Supporting Information (SI)

All references refer to the bibliography of the main paper.

S1 Textures of pristine SmC shells, directly after production

An interesting experiment starting out from non-equilibrium conditions is to heat shells directly after production. Representative of this experiment is Fig. S1, which shows the progression of the disordered lunes formed by the rapid drop in temperature from the isotropic phase experienced during shell production. Since the lunes formed from the initial cooling are very small and disorganized, the SmC texture directly after production presents chunks of lunes rather than fully formed domains. As the lunes terminate rather than extend throughout the shell, they resemble focal conic domains that would be seen in a traditional flat geometry. Once the shell has reached the SmA phase in heating (Fig. S1d), the lunes become more clear and the secondary modulation can be seen. Upon heating into the nematic phase, a +1/2 and -1/2 defect pair can be seen along the domain boundary where lunes on the top of the shell had grown in different directions (Fig. S1d SmA, Fig. S1e N). The two defects then quickly annihilate yielding a near-equilibrium N phase in Fig. S1f

S2 Why do shells break at the N-SmA transition on fast cooling but not on slow cooling?

To find a possible explanation to why our shells consistenly break at the N-SmA transition if this is approached on slow cooling, we suggest to consider the following arguments. The two phenylpyrimidine mesogens used in this study (Fig. 3a) lack the polar cyano group that terminates the more commonly used 5CB and 8CB mesogens at one end, where it provides efficient hydrogen bonding with the aqueous phase even if $\mathbf{n}(\mathbf{r})$ is normal to the interface[14]. Because our mesogens are instead terminated by nonpolar alkyl chains at both ends, our mixture should have significantly greater interfacial tension to water for normal $\mathbf{n}(\mathbf{r})$. At the lune boundaries of SmA shells, the smectic layer bend forces $\mathbf{n}(\mathbf{r})$ into an alignment between tangential and normal, yielding an increased interfacial tension that for our mixture may be significant. This might explain the persistent breaking at the N–SmA transition upon fast cooling. Upon fast cooling, the rapid development of the one-dimensional long-range positional order characterizing the smectic structure renders the phase less fluid, which might provide an energy barrier against shell rupture, which could then explain the greater stability of the shells cooled quickly past the transition. A thorough test of these ideas is outside the scope of this paper, but may be a worthwhile task for a future study.

S3 Avoiding the secondary modulation by kinetically arresting the initial lune texture through fast cooling

Liang et al. noted that the secondary modulation follows after the lune formation in time[22], at least if the cooling rate is not very slow. Since in this study we must cool the shells very fast to avoid shell breaking, we can take this to the extreme and explore if we can kinetically trap the original lune configuration without any secondary modulation developing in SmA. We thus cool the shells at ∼30-40°C/min from an annealed nematic phase through the SmA phase and to the SmC phase. Fig. S2 and Supporting Video 5 show the textures observed during an experiment with -40°C/min cooling rate. Not only do we succeed in avoiding the secondary modulation, but the lunes remain very thin throughout the SmA phase and high-temperature region of the SmC phase. At lower temperature in the SmC phase, e.g., Fig. S2f, the lunes are again significantly wider than in the SmA phase, but they are not as wide as after slower cooling, demonstrating that it is the lune width in SmA that dictates the final lune width in SmC, even if the latter is always greater than in SmA. The very fast cooling rate of course leads to an even more irregular lune arrangement than usual, and a relatively high number of defects can be seen in the texture.

S4 Kinetically arresting surplus defects through fast cooling

The means of kinetically arresting non-equilibrium textures by fast cooling into and through the smectic phases can be used in other interesting ways. In an attempt to lock in surplus defects in the SmC phase, yet obtain more uniform texture than in the pristine shells, a shell was brought to the isotropic state and then quickly cooled back to room temperature at -30°C/min, see Fig. S3. This experiment shows that the shell is riddled with defects upon transition from isotropic to nematic, and that these defects will rapidly annihilate as can be seen in Fig. S3a-c. Once the shell has made the transition from N-SmA however, whatever defects are still present are locked in place due to the higher viscocity of the smectic phase which impacts the structure of lune formation. Fig. S3c-d shows the formation of the smectic lunes around two adjacent defects of opposite sign which would normally annihilate, and as the shell cools further into the SmC phase it is apparent that the defects do not move throughout the shell as the lunes hold their shape around the defects in the same configuration as they had formed.

S5 Overview of Supporting Videos

1. POM observation of a shell of our phenylpyrimidine mixture as it is cooled at 6°C/min. from nematic to SmC. The photos in Fig. 4 are extracted from this video.

2. POM observation of a shell of our phenylpyrimidine mixture as it is cooled at 25°C through the SmA-SmC transition, all the way to room temperature. The photos in Fig. 5 and Fig. 6 are extracted from this video.

3. POM observation of a shell of our phenylpyrimidine mixture as it is cooled so fast past the N-SmA transition that the original thinnest lune width remains. The photos in Fig. S2 are extracted from this video.

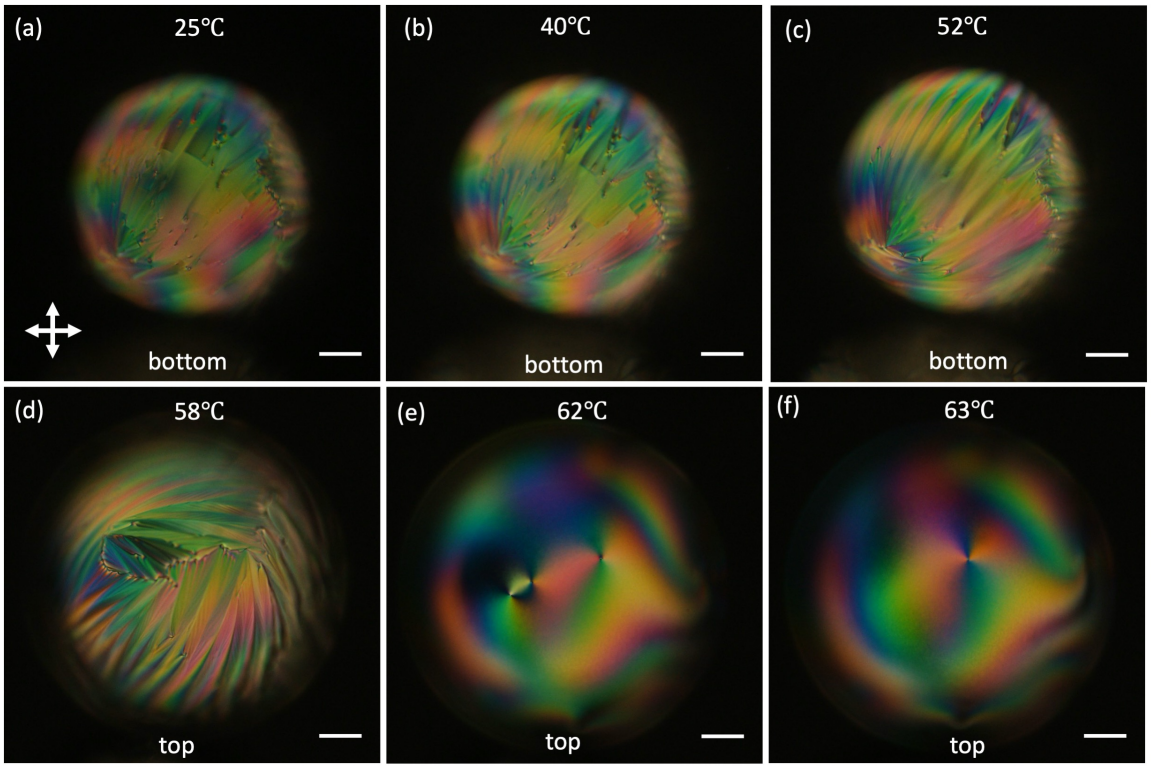

Fig. S1 POM images of a shell collected at 25°C and then heated at 30° C/min. The smectic lunes of the pristine shell appear disorganized, lacking clear domain boundaries (a). Heating through SmC yields some definition of lune domains (b) but individual well-defined domains cannot be distinguished until reaching the SmA phase (c). The top of the shell in the SmA phase (d) shows the formation of lunes which have propagated in different directions due to a surplus defect pair caught by the rapid cooling. These defects are better visualized in the nematic phase (e) before they quickly annihilate (f), leaving an annealed nematic shell with optimum defect configuration. Scale bar: 50μm.

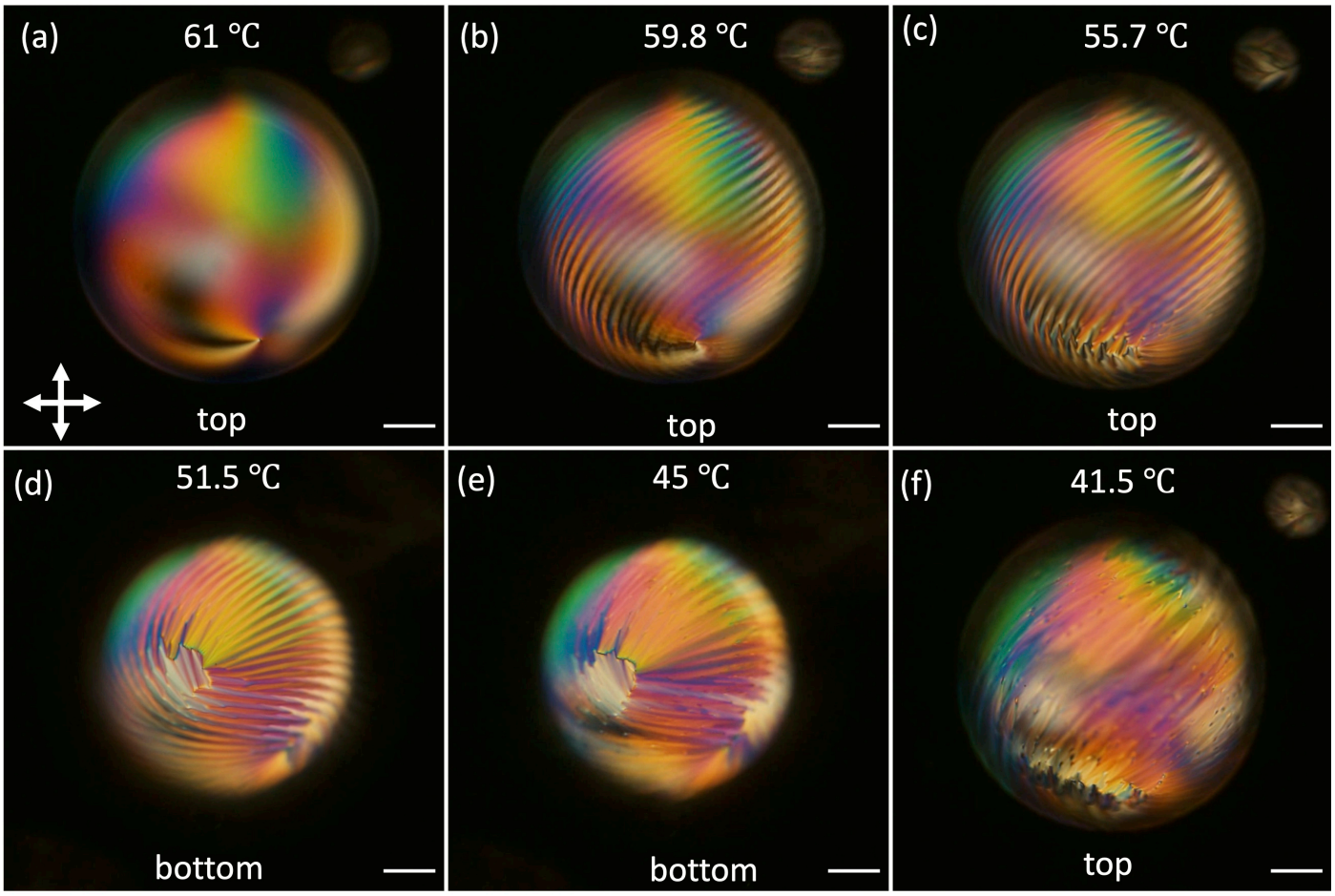

Fig. S2 POM images of a shell on cooling from an annealed nematic phase to the SmA and then the SmC phase with 40° C/min rate. Image (a) is in the nematic phase with one +1 defect towards the equator. Images (b-c) display the top of the shell with the thin, ribbon-like kinetically trapped lunes in the SmA phase, the bottom of which can be seen in Image (d). Image (e) shows the bottom side of the shell 4.7°C below the SmA-SmC transition. The distorted kinetically trapped lunes can be seen 8.2°C below the SmA-SmC phase transition can be seen clearly at the top part of the shell (f). Photos are still frames from Supporting Video 5. Scale bar represents 50μm.

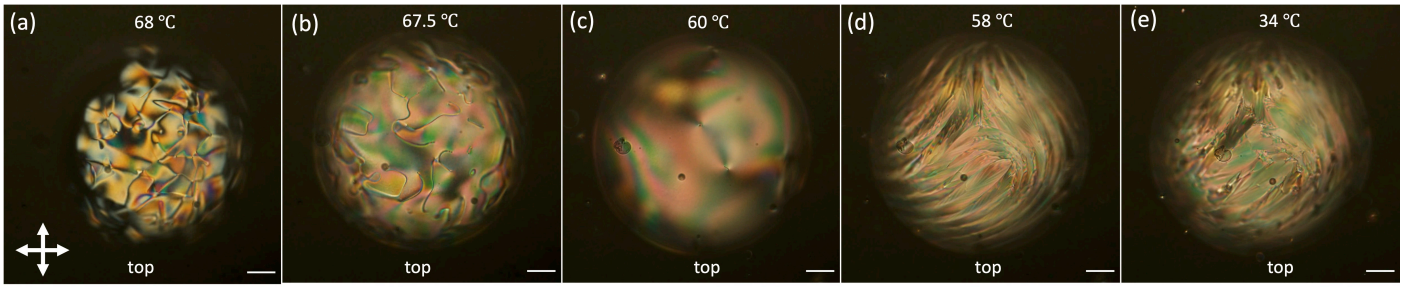

Fig. S3 POM images of a shell on cooling from nematic to SmC phase with 30° C/min rate. Image (a) is taken at the transition from isotropic to nematic with many defects at the top side of the shell forming as the N phase grows in. On cooling further most defects annihilate (b-c) but a +1/2 -1/2 defect pair at the top of the shell can still be seen in the nematic phase and are trapped on transition to the SmA phase (d). Image (e) shows the shell at SmC phase with distorted lunes around the trapped defect pair. Scale bar represents 50μm.