

### Experimental conditions for X-ray scattering

Powder X-ray investigations were carried out with a Guinier film camera and a Guinier Goniometer (Huber Diffraktionstechnik, Germany). Samples in glass capillaries ( $\varnothing$  1 mm) in a temperature-controlled heating stage, quartz-monochromatized  $\text{CuK}\alpha$  radiation, 30 to 60 min exposure time, calibration with the powder pattern of  $\text{Pb}(\text{NO}_3)_2$ . 2D patterns for aligned samples on a glass plate on a temperature-controlled heating stage (alignment at the sample – glass or at the sample – air interface) were recorded with a 2D detector (HI-STAR, Siemens) using  $\text{CuK}\alpha$  radiation monochromatized by a Ni filter.

**Table S1.** X-ray data from Guinier powder patterns ( $\theta_{\text{obs}}$ : experimental scattering angle;  $d_{\text{obs}}$ : experimental and  $d_{\text{calc}}$ : calculated d spacing;  $hk/n$ : assigned indices for  $\text{Col}_{\text{hex}}$  phases / order of reflection for SmA phases, Parameter used: Lattice parameters or  $d$  values used to calculate  $d_{\text{calc}}$  with an error of the calculated parameters in the order of 0.1 nm)

Compound	$T$ (°C)	Phase	$\theta_{\text{obs}}$ (°)	$d_{\text{obs}}$ (nm)	$hk/n$	$d_{\text{calc}}$ (nm)	$d_{\text{obs}} - d_{\text{calc}}$ (nm)	Parameter used (nm)
<b>5b</b>	120	$\text{Col}_{\text{hex}}$	1.713	2.58	10	2.55	0.03	$a = 2.95$
			3.021	1.46	11	1.47	-0.01	
			3.450	1.28	20	1.28	0.00	
<b>5c</b>	160	$\text{Col}_{\text{hex}}$	1.712	2.58	10	2.59	-0.01	$a = 2.99$
			2.953	1.49	11	1.49	0.00	
			3.400	1.30	20	1.29	0.01	
<b>6b</b>	115	SmA	1.472	3.00	1	3.00	0.00	$d = 3.00$
			2.952	1.50	2	1.50	0.00	
<b>6c</b>	140	SmA	1.450	3.04	10	3.00	0.04	$d = 3.00$
			2.923	1.51	11	1.50	0.01	
			4.507	0.98	20	1.00	-0.02	