Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644168

Computer Simulation of the Pentagonal Columnar Phase of Liquid Crystalline Bolaamphiphiles

Martin A. Bates[a]; Martin Walker[a]
[a] Department of Chemistry, University of York, York

First published on: 13 July 2010

To cite this Article Bates, Martin A. and Walker, Martin(2010) 'Computer Simulation of the Pentagonal Columnar Phase of Liquid Crystalline Bolaamphiphiles', Molecular Crystals and Liquid Crystals, 525: 1, 204 — 211
To link to this Article: DOI: 10.1080/15421401003799797
URL: http://dx.doi.org/10.1080/15421401003799797

Mol. Cryst. Liq. Cryst., Vol. 525: pp. 204–211, 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421401003799797

Taylor & Francis
Taylor & Francis Group

Computer Simulation of the Pentagonal Columnar Phase of Liquid Crystalline Bolaamphiphiles

MARTIN A. BATES AND MARTIN WALKER

Department of Chemistry, University of York, York

We use dissipative particle dynamics (DPD) simulations to explore the nature of triblock liquid crystalline bolaamphiphiles. We show that the simulations can reproduce the relationships, previously established experimentally, between the molecular dimensions and the phase behaviour. In contrast to other recent simulation studies of bolaamphiphiles, we observe a columnar phase with a pentagonal cross section.

Keywords Bolaamphiphiles; columnar liquid crystals; computer simulation; dissipative particle dynamics; pentagonal tiling

Introduction

Bolaamphiphiles and facial amphiphiles have recently received much attention both experimentally [1–6] and in computer simulations [7–9]. These differ from the more usual liquid crystal mesogens in the rich and predictable phase behaviour that can be obtained from small molecular alterations [1,8]. Liquid crystalline T-shaped bolaamphiphiles are composed of a rod-shaped core, with terminally attached polar groups and a laterally attached aliphatic chain, whereas facial amphiphiles have a similar structure but the aliphatic chains are located at the ends of the rigid cores, and the lateral chain is hydrophilic (see Fig. 1). For these classes of molecules, the different chemical groups microphase segregate such that the resultant phases are ordered liquids that significantly differ in structure from the more usual liquid crystalline systems. Typically, short chained bolaamphiphiles show columnar ordering [1]. These columnar phases differ from the columnar phases exhibited by disc-shaped molecules in that the central rod-like core forms the walls of the column, the hydrophilic end groups form the vertices and the flexible, laterally attached aliphatic chains form the interior. The rigid units tend to lie normal to the column axis which gives each column a defined shape (square, pentagonal, hexagonal, etc.), such that the perimeter tends to be an integer number of rod lengths (Fig. 2). The cross sectional area and hence shape of the column can be controlled by adjusting the length of the laterally attached chain. A short arm requires a relatively small volume and so favours shapes with fewer sides, whilst a longer arm requires a greater volume and so favours shapes with more sides. The complexity of the molecules forming these phases means that there are a number of parameters (aliphatic and hydrophilic chain lengths, length

Address correspondence to Martin A. Bates, Department of Chemistry, University of York, York YO10 5DD. E-mail: mb530@york.ac.uk

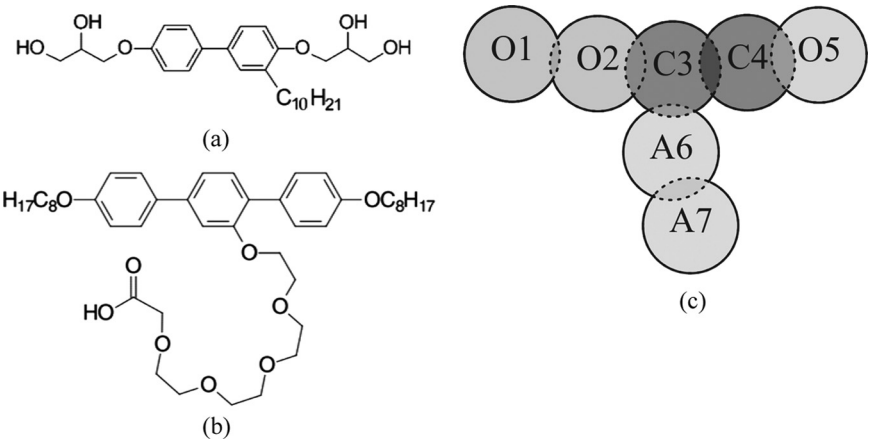

Figure 1. Molecular structures of typical (a) bolaamphiphiles [3] and (b) facial amphiphiles [5]. (c) A coarse grained representation of a T-shaped bolaamphiphile suitable for dissipative particle dynamics simulations. The beads are coloured and labelled according to their type. Dark grey (C): aromatic core; light grey (O): polar group, green (A): alkyl chain.

of the rod-like core, chemical nature of the aliphatic and hydrophilic groups, etc.) that can be adjusted; however, the basic features of the phase diagram remain. As the lateral chain length is extended whilst keeping other parameters the same, a

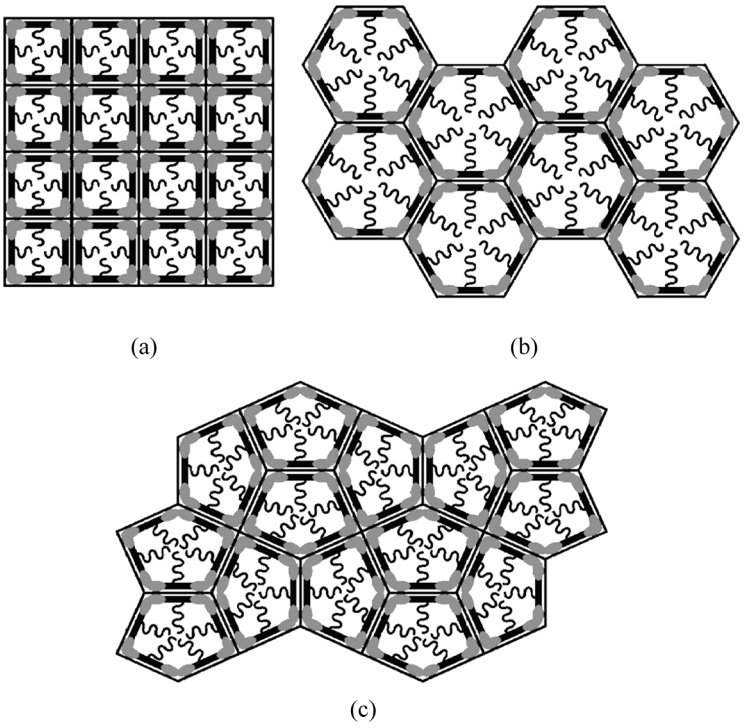

Figure 2. Schematic illustration of the in-plane tiling for the (a) square, (b) hexagonal, and (c) pentagonal columnar phases of T-shaped bolaamphiphiles [5].

sequence of columnar phases is observed, followed by lamellar phases for much longer chains lengths. Facial amphiphiles have a similar series of phases, but here the vertices are formed by the aliphatic chains and the lateral hydrophilic chains form the column interiors. As noted by Chen *et al.* [5], there is a topological duality between the sequence of phases for the two classes of materials.

Recent computer simulations of bolaamphiphiles have, to some extent, reproduced the experimental phase sequences. Thus square and hexagonal columnar phases have been observed in simulations [7–9]. Simulations have predicted more complex phase behaviour for X-shaped bolaamphiphiles where frustration must be relieved [9]; they have also identified and helped characterise a columnar phase with a Kagome lattice cross section [10]. However, in the previous simulations, the pentagonal columnar phase observed for T-shaped molecules has not yet been observed. In this paper, we present a model for which the pentagonal columnar phase is observed between the square and hexagonal columnar phases on increasing the lateral chain length.

Computational Methods

The large primitive unit cell of the pentagonal columnar phase necessarily requires a coarse grained technique in which the molecular detail is simplified to allow for simulations over large length and time scales. This means that the molecule is broken into its constituent parts, with a single sphere or bead representing a number of atoms (see Fig. 1c). The dissipative particle dynamics technique [11,12] has already been used to simulate T and X-shaped bolaamphiphiles [8,9]. Full implementation details of this technique are given in the original references and so are not presented here; essential simulation parameters, based on those previously used [8,9], are shown in Tables 1 and 2. As already noted, the previous models used did not reproduce phe pentagonal columnar phase. The omission of this phase suggests that subtle adjustments to the model are required to account for this presumably narrow area in phase space. Unfortunately, using a coarse grained model means that small adjustments are not always possible. For example, it is not possible to extend a chain by only a few atoms as each chain must consist of an integer number of beads. Thus if the pentagonal phase exists only for a narrow subset of chain lengths for the real molecule, this detail may be missed by the coarse grained simulation models. Here we adjust the lengths of the aromatic core and one of the terminal hydrophilic chains, as shown in Figure 1e. Similar to our previous studies, we examine a series

Table 1. Simulation parameters

Number of molecules	5000
Density	3.0
Timestep	0.02
Noise amplitude	3.67
Simulation length (per state point)	2500000 steps
Connectivity spring constant [8]	4.0
Angle spring constant (beads 1-2-3) [8]	4.0
Angle spring constant (beads 2-3-4) [8]	12.0
Angle spring constant (beads 3-4-5) [8]	4.0

Table 2. DPD repulsion parameters [8]

$a_{\alpha\beta}$	C	O	A
C	15	15	40
O	15	5	40
A	40	40	20

of models for different length aliphatic chains. For each model, the system is examined over a range of temperatures, cooling from an isotropic liquid.

Results

We investigated five models, varying the lateral chain length (N_c) from one to five beads. For the longer chain lengths ($N_c = 4$ and 5), lamellar phases were observed. These are similar to those in the previous studies [8] and so shall not be discussed here; we shall concentrate only on the shorter chain lengths for which columnar phases are observed. We show snapshots of the first ordered phase observed on cooling from the isotropic liquid for each model in Figure 3. It is clear that for the shortest chain ($N_c = 1$, Fig. 3a), the columnar phase has a square cross section, as observed for the shortest chains in our previous study of T-shaped bolaamphiphiles [8]. As before, the walls of the columns are formed by the central aromatic cores, the vertices by the polar regions and the interior of the columns by the lateral chains. Note also, that as for real [6] and model [8] T-shaped bolaamphiphiles, the walls tend to be two cores thick, in comparison to the single thickness walls observed for X-shaped bolaamphiphiles. For the square columnar phase, there is a single type of vertex. This is formed by four walls converging at the vertex, such that the angle between the walls is 90°. For a longer chain bolaamphiphile ($N_c = 3$, Fig. 3b), the volume required by the chain is much larger, whilst the length of the core, and hence the length of the walls, is unchanged. This columnar phase is hexagonal, again similar to that seen in previous studies [8]. As we expect for a hexagonal lattice, the vertices of this columnar phase are of a single type, each formed by three walls converging at 120°. In contrast to previous simulations, a different columnar phase is observed for the intermediate chain length ($N_c = 2$, Fig. 3c). In this columnar phase, we observe a unit cell which is significantly larger than that for the square and hexagonal columnar phases, which possesses two types of vertex. For one type, four walls converge at the vertex; in the other, three walls converge. This is therefore a possible candidate for the pentagonal columnar phase [5] (see Fig. 2c). Of course, regular pentagons cannot tile space in two dimensions and, therefore, the pentagonal columnar phase cannot have a regular pentagonal cross section. Therefore, the pentagons must deform in some way to accommodate the structure if a columnar phase is to be observed. This can be achieved in two ways; either the angles of the pentagon must deform or the lengths of the sides must deform (or both). The latter should be restrained, given that the length of the walls between the vertices is defined by the dimensions of the molecular core. Indeed, we find that the distribution of molecular lengths in the simulations (i.e., the length of the vector joining O1 and O5), is unimodal, suggesting a uniformity amongst the molecules. Moreover, the distribution is peaked at the same value for the models with different lateral chain lengths,

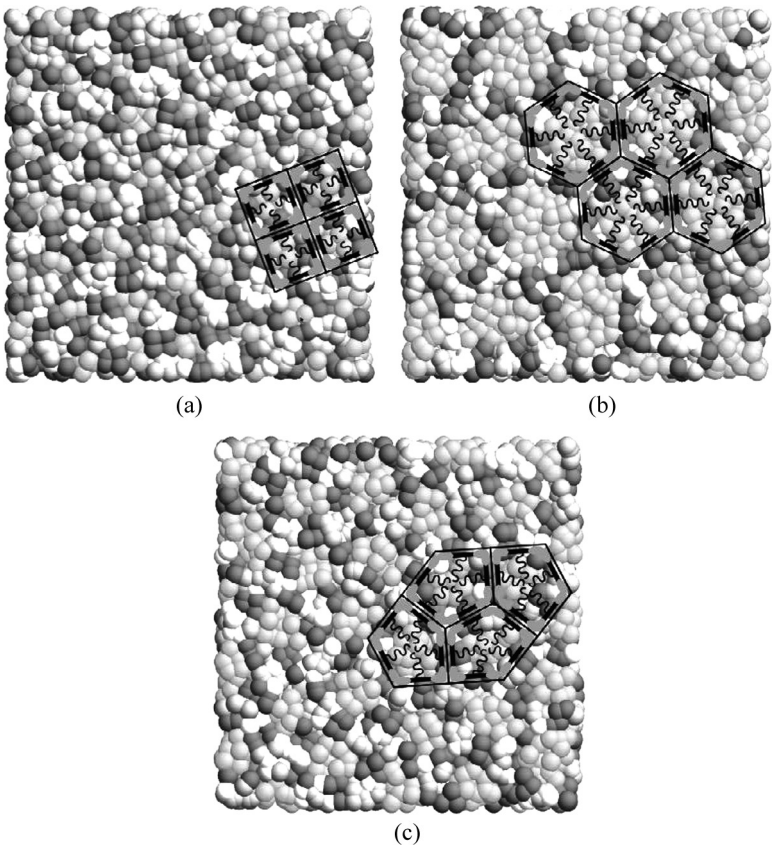

Figure 3. Snapshots of the ordered phases from the simulations of (a) the square ($N_c = 1$), (b) hexagonal ($N_c = 3$), and (c) pentagonal ($N_c = 2$) columnar phases. The beads are coloured as in Fig. 1e. Note that, to construct these snapshots, we have surrounded the original simulation box by its periodic images and rotated it so that the view is down the column axis. The box dimensions shown are the same as in the original simulations. This means that the boundaries do not necessarily match in the snapshots, but the size of the system gives an indication of total number of molecules simulated. The snapshots were taken from simulations at the following scaled temperatures [8]: (a) 0.4, (b) 0.8, and (c) 0.4.

indicating that the straight sections of the perimeters of the different columnar phases are equal. This is in agreement with experimental data. Thus it seems likely that the angles should deform to fit the irregular pentagonal tiling pattern in this columnar phase.

To test this idea, we have determined the angles formed by the walls at the vertices directly from the simulations. To do so, we define an angular distribution function, $f(\theta)$, as follows. We cut the simulation box into a number of slabs, with a normal vector parallel to the column axis (as defined by the algorithm of Ref. [8]). Within each slab, the positions of the terminal polar groups (O1 and O5) were projected onto the perpendicular plane. A clustering algorithm was then employed to merge nearby hydrophilic groups in this plane. This allows us to determine the average location of the terminal groups that form a single vertex,

and hence the location of the vertex itself. Once we have determined the location of all the vertices, the calculation of the vertex angles is straightforward. For each vertex in turn, we identify the subset of all neighbouring vertices within a distance of 1.2 L, where L is the average molecular length. For each unique pair of vertices in this subset, we calculate the angle formed at the original vertex and store this in a histogram. This is then averaged over all vertices, slabs and stored configurations from the simulation (typically 100 configurations, at 1000 step intervals). The angular function, $f(\theta)$, is shown for the square columnar phase in Figure 4a. We observe two peaks, one at 90° and the other at 180°, with an intensity ratio of 2:1. The locations and intensities of the peaks are easily understood since, around any vertex in a square lattice we expect four other vertices. There are four unique pairs for which the angle is 90° and two unique pairs at 180°. A similar analysis for the hexagonal columnar phase (Fig. 4b) reveals a single peak at 120°, as we expect. The situation is more complicated for pentagonal tiling. To determine the theoretical values for the angles for irregular pentagonal tiling, we make the assumption that the walls meeting at the 4-fold vertices form angles of 90°. With this assumption, the angles at the 3-fold vertices should be equal to 114.3° and 131.4°. The intensity ratios of the four expected peaks are 2 (90°): 2 (114.3°): 1 (131.4°): 1 (180°). The predicted locations and intensities of the peaks in $f(\theta)$ appear to give a reasonable fit to the data obtained for the simulations with $N_c = 2$ (Fig. 4c). Thus

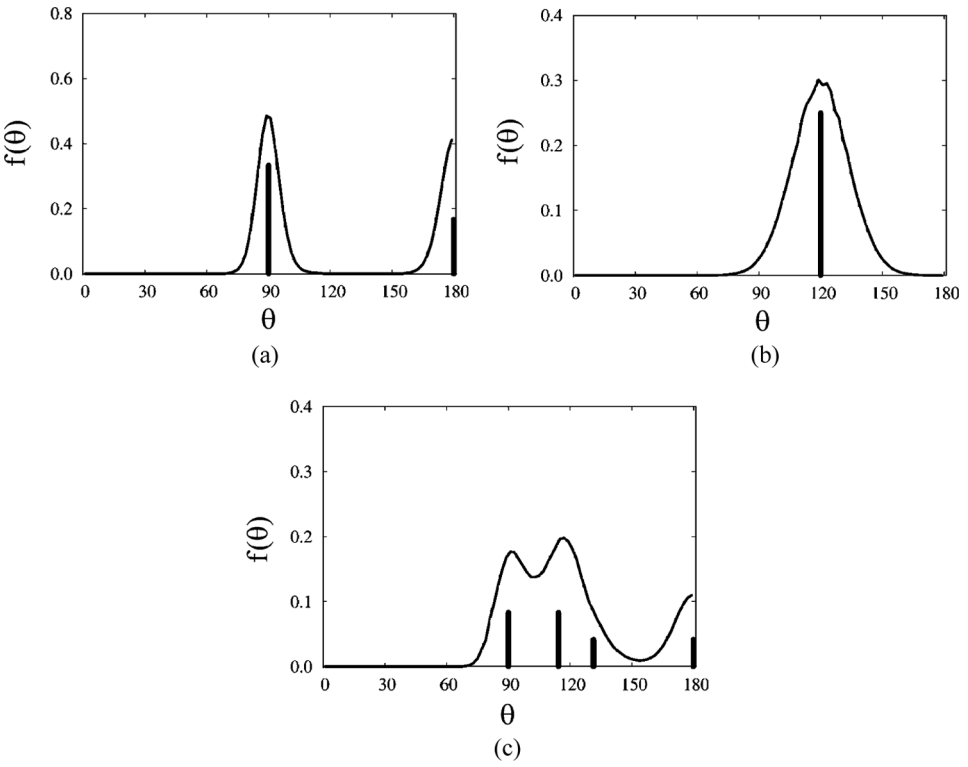

Figure 4. The distribution function, $f(\theta)$, of the angles formed at the vertices for (a) the square ($N_c = 1$), (b) hexagonal ($N_c = 3$), and (c) pentagonal ($N_c = 2$) columnar phases. The vertical bars show the expected locations and intensities of the peaks for ideal lattices.

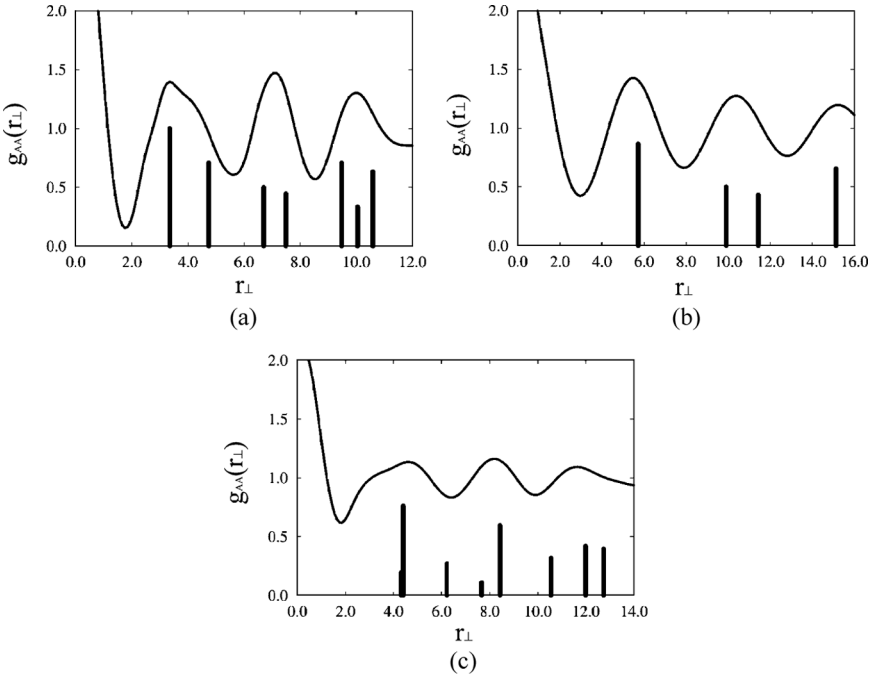

Figure 5. The in-plane distribution function, $g_{AA}(r_\perp)$, for the ends of the lateral aliphatic chains for the (a) the square ($N_c = 1$), (b) hexagonal ($N_c = 3$), and (c) pentagonal ($N_c = 2$) columnar phases. The vertical bars show the expected locations and intensities of the peaks for ideal lattices.

this phase is characterised as a pentagonal columnar phase. This characterisation can be complemented by other in-plane distribution functions, as used to examine the columnar phase structures in other bolaamphiphile simulations [8,9]. For example, we show the in-plane distribution function, $g_{AA}(r_\perp)$, for the distance between the ends of the lateral chains [9] for the three columnar phases in Figure 5, along with the expected peak locations and intensities. We again observe a good agreement between the predicted and simulation values for each columnar phase, confirming their characterisation.

The pentagonal columnar phase also presents another interesting question, relating to the hydrophilic groups. In our model, we have used different length hydrophilic groups at each end. We may, therefore, wonder if there is any preferential segregation of these between the two different types of vertices in the pentagonal phase. However, this is not found to be the case; both types of terminal groups (O1 + O2 and O5) are equally likely to be found at both the 3-fold and the 4-fold vertices.

Conclusions

We have used dissipative particle dynamics with a simple soft potential model to represent T-shaped bolaamphiphiles. The simulations reveal, on increasing the lateral chain length, a square, irregular pentagon and hexagonal columnar phase, with lamellar phases for longer chain lengths. Whilst square and hexagonal columnar phases have been observed in simulations of bolaamphiphiles, pentagonal columns

have not been observed until now. Here we observe irregular pentagonal columns that tile to fill space. If we take cross sections through the pentagonal columnar phase, we observe that two types of vertex are found, as opposed to one for both the square and hexagonal columnar phases. The distribution of angles observed at the vertices is relatively wide but appear to be in reasonable agreement with the model for the pentagonal columnar phase in which the different sections of the perimeter walls are of equal length. The frustration of tiling two dimensional space with regular pentagons is released by both the formation of these two different types of vertices and by the deviation of the internal angles of the pentagons from their ideal value of 108°.

References

[1] Tschierske, C. (2007). *Chem. Soc. Rev.*, *36*, 1930.
[2] Chen, B., Baumeister, U., Pelzl, G., Das, M. K., Zeng, X., Ungar, G., & Tschierske, C. (2005). *J. Am. Chem. Soc.*, *127*, 16578.
[3] Cheng, X. H., Prehm, M., Das, M. K., Kain, J., Baumeister, U., Diele, S., Leine, D., Blume, A., & Tschierske, C. (2003). *J. Am. Chem. Soc.*, *125*, 10977.
[4] Liu, F., Chen, B., Glettner, B., Prehm, M., Das, M. K., Baumeister, U., Zeng, X., Ungar, G., & Tschierske, C. (2008). *J. Am. Chem. Soc.*, *130*, 9666.
[5] Chen, B., Zeng, X., Baumeister, U., Ungar, G., & Tschierske, C. (2005). *Science*, *307*, 96.
[6] Kieffer, R., Prehm, M., Glettner, B., Pelz, K., Baumeister, U., Liu, F., Zeng, X., Ungar, G., & Tschierske, C. (2008). *Chem. Comm.*, 3861.
[7] Crane, A. J., Martinez-Veracoechea, F. J., Escobedo, F. A., & Muller, E. A. (2008). *Soft Matter*, *4*, 1820.
[8] Bates, M. A.. & Walker, M. (2009). *Soft Matter*, *5*, 346.
[9] Bates, M. A., & Walker, M. (2009). *Phys. Chem. Chem. Phys.*, *11*, 1893.
[10] Glettner, B., Liu, F., Zeng, X., Prehm, M., Baumeister, U., Walker, M., Bates, M. A., Boesecke, P., Ungar, G., & Tschierske, C. (2008). *Angew. Chem. Int. Ed.*, *47*, 9063.
[11] Groot, R. D., & Warren, P. B. (1997). *J. Chem. Phys.*, *107*, 4423.
[12] Groot, R. D., & Madden, T. J. (1998). *J. Chem. Phys.*, *108*, 8713.