Electronic supplementary information (ESI) to accompany

Molecular Dynamics Simulation of the Mesophase Behaviour of a Model Bolaamphiphilic Liquid Crystal with a Lateral Flexible Chain

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S1 (movie; see file S1.mov) Flipping Mechanism

A system of $N_{\mathrm{flx}}=2$ (c.f. figure 5(a)) is observed in equilibrium at $T^*=0.47$ (close to the solid-LC transition). In the movie three molecules are highlighted. The blue molecule vibrates locally in the columnar structure. The green molecule vibrates locally in the columnar structure, before flipping to a new locally vibrating position. The red molecule is vibrating outside of the columnar structure. The movements of these three molecules are described qualitatively in the text of the main paper. Figure 7 gives a graphical description of these three cases.

S2 (movie; see file S2.mov) Self-assembly by quenching

A disordered fluid of $N_{\mathrm{flx}}=5$ is quenched from an isotropic state to $T^*=0.73$. The system self-assembles into a columnar hexagonal phase, similar to the one shown in Figure 5(d). Three views of the same process are given; in the left the whole system, in the center the system with the flexible side chains removed for clarity; at the right the system seen from the side. The run is typical of the ones reported in this work. A plot of the evolution of the planar order parameter S_2 is also included.

S3 Simulation details

S3.1 Generic information

Simulations were performed in continuum space via Molecular Dynamics in the NVT, NσT, NPT and NVE ensembles using the simulation suite DL_POLY[i]. Integration was carried out using the leap frog algorithm. Temperature control was achieved by means of the Nosé-Hoover thermostat[ii] while pressure was controlled with the barostat of Melchionna *et al.*[iii]

S3.2 Initial Setup

Initial simulations, performed in both the NVT and NPT ensembles, were started from random high T* configurations and then quenched to a target T*, over typical runs of 10^6 – 10^7 integration steps, that depended upon the size of the lateral chain. An integration step size of $\Delta t^{*}= \delta t[\varepsilon/(m\sigma^2)]^{1/2}=0.012$ was used for all simulations. Simulations generally involved a number of molecules, N, in the range 400-700, although in some cases larger system sizes were run (up to four times). No solvent was present in the system, that is, only pure fluids were considered. Experimental results are sometimes interpreted in terms of the volume fraction occupied by the fluid molecules, and these were broadly used as a guide to deciding the initial system volumes for the NVT simulations. For soft matter, volume fraction is an ill-defined property, as the volume of a molecule can only be approximated. For this work, a coarse approach of assuming the rigid rod unit to have spherocylinder geometry and assuming each lateral bead as a separate sphere, gave a basic approximation of the molecular volume, V_{mol}, in terms of σ as

$$V_{mol} = V_{rig} + V_{flx} = \left[5\times\frac{\pi\sigma^2}{4}\times 0.7\sigma + \frac{\pi\sigma^3}{6}\right] + \left[\frac{\pi\sigma^3}{6}\times N_{flx}\right] \qquad \textbf{S3.1}$$

where V_{rig} and V_{flx} are the approximated volumes of the rigid and flexible model components respectively. The preliminary NVT simulations were carried out at a simulation cell volume, V, such that the volume fraction, η, defined by

$$\eta = \frac{N_{mol}V_{mol}}{V} \qquad \textbf{S3.2}$$

was 0.4, using the volume approximation above. Experimentally this volume fraction corresponds to a dense fluid phase. The NPT simulations were fixed at pressures that approximately kept this value of η for the temperatures studied. In order to facilitate pressure isotropy in the NPT simulations, the algorithm was slightly modified in these runs to allow independent changes of the simulation box size in each direction whilst keeping 90° angles between the boxes edges.

It is expected that these fluids, as is common in liquid crystals and polymers, have extremely low vapour pressures. Thus all studies were centred at the high end of the packing fraction, typical of the dense liquid state. For the same reasons, the isothermal compressibility was expected to be high, so the pressure was not expected to have a major impact on the actual phases observed.

S3.3 Phase diagram simulation runs

Following the determination of structured phases through the preliminary simulations, the global phase diagram of the coarse-grained model liquid crystal system was probed by performing a series of simulations on systems of different lateral chain length for a range of temperatures in the NσT ensemble. Use of this ensemble allowed a flexible simulation box without edge angle restraint and was appropriate for the crystalline phases.[iv] By using a higher barostat parameter the elongation of the simulation cell was minimised when simulating the liquid phase. For each lateral chain length system, a representative ensemble of N molecules, similar to that used in the initial simulations runs, were slowly cooled in temperature increments of $\Delta T^*=0.03$, to a temperature of $T^*=0.16$, in typical simulation run times of $t^*=5000$. The systems were then reheated to well into their isotropic phase, in temperature increments of $\Delta T^*=0.03$. Each of these simulations was run for a total time of $t^*=7500$, and configuration data were sampled at time intervals of $t^*=62$. This data was used to calculate order parameters, defined in the following section. The final configuration of each fixed temperature NσT ensemble simulations, were used as input configuration of NVE simulations used to calculate mobility coefficients, that are defined in the following section. Each of the NVE simulations, were equilibrated for a time of $t^*=250$, before collecting bead configuration data, at time intervals of $t^*=25$, for a further time of $t^*=10000$. As with the preliminary simulation runs, a time step of $\Delta t^*=0.012$ was used in both the NVE and NσT ensemble simulations. For the NσT simulations a value of $P^*=0.78$ was used. In all cases, energy, density, and temperature fluctuations and averages were closely monitored to ensure equilibrium was attained.

S4 Lateral Chain End-to-End distance

To study the influence of the mesophase structure on the lateral flexible chain structure the distribution of end-to-end distance of the flexible chains was investigated as a function of temperature. The end-to-end distance of a single molecule is calculated through the expression

$$r^{j}_{ee} = \left| \mathbf{r}^{j,6+1} - \mathbf{r}^{j,6+N_{flx}} \right| \qquad \textbf{(S4.1)}$$

where $\mathbf{r}^{j,6+1}$ and $\mathbf{r}^{j,6+Nflx}$, are respectively the vector positions of the first and last flexible bead of molecule j. Figure S4.1 shows the distributions found for the $N_{flx}=5$ system at temperatures of T*=0.13, T*=0.57 and T*=1.00, which correspond to crystalline, liquid crystalline and isotropic phases of the system. At T*=0.13, in the crystalline phase, there are four resolved peaks in the distribution. These relatively sharp peaks suggest the lateral flexible chains reside in only a small number of distinct low energy conformations, mostly bent upon themselves as coils. Figure S4.2 shows two snapshots of typical lateral chain configurations. On increasing the temperature further to T*=0.57 three distinct peaks remain, but these are now less resolved. This is likely due to greater movement of the beads with respect to the molecular centre of mass and possible adoption of distinct conformations by the lateral chains. Finally at T*=1.00, in the isotropic phase, there is now a single dominant peak.

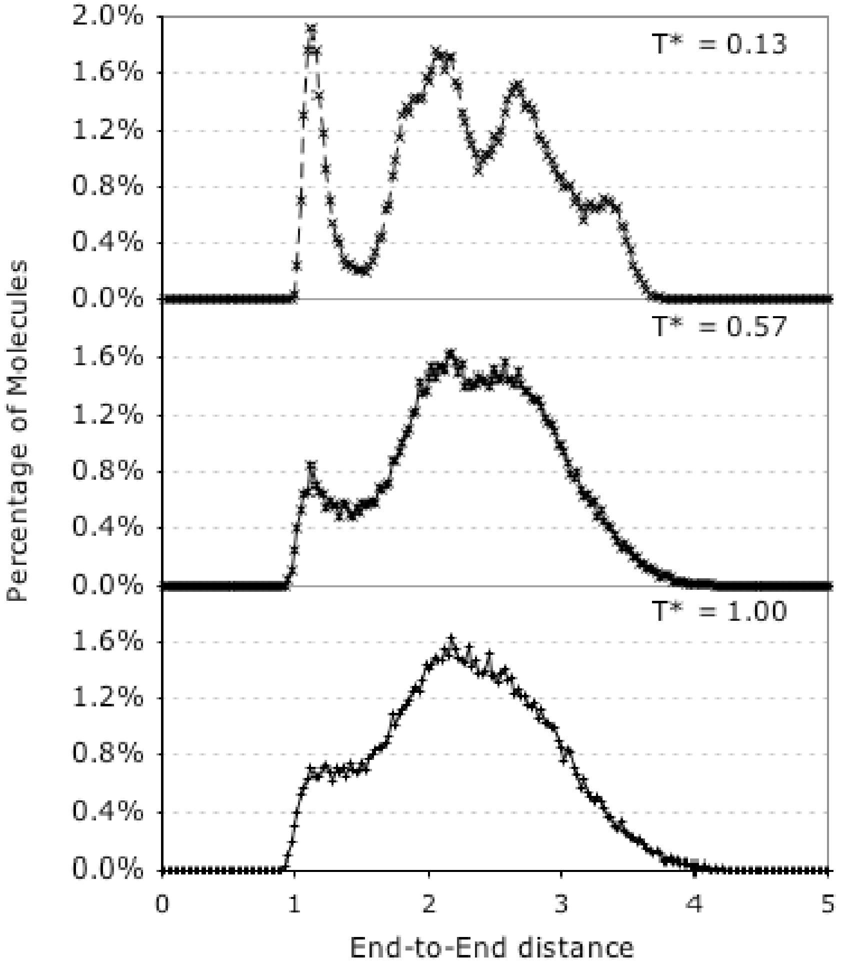

Figure S4.1 End to end distance, r_{ee}, of the flexible side chains for N_{flx}=5 at three distinct temperatures corresponding to the crystalline state (T*=0.13), the LC region (T*=0.57) and the isotropic liquid (T*=1.00)

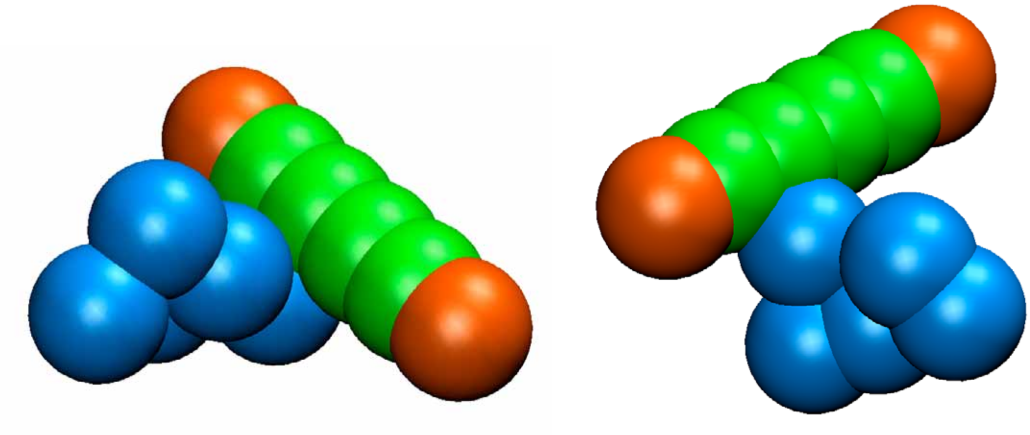

Figure S4.2 Snapshots of equilibrium configurations of two typical molecules of N_{flx}=5 at T*=0.13, corresponding to a solid state. Molecules are depicted removed from their environment to highlight the lateral chain structure.

References

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[i] www.ccp5.ac.uk/DL_POLY/. For a recent review see W. Smith, *Molecular Simulation*, 2006, **32**, 933-1121.

[ii] W.G. Hoover, *Phys. Rev. A*, 1985, **31**, 1695–1697.

[iii] S. Melchionna, G. Ciccotti, and B. L. Holian, *Mol. Phys.*, 1993, **78**, 533–544.

[iv] M. Parrinello and A. Rahman, *Phys. Rev. Lett.*, 1980, **45**, 1196–1199.