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Phase behaviors and supra-molecular structures of a series of symmetrically tapered bisamides

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A series of symmetrically tapered 1,4-bis[3,4,5-tris(alkan-1-yloxy)benzamido] benzene bisamides (CnPhBA, where \( n \) is the number of carbon atoms in the alkyl chains, \( n = 10, 12 \) and 16), was synthesized in order to investigate the effect of alkyl chain length on supra-molecular ordered structures induced by hydrogen (H)-bonding and micro-phase separation. These bisamides consist of a rigid aromatic bisamide core with three flexible alkyl chains at each end of the core. Major phase transitions and their origins in CnPhBA bisamides were studied with differential scanning calorimetry, one-dimensional (1D) wide angle X-ray diffraction (WAXD), infrared spectroscopy, and solid-state carbon-13 nuclear magnetic resonance experiments. The structures of these compounds in different phases were identified using 2D WAXD from oriented samples and were also confirmed by selected area electron diffractions in transmission electron microscopy from stacked single crystals and by computer simulations. All of the CnPhBA bisamides in this series formed a highly ordered oblique columnar (\( \Phi_{\text{OK}} \)) phase and a low-ordered oblique columnar (\( \Phi_{\text{OB}} \)) phase, similar to a recent report on C14PhBA.1 The two main driving forces in the formation of these two supra-molecular columnar structures were identified: One was the H-bond formation between N–H and C=O groups, and the other was the micro-phase separation between the bisamide cores and the alkyl chains. With increasing the length of alkyl tails, the isotropization temperature decreased, while the disordering temperature of the alkyl tails increased. The 2D lattice structures perpendicular to the columnar axis also increasingly deviated from the pseudo-hexagonal packing with increasing the alkyl tail length. However, the alkyl tail length did not have a significant influence on the packing along the columnar axis direction. Utilizing polarized optical microscopy, the phase identifications were also supported by the observation of texture changes and molecular arrangements inside of the micro-sized domains.

Introduction

Since columnar discotic liquid crystals (LCs) show many extraordinary properties such as one-dimensional (1D) electrical conductivity,2–5 fast photoconductivity6–11 and ferroelectricity,12,13 the structures and dynamics of discotic LCs have been studied extensively. Traditional columnar phases are normally constructed with discogenic (disc-like) molecules as building blocks which possess a rigid core with flexible tails (most of them are alkyl chains), and they usually exhibit three-, four- or six-fold rotational symmetry. Recently, many novel discotic LC systems have been identified, including those with building blocks that are chiral molecules,14 inverted molecules,15 tapered molecules,16 half disc molecules,17 dendrimers,18 or symmetric-tapered molecules.19

Supra-molecular discotic mesophase structures driven by molecular recognition processes through non-covalent interactions have become an interesting research topic and a promising approach for practical applications and scientific challenges.20,21 Non-covalent interactions include hydrogen (H)-bonding, electrostatic (ion–ion, ion–dipole, and dipole–dipole) interactions, \( \pi–\pi \) stacking interactions, van der Waals interactions, and hydrophobic–hydrophilic effects along with others.22–31 Since Lehn first discovered H-bonding induced supra-molecular LC phases, H-bonding has become a topic of major research due to its moderate bonding energy, directionality, selectivity and reversibility.25–31 In these H-bonding systems, self-assembled columnar LC phases are not formed via discotic molecules or main chain macromolecules, but rather by supra-molecular “discs” as building blocks generated through intra/inter-molecular H-bonding.1,30,31 In addition to H-bonding, the micro-phase separation between two incompatible yet chemically bonded components is another driving force to facilitate the formation of self-assembled LC structures.22–31 This can happen between rigid aromatic cores and flexible alkyl parts. Since the rigid cores and flexible parts are covalently bonded, only microscopic phase separation is allowed.

Similar to a recent study,32 we have reported discotic LC phases from the symmetric tapered bisamide ( abbreviated as CnPhBA, here \( n \) is the number of carbon atoms in each tail, \( n = 14 \) ) having three alkyl chain tails at each end of the core.1 It was found that a disc was generated through inter-molecular
H-bonding of four C14PhBA, and these supra-molecular discs further assembled into oblique columnar phases. The question remains: what is the role of alkyl tail length in the construction of stable columnar phases in this series of CnPhBA compounds?

In order to study the effect of alkyl chain length on phase behaviors and structures, a series of symmetrically tapered bisamides (CnPhBA, n = 10, 12 and 16) were designed and synthesized. These bisamides contain 1,2-bis[3,4,5-tris(alkan-1-yloxy) benzamido] benzene as a rigid core, and three flexible alkyl chains at each end of the core. The difference among these three bisamides is that they have different numbers of methylene units (n). Differential scanning calorimetry (DSC) experiments were first utilized to detect the thermal transitions in this series of CnPhBA samples. The phase structures of this series of CnPhBA were identified by wide angle X-ray diffraction (WAXD) and selected area electron diffraction (SAED). Their molecular conformations and packing schemes were deduced from structural characterization and supported by computer simulations. The phase morphologies in the ordered phases were investigated via polarized light microscopy (PLM). The H-bonding between N–H and C=O groups were studied using Fourier transform infrared spectroscopy (FT-IR). The dynamic conformational changes of the aromatic and aliphatic parts in this series of CnPhBA at different temperatures correspond well with the thermal transitions via solid-state carbon-13 nuclear magnetic resonance (13C NMR) experiments.

**Experimental**

**Materials and sample preparation**

A series of twin-tapered bisamides (CnPhBA, here n is the even number of carbon atoms in each tail; n = 10, 12 and 16) was designed and synthesized. The final compounds were purified through repeated chromatography with a silica gel using an ace tone-benzene (5 : 95) mixture as the eluting solvent, followed by re-crystallization from an ethanol–benzene mixture and vacuum drying. The purity of the materials was verified by thin layer chromatography (TLC) and nuclear magnetic resonance (NMR). A detailed synthetic procedures for 1,2-bis[3,4,5-tris (alkan-1-yloxy) benzamido] benzenes (CnPhBA) can be found in refs 1 and 33. The general chemical structure of this series of compounds is

\[
\text{H}_2C\left(\text{H}_2C\right)_{n-1}\text{O} \quad \text{H}_2C\left(\text{H}_2C\right)_{n-1}\text{O} \quad \text{H}_2C\left(\text{H}_2C\right)_{n-1}\text{O}
\]

\[
\text{CnPhBA, here } n = 10, 12 \text{ and } 16
\]

For 1D WAXD powder measurements, film samples with a thickness of about 1 mm were prepared by melting the compounds on an aluminium plate. In order to determine various phase structures, oriented samples for 2D WAXD experiments were obtained by mechanical shearing in the low-ordered oblique columnar phase and thermally treated at different temperatures. A typical sample thickness was about 0.2 mm. The samples prepared for PLM had a typical thickness of 10 μm, and they were melt-processed between two bare cover glass sides. In the shearing experiments in the PLM, the sample was first heated to the isotropic melt (I) and sheared in the low-ordered columnar phase. The sample was then immediately quenched to room temperature. The film samples for Fourier transform infrared spectroscopy (FT-IR) were prepared by film casting from a CHCl₃ dilute solution onto KBr plates and the solvent was evaporated. The powder samples were used for solid-state carbon-13 (13C) nuclear magnetic resonance (NMR). Thin film samples prepared for transmission electron microscopy (TEM) via solution casting from a 0.05% (w v⁻¹) chloroform solution onto carbon-coated mica had a thickness of 50–150 nm. After crystalization, the films were floated onto the water surface and recovered using the TEM copper grids.

**Equipment and experiments**

The thermal behavior of the phase transitions was studied using a Perkin-Elmer PYRIS Diamond DSC with an Intracooler 2P apparatus. The temperatures and heat flows were calibrated using material standards at cooling and heating rates ranging from 5 to 20 °C min⁻¹. The heating experiments always preceded the cooling experiments in order to eliminate previous thermal histories, and the cooling and heating rates were always kept identical. The transition temperatures were determined by measuring the onset temperatures from both the cooling and heating scans at different rates.

One-dimensional WAX powder experiments were conducted in the reflection mode of a Rigaku 12 kW rotating-anode X-ray (Cu Kα radiation) generator coupled to a diffractometer. The diffraction peak positions and widths were calibrated with silicon crystals in the high 2θ-angle region (>15°) and silver behenate in the low 2θ-angle region. A hot stage was coupled to the diffractometer in order to study the structural evolutions with temperature changes during heating and cooling. The temperature of this hot stage was calibrated to be within ±1 °C. Samples were scanned across a 2θ-angle range of 1.5° to 30° at a scanning rate of 6° min⁻¹. The oriented 2D WAXD patterns were obtained using a Rigaku X-ray imaging system with an 18 kW rotating anode X-ray generator. Silicon crystal powders, used as an internal reference, show a diffraction ring at a 2θ value of 28.47°. A hot stage was also used to obtain diffraction peaks from the ordered structures at elevated temperatures. A 30 min exposure time was required for a high-quality pattern. In both 1D and 2D WAXD experiments, background scattering was subtracted from the sample scans.

Bright images of TEM (FEI Tacnai 12) were obtained to examine crystal morphology on the nanometre scale using an accelerating voltage of 120 kV. The camera length was set at 4.2 m and calibration of the SAED spacing smaller than 0.384 nm was carried out using evaporated thallous chloride, which has a largest first-order spacing diffraction of 0.384 nm. Spacing values larger than 0.384 nm were calibrated by doubling the d-spacing values of the first-order diffractions.

Optical textures of the ordered phases at different temperatures were observed with a PLM (Olympus BH-2) coupled
with a Mettler heating stage (FP-90) in order to investigate morphology on the micrometre scale. A tint retardation plate (530 nm) was also placed between the objective lenses and the eyepieces in order to identify the orientation of molecules in the PLM textures. H-bonding and molecular chain conformations were studied using a FT-IR (Digilab Win-IR Pro FTS 3000) equipped with a Bruker heating stage. The resolution was 1 cm⁻¹ and 20 scans were averaged for each spectrum. The temperatures of this hot stage were calibrated to be within ±0.5 °C. The dynamics of each carbon and the conformations of the alkoxyl chain in CnPhBA compounds at different temperatures were also studied using a solid-state ¹³C NMR (Chemagnetics CMX 200) operating at 201.13 and 50.78 MHz for ¹H and ¹³C nuclei. The samples were spun in nitrogen gas at 4.5 kHz at the magic angle. The magic angle was optimized by the intensity calibration of the aromatic carbon resonance of hexamethylbenzene. The ¹³C cross polarization/magic angle spinning/dipolar decoupling (CP/MAS/DD) NMR spectra were acquired to selectively investigate the rigid components and the Bloch decay spectra with MAS/DD was used to selectively study the mobile components. The CP contact time was 1 ms, while the recycle time of the pulse was 5 s. Each spectrum consisted of an accumulation of 1000 scans. The temperature of the solid-state ¹³C NMR experiment was 1 ms, while the recycle time of the pulse was 5 s. Each spectrum consisted of an accumulation of 1000 scans. The temperature of the solid-state ¹³C NMR experiment was controlled using a REX-F900 VT unit covering the temperature range from 25 to 170 °C.

Crystallographic simulation was performed using Cerius² (Version 4.6) simulation software from Accelrys utilizing the COMPASS force field. To make the simulation practical, aliphatic alkyl chains at each end of the core were replaced by methyl groups. First, the global equilibrium conformation of the single CnPhBA was constructed at 0 K using the COMPASS force field. And then, a disc as a building block was generated through inter-molecular H-bonding of four energy-minimized CnPhBAs. In order to build the crystal unit cell, basic unit cell parameters determined by crystallographic experimental data from 2D WAXD were used. The positions of atoms in this unit cell were judged by comparing their calculated diffraction patterns with those of experiments. Overlapped peaks in 2D WAXD and β carbon peaks in solid-state ¹³C-NMR were resolved using the PeakFit peak separation program (Jandel Scientific). Gaussian and/or Lorentzian functions were used to obtain the best fit.

**Results and discussion**

**Thermal transitions and their corresponding structural evolutions**

Figs. 1a and 1b show two sets of DSC cooling and subsequent heating diagrams respectively, for a series of symmetrically tapered bisamides CnPhBA (n = 10, 12, 14 and 16) at a scanning rate of 5 °C min⁻¹. During cooling, two thermal transition processes are observed when n is 14 and 16, while three transition processes for n = 10 and 12. The CnPhBA samples containing the longer alkyl tails at ends of the amide core exhibit lower transition temperatures for the high-temperature transitions, but higher transition temperatures for the low-temperature transitions. For C14PhBA, the two transition processes are observed at 146 °C and 52 °C and their heats of transition measured during cooling were 40.5 kJ mol⁻¹ and 54.7 kJ mol⁻¹, respectively. In the case of C16PhBA, these two transition processes are observed at 139 °C and 60 °C and their heats of transition measured during cooling were 40.8 kJ mol⁻¹ and 67.9 kJ mol⁻¹ respectively. As an example of CnPhBA, different cooling and subsequent heating rates between 5 and 20 °C min⁻¹ for C16PhBA were shown in Fig. 2a. Both transition temperatures and their heats of transitions are independent of cooling and heating rates. The onsets of the cooling at the high temperature side and the heating at the low temperature side at equal cooling and heating rates show differences of a few degree. Therefore, these two-phase transitions must correspond to transitions from the isotropic (I) state to a LC phase at the high-temperature transition and a LC to another LC phase transition at the low-temperature transition.

Compared with thermal transitions of C14PhBA and C16PhBA, both C10PhBA and C12PhBA exhibited three transition processes during cooling as shown in Fig. 1a. For example the case of C12PhBA, in addition to the high-temperature exothermic transition at 148 °C with a heat of transition of 39.6 kJ mol⁻¹, a broad low-temperature exothermic process can be deconvoluted into two exothermic peaks at 45 °C with 25.7 kJ mol⁻¹ and at 42 °C with 3.2 kJ mol⁻¹. This deconvolution can also be verified by subsequent heating DSC diagram of C12PhBA as shown in Fig. 1b. Similarly, the C10PhBA compound also exhibits three thermal transition
C16PhBA is in the I phase exhibiting only two amorphous halos. One is at $2\theta = 3.05^\circ$ ($d = 2.90$ nm), which may correspond to the average periodicity of electron density fluctuations between the micro-phase separated aromatic amide cores and alkyl tails, and the other is at $2\theta = 18.8^\circ$ ($d = 0.47$ nm), which is attributed to the average distance among the amorphous chains. When the temperature reached $139^\circ$ C, two apparent low-angle reflections are observed (actually, there are three overlapped reflections, see below in 2D WAXD results for the detail explanation). In addition to the changes of low $2\theta$-angle region, the scattering halo at $2\theta = 18.8^\circ$ ($d = 0.47$ nm) suddenly shifts toward a $2\theta$-angle of $19.2^\circ$ ($d = 0.46$ nm) in the high $2\theta$-angle region. Below $60^\circ$ C, which corresponds to the lower temperature thermal transition in Fig. 2a, there is a broad reflection in the low $2\theta$-angle region, which is caused by overlapped reflections (see below in 2D WAXD results for the detail explanation). Another relatively weak reflection at $2\theta = 5.38^\circ$ ($d = 1.64$ nm) can also be seen. In the wide-angle region, a $2\theta = 21.1^\circ$ ($d = 0.42$ nm) peak appears, which sits on the scattering halo at $2\theta = 19.5^\circ$ ($d = 0.46$ nm). This reflection at $2\theta = 21.1^\circ$ may originate from the ordered alkyl chain structure. The 1D WAXD powder patterns during heating also agree with the thermal transitions observed in the DSC heating results.

**Identifications of supra-molecular structures of CnPhBA**

Even though the 1D WAXD powder experiments at different temperatures combined with the DSC results can monitor the structural evolutions in this series of CnPhBA compounds, 2D WAXD experiments on oriented CnPhBA samples should be conducted to obtain detailed structures and symmetry. As an example of this series, a 2D WAXD pattern of an oriented C16PhBA sample is shown in Fig. 3a. The oriented sample was prepared by mechanical shearing at $95^\circ$ C followed by annealing at $50^\circ$ C for 1 day. This 2D WAXD pattern exhibits diffractions not only on the equator and meridian, but also in the quadrants. As indicated in this figure, the $a^*$ and $b^*$ axes are assigned to be on the equator, and the $c^*$ axis is along the shear direction (SD). On the equator, the overlapped diffractions in the low $2\theta$-angle region can be deconvoluted as three diffractions at $2\theta = 2.44^\circ$ ($d = 3.62$ nm), $2.72^\circ$ ($d = 3.24$ nm) and $3.00^\circ$ ($d = 2.95$ nm), respectively, as shown in Fig. 3b. These three deconvoluted diffractions are assigned to be the (010), (110), and (100) diffractions, respectively, based on the triangulation method of building a 2D $a^*b^*$ lattice of the unit cell.25 A series of weak diffractions on the equator between $2\theta = 4.7^\circ$ and $17.5^\circ$ fit well with the 2D $a^*b^*$ lattice, and they can be assigned as shown in Fig. 3c. A relatively diffuse diffraction arc at $2\theta = 18.5^\circ$ ($d = 0.48$ nm) is observed on the meridian. This diffuse diffraction can be assigned as the (002) since the (001) diffraction on the meridian is extinct at $2\theta = 9.2^\circ$ ($d = 0.96$ nm). This assignment is supported by a series of weak and diffused diffractions of the first layer $(hk1)$ of the 2D WAXD pattern. The order along the meridian direction is quasi-long-range but not a long-range order.26,27 In the high $2\theta$-angle region above $20^\circ$, there are two arc diffraction pairs in the quadrants and on the equator at $2\theta = 20.8^\circ$ ($d = 0.427$ nm) and $2\theta = 21.4^\circ$ ($d = 0.415$ nm), respectively. These two arc
diffraction pairs can be assigned to the inter-chain packing of the ordered alkyl tails based on the FT-IR and solid-state $^{13}$C NMR results at different temperatures (see below for the detail explanations). Thus, they should be excluded from the construction of supra-molecular structure unit cell lattice. Careful structural analysis gives a pseudo-3D monoclinic unit cell with dimensions of $a = 3.44$ nm, $b = 4.22$ nm, $c = 0.96$ nm, $a = b = 90^\circ$ and $c = 59.1^\circ$ via the refinement of the reciprocal lattice, and this phase is abbreviated as the $W_{OK}$ phase, and it is close to a hexagonal lattice. The experimentally observed and the calculated $2\theta$ values and $d$-spacings based on this unit cell lattice are listed in the Table 1. Its calculated crystallographic density is 0.98 g cm$^{-3}$ based on four C16PhBA molecules per unit cell. The experimentally observed density is 0.98 g cm$^{-3}$, which fits well with the calculated data.

Even its second order diffraction can be clearly seen at the $d$-spacing of 1.8 nm. Therefore, the column direction is parallel to the surface of the substrate, and is highly ordered. The arrow in Fig. 4a points to the long axis of the columns which corresponds to the $c^*$ axis of the $W_{OK}$ unit cell. The assignment

Table 1 Experimental and calculated crystallographic parameters of the highly ordered columnar $W_{OK}$ phase of C16PhBA

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<th>Calc$^b$</th>
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$^a$ The accuracy of the experimental data is $\pm 0.005$ nm. $^b$ The calculated data listed are based on the $W_{OK}$ monoclinic unit cell with $a = 3.44$ nm, $b = 4.22$ nm, $c = 0.96$ nm, $a = b = 90^\circ$ and $c = 59.1^\circ$. $^c$ The intensities are semi-quantitatively estimated via a micro-densitometer and classified as very strong (vs), strong (s), medium (m), weak (w), and very weak (vw).
of (002) diffraction at 2h = 18.5° (d = 0.48 nm) on the meridian of 2D WAXD of C16PhBA (Fig. 3a) can be confirmed by the observation of electron diffraction at d = 0.24 nm, which belongs to (004) diffraction as indicated in Fig. 4b. Furthermore, two pairs of electron diffractions at d = 0.43 nm which belong to the (042) X-ray diffraction of the 2D WAXD pattern (Fig. 3a) are observed at +31° out of the c* axis. This explains that the discotic building blocks generated by H-bonding self-assembly are tilted +31° with respect to the ab-plane.

Confirmation of this structural determination and the positions of atoms in the φOK unit cell of four C16PhBA molecules can be provided via computer calculations. To make the simulation practical, we focus on the assembly of the amide cores of C16PhBA. The alkyl tails at each end of the amide core are replaced by methyl groups. First, the global equilibrium conformation of the single C16PhBA was constructed at 0 K using the COMPASS force-field. And then, a disc building block is generated through the inter-molecular H-bondings between the C=O and N–H groups in the amide cores. Four energy-minimized C16PhBA molecules create one disc, which then can build a column by stacking the discs perpendicular to the disc plane. In this disc model, two C16PhBA molecules are located face-to-face at a distance of 0.7 nm apart from each other. The other two neighboring C16PhBA molecules at the bottom facing parallel to each other are rotated 90°, and they are separated from the upper pair by a distance of 0.49 nm. In order to build the crystal unit cell, basic unit cell parameters determined by crystallographic experimental data are used. The positions of the atoms in this unit cell are judged by comparing their calculated diffraction patterns with experimental ones. An energy minimization is carried out with the fixed unit cell dimensions. The results are shown from the top (Fig. 5a) and side (Fig. 5b) views, respectively. In this model, the H-bonds are between two neighboring pairs along the column direction, while the phenylene rings of the amide cores are tilted with respect to the column direction, and the phenylene rings of two amide cores in the pair are in a tilted face-to-face configuration. The angle between two adjacent amide pairs along the column direction becomes 50°. Based on the 2D WAXD of oriented samples and SAED of single crystal experiments combined with the computer simulation, a schematic illustration representing the unit cell lattice and the supra-molecular columnar structure of the φOK phase of C16PhBA is shown in Fig. 5c.

Two-dimensional WAXD patterns of highly ordered supra-molecular structures of the other two CnPhBA compounds (n = 10 and 12) are similar to that of the C16PhBA (the supra-molecular structure of C14PhBA has been reported in ref. 1). Detailed structural determinations of the highly ordered supra-molecular structures in these two CnPhBA compounds lead to similar pseudo-3D monoclinic lattices. Their lattices, unit cell dimensions and density data are listed in Table 2. As shown in this table, with decreasing the number of methylene units in the alkyl tails at the end of amide cores, the γ angle increasingly deviates from 60° yet the c-axis dimension is almost identical.

The supra-molecular structure at the high-temperature phase also can be identified using the 2D WAXD experiments from the oriented samples. The oriented C16PhBA sample was prepared by mechanical shearing at 95°C and quenched to room temperature followed by increasing temperature up to

![Fig. 4](image)

**Fig. 4** Bright-field TEM morphology of the highly ordered columnar φOK phase of C16PhBA (a). The arrow is pointing along the long axis of the columns (c* axis). SAED pattern from the circled area of the bright-field TEM morphology in Fig. 4a (b).

![Fig. 5](image)

**Fig. 5** Computer energy-minimized φOK phase with top (a) and side (b) views, and a schematic unit cell model with four C16PhBA compounds for the φOK highly ordered columnar phase of C16PhBA (c).
95 °C. The 2D WAXD pattern of the mechanically sheared C16PhBA at high-temperature phase at 95 °C is shown in Fig. 6a. As indicated in this figure, the \( a^* \) and \( b^* \) axes can still be assigned to the equator, and the \( c^* \) axis is along the SD.

On the equator of this oriented sample at 95 °C, the overlapped diffractions in the low 2\( \theta \)-angle region can again be deconvoluted into three diffractions at 2\( \theta \) = 2.16° (\( d = 4.09 \) nm), 2.63° (\( d = 3.36 \) nm) and 2.93° (\( d = 3.02 \) nm), respectively as shown in Fig. 6b. These three deconvoluted diffractions are assigned as the (010), (110), and (100) diffractions, respectively, if the self-assembled disc packing in this phase still retains the molecular orientation and positional order of the \( \Phi_{\text{OB}} \) phase. On the meridian, the diffraction assigned as the (002) planes can still be observed at d-spacing of 0.48 nm. However, all of the diffractions above 2\( \theta \) = 20° disappear because the ordered alkyl tails melt (see below of FT-IR and solid-state \(^{13}\)C NMR experiments). Careful structural analysis gives a pseudo-hexagonal lateral packing unit cell with dimensions of \( a = 3.49 \) nm, \( b = 4.71 \) nm, \( c = 0.96 \) nm, \( \alpha = \beta = 90° \) and \( \gamma = 60.1° \) via the refinement of the reciprocal lattice, and this phase is abbreviated as the \( \Phi_{\text{OB}} \) phase.

Two-dimensional WAXD patterns of low-ordered supra-molecular columnar structures of the other three CnPhBA compounds \((n = 10, 12, \text{and} 14)\) are very similar to the \( \Phi_{\text{OB}} \) phase of C16PhBA. Detailed structural determinations of the low-ordered supra-molecular structures in these three CnPhBA compounds and density data are listed in Table 3. As shown in this table, with decreasing the number of methylene units in the alkyl tails at the end of amide cores, again, the 2D \( ab \) unit cell lattices are shrunk and the \( \gamma \) angle increasingly deviates from 60°, while the \( c \)-axis dimension is not changed.

### Hydrogen bonding associations and molecular mobility in the phases

Structure sensitive characterization experiments such as 2D WAXD and SAED need to be combined with FT-IR and solid-sate \(^{13}\)C-NMR spectroscopic experiments in order to understand the inter-molecular H-bonding between C=O and N–H groups, which form the self-assembled discs, as well as to identify the conformations of alkyl tails at the end of amide cores, which can provide information on the origins of the phase transformations. Figs. 7a and 7b show two sets of FT-IR spectra of C12PhBA at different temperatures. These sets of data were obtained during heating at 5 °C min\(^{-1}\). In the \( \Phi_{\text{OB}} \) phase at 30 °C, the amide cores exhibit the characteristic phenylene vibration bands at 1608, 1582, 1527, and 1493 cm\(^{-1}\), the N–H stretching vibration (\( v_{\text{N–H}} \), \( v \): stretching vibration) at 3300 cm\(^{-1}\), and the C=O stretching vibration (\( v_{\text{C=O}} \)) at 1648 cm\(^{-1}\). The alkyl tails show the characteristic bands of CH\(_3\) asymmetric stretching \( \{ v_{\text{as}}(\text{CH}_3) \} \) at 2957 cm\(^{-1}\), CH\(_3\) symmetric stretching \( \{ v_{\text{s}}(\text{CH}_3) \} \) at 2873 cm\(^{-1}\), CH\(_2\) asymmetric stretching \( \{ v_{\text{as}}(\text{CH}_2) \} \) at 2921 cm\(^{-1}\), CH\(_2\) symmetric stretching \( \{ v_{\text{s}}(\text{CH}_2) \} \) at 2851 cm\(^{-1}\), as well as 1468 cm\(^{-1}\) \( \{ \delta(\text{CH}_2) \} \), 1382 cm\(^{-1}\) (CH\(_3\) umbrella). Molecular interactions and conformations affect the wavenumber, intensity and shape of the infrared absorption bands,\(^{41}\) while H-bonding is one of the best-known factors that have such effects. It is observed that

### Table 2 Crystal system, axial system, and density of the highly ordered columnar \( \Phi_{\text{OK}} \) phase of CnPhBA at room temperature

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Axial system</th>
<th>Density/g cm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( a/\text{nm} )</td>
<td>( b/\text{nm} )</td>
</tr>
<tr>
<td>10 Monoclinic</td>
<td>2.40</td>
<td>5.21</td>
</tr>
<tr>
<td>12 Monoclinic</td>
<td>3.10</td>
<td>3.83</td>
</tr>
<tr>
<td>14 Monoclinic</td>
<td>3.28</td>
<td>3.87</td>
</tr>
<tr>
<td>16 Monoclinic</td>
<td>3.44</td>
<td>4.22</td>
</tr>
</tbody>
</table>

16 Monoclinic 3.49 4.71 0.96 90 90 60.1 0.97 0.98

14 Monoclinic 3.34 4.62 0.96 90 90 56.6 0.98 1.01

12 Monoclinic 3.15 4.58 0.96 90 90 54.8 0.99 1.00

10 Monoclinic 2.43 4.96 0.96 90 90 46.7 1.00 1.01

Fig. 6 Two-dimensional WAXD pattern of the low ordered columnar \( \Phi_{\text{OB}} \) phase of C16PhBA at 95 °C (a). The oriented sample was prepared by mechanical shearing at 95 °C and quenched to room temperature followed by increasing temperature up to 95 °C. The deconvolution of the low 2\( \theta \)-angle diffraction between 2\( \theta \) = 1.5° and 2\( \theta \) = 3.5° into three peaks using the PeakFit peak separation program (b). Gaussian functions were used to obtain the best fit.
Although FT-IR is not sensitive to the conformation changes of the non-polar carbon backbones, the \( v_s(CH_2) \) and \( v_{as}(CH_2) \) bands may still be used to detect alkyl tail conformation changes during heating. The \( v_s(CH_2) \) and \( v_{as}(CH_2) \) are in the ranges of 2846–2850 and 2916–2920 cm\(^{-1}\) for all-trans alkyl chains, and these two vibration bands shift to 2854–2856 and 2924–2928 cm\(^{-1}\) for disordered alkyl chains.\(^{42-44}\) In Fig. 7b, the \( v_s(CH_3) \) and \( v_{as}(CH_2) \) of the \( \Phi_{OB} \) phase are at 2851 cm\(^{-1}\) and 2921 cm\(^{-1}\) for the C16PhBA at 30 °C, indicating the co-existence of both ordered all-trans conformation and disordered alkyl chains. When the temperature increases and passes through the \( \Phi_{OB} \leftrightarrow \Phi_{OK} \) transition, the wavenumber of \( v_s(CH_2) \) increases continuously at temperatures below 40 °C, and then, a small change is seen at 40 °C while another sudden shift, about 2 cm\(^{-1}\), occurs at 50 °C. This band then remains almost unchanged until 95 °C. The concentration of the disordered conformations thus suddenly increases at 50 °C, during the \( \Phi_{OB} \leftrightarrow \Phi_{OK} \) transition. However, these spectroscopic changes are small, solid-state \(^{13}\)C NMR experiments were also carried out to further support this conclusion.

One of the advantages of solid-state \(^{13}\)C NMR is that it can give a quantitative population estimate of the ordered (all-trans) and disordered (mixture of trans and gauche) alkyl tail conformations.\(^{1,3,6,44-48}\) Figs. 8a and 8b show CP/MAS/DD and Bloch decay spectra of C12PhBA during heating at different temperatures, respectively. The CP/MAS/DD method is sensitive to the rigid components, and the mobile components can easily be detected by the Bloch decay method.\(^{1,3,6,44}\) Chemical shift identifications are carried out by both the solution \(^{13}\)C NMR and theoretical calculations based on the tabulated data.\(^{41}\) The ordered alkyl tail conformations give a chemical shift around 33–35 ppm, while the disordered alkyl chain conformations give a chemical shift around 30–32 ppm. In the \( \Phi_{OK} \) phase at 30 °C, the chemical shift at 34 ppm corresponds to the methylene carbon atoms in the ordered segments of alkyl tails, while the chemical shift peak at 32 ppm corresponds to the methylene carbon atoms in the disordered segments of the alkyl tails. From the area ratio of these two chemical shifts, the population of methylene carbons in the ordered segments of the alkyl tails was estimated to be 40%. With increasing temperatures, the intensity and area of the chemical shift representing the ordered conformations decreases and those of the disordered conformations increases.

This area ratio of these two chemical shifts continuously decreases with increasing temperatures. However, when temperature reaches the lowest transition temperature at 40 °C, a sudden decrease of this ratio to around 35% is observed, indicating a sudden conformational change of the alkyl tails is involved in this transition. With the further increase of temperature, the percentage of ordered carbons does not change much until 50 °C, at which point this percentage abruptly drops to around 15%. This indicates that sudden conformation changes of the alkyl tails are involved in two steps in the two low-temperature phase transitions. After these phase transitions, very little change of the chemical shift area ratio can be observed even after C12PhBA enters the I phase at 175 °C. This suggests most of the ordered alkyl tails are
already melted. Therefore, we can conclude that at the $\Phi_{\text{OK}}$ phase, there about 40% of the methylene carbons are in the ordered all-trans conformation in the C12PhBA sample. With increasing temperatures, this ratio decreases, and the low-temperature transition ($\Phi_{\text{OK}} \leftrightarrow \Phi_{\text{OB}}$) is attributed to the sudden decrease of this ratio, where most of the methylene carbons transform into the liquid-like disordered state. The alkyl tail conformation changes, on the other hand, contribute little to the high-temperature transition ($\Phi_{\text{OB}} \leftrightarrow I$).

**Supra-molecular phase morphologies and molecular orientations**

The texture changes in PLM can give morphological information on the micrometre length scale, while the WAXD and computer simulation provide microscopic structure of the materials. Fig. 9a shows the PLM micrograph of C16PhBA sheared at 120 °C and then annealed at room temperature. The bright “lines” are the oriented bulk sample and the shear direction is along the “lines”. The “lines” are bright because the molecules are in the ordered columnar phase ($\Phi_{\text{OK}}$) and the directions of refractive indexes are not parallel to the directions of the polarizers of the PLM. A tint retardation plate (530 nm) was also applied between objective lenses and eyepieces in order to identify the orientation of molecules in the PLM textures, as shown in Fig. 9b. The sheared “lines” are yellow in color, which means that the refractive index perpendicular to the “lines” ($n_\perp$) is higher than the refractive index parallel to the “lines” ($n_\parallel$). Therefore, the column direction of this supra-molecular columnar phase should align along the “lines” (shear direction, SD) under PLM. This observation is also consistent with the 2D WAXD result (Fig. 3a), the SAED experiment (the inset of Fig. 4) and the computer simulation (Figs 5a–5c).

Fig. 10a shows the morphologies of the $\Phi_{\text{OB}}$ phase observed in PLM. The sample was between two pieces of glass and first heated to the I phase, and then, cooled to 138.5 °C and annealed there for 1 day. Both ribbon-like and spherulite-like textures are observed. Some of the ribbons fold back and forth and others form half circles. The ribbon width is around 5–10 µm. Fig. 10b shows the PLM micrograph after inserting the tint plate. All the ribbons go along the direction of left-up to right-down are blue and all the ribbons go along the direction of right-up to left-down are yellow. This provides evidence that the refractive index perpendicular to the ribbons ($n_\perp$) is higher than the refractive index parallel to the ribbons ($n_\parallel$). Similar to the case of $\Phi_{\text{OK}}$ phase, the column direction is aligned along the ribbon long axis (see the TEM image in Fig. 4). It is interesting that the bright and dark ribbons always appear in an alternating manner and both positive in Fig. 10c and negative in Fig. 10d optical spherulite-like textures are observed. The positive spherulite-like textures are formed by the supra-molecular columns rotating circularly in the glass...
of this series of samples include the melting of alkyl tails and the isotropization originated from H-bond dissociation. It has been concluded that the isotropization temperature decreases with increasing length of the alkyl tails, while the alkyl tail melting temperatures increase with increasing length of the alkyl tails. C16PhBA with the longest alkyl tails among this series of twin-tapered bisamides possesses 2D lattices close to hexagonal packing. By decreasing the length of the alkyl tails at each end of the amide core, the 2D lattice of CnPhBA increasingly deviates from the pseudo-hexagonal packing. This may result from the fact that shorter alkyl tails result in relatively weaker effectiveness in micro-phase separation. However, the alkyl tail length does not have a significant influence on the packing along the column direction (the c axis and shear direction). Phase identifications are supported by the observation of texture changes in polarized optical microscopy and molecular arrangements inside of the micro-size domains were also investigated by introducing a tint plate.

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References


Fig. 10 PLM morphological observation of C16PhBA annealed at 138.5 °C for 1 day (a) and PLM texture with a tint plate between the objective lens and eyepieces (b). Schematic illustration of positive (c) and negative (d) spherulites.
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