

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 (θ_{obs} : experimental scattering angle; d_{obs} : experimental and d_{calc} : calculated d spacing; hk/n : assigned indices for Col_{hex} phases / order of reflection for SmA phases, Parameter used: Lattice parameters or d values used to calculate d_{calc} with an error of the calculated parameters in the order of 0.1 nm)

Compound	T (°C)	Phase	θ_{obs} (°)	d_{obs} (nm)	hk/n	d_{calc} (nm)	$d_{\text{obs}} - d_{\text{calc}}$ (nm)	Parameter used (nm)
9b	170	Col_{hex}	1.816	2.43	10	2.43	0.00	$a = 2.81$
	150		1.831	2.41	10	2.43	-0.02	$a = 2.81$
			3.120	1.41	11	1.40	0.01	
			3.625	1.22	20	1.21	0.01	
	130		1.837	2.40	10	2.42	-0.02	$a = 2.80$
			3.150	1.40	11	1.40	0.00	
			3.625	1.22	20	1.21	0.01	
	110		1.844	2.39	10	2.41	-0.02	$a = 2.78$
			3.162	1.40	11	1.39	0.01	
			3.650	1.21	20	1.20	0.01	
9a	72	?	1.871	2.36				
11a	102	SmA	1.414	3.12	1	3.13	-0.01	$d = 3.13$
			2.813	1.57	2	1.56	0.01	
	92		1.399	3.16	1	3.16	0.00	$d = 3.16$
			2.800	1.58	2	1.58	0.00	
11b	130	SmA	1.374	3.21	1			$d = 3.21$
	120		1.365	3.23	1			$d = 3.23$
	110		1.345	3.28	1			$d = 3.28$

Figure S1. The inner diffuse scattering in the SmA phase of **11b**: **a)** diffuse X-ray scattering scanned along a conical segment ($\Delta\chi = 60^\circ$) of the 2D-pattern about a line perpendicular to the layer normal, **b)** distribution of the intensity integrated over θ from 3.2 to 3.9° ($d \approx 2.50$ nm) showing a fit by two Gaussian functions and the corresponding position of the intensity maxima, **c)** distribution of the intensity for the outer diffuse scattering integrated over θ from 7.5 to 10.5° ($d \approx 0.50$ nm, maxima at about 116 and 298°) for comparison, [**b)** and **c)**: relative intensity calculated by $I_{\text{rel}} = I(120^\circ\text{C}) / I(\text{isotropic liquid})$. The black arrow points to the position of the intensity maximum for the layer reflections.]

