

(Supplementary File)

Isotropic–isotropic phase separation and spinodal decomposition in liquid crystal–solvent mixtures

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1 Brief summary of the key aspects of spinodal decomposition versus nucleation and growth

A uniform multicomponent phase undergoes phase separation by spinodal decomposition when it becomes unstable and immediately separates into two new phases having distinct compositions. There is a direct reduction in free energy from the phases separating in this way [1]. The phenomenon is characterized by the immediate appearance of the new phases in an interdigitated (bicontinuous) fashion, as opposed to phase separation via nucleation and growth. Spinodal decomposition can occur at any overall mixture composition that encompasses the spinodal curve (the bell-shaped regime with top-right-to-bottom-left dashed pattern in Fig. 1 in the main paper), specifically at the temperature where the uniform phase composition crosses the spinodal. At the critical concentration, where the spinodal curve reaches its maximum temperature, spinodal decomposition is the only possible phase separation mechanism.

If we move away from the critical concentration, an alternative phase separation mechanism, nucleation and growth, becomes possible. Below the binodal curve (solid lines outside the spinodal regime in Fig. 1 in the main paper) the uniform isotropic phase can persist although it no longer corresponds to thermodynamic equilibrium. In the region between the binodal and the spinodal curves, an energy barrier must be overcome to reach the separated states on either side of the binodal curve that together correspond to the global free energy minimum. As a consequence the original isotropic phase can remain as a supercooled metastable state. However, the energy barrier may be overcome through a concentration fluctuation and the separation then starts from a nucleus at the maximum fluctuation point. This makes the nucleation and growth process distinct from spinodal decomposition. The limit of how far the metastable phase can be supercooled is given by the spinodal curve. If nucleation and growth has not occurred before the spinodal is crossed, spinodal decomposition will take place at that temperature.

2 Preparation of anhydrous and aqueous ethanol–5CB mixtures

Tables 1 and 2 list the masses of ethanol (anhydrous and diluted, respectively) and 5CB used to create the mixtures (defined by their mol.%, x , of 5CB) studied using the temperature control stage and POM. The masses of each component were obtained using a Sartorius MC1 research grade six digit balance. Using the molar mass values of ethanol ($M_e = 46.07 \text{ g}\cdot\text{mol}^{-1}$), 5CB ($M_{5\text{CB}} = 249.357 \text{ g}\cdot\text{mol}^{-1}$) and water ($M_w = 18.015 \text{ g}\cdot\text{mol}^{-1}$), respectively, and the fact that the aqueous ethanol contained 96 mass-% anhydrous ethanol and 4 mass-% water, the experimental mixture compositions could be determined from Tables 1 and 2 as follows (x = mol% of 5CB, with index 'e' signifying anhydrous ethanol as solvent and 'ae' signifying aqueous ethanol as solvent):

$$x_e = \frac{\frac{m_{5\text{CB}}}{M_{5\text{CB}}}}{\frac{m_{5\text{CB}}}{M_{5\text{CB}}} + \frac{m_e}{M_e}} \cdot 100 \quad (1)$$

$$x_{ae} = \frac{\frac{m_{5\text{CB}}}{M_{5\text{CB}}}}{\frac{m_{5\text{CB}}}{M_{5\text{CB}}} + 0.96 \frac{m_e}{M_e} + 0.04 \frac{m_w}{M_w}} \cdot 100 \quad (2)$$

Table 1: Component masses for all mixtures containing 5CB in anhydrous ethanol.

Ethanol (g)	5CB (g)	5CB conc. (mol.%)
0.690	0.411	9.9
0.526	0.495	14.8
0.055	0.068	18.6
0.524	1.092	27.8
0.493	1.092	29
0.051	0.118	30
0.050	0.180	40
0.054	0.291	49.9
0.174	3.200	77.2
0.024	2.505	95

Table 2: Component masses for all mixtures containing 5CB in aqueous ethanol.

Aqueous ethanol (g)	5CB (g)	5CB conc. (mol.%)
0.43	0.26	9.6
0.38	0.26	11
0.21	0.32	21
0.12	0.32	32
0.057	0.34	51
0.021	0.34	74
0.011	0.21	77
0.011	0.36	85

The 5CB was acquired from two sources: Synthron Chemicals GmbH Co., and Yantai Xianhua Chem-Tech. Co. Ltd. The pure compound from both companies shared a similar nematic to isotropic clearing point between 35.7°C and 35.8°C. To confirm this clearing temperature, samples from each bottle were placed in planar-aligning test cells (E.H.C Co. Ltd, 10 μm substrate spacing), and heated until they cleared using a Linkam T95 series LTS120E temperature control stage (0.1°C resolution). The heating rate used for testing the purity was as follows: 2°·min⁻¹ until 30°C, then 0.5°·min⁻¹ until 34.5°C, then 0.1°·min⁻¹ until the clearing point.

3 Capillary filling for POM examination

Selected mixtures from Tables 1 and 2 were filled into rectangular glass capillaries (0.10 mm × 1.00 mm cross section, ~ 3 cm long, CM Scientific Ltd.) for POM experiments according to the process shown in Fig. S1. All filled capillaries studied were free of air bubbles, and were mounted on uncoated glass slides (76 mm × 26 mm, Duran Group) for easy handling. A two-component epoxy sealant used for closing the capillary ends, and for attaching the capillaries to the glass slides, was purchased from Pattex Henkel Adhesives (type: "5 min. drying, power epoxy super metal mix" with temperature range: +150°C to -30°C). The final capillary-glass slide units, shown in Fig. S1(d) were analysed within 1-4 days after assembly.

4 Qualitative observations of phases by POM: 5CB in anhydrous ethanol

Supporting movies (SM) #1, 2, 4 and 6 were sped up by 15 times their original speed to minimize the file sizes. Supporting Movie #5 was sped up by 10 times. Scale bars are shown at each moment when the magnification was changed between the 4x and 10x objectives. The magenta background seen in most movies corresponds to moments when the first-order λ plate was inserted. The heating and cooling rates, along with temperature ranges, are also specified in the videos.

- SM 1 – mixture containing 18.6 mol.% 5CB in anhydrous ethanol. This movie shows one round of cooling (3.1°C to -16.3°C), and heating (-16.3°C to 10.3°C).
- SM 2 – mixture containing 29.0 mol.% 5CB in anhydrous ethanol. This movie shows the first and third round of cooling and heating to show the differences in the phases that nucleate first. The first round:

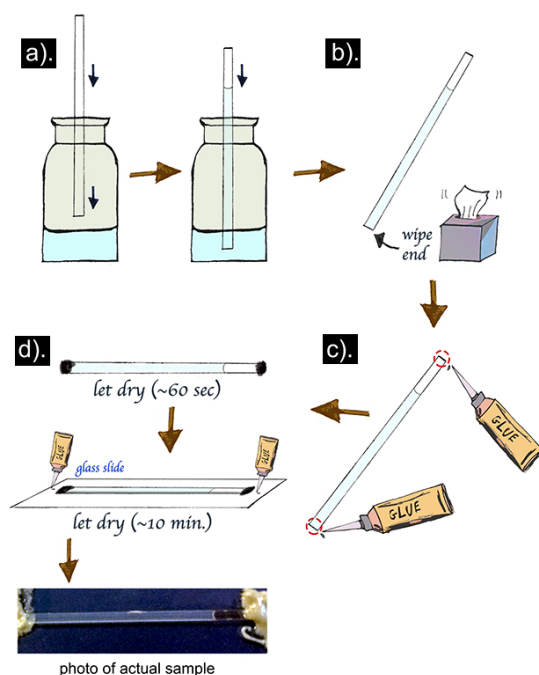


Figure S1: The process for filling rectangular capillaries with the 5cb-ethanol mixtures begins with first vertically inserting the capillary end into the vial containing the homogeneous, non-separated mixture (a). If the mixture has separated, it should be heated gently such that it becomes homogeneous but does not start bubbling. The thin capillary should be wiped to remove any debris and excess solution coating the outside of the capillary, (b), and the ends of the capillary should quickly be sealed with dabs of temperature resistant glue, (c). Finally, the capillary is mounted on a glass slide, (d), for placement into the temperature control stage for POM observation.

cooling (17.5°C to -11.6°C) and heating (-12.0°C to 9.2°C). The third round: cooling (-0.8°C to -8.5°C) and heating (-8.5°C to 0.2°C)

- SM 3 – mixture containing 20 mol.% 5CB in anhydrous ethanol. This movie (cooling, real time, no analyzer) shows the characteristic bicontinuous textural pattern developing at the isotropic-isotropic spinodal decomposition.
- SM 4 – mixture containing 9.9 mol.% 5CB in anhydrous ethanol. This movie shows one round of cooling (0.3°C to -13.5°C) and heating (-13.5°C to -7.9°C), plus an extra cooling trial (-7.9°C to -12.2°C) to show the that the nematic droplets nucleating are not related to the smudges present on the outside of the capillary.
- SM 5 – mixture containing 49.2 mol.% 5CB in anhydrous ethanol. This movie shows one round of cooling (19.5°C to -15.3°C), and heating (-15.3°C to 14.0°C). Once a uniform and homogeneous isotropic phase is reached at the end of the video there are some smudges and dirt visible that were not apparent at the start of the video. This is because the position of the capillary was moved horizontally since the start of the experiment to track the phase separation, and the smudges/dirt particles are on the outside of the capillary.
- SM 6 – mixture containing 77.2 mol.% 5CB in anhydrous ethanol. This movie shows one round of cooling (22.2°C to -16.0°C), and heating (-16.3°C to 20.0°C).

The descriptions for supporting movies of the mixtures containing 5CB in aqueous ethanol are shown on page 10, Section 6.

4.1 POM observations for the 9.9 mol.% mixture

Figure showing the isotropic and nematic phases in coexistence on cooling and heating

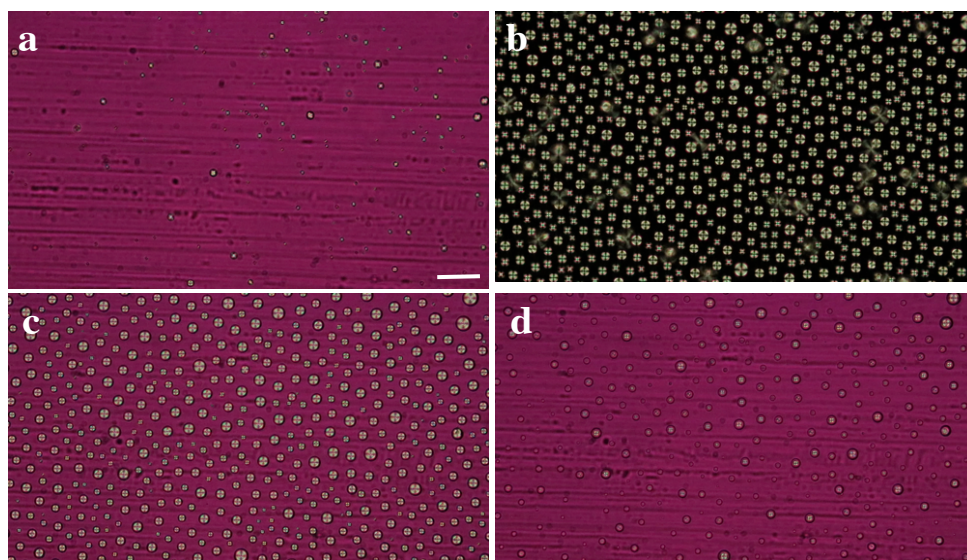


Figure S2: POM images of the 9.9 mol-% 5CB mixture in a 100 μm thick flat capillary. Top row: on cooling at 2 K/min., at the onset of the isotropic–nematic transition at -11.8°C (a) and deeper in the coexistence regime at -13.5°C (b). Bottom row: on heating, at -9.6°C (c) and close to complete clearing at -8.8°C (d). Micrographs with a purple background are obtained with a first-order λ plate inserted. Scale bar (applies to all panels): 200 μm .

4.2 POM observations for the 29.0 mol.% mixture

Figure showing the phases in coexistence on cooling and heating

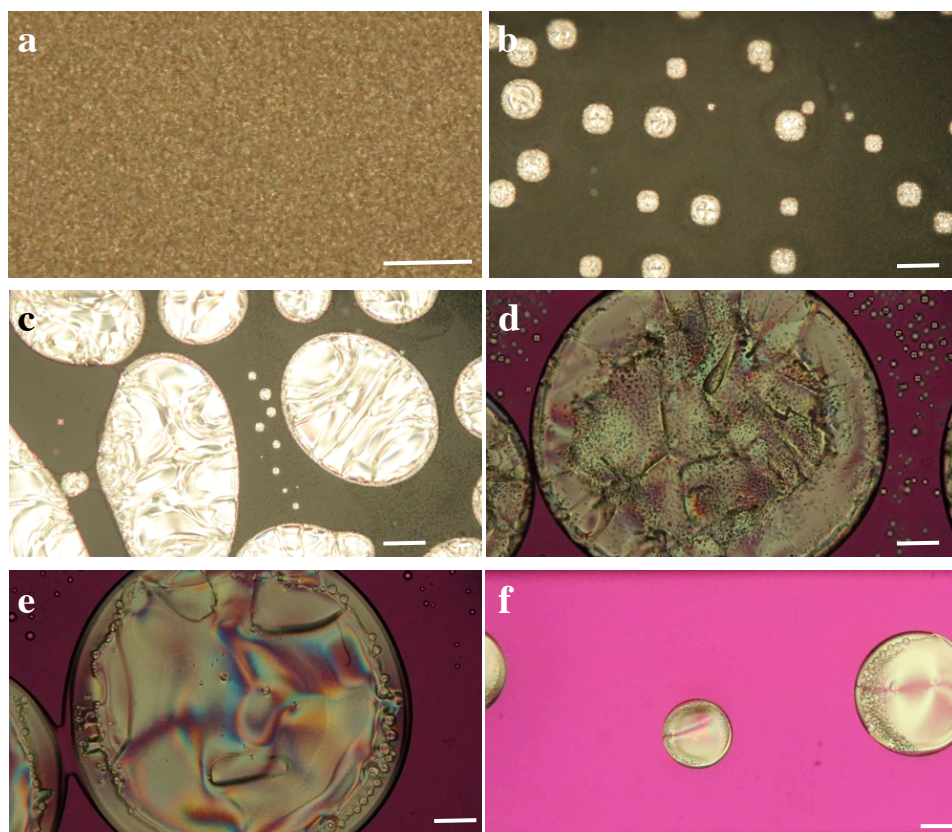


Figure S3: POM images of the 29.0 mol-% 5CB mixture in a 100 μm thick flat capillary, on cooling (a–d) and on subsequent reheating (e–f). The original uniform isotropic phase rapidly breaks up into two new isotropic phases, probably by spinodal decomposition, around -4.7°C (panel (a) is taken (with the analyzer removed) somewhat later, at -5.6°C). Just below -7°C the nematic phase starts nucleating (b) and at -7.9°C (c) its growth becomes very fast, with one of the two isotropic phases disappearing. At -9.9°C (d) many small isotropic droplets nucleate within large nematic domains. As we reheat, they gradually disappear and at -5.4°C (e) we again detect isotropic–isotropic phase separation in the regions surrounding large nematic domains. The two isotropic phases merge at about -1°C (not shown). The nematic phase persists until about $+9^\circ\text{C}$ (panel (f) is taken at $+3.9^\circ\text{C}$). Micrographs with a purple background are obtained with a first-order λ plate inserted. Scale bars: 100 μm .

4.3 Additional comments concerning the 49.2 mol.% mixture

As we cool below point (2) in the phase diagram (Fig. 1 in the main paper), only the left-most isotropic phase can coexist with the nematic phase, which now appears to dominate strongly (Fig. 3c in the main paper). This dominance is surprising, considering that the 49.2 mol% overall concentration is not drastically closer to the nematic than to the isotropic boundary, hence we should have almost as much isotropic as nematic phase. The observation may suggest that we now have phase coexistence mainly in the *vertical* direction of the capillary, along the direction of gravity. Since this is also along the viewing direction, detecting the phase separation is then not easy.

The less 5CB-rich isotropic phase may largely adhere to the top of the capillary, above the denser nematic phase. In fact, the observed birefringence of the nematic phase is rather low for a 100 μm thick capillary, with a color in Fig. 3c in the main paper that over large areas resembles the pink of the first-order λ -plate, thus suggesting close to no contribution from the nematic. Such a situation might be expected if we are looking through an isotropic layer on top of the nematic. The texture is also very irregular and does not feature the *schlieren* that are characteristic for a nematic phase (see, e.g., Fig. S4c for a typical example).

4.4 POM observations for the 77.2 mol.% mixture

The 77.2 mol-% sample has high enough 5CB content to have the nematic phase present at room temperature. As expected, the phase enters directly from the isotropic at 15.8°C without any sign of isotropic–isotropic phase separation (see Fig. S4a and Movie SM6). However, the sample remains mainly isotropic down to about +12°C, where the full sample rapidly turns nematic (Fig. S4b). This may reflect the significantly larger 5CB content in the nematic phase of the two-phase region, requiring cooling until about 10°C until the nematic phase (Fig. S4d), has the 77.2 mol.% 5CB composition of the overall sample.

At that point the full sample should have turned nematic, but a minority isotropic phase still remains until +5.1°C where the nematic phase extends throughout the sample (Fig. S4c). This may again be a consequence of the concentration gradients and non-equilibrium phenomena while these are slowly evened out. For the same reason, it is not until –11.3°C that we see the first isotropic droplets nucleate within the nematic phase (Fig. S4d), although the lower boundary of the stable nematic phase range with 77.2% 5CB is about –5°C, as established by DSC.

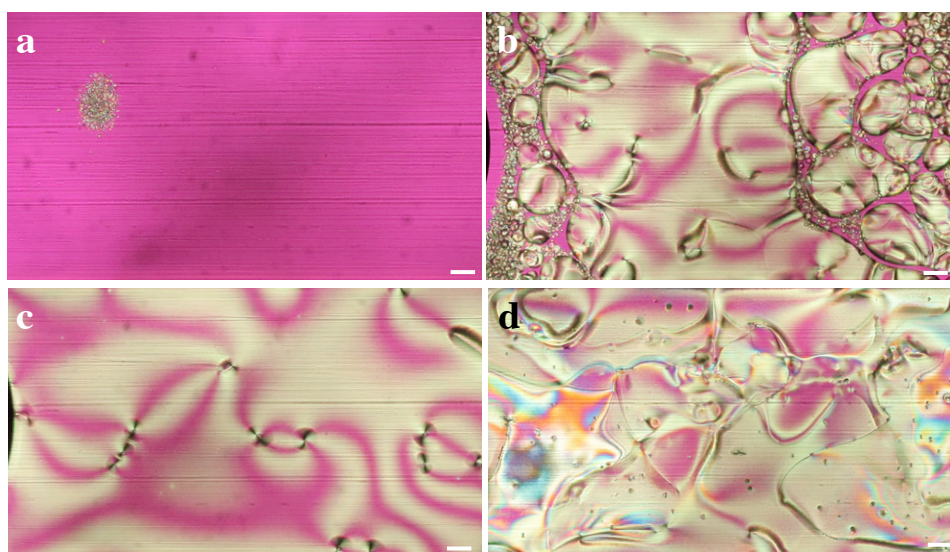


Figure S4: POM images (with a first-order λ plate inserted) of the 77 mol-% 5CB mixture in a 100 μm thick flat capillary on cooling from uniform isotropic phase. The nematic phase enters at +15.8°C (a), initially growing only slowly on further cooling. However, at about +12°C most of the remaining isotropic phase rapidly turns nematic, the image in panel (b) captured at 11.8°C. The sample becomes fully nematic at +5.1°C (c). At –11.3°C (d) we start seeing a few small isotropic droplets nucleating, signifying that we have crossed the lower boundary of the stable nematic phase range. Scale bars: 100 μm .

5 Quantitative measurement of transition temperatures by DSC: 5CB in anhydrous ethanol

The strong concentration gradients that arise as a result of phase separation in the large-scale capillary make accurate conclusions about the transition temperatures difficult from the microscopy investigations. We therefore carried out DSC experiments on heating and cooling for selected concentrations. The sample extension for DSC is smaller, reducing the time for evening out phase separation-induced concentration gradients, hence the DSC transition temperatures are more reliable. The heating as well as cooling runs were repeated at least once, confirming in the majority of cases that peaks were almost perfectly reproducible. The exceptions are mentioned and discussed in the following.

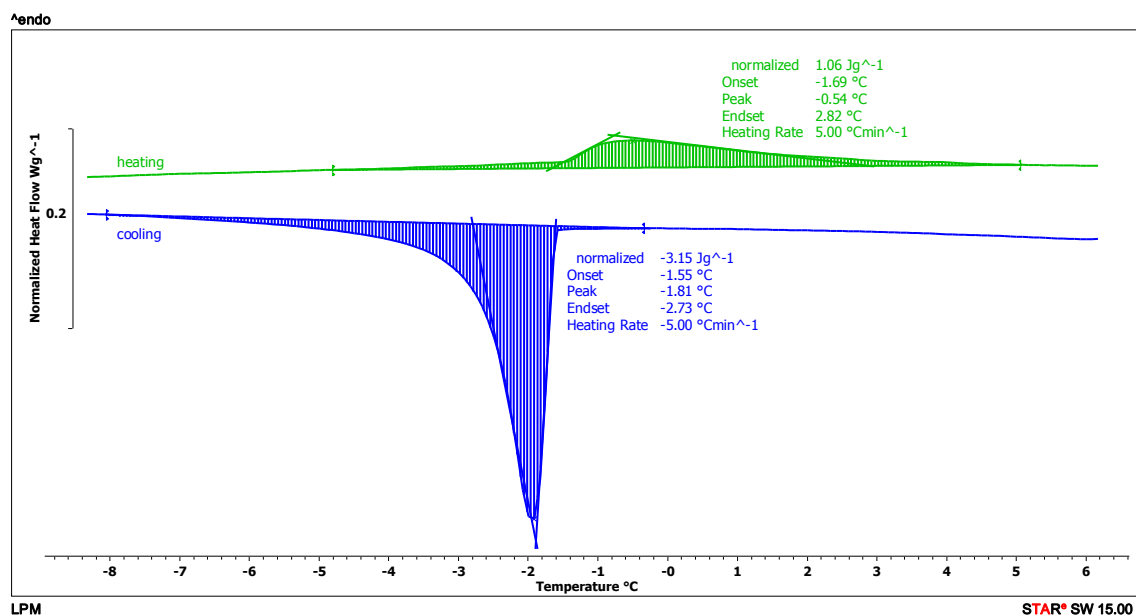


Figure S5: DSC traces on heating and cooling for the 14.8 mol.% 5CB mixture

On cooling the 14.8 mol.% 5CB mixture the first peak that can be correlated with a phase transition is a very sharp drop in the heat flow with onset at -1.5°C . We interpret this as the crossing of the spinodal curve, inducing the sudden separation of the original isotropic phase into an isotropic phase with somewhat lower 5CB content and a nematic phase with much higher 5CB content. The reason that we do not expect isotropic–isotropic phase separation is because the spinodal is crossed at a temperature below the eutectic point of the isotropic phase, point (2) in Fig. 1 in the main paper, hence phase separation produces the nematic phase right away.

On heating, the curve is somewhat noisy and repeatability between runs is not perfect. An extended and less well-defined peak with lower area than the peak on cooling can be seen with onset at about -1.5°C . We believe that the concentration differences between the two resulting phases upon low temperature phase separation in this mixture are so extreme, the isotropic fraction at -10°C having a 5CB concentration of about 9 mol.% while the corresponding nematic fraction has about 75 mol.% 5CB, that concentration gradients influence the behavior of this sample even within the DSC measurement. This is why we do not see a sharp peak corresponding to complete clearing when we heat past the 14.8 mol.% 5CB binodal at about -1.5°C . The peak is extended considerably by non-equilibrium effects as concentration gradients are evened out upon heating.

Fig. S6 shows the salient features of the DSC traces for the 27.8 mol.% 5CB mixture. Similar to the behavior in the 14.8 mol.% sample, the first peak on cooling is a rapid drop of the heat flow, this time with an onset at $+1.4^{\circ}\text{C}$, which we interpret as spinodal decomposition of the uniform isotropic phase into two new isotropic phases. The peak has a considerable extension on the low temperature side and it is clear that it is composed of two partially overlapping peaks. We believe that the second sub-peak corresponds to cooling past the eutectic point of the isotropic phase, point (2), at which the nematic phase at much higher 5CB concentration must be rapidly formed from the isotropic fraction with higher 5CB content.

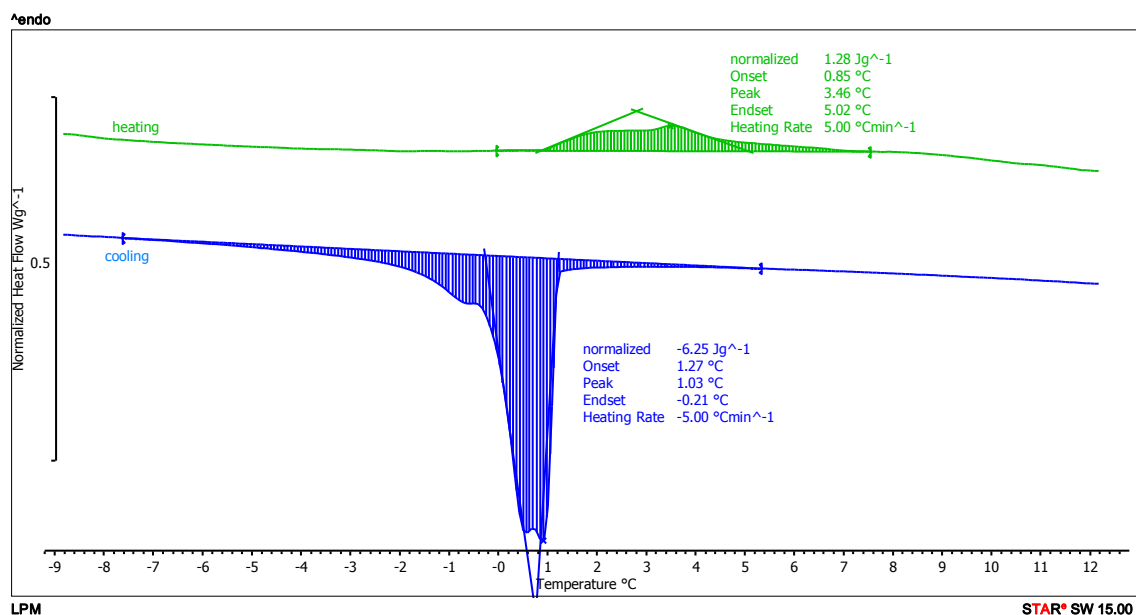


Figure S6: DSC traces on heating and cooling for the 27.8 mol.% 5CB mixture

Upon heating we again see an extended peak with lower integrated area, suggesting that also in this sample some concentration gradients remain, inducing non-equilibrium phenomena. The onset of the heating peak is just above 0°C and we interpret this peak as the gradual disappearance of the nematic phase, initially into a second isotropic phase, eventually leaving only the single uniform isotropic phase prevailing at high temperatures in the 27.8 mol.% mixture.

With the 49.2 mol.% mixture, the key DSC traces of which are shown in Fig. S7, we are on the right side of the eutectic point (2) in the phase diagram. On cooling we now see a strong initial peak with onset at about +3.2°C, corresponding to the development of nematic phase in coexistence with the original isotropic phase, and this is partially overlapping with a peak starting slightly above 0°C, most likely again corresponding to the eutectic point. Whereas this for lower 5CB concentration corresponded to nematic phase developing from isotropic, now it is the other way around: as the initial 5CB-rich isotropic phase reaches the eutectic point it becomes unstable with respect to the isotropic phase on the far left in the phase diagram, with much less 5CB, inducing a phase separation that gives rise to the additional smaller peak.

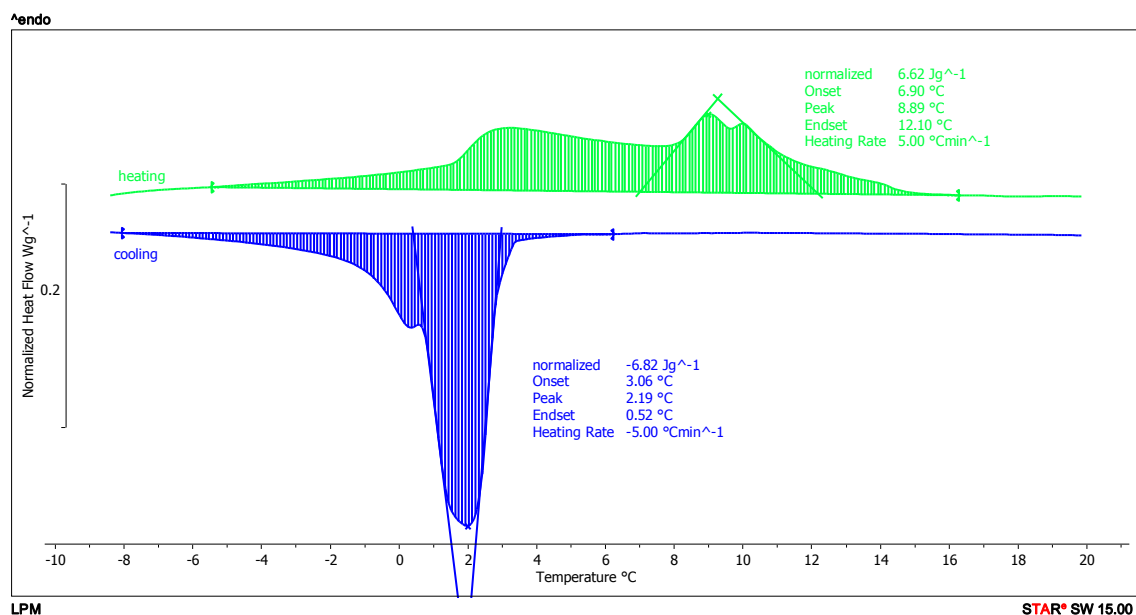


Figure S7: DSC traces on heating and cooling for the 49.2 mol.% 5CB mixture

The repeatability of the traces is not perfect even on cooling in this case, reflecting the strong concentration gradients building up as phases on opposite sides of the phase diagrams are nucleated or disappear. On heating, the repeatability is even poorer, but we see an extended peak starting at around 0°C. We believe that this corresponds to the gradual disappearance of the very low-5CB-concentration isotropic phase, later on the disappearance of the nematic phase, until only a single isotropic phase remains at about +16°C, much higher than the binodal at this overall mixture composition. This is, again, a strong testimony to the great impact of concentration gradients.

The DSC traces for the 77.2 mol.% mixture, finally, are shown in Fig. S8. In this case repeatability is good on cooling and on heating. On cooling, a clear peak with onset at +16.8°C signifies the beginning of the isotropic–nematic transition, thus crossing the binodal, and this ends at about 8°C, which we interpret as the upper boundary of the stable nematic phase range. A weak peak can be distinguished starting at about –5°C. Because it is perfectly repeatable we consider it to correspond to a phase transition, thus suggesting the lower boundary of the stable nematic phase.

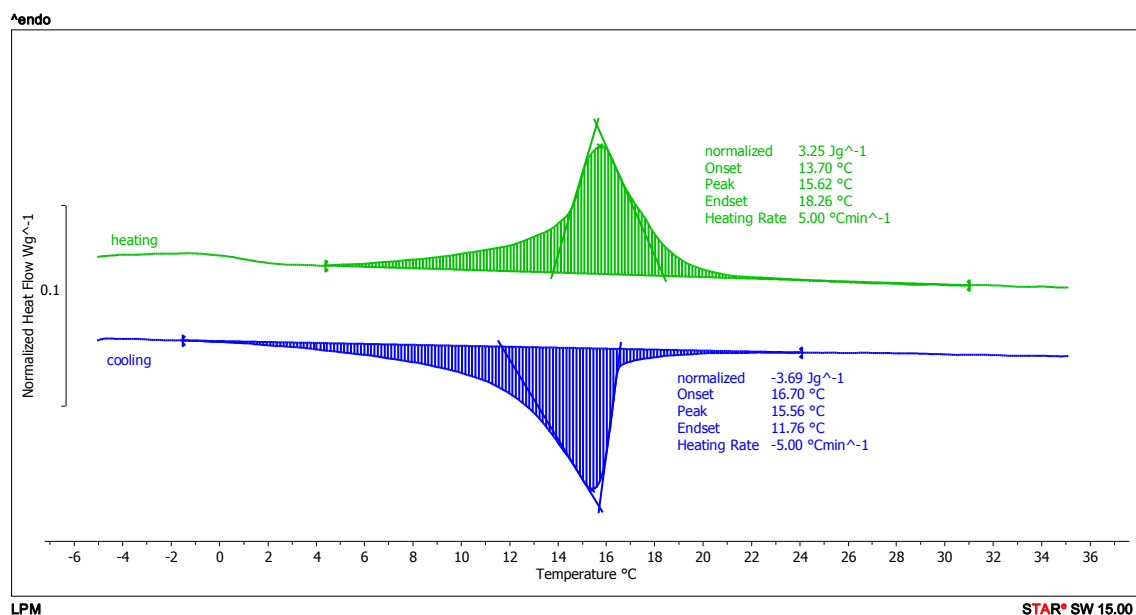


Figure S8: DSC traces on heating and cooling for the 77.2 mol.% 5CB mixture

6 Qualitative observations of phases seen macroscopically and by POM: 5CB in aqueous (3 vol.% water added) ethanol

Supporting movie (SM) #7 was sped up by 15 times its original speed to minimize the file size. Scale bars are shown for each moment when the magnification was changed from the 4x to 10x objectives using the POM. The magenta background seen corresponds to the first-order λ plate was inserted. The heating and cooling rates, along with temperature ranges, are also specified in SM 7.

For SM 8 all three mixtures shown were contained in 2 mL vials. They were filmed using an iPhone 5s in rooms having a temperature of roughly 23°C and relative humidity roughly equal to 30%. This movie was sped up by 2 times the original speed.

- SM 7 – mixture containing 19 mol.% 5CB in ethanol with 3 vol.% water added. Since the capillary starts off with the coexisting isotropic phases at room temperature it is first heated (28.0°C to 49.5°C) so that there is one homogeneous isotropic phase. Then the movie shows one round of cooling (49.5°C to -19.6°C) and heating (-19.6°C to 45.5°C). Melting ice crystals appear at roughly 2:15 (the blurry dotted pattern seen when the focus is briefly altered), but these are from water that condensed on the outside of the capillary and do not impact the phase separation seen within.
- SM 8 – three videos show that two isotropic phases in mixtures containing 9.6 mol.%, 20.2 mol.% and 50.9 mol.% 5CB in ethanol plus 3 vol.% water can coexist at room temperature. The videos collected here correspond to the screen shots labeled a, b, and c, in Fig. 5 of the main paper.

7 Quantitative measurement of transition temperatures by DSC: 5CB in aqueous (3 vol.% water added) ethanol

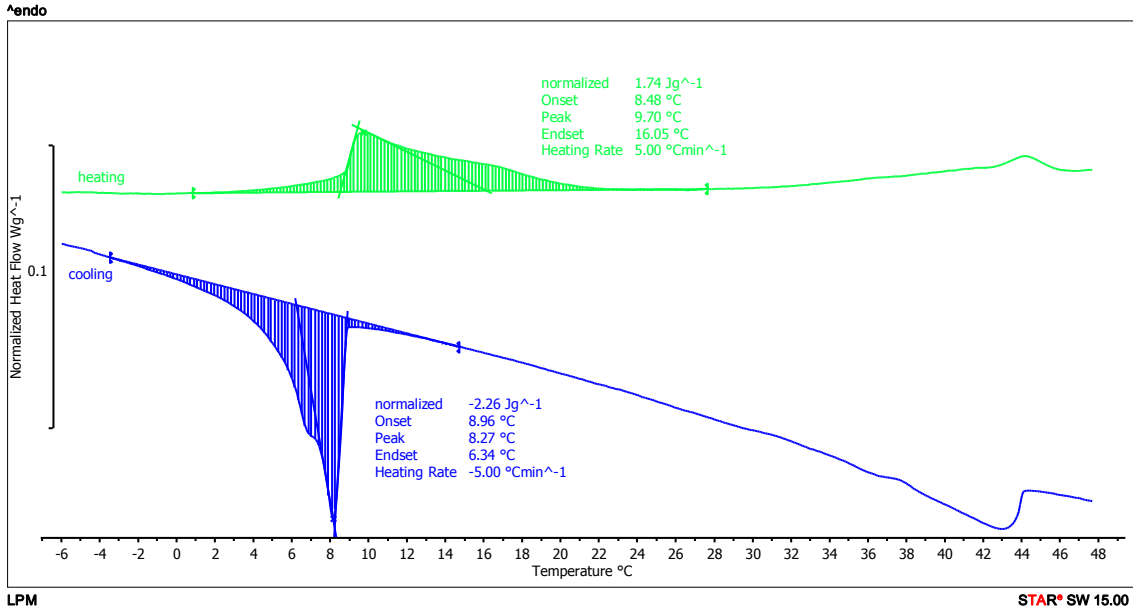


Figure S9: DSC traces on heating and cooling for the 40.9 mass-% 5CB mixture

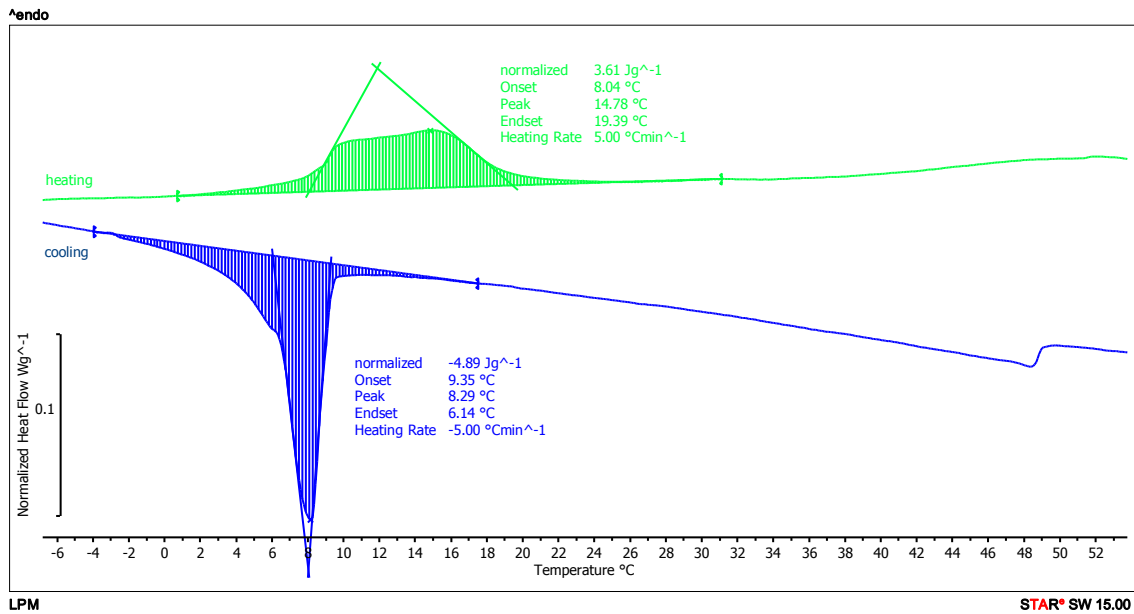


Figure S10: DSC traces on heating and cooling for the 72.8 mass-% 5CB mixture

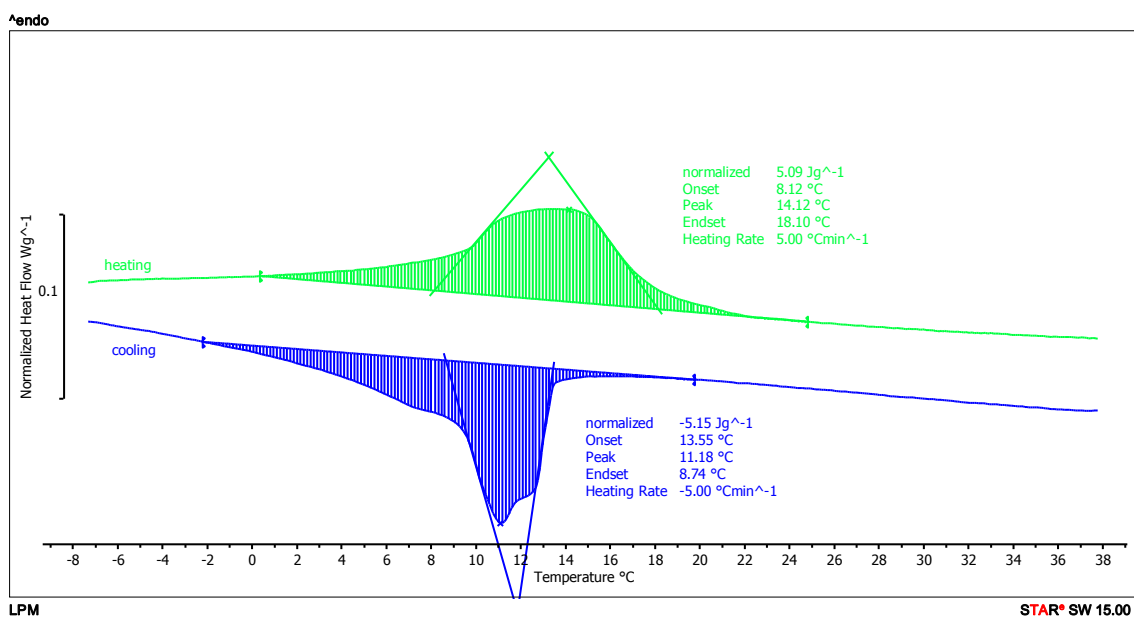


Figure S11: DSC traces on heating and cooling for the 94.2 mass-% 5CB mixture

References

- [1] E. Favvas and A. C. Mitropoulos, "What is spinodal decomposition?" *J. Eng. Sci. Technol. Rev.*, vol. 1, pp. 25–27, June 2008.