Probably their height is significantly larger. For clarity a copy of a transparent overlay is given in Fig. 6. This remarkable height of defect-free columns results from the polysiloxane which prevents the columns from breaking. In combination with the rapid charge transport of such materials[7] these seem to be very promising for electronic devices such as graphitic nanowires. Their electronic properties can, in principle, be modified by different substituents or by intercalation of low molecular weight molecules. Knowledge of graphite and carbon fiber intercalation compounds[16] can be used for the modification of the electrical properties of the graphitic nanowires. To our knowledge the **c** form the highest known intracolumnar order of discotic mesophases reported to date. By contrast, very high correlation lengths of two-dimensional lattices in hexagonal columnar phases, greater than 400 nm, have already been described.[17]

Thermal and mechanical properties

The thermal and the mechanical properties of **c** were investigated by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Typical DSC traces for heating and cooling scans, measured with a heating rate of 10 K min^{-1}, are given in Fig. 7. An endothermic transition with a maximum at 85 °C was found upon heating with a width of 16 °C (lower temperature onset at 76 °C, higher temperature onset at 92 °C). After cooling the transition was found to be at a maximum at 57 °C and at a width of 16 °C (left onset at 46 °C, higher temperature onset at 62 °C). The large hysteresis of the transition at a width of 30 °C indicates that the bulky aromatic cores are involved in the transition, their reorientation is known to show slow kinetics.[8] We assign this transition to the order–order transition from Col_1 to Col_2, similar to that which we reported on recently for a complex of **b** with a hydrophobically modified polyethyleneimine.[8] The influence of the temperature on the storage shear modulus can be seen in Fig. 8. At –120 °C the modulus is in the range of 9 MPa to 10 MPa, at 0 °C it is in the range of 2.5 to 2.7 MPa and at 30 °C it is 2.0 to 2.2 MPa. During further heating a step-like decrease of the modulus from about 1.5 MPa to 0.6 MPa was found with the point of inflection at 95 °C. During heating a step-like increase of the same height can be seen whose point of inflection is at 46 °C. The step-like decrease of the modulus during heating has the same position as the high temperature onset of the peak in the DSC heating trace (92 °C) and the step-like decrease during cooling has the position of the low temperature onset of the peak in the DSC curve (46 °C). From this we conclude that the origin of the transition found in DSC is the same as in the shear modulus. Furthermore from the positions of the transitions it can be concluded that the transition from Col_1 to Col_2 must be almost thermally complete before it becomes mechanically effective. An origin of the small step seen in Fig. 8 on the heating scan at around 30 °C, which was not observed on the cooling scan or in the DSC curve, is not clear yet. The mechanical properties identify **c** in the α phase as a highly flexible material whose modulus decreases smoothly by a factor of 5 in the range from −120 °C to 90 °C. The Col_2 phase is even more flexible. The flexibility of the complex over a wide range of temperatures can be attributed to the relatively high polysiloxane content which acts as soft segments in the mesophase. The mechanical properties of the material may be improved by cross-linking reactions, which are established in the chemistry of polysiloxanes. Examples for effective cross-linking catalysts are heavy metal compounds such as dibutyltin dilaurate.

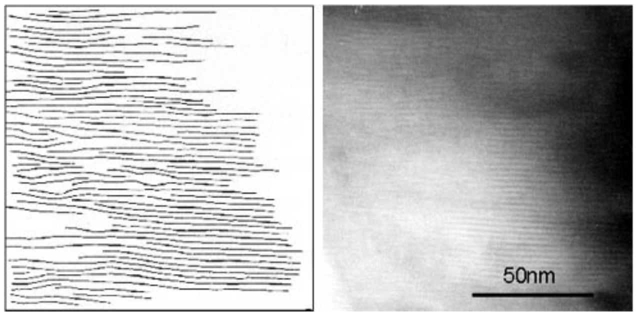

Fig. 6 High resolution electron micrograph (TEM) of a cut along the columns of the Col_1 phase (right). The brighter lines correspond to the columns and the dark ones to the surrounding siloxane matrix. The average distance between two equal stripes is 2.3 nm. For clarity the copy of a transparent overlay (left) shows the height of the columns.

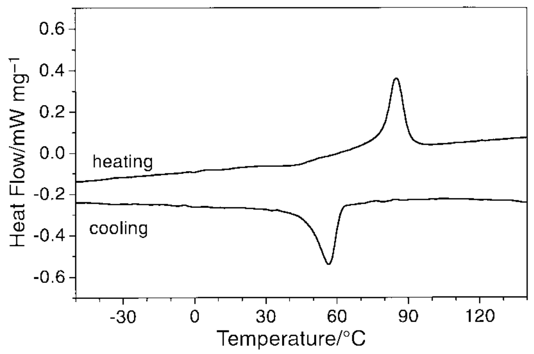

Fig. 7 DSC traces of complex **c** while heating and cooling. The exothermic transition at 85 °C in the heating scan and the endothermic transition at 57 °C indicate a reversible order–order transition form a column phase α to a column phase β.

Summary

It has been shown that the complexation of carboxylic acid functionalized hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene with a commercially available polysiloxane results in a hybrid material which shows interesting highly ordered columnar phases. The columns are remarkably long and the structures

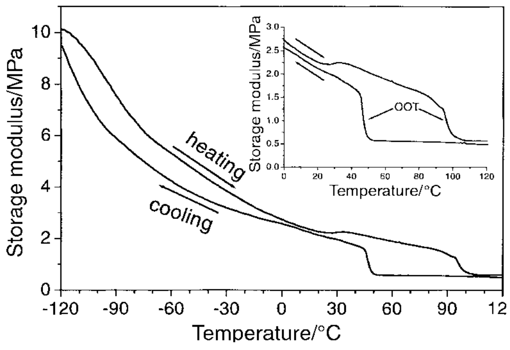

Fig. 8 Storage shear modulus of complex **c** while heating and cooling. The insert shows a magnification in the region of the columnar order–order transition.

are essentially free of defects. The material is highly elastic over a wide range of temperatures and may function as a basic material for molecular nanowires.

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