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Columnar Phases in Liquid Crystal Dendrimers: Variable Pressure X-Ray Diffraction

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The structures of the third and fifth generation of a liquid crystal dendrimer have been studied as a function of temperature and pressure using X-ray diffraction. The third generation LC dendrimer showed a crystal to smectic transition and increasing pressure simply increased the transition temperature. The fifth generation showed two different rectangular columnar phases and one hexagonal columnar phase. The application of pressure did not induce either of the rectangular phases to transform to a simple smectic phase, suggesting that they are slightly modified smectic phases. The hexagonal phase was more easily suppressed by the application of pressure, suggesting that the molecules are splayed into a disc-like conformation and become more cylinder-like under pressure.

Keywords Columnar phase; liquid crystal dendrimer; non-ambient pressure; X-ray diffraction

1. Introduction

Liquid crystal dendrimers are formed by attaching mesogenic units to a dendritic core via flexible spacer units. They provide an interesting example of the nanoscale structures formed by two antagonistic influences. The long axes of the mesogenic units tend to be parallel but the dendritic cores tend to make the units splay radially. The dendritic cores are made from chains with a bifunctional group at one end so the core size may be increased by adding another "layer" of chains. Each additional generation of chains doubles the number of functional groups at the periphery of the core with the first generation having eight and rising to 128 for the fifth generation. X-ray diffraction studies [1,2] have shown that if the dendritic core is small (i.e., first to third generation) the parallel tendency dominates so the each molecule forms a cylindrical shape and they merge into layers to form smectic phases. The flexible link between mesogenic unit and dendritic core is crucial in accommodating the two

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opposing tendencies. However, for larger generation numbers (e.g., fifth generation) the molecules cannot form cylindrical shapes because the flexible links are not long enough to reach the extremal mesogenic units. In this case, the shape of the molecule is believed to be more disc-like and columnar phases are formed.

This behaviour has been rationalized by a theory [3] built of micro-segregation of the dissimilar units (core and mesogenic unit). One possibility that emerged from the theory was a pressure induced transition from disc-shaped molecules, forming columnar phases, to cylindrically shaped molecules, forming smectic phases. This might be expected if there were differences in free volume and was a further motivation for the exploration of the pressure dependent structural study reported in this paper.

2. Experimental Methods

X-ray diffraction has been done at elevated pressure on the third and fifth generation of a series of liquid crystal dendrimers that have already been extensively studied at ambient pressure [2]. Figure 1 shows the structure of the third generation core and one mesogenic unit plus spacer. Some of the hydrogen sites in the phenyl rings were deuterated because the materials were originally made for a neutron scattering study but this does not influence the phase behaviour or transition temperatures. The third generation dendrimer was a 50:50 mixture of normal hydrogenous molecules and one with the inner phenyl ring deuterated and will be designated G3HD. Its transition temperatures and phase structure from X-ray diffraction were reported previously to be:

Cr 20°C C Sm A 108°C I

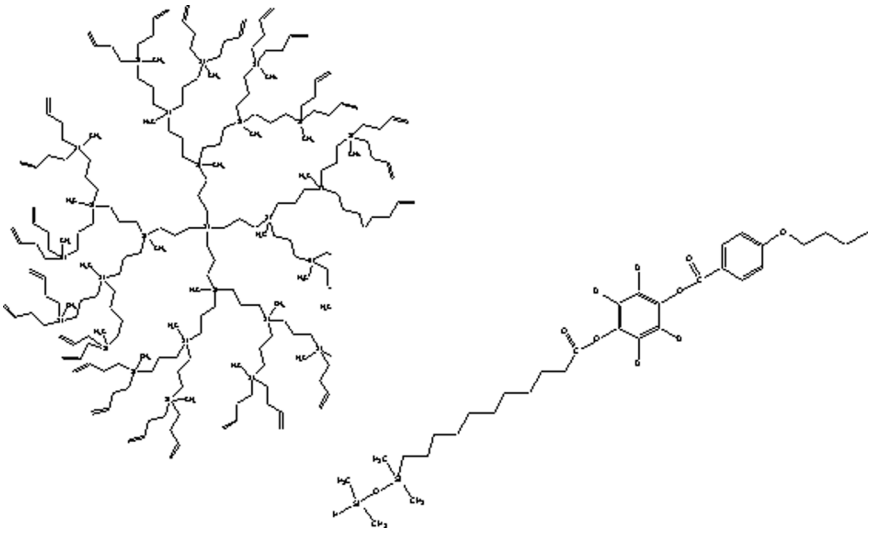

Figure 1. Showing 3rd generation dendritic core and one of 32 mesogenic units with a flexible spacer. In the liquid crystal dendrimer, the terminal Si atom of a mesogenic unit is joined to every extremal double bonded C atom on the core.

In the previous work, the fifth generation LC dendrimer was also studied as a 50:50 mixture of normal hydrogenous molecules and phenyl ring deuterated ones, designated G5HD. Two columnar phases were observed in this material:

$$\text{Cr } 23^{\circ}\text{C } D_{rect} 90^{\circ}\text{C } D_{hex} 140^{\circ}\text{C I}$$

However, in this study a statistical co dendrimer has been used. Each dendritic core has on average 50% of normal hydrogenous mesogenic units and 50% with the inner phenyl ring deuterated and will be designated G5CO. The previous work [2] also revealed strong evidence for a significant heterogeneity between the molecules with a substantial fraction of the cores having less than the maximum number of mesogenic units attached. This is analogous to polydispersity in linear polymers and may account for the gradual nature of the transitions between mesophases. It is also a possible cause of variation in transition temperatures and phase structure between samples prepared under different conditions.

The elevated pressure X-ray diffraction experiments were done at the I22 instrument [5] for small angle scattering at the Diamond Light Source. The pressure and temperature were applied to the sample using apparatus constructed at Imperial College [4]. The cell windows were made of diamond and pressure up to 4 kb could be applied hydraulically. An incident wavelength of 0.73 Å (energy = 17 keV) was used to maximise transmission through the sample cell windows and a sample to detector distance of 1.2 m was used to achieve a scattering vector range covering the important Bragg peaks. The samples were not aligned so the diffraction appeared as Debye Scherrer rings on the area detector.

The sample to detector distance was determined using a silver behenate standard so that the scattering vector, Q, could be determined for each pixel. The data was then processed into one dimensional intensity vs. scattering vector, Q as follows.

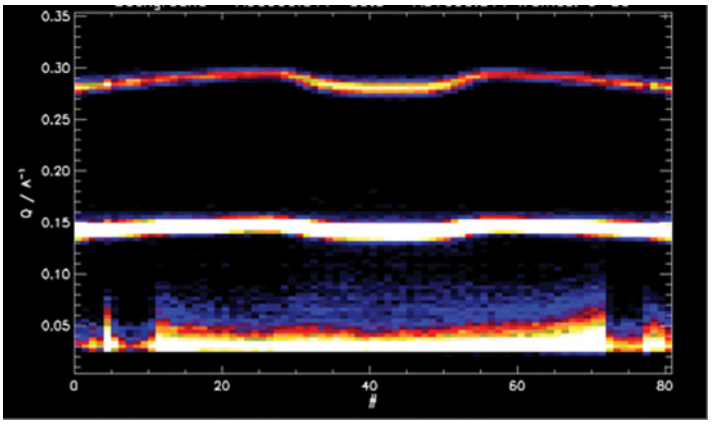

Figure 2. Showing the intensity vs run number, #, and scattering vector, Q, for the G3HD liquid crystal dendrimer at 60°C. The applied pressure has been raised in 40 steps from zero to 4.0 kb and then reduced to zero in the same steps. The transition from smectic to crystal phase takes place between 2.9 and 3.4b with increasing pressure and 3.1 and 2.6 kb during pressure reduction. The colours represent the scattered intensity with black being the lowest then blue, red and yellow with white being the highest. (Figure appears in color online.)

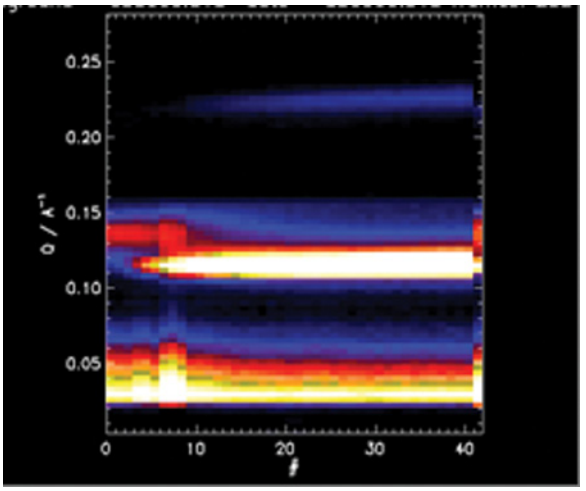

Figure 3. Showing the intensity vs run number, #, and scattering vector, Q, for the G5CO liquid crystal dendrimer at 105°C. The applied pressure has been raised in 40 steps from zero to 4.0 kb and then reduced to zero in a single step. The transition from hexagonal to rectangular columnar phase takes place between 0.2 and 0.9 kb. (Figure appears in color online.)

The background from the empty cell at ambient pressure was subtracted from each data set and then the two dimensional data were regrouped to intensity vs Q by taking an azimuthal average using procedures written for IDL [6].

The experimental measurements were performed by stepping the pressure in 100b increments at a fixed temperature. For each temperature, the data were presented as a two dimensional plot of intensity vs. Q and pressure number

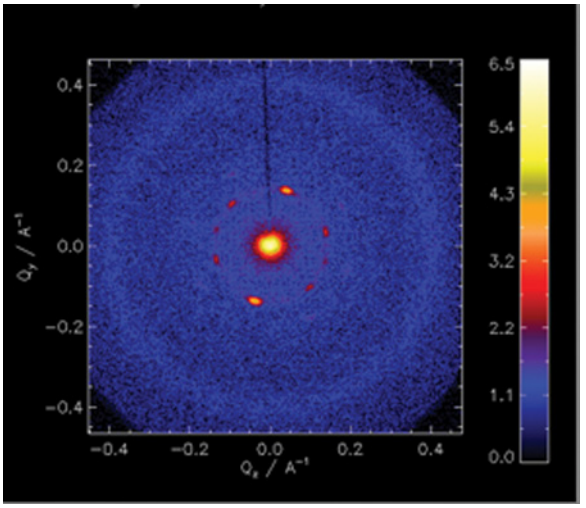

Figure 4. Showing the diffraction pattern from a magnetically aligned sample of the G5CO liquid crystal dendrimer heated to 130°C. It has been interpreted as a hexagonal phase with $c = \sqrt{3}a = 86$A. (Figure appears in color online.)

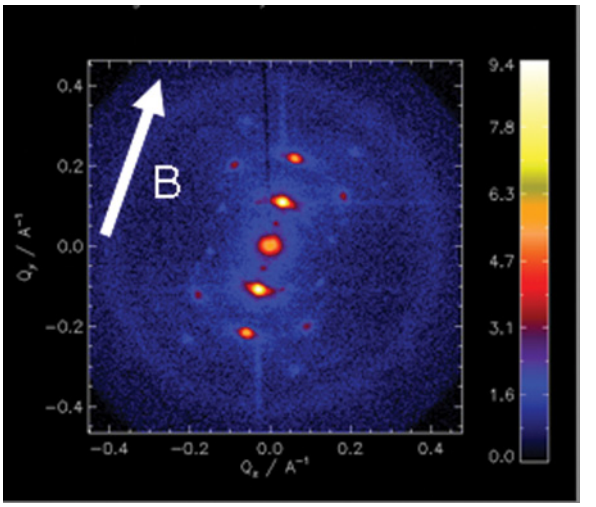

Figure 5. Showing the diffraction pattern from a magnetically aligned sample of the G5CO liquid crystal dendrimer heated to 90°C. The weak peaks at 001 are probably from half-wavelength contamination in the incident X-ray beam. Only the $l = 1$ and 3 (odd) rows show peaks at $h \neq 0$. (Figure appears in color online.)

(see Figs. 2, 3, 7 and 10). Some diffraction patterns of the fifth generation LC dendrimer were also measured using small angle scattering apparatus at Bristol. For these, the sample was cooled from the isotropic phase in a 9.4 T magnetic field. Calculation of the components of **Q** parallel and perpendicular to the alignment direction was done using procedures written for IDL.

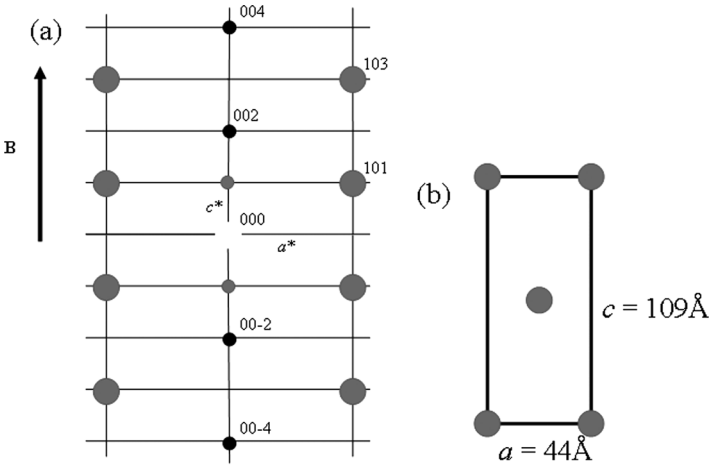

Figure 6. (a) The 2D reciprocal lattice deduced from the aligned sample of G5CO in the high temperature rectangular columnar phase, D_{rect}, and (b) is the corresponding centred cell. The axis of a disordered column would be placed on each lattice point in the mesophase structure.

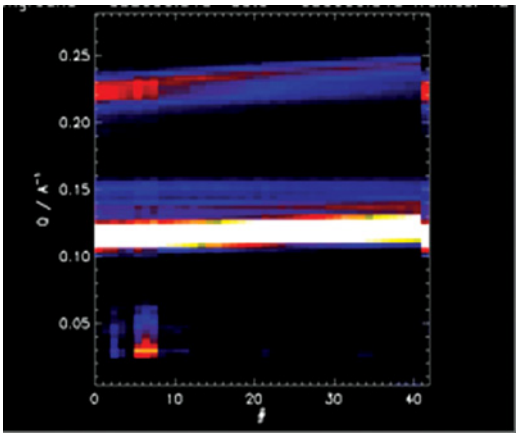

Figure 7. Showing the intensity vs run number, #, and scattering vector, Q, for the G5CO liquid crystal dendrimer at 60°C. The applied pressure has been raised in 40 steps from zero to 4.0 kb and then reduced to zero in a single step. The transition from a rectangular columnar phase with disordered to ordered columns takes place around 1.5 kb and can be seen as a growth in the peak at $Q = 0.135\,\text{Å}^{-1}$ and a weakening of a peak at $Q \sim 0.22\,\text{Å}^{-1}$. (Figure appears in color online.)

3. Results and Discussion

3.1. *Pressure Variation on G3HD*

Pressure scans were taken on G3HD at temperatures of 18, 40 and 60°C. Figure 2 shows the intensity as a function of Q and run number at 60°C. The applied pressure

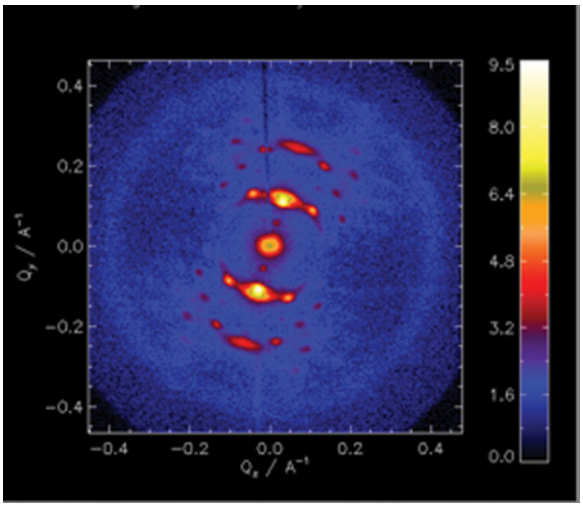

Figure 8. Showing the diffraction pattern from a magnetically aligned sample of the G5CO liquid crystal dendrimer heated to 30°C. The weak peaks at 001 are probably from half-wavelength contamination in the incident X-ray beam. Peaks with $k \neq 0$ can be seen on the $l = 2$, 3, 4 rows. (Figure appears in color online.)

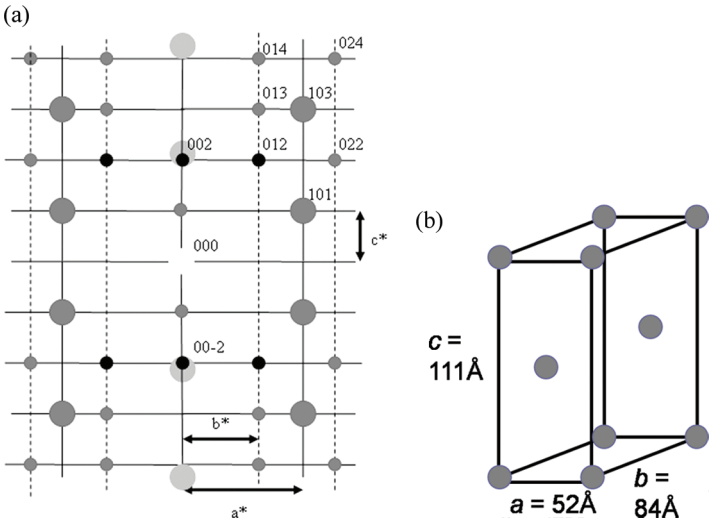

Figure 9. (a) The fibre pattern for the 3D reciprocal lattice deduced from the aligned sample of G5CO in the low temperature rectangular columnar phase, D_{rect2}, and (b) is the corresponding 3D cell. The axis of a column would be placed parallel to *b* on each lattice point and there is a periodicity of 84 Å within the columns. However, in the mesophase structure, the columns are not necessarily correlated in the *b* direction.

has been scanned in steps of 100b from 0b to 4 kb and back to 0b. It can be seen that the scattering vs. *Q* consists of two peaks which are the first and second order layer reflections from a lamellar structure. These have miller indices 001 and 002. At low pressure, the peak positions increase with pressure indicating a decrease in the layer

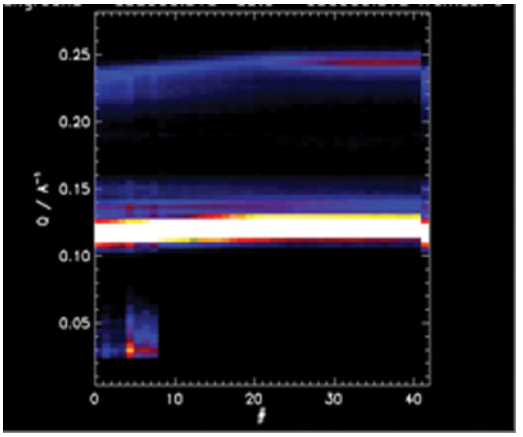

Figure 10. Showing the intensity vs run number, #, and scattering vector, *Q*, for the G5CO liquid crystal dendrimer at 40°C. The applied pressure has been raised in 40 steps from zero to 4.0 kb and then reduced to zero in a single step. The transition from a rectangular columnar phase with ordered columns to crystal takes place around 2.3 kb and can be seen as a loss of the peak at $Q = 0.135\,\text{Å}^{-1}$ and the layer spacing becomes pressure independent. (Figure appears in color online.)

spacing (since $d = 2\pi/Q_{001} = 4\pi/Q_{002}$). For zero applied pressure the corresponding layer spacing is 44 Å, in agreement with the previous measurements at ambient pressure. Around run number 32 (3.2 kb) there is a rapid decrease in the Q values followed by a constant Q value until run number 40 (4.0 kb). This corresponds to a transition to a phase with slightly thicker but non-compressible layers. On reducing the pressure to zero in 100b steps, the transition took place at a slightly lower pressure (2.8 kb). This is identified as a smectic to crystal transition and on Figure 11 the transition pressures have been plotted against temperature. Keeping in mind the hysteresis, the extrapolation to zero applied pressure gives a transition temperature of approximately 20°C in agreement with the value previously determined by microscopy and calorimetry.

3.2. *Pressure Variation on G5CO*

Pressure scans were taken on G5CO at temperatures of 15, 20, 25, 30, 34, 40, 60, 80, 90, 95, 100, 105, 113 and 124°C. Four different X-ray patterns were observed from the G5CO LC dendrimer and the transitions between them may be seen in the Q-pressure diagrams. Figure 3 shows the intensity as a function of Q and run number at 105°C. At $p < 0.5$ kb, there is a single peak at $Q = 0.135\,\text{Å}^{-1}$ but at higher pressure this peak has faded and is replaced by pressure dependent peaks at $Q \sim 0.115\,\text{Å}^{-1}$ and $0.23\,\text{Å}^{-1}$, and a weaker one at $Q = 0.15\,\text{Å}^{-1}$. The pressure of this transition has been plotted against temperature in Figure 11. Figures 4 and 5 show diffraction from an ambient pressure aligned sample at 90°C and at 130°C which should be in each of the two phases of the transition in Figure 3 (i.e., D_{rect} and D_{hex}). The three peaks from the higher pressure phase have been indexed with the help of the diffraction (Fig. 5) from an ambient pressure aligned sample at 90°C as 002, 004 and 101 of a rectangular unit cell whose dimension in the c direction is approximately double the thickness of a smectic layer. Figure 6a shows the reciprocal lattice deduced from the data in Figure 5. The 103 peaks are clearly seen in the aligned sample but are not seen in the unaligned because they have nearly the same Q value as

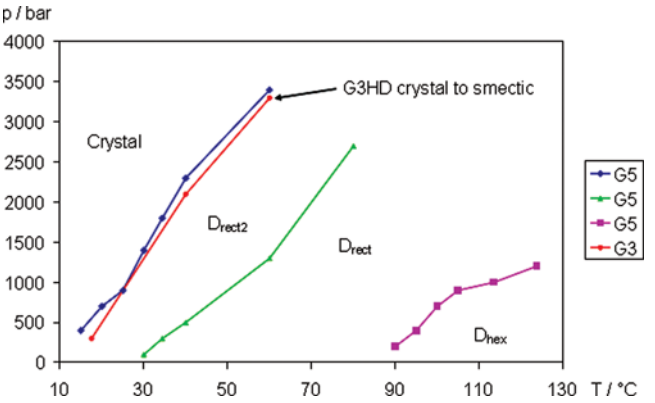

Figure 11. Showing pressure temperature phase diagram for G3HD and G5CO LC dendrimers. The mesophase to mesophase transitions are quite gradual and the points are just an estimate of their position. Typically, there would be a spread of ±300 b. (Figure appears in color online.)

the 004 peaks. Since *hk* are both odd or both even the *b*-face of the cell must be centered. Since only $k = 0$ peaks are observed the structure must be uniform in the *b* direction, i.e., a columnar phase. The unit cell corresponding to this reciprocal lattice is shown in Figure 6b. This is the same structure as previously observed for the G5HD dendrimer in the temperature range 90 to 140°C. The higher temperature phase showed only one strong peak but the aligned sample showed hexagonal symmetry (as in Fig. 4) so it was designated as a hexagonal columnar phase. This phase was also found for the G5HD [2] and labeled D_{rect}.

Figure 7 shows the intensity as a function of Q and run number at 60°C. As the pressure increases the peak at $Q = 0.15\,\text{Å}^{-1}$ fades but is not extinguished but a peak at $Q = 0.135\,\text{Å}^{-1}$ appears. The temperature dependence of this transition has been tracked and plotted in Figure 11. The new peaks at the higher pressure have been indexed with the help of diffraction, shown in Figure 8, from an aligned sample at 30°C as 012 and 022 reflections from a 3D cell. The fibre diffraction pattern is clarified in Figure 9a. The data also shows two diffuse peaks growing near but not at the 002 and 004 positions. These are probably signaling the approach of the transition to the crystal phase (which is seen in Fig. 10) so they have not been considered as part of the major phase at 30°C. The *c* lattice parameter for all peaks on the layer lines is the same as for the rectangular columnar phase observed at 90°C. However two different sets of spots are observed along the $l = 2$, 3 and 4 layer lines, so the presence of a phase with 3D periodicity is strongly suggested. It is probably not a full 3D crystal because no $h \neq 0$ and $k \neq 0$ peaks are seen. It could be a periodicity along the columns that has no correlation between adjacent columns. This phase was not seen in the previously studied G5HD sample [2] and has been labeled D_{rect2}. Figure 10 shows the intensity as a function of Q and run number at 35°C. It shows the transition to an incompressible phase which is probably the crystal phase. This transition has also been plotted on the phase diagram in Figure 11. The zero pressure transition is at about 20°C in agreement with previous observations [2].

4. Conclusions

Figure 11 summarizes the phase diagram for G3HD and G5CO liquid crystal dendrimers as a function of temperature and pressure. It is clear from the results that the application of modest pressure to the rectangular columnar phases of a LC dendrimer does not induce the formation of a smectic phase since the D_{rect} phase transforms to a crystal phase.

The Clausius equation ($dp/dT = \Delta S/\Delta V$) relates the slope of a line on a pressure – temperature phase diagram to the entropy and volume changes of transition, ΔS, and ΔV respectively. The enthalpy of crystallization of the G3 and G5 dendrimers are quite similar ($\sim$8 and $\sim 6\,\text{Jg}^{-1}$) [2] indicating their entropies of crystallization are similar. The similarity of the dp/dT slopes for the crystallization transitions in Figure 11 suggests that the volume changes on crystallization are also similar. This supports the conclusion that the free volume of the smectic phase of G3 is not significantly less than that of the rectangular columnar phase (D_{rect2}) of G5. Thus it may be concluded that the columnar phase is a small modification of the smectic with cylinder-like molecules (as indicated schematically in Fig. 12a) rather than a completely different disk-like conformation as in Figure 12b.

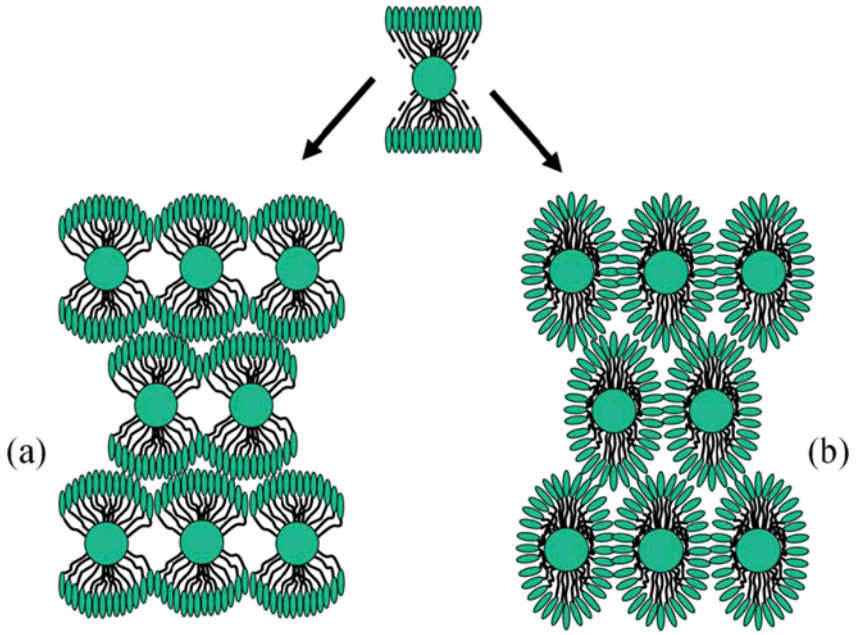

Figure 12. Showing schematically two possible distortions of the cylindrical molecules that occur for high generation numbers. The mesogenic units in (a) are much less splayed than in (b). The pressure dependency of the observed phases suggests that (a) is a more realistic representation of the rectangular columnar phases. (Figure appears in color online.)

The hexagonal phase of G5 does transform into the rectangular columnar phase with the application of modest pressure (and with low dp/dT). Unfortunately the enthalpies of mesophase to mesophase transitions have not been determined accurately for G5 because the transitions are weak and spread over temperature. However, it is reasonable to take the low slope as an indicator of a relatively large volume change (ΔV) of transition. This would suggest that D_{hex} does consist of columns formed from disc-like molecules with splayed mesogenic units and a large free volume in contrast to the rectangular phases. The pressure induced transition from disc-like to cylinder-like liquid crystal dendrimer molecules is qualitatively similar to the prediction of reference 3 (e.g., Fig. 2).

The observation of the 3D phase is surprising in that it was not seen in the previously studied sample of G5HD [2]. It is possible that the codendrimers sample G5CO happened to have a different degree of substitution from the G5HD and this could favour the ordered columns. The long periodicity that develops in the column direction could result from a distortion wave that fills the volume more effectively.

Acknowledgment

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