ESRF	**Experiment title:** Liquid crystalline behaviour of Polyhedral Oligomeric Silsesquioxanes (POSS)	**Experiment number**: SC 2317
Beamline: Bm26b	**Date of experiment**: from: 22/02/08 to: 25/02/07	**Date of report**: 26/02/09
Shifts: 9	**Local contact(s)**: Kristina Kvashnina	*Received at ESRF:*

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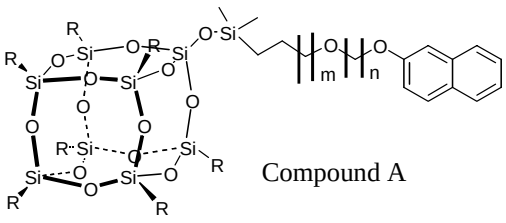
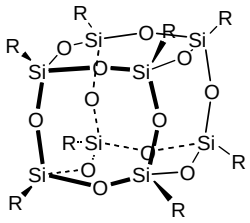
Experimental: Several Polyhedral Oligomeric Silsesquioxanes (POSS) compounds [1-4] were synthesised and the LC behaviour of the mesogens with which were tethered to the POSS T_8 cage (Fig. 1) were investigated during several heat/cool regimes. The heat-cool regimes where performed at a rate of 20 ^{o}C/min and 5 ^{o}C/min.





R =$C_{18}H_{37}$

Compound B

Fig 1. POSS-LC T8 cages with 8 mesogens. Compound A (m = 11, and n =9) and B (R = $C_{18}H_{37}$).

Results: Fig 2, shows individual frames of SAXS data for the heat-cool of the POSS cage compound A. The heat cool regime was -10 ^{o}C to 50 ^{o}C to -10 ^{o}C at a rate of 20 ^{o}C/min. the disorder/melt transition was seen at ~ 44 ^{o}C.

Table 1: Peak positions from beamstop position.

Peak	D /Å
1 (weak)	108
2 (weak)	70
3 (strong)	60
4 (weak)	30

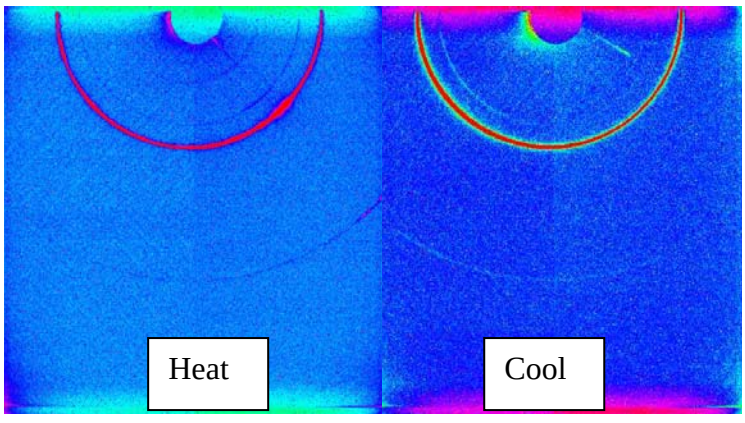


Fig 2. SAXS data for heat-cooling of compound A, POSS-LC T8 cage.

From the SAXS data it can be seen that compound A has several sharp peaks. The distances are given in Table 1. During the heating regimes the peaks start to disappear as the crystalline nature of the material melts. On cooling the peaks reappear, again they are sharp but not all can be observed as the intensity may be very low. However, Fig 3 shows a slow cool for compound A (rate 5 ^{o}C/min). Here, the crystalline reflections do return but are diffuse, compared with the sharp peaks at a high cooling rate.

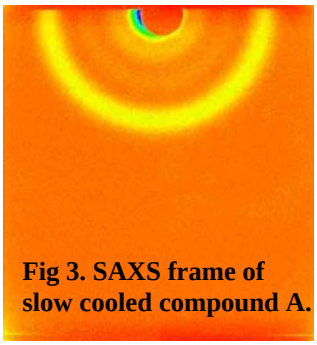


Fig 3. SAXS frame of slow cooled compound A.

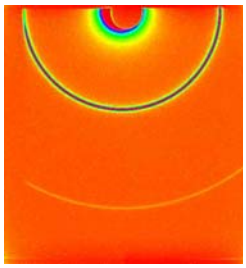


Fig 4. SAXS frame of compound B during heating.

In Fig 4, an individual SAXS data frame for the heat of compound B is shown. Here, again the sharp peaks are seen but the spacing of the peaks differ slightly (Table 2). The spacing of the peaks for both compounds indicated a periodicity is formed. This s linked to the size of the POSS cage and mesogen arms and the way that they pack into layers.

Table 2: Peak positions from beamstop position for compound B.

Peak	D /Å
1 (strong)	50
2 (weak)	26

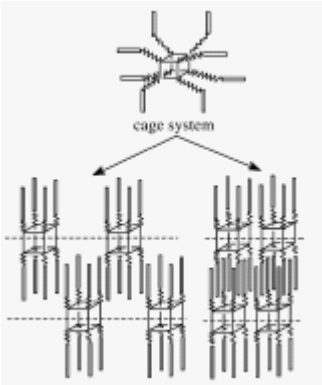


Fig 5. Cage POSS-LC packing models.

This layer formation is indicative of when the mesogens interdigitate with each other. From the SAXS data, the structures formed in compounds A and B have are thought to have the mesogen units forming interdigitated bilayers, while the silyloxane cores have a monolayer arrangement (fig. 5.). However, the phase structure is dependant upon the length and type of mesogen tethered to the cage system and if they are able to interdigitate. The main periodicity for compounds A is 60 Å and for compound B 50 Å. This ties in well with the POSS core being ~ 15 Å in both compounds and the mesogen in A ~45 Å. In Compound B the mesogens are slightly smaller ~ 30 Å. Hence, an interdigitated bilyer is likely to be present in both the compounds. The other peaks that do not appear to be part of the regular repeat peaks, may be due to the presence of a mixture of layers (biphasic). The broadening of the peaks during slow cooling also suggests that the bilayers have a range of repeat distances and are not as ordered compared with the compounds undergoing faster cooling. No orientation in the SAXS data is seen indicating no preferred direction of the bilayers is present in the compounds.

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2. A.R. Bassindale, Z. Liu, D.J. Parker, P.G. Taylor, P.N. Horton, M.B. Hursthouse, M.E. Light, J. Organomet. Chem (2003), 687, 1.
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4. J. Hardy, PhD thesis, OU, 2001.