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Pretransitional Orientational Ordering of a Calamitic Liquid Crystal by Helical Nanofilaments of a Bent-Core Mesogen

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Mixtures of 8CB (a calamitic mesogen) and NOBOW (P-9-O-PIMB, a bent-core mesogen) have been investigated using differential scanning calorimetry, nuclear magnetic resonance spectroscopy, and freeze fracture transmission electron microscopy. On cooling the isotropic mixture, the NOBOW component phase separates, forming a dilute, random network of helical nanofilaments in the B4 phase with isotropic 8CB material filling the interstitial volume. At lower temperature, but still far above the bulk isotropic–nematic transition of pure 8CB, a significant fraction of the 8CB becomes prealigned on the filament surfaces. We propose that this pretransitional ordering is induced by short-range interactions of the polar 8CB molecules with the NOBOW filaments, leading to the formation of an adsorbed film of orientationally frozen 8CB around each filament.

Introduction

Mixtures of liquid crystals (LCs) sometimes yield new phases and may show phase sequences not present in any of the individual components.¹ In many cases, desirable liquid crystalline properties and phases with broad temperature ranges can be obtained more easily by mixing compounds of different shapes and properties than by performing systematic variations in the synthesis of pure compounds.

Mixtures of bent-core and calamitic (rod-shaped) mesogens are particularly interesting systems for exploring the role of molecular shape in determining liquid crystal ordering. Transitions between the B2 banana phase and mesophases more typically found in calamitic compounds, for example, the phase sequence SmA-SmC-B2, have been reported in pure bent-core mesogens.² The experiments indicate that an essential condition for such phase sequences is a change of the molecular conformation as a function of temperature. Studies of the binary mixtures of bent-core and calamitic mesogens have led to the observation of the phase sequences SmA-B2, SmC-B2, and N-SmA-SmC-B2.³ The calamitic/bent-core binary system reported by Pratibha et al.^{4,5} shows an orientational transition of bent-core molecules, which, at low concentration (3–4 mol %), order within the smectic layers of the rodlike molecules with the director orthogonal to the layer normal and display a biaxial smectic A₂ (SmA_{2b}) phase. Rodlike chiral dopants have also been used to control the proportion of left- and

right-handed chiral domains in thin cells of achiral bent-core compounds.⁶

In 2005, Takezoe and co-workers prepared mixtures of the bent-core molecule NOBOW (Figure 1a) with the calamitic LC 5CB,⁷ obtaining large homochiral domains, a promising development for nonlinear optic applications.⁸ These experiments were interpreted assuming the mixture to be a single phase. Following the identification of the structure of the B4 phase as an array of helical nanofilaments,^{9,10} X-ray diffraction studies showed that mixtures of NOBOW with 8CB (Figure 1a), a homologue of 5CB with a smectic A phase below the nematic, form a single, homogeneous phase only in the high temperature, isotropic range.¹¹ At lower temperatures, the NOBOW B4 phase separates into a network of helical nanofilaments, leaving the 8CB to fill the interstitial spaces. Such segregation combined with mixing offers the possibility for a wide variety of novel materials based on spontaneous nanoscale self-assembly. For example, the Takezoe group recently showed that the optical activity of the 5CB/NOBOW mixtures is enhanced when 5CB changes from isotropic to nematic,¹² ascribing this effect to the formation of macroscopic chiral domains in the 5CB nematic templated by the chiral nanofilaments. Here we probe in detail the interaction of the helical nanofilaments of the NOBOW B4 phase with 8CB in mixtures. We find that there is substantial prealignment of the

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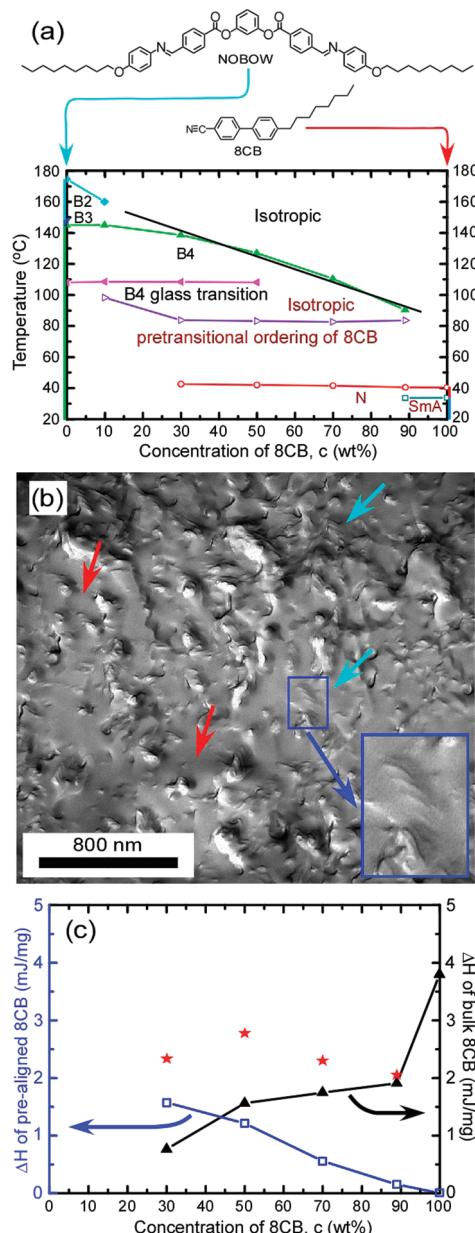


Figure 1. Phase behavior of 8CB/NOBOW mixtures showing nanophase separation and prealignment of 8CB far above its Iso-N transition. (a) Chemical structure and phase diagram of the binary system obtained from DSC measurement and optical observations (NOBOW states in black, 8CB states in red). The linear reduction of the NOBOW Iso-B4 transition (the black line is a guide to the eye) corresponds to conventional freezing point depression. The DSC peak around 83 °C observed in the mixtures (open purple triangles) arises from local pretransitional orientational ordering of 8CB around the surface of NOBOW B4 helical nanofilaments. (b) FFTEM image of $c = 75\%$ 8CB/NOBOW mixture obtained after quenching an open hemispherical sample at $T \approx 80\text{ }^{\circ}\text{C}$ and cutting it deep into the bulk. Randomly oriented helical imprints of the NOBOW B4 phase are uniformly distributed in the bulk (blue arrows, one magnified in the inset), while the isotropic 8CB appears as smooth regions between the helical imprints (red arrows). (c) Normalized latent heat of the 8CB bulk Iso-N transition ($T \approx 40\text{ }^{\circ}\text{C}$, black triangles) and that of 8CB prealigning around the B4 filament surfaces ($T \approx 83\text{ }^{\circ}\text{C}$, blue squares) in a series of 8CB/NOBOW mixtures. The latent heat of the surface-prealigned 8CB increases as the concentration of B4 filaments increases, with a corresponding decline for that of the bulk 8CB Iso-N transition. The red stars show the sum of the 8CB bulk Iso-N transition and prealigned latent heats in the mixture.

8CB by the nanofilaments far above the 8CB bulk isotropic–nematic transition temperature, which we believe must be due to a thin film of 8CB adsorbed to the nanofilament surface.

Results and Discussion

The phase sequences of the pure materials on cooling are as follows: for NOBOW, Iso(175°)B2(147°)B3(143°)B4; for 8CB, Iso(40°)N(33°)SmA. The chemical structures of NOBOW and 8CB, and the phase diagram of the binary system based on differential scanning calorimetry (DSC)¹³ (also see Supporting Information S.1 and 2) and optical observations,¹⁴ are shown in Figure 1a. As the concentration of 8CB is increased, the NOBOW B2 and B3 phases disappear and the transition to the B4 phase is depressed, decreasing approximately linearly with 8CB concentration (black line in Figure 1a is a guide to the eye). Below the I-B4 phase transition temperature, freeze fracture transmission electron microscopy (FFTEM) shows the formation of helical nanofilaments similar to those found in pure NOBOW.¹⁰ These filaments are observed in the mixtures at all concentrations of 8CB, both in the bulk (Figure 1b) and near the cell surface (see Figure 2E in ref 10 and Figure 2 in ref 13). Figure 1b is an FFTEM image of a plane cutting the bulk of the mixture, showing randomly oriented helical B4 imprints (blue arrows in Figure 1b, one region magnified in the inset) with smooth regions of isotropic 8CB between them (red arrows). Such images provide direct confirmation of nanophase separation in this binary system, with the NOBOW B4 helical nanofilaments forming a dilute random network uniformly distributed in the bulk and the 8CB filling the interstitial volume. When the fracture plane is near the cell surfaces, FFTEM images show individual twisted nanofilaments, allowing the direct measurement of the filament diameter and helix pitch, which we find to be independent of the 8CB concentration.¹⁴ Precision X-ray diffraction measurements show that the smectic layer spacing in the B4 nanofilaments is also independent of the 8CB concentration.¹³ In addition to reflections from the B4 filaments, the diffraction pattern shows at lower temperatures a separate Bragg peak from the 8CB smectic A layers, with a spacing $d \approx 33\text{ \AA}$ at temperature $T \approx 33\text{ }^{\circ}\text{C}$, also independent of the 8CB concentration. This suggests that NOBOW is insoluble in the 8CB, indicating an essentially complete phase separation of the two components once the B4 forms, with NOBOW forming nanofilaments and 8CB occupying the space between them. The linear reduction of the Iso-B4 transition temperature of NOBOW with increasing 8CB concentration corresponds to classical freezing point depression, where the latent heat obtained from fitting the slope of this phase boundary, $\Delta H_{\text{Iso-B4}} \approx 51\text{ kJ/mol}$, matches the value $\Delta H_{\text{Iso-B4}} \approx 53\text{ kJ/mol}$ obtained from the extrapolation of DSC data. The overall picture that emerges from these structural studies is of a strongly nanosegregated mixture of NOBOW filaments of diameter $D \approx 36\text{ nm}$, with 8CB in nanosized pores whose average dimension decreases as the 8CB concentration is reduced. At smaller 8CB concentrations, the confinement of the 8CB leads to a broadening of the thermal anomalies associated with its Iso-N and N-SmA phase transitions¹³ similar to what is observed in 5CB,¹⁵ indicating that 8CB is interacting with the filament surfaces and that orientational or layer ordering of the 8CB is limited to smaller and smaller volumes. DSC and NMR experiments provide clear evidence

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for the existence of an adsorbed 8CB film on the nanofilament surfaces above the 8CB Iso-N transition, as we shall see below.

8CB/NOBOW mixtures of concentration c , where c is the wt % of 8CB in the mixture, were prepared in the range $0\% < c < 100\%$. The DSC data show an additional peak at $T \approx 83^\circ\text{C}$ (open purple triangles in Figure 1a), more than 40°C above the clearing point of pure 8CB, which appears neither in pure NOBOW nor in pure 8CB. At the same time, the normalized latent heat of the bulk 8CB Iso-N transition at $T \approx 40^\circ\text{C}$ in the mixtures (black triangles in Figure 1c) is substantially reduced compared with that of pure 8CB. This strongly indicates that some fraction of 8CB is prealigned by the NOBOW B4 helical nanofilaments, inducing orientational ordering of 8CB at elevated temperature. Indeed, in mixtures which are almost 8CB, with few B4 nanofilaments available to prealign the 8CB, the normalized latent heat of the bulk 8CB Iso-N transition approaches the bulk value, while the contribution from prealigned 8CB becomes very small (Figure 1c). The prealignment transition of the 8CB is not noticeable in the depolarized transmitted light microscope, presumably because any additional birefringence from pretransitional orientational ordering of the 8CB is averaged out by the global orientational disorder of the B4 nanofilaments. However, NMR provides a sensitive alternative probe of the local orientational ordering of the 8CB molecules.

Solid-state NMR spectra were acquired using a Varian Inova 400 spectrometer equipped with an extended variable-temperature 4 mm cross-polarization, magic-angle-spinning (CPMAS) probe, operating at 100.63 MHz for ^{13}C observation. CPMAS spectra were acquired using a 90° pulse of $3.4\ \mu\text{s}$ and a typical MAS spinning frequency of 11 kHz, with a Hartmann–Hahn spin locking field of 71.5 kHz for both ^1H and ^{13}C . Typical cross-polarization contact times were 4.0 ms, and TPPD ^1H decoupling was applied during acquisition. Single-pulse ^{13}C MAS NMR was done using a $3.5\ \mu\text{s}$ 90° excitation pulse. The relaxation delay was 3.0 s for all experiments. Actual sample temperatures were calibrated using the ^{207}Pb chemical shift of lead nitrate, as described in ref 16. Using careful matching of air flows and spinning speeds with the calibration standard, we were able to achieve reproducible sample temperatures of $\pm 2^\circ\text{C}$.

In CPMAS NMR, the observed ^{13}C NMR signal arises via the heteronuclear, first-order dipole–dipole coupling between the ^1H nuclei and the ^{13}C nuclei. In a rapidly tumbling, isotropic environment, this interaction is zero, and the cross-polarization (CP) mechanism vanishes. Therefore, the observation of a ^{13}C NMR signal via CP indicates either that the molecule is tumbling slowly on the NMR/dipolar-coupling time scale (~ 10 –100 kHz) or that the molecular motion is anisotropic in nature. In addition, in CPMAS experiments, only the proton nuclei need to relax between transient acquisition, and in condensed phases ^1H spin–lattice relaxation time constants (T_1) are generally significantly smaller than those of ^{13}C , often by one or more orders of magnitude. In a single-pulse, MAS spectrum, all of the net ^{13}C magnetization present in the sample is excited by the pulse; however, in rigid solids, the T_1 relaxation time is so long that no signal is observed under signal averaging unless very long relaxation delay times are used. In this work, when performing single-pulse MAS NMR, only highly mobile molecules having solution-like T_1 relaxation behavior are observed with significant intensity.

To illustrate this, in the $c = 75\%$ 8CB/NOBOW mixture observed with the sample at $T \approx 80^\circ\text{C}$, above the Iso-N transition temperature of pure 8CB but still well below the clearing point of

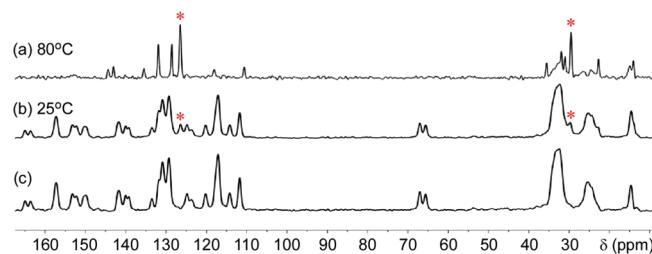


Figure 2. Single-pulse and CPMAS NMR spectra of $c = 30\%$ 8CB/NOBOW mixture. (a) The single-pulse NMR spectrum taken at $T \approx 80^\circ\text{C}$ is dominated by the 8CB signal. At low chemical shift, there is some signal from the tails of NOBOW, which are more mobile than their cores. (b) The CPMAS NMR spectrum at $T \approx 25^\circ\text{C}$ shows both NOBOW and 8CB peaks. Fortunately, the two strongest peaks from 8CB do not overlap significantly with the NOBOW spectrum (marked with red stars). (c) The NOBOW spectrum obtained by subtracting the scaled single-pulse signal (a) from the CPMAS signal (b) agrees well with the spectrum of pure NOBOW reported previously.¹⁶

NOBOW, the single-pulse spectrum (Figure 2a) is predominantly from 8CB, both bulk and prealigned, except at small chemical shift where there is some signal from the NOBOW tails, which are more mobile than the cores. Using this isotropic liquid-phase ^{13}C data, it is possible to assign nearly all of the resonances of the 8CB molecule, assisted by the predicted ^{13}C NMR shifts using the ACD/Laboratories NMR software (version 12.0). Fortunately, in the NMR spectrum, the two strongest 8CB peaks (around 29 and 126 ppm, marked by red stars in Figure 2) do not significantly overlap with the NOBOW spectrum and can easily be distinguished in the CPMAS NMR spectrum in Figure 2b. When subtracting an appropriately scaled single-pulse NMR signal (Figure 2a) from the CPMAS NMR signal (Figure 2b), we obtain the CPMAS NMR spectrum of pure NOBOW (Figure 2c), which is consistent with that reported in ref 16.

We recorded a series of CPMAS NMR spectra while cooling the $c = 30\%$ 8CB/NOBOW mixture, shown in Figure 3. As expected, at high temperature, all of the 8CB is isotropic and the spectrum is purely from the NOBOW B4 phase (Figure 3a). At slightly lower temperature, the two strongest 8CB peaks appear (Figure 3b, marked by red stars), indicating that there is anisotropic 8CB which is orientationally ordered far above the Iso-N transition of bulk 8CB. On further cooling, the 8CB peaks persist all the way down to room temperature (Figure 3c–f). To analyze the 8CB peak intensity quantitatively as a function of temperature, we first normalize each scan by setting the integrated intensity of the two peaks around 68 ppm to a value of 100, for they are due only to NOBOW and are independent of 8CB below the NOBOW clearing point. As shown in Figure 3g and h, 8CB signals appear at $T \approx 93^\circ\text{C}$, a temperature that is slightly higher than that obtained by DSC, indicating the onset of orientational ordering of 8CB around the nanofilament surfaces. On further cooling, the 8CB signal strength increases steadily, indicating that the orientational ordering of 8CB is progressively enhanced. When the sample is cooled through the bulk 8CB Iso-N transition (blue dashed line in Figure 3g and h), there is a large increase of the 8CB signal as the remaining 8CB becomes nematic.

The CPMAS NMR spectra of the $c = 70\%$ 8CB/NOBOW mixture are qualitatively different from those of the $c = 30\%$ 8CB/NOBOW mixture. At high temperature (Figure 4a), well below the NOBOW Iso-B4 transition, there is no signal from either NOBOW or 8CB, even though the NOBOW is in the B4 phase. This is because there are fewer B4 filaments than in the $c = 30\%$ 8CB/NOBOW mixture and those that are present are

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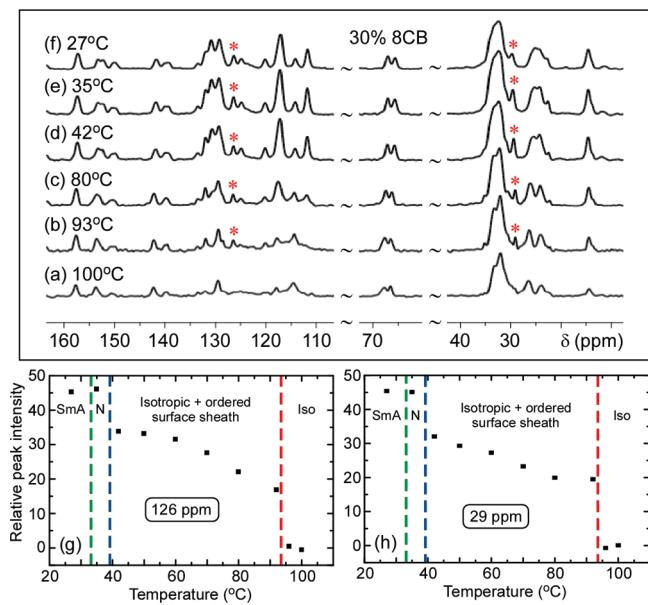


Figure 3. CPMAS NMR spectra of $c = 30\%$ 8CB/NOBOW mixture at different temperatures. (a) At high temperature, there is no contribution from 8CB and the spectrum is the same as that of pure NOBOW.¹⁶ (b) 8CB peaks (indicated by red stars) appear on cooling, indicating the presence of anisotropic 8CB far above the bulk 8CB Iso-N transition. (c–f) 8CB signal persisting all the way down to room temperature. (g,h) Relative intensities of 8CB peaks around 126 and 29 ppm, respectively, obtained by setting the integrated intensity of the NOBOW peaks near 68 ppm to a value of 100 in each scan and then subtracting the high temperature isotropic background. On cooling, the anisotropic 8CB signal first appears at about $T \approx 93^\circ\text{C}$ (red line) as a first order transition, which is slightly higher than the temperature predicted by DSC (around $T \approx 83^\circ\text{C}$). This may be due to the different environment of the NMR sample holder. The 8CB peak intensities increase slightly on further cooling, with a strong enhancement of the NMR signal below the 8CB bulk Iso-N transition temperature ($T \approx 39^\circ\text{C}$, blue line).

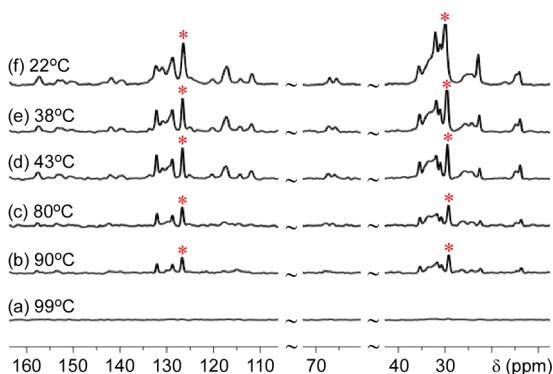


Figure 4. CPMAS NMR spectra of $c = 70\%$ 8CB/NOBOW mixture at different temperatures. (a) At high temperature but well below the NOBOW Iso-B4 transition, the B4 nanofilaments are mobile and float around in the isotropic 8CB solution, resulting in no NMR signal either from 8CB or from NOBOW. (b) At slightly lower temperature, the B4 filaments become more rigid and both B4 and 8CB peaks (the latter marked with red stars) appear. (c–f) On further cooling, both the B4 and 8CB signals become more intense.

mobile, floating around in the 8CB medium, with no orientational order. As the sample is cooled and the B4 filaments become more rigid, the NOBOW signal begins to appear, together with 8CB peaks (Figure 4b–f). As before, we observe 8CB peaks in the

CPMAS NMR spectra at temperatures far above the bulk 8CB Iso-N transition temperature, confirming the pretransitional orientational ordering of 8CB by the B4 filaments. The simultaneous appearance of the 8CB and NOBOW signals on cooling indicates a strong dependence of 8CB prealignment on the presence of the B4 filaments.

In contrast to the case of pure NOBOW, where smectic layer edges are seen in FFTEM images of the helical nanofilaments (right inset, Figure 5a),¹⁰ no layer edges are visible in the mixtures with 8CB (Figure 5a, magnified in the left inset), consistent with the idea that each B4 filament in the mixture is coated by an aligned layer of 8CB (Figure 5b), with the 8CB molecules adhering to the filament at some fixed orientation relative to the local NOBOW smectic layering. We can use the latent heat data to obtain a quantitative estimate of the thickness of the ordered 8CB coating. We approximate the helical B4 filaments as cylinders and assume that only 8CB in a thin layer around each filament is prealigned (Figure 5b). We expect that a substantial fraction of the 8CB can be prealigned because the surface area to volume ratio of the B4 filaments is large ($\approx 10^8 \text{ m}^{-1}$). Assuming that the latent heat release per 8CB molecule is the same for molecules orientationally ordering at the nanofilament surface or becoming nematic in the bulk liquid crystal, the ratio of $\Delta H_{\text{prealign}}$, the latent heat release at the prealignment transition, to $\Delta H_{\text{I-N}}$, that of the bulk 8CB Iso-N phase transition, as a function of 8CB concentration c depends only on the relative volumes of the surface (red region) and bulk (blue region) 8CB:

$$\Delta H_{\text{ratio}} = \frac{\Delta H_{\text{prealign}}}{\Delta H_{\text{I-N}}} = \frac{a(1-c)}{c-a(1-c)}$$

where

$$a = \frac{\rho_{\text{8CB}}}{\rho_{\text{NOBOW}}} \left(\frac{r_{\text{total}}^2 - r_{\text{NOBOW}}^2}{r_{\text{NOBOW}}^2} \right)$$

The best fit to the ratios obtained by DSC at different 8CB concentrations is $a \approx 0.29$, shown in Figure 5c. Assuming similar liquid crystal densities ($\rho_{\text{NOBOW}} \approx \rho_{\text{8CB}} \approx 1 \text{ g/cm}^3$) and taking a typical bare filament radius measured from FFTEM images ($r_{\text{NOBOW}} \approx 18 \text{ nm}$), we obtain $r_{\text{total}} \approx 20.4 \text{ nm}$, implying that 8CB is prealigned in a sheath about 2.4 nm thick around the nanofilaments. Several factors may cause this simple model to underestimate the thickness of the prealigned 8CB sheath. First, the aggregation of filaments, as seen in Figure 5a, reduces the overall exposed filament surface area and thus reduces the measured $\Delta H_{\text{prealign}}$. Second, the orientational ordering of the 8CB may well occur inhomogeneously on the nanofilaments, given that the chemical potential of the smoothly helixing smectic ribbon surfaces are different from that of the exposed layer edges. Finally, we see from Figure 1c that the latent heat sum $\Delta H_{\text{prealign}} + \Delta H_{\text{I-N}}$ in the mixtures (red stars in Figure 1c) is noticeably smaller than $\Delta H_{\text{I-N}}$ of pure 8CB Iso-N transition, implying that the prealignment latent heat release per molecule is in fact smaller than that of the bulk Iso-N transition.

The elevated temperature of the prealignment indicates that the 8CB/NOBOW surface interaction is strong, with its appearance as a transition over a rather narrow temperature range implying that a well-defined interfacial complex is being formed. Although the prealignment can basically be viewed as the coating of a cylindrical filament by a uniform layer of 8CB, in actuality the NOBOW filaments present two quite distinct surfaces to the 8CB, the layer surfaces S and the layer edges E, indicated in Figure 5b.

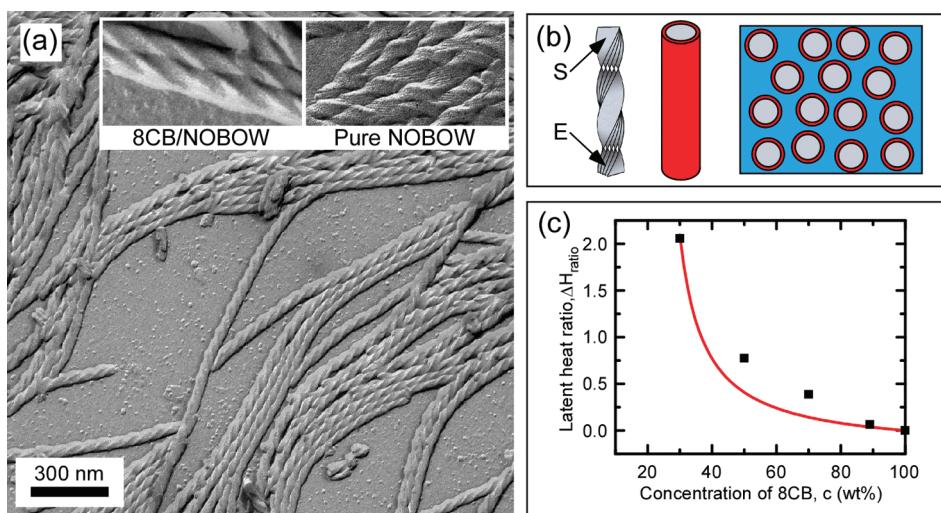


Figure 5. Structural model for the prealignment of 8CB by NOBOW B4 helical nanofilaments. (a) FFTEM image of $c = 75\%$ 8CB/NOBOW mixture quenched at $T \approx 37^\circ\text{C}$ and then fractured at $T \approx -140^\circ\text{C}$. The image shows helical filaments of the NOBOW B4 phase near the glass surface (magnified in the left inset). No layer edges are visible, suggesting that the filaments are smoothly coated with 8CB, in contrast with pure NOBOW (right inset), where layer edges are easily identified. (b) In our model, the filaments are approximated as cylinders (gray region), with prealigned 8CB forming a thin sheet around each cylinder (red region) and the rest of the 8CB being isotropic (blue region). (c) Analysis of the latent heat ratios of prealigned to bulk 8CB Iso-N transition, $\Delta H_{\text{ratio}} = \Delta H_{\text{prealign}} / \Delta H_{\text{I-N}}$, as a function of 8CB concentration implies that a 2.4 nm thick layer of 8CB is prealigned around each filament.

Since these surfaces most likely have very different adsorption characteristics for 8CB, it is probable that only one surface subset, the S or the E, is involved in the prealignment. A requirement for the prealignment to occur as a distinct transition is that the adsorption surface have a well-defined, repeating nanostructure. Figure 5a shows that the filaments grow in a very regular way, suggesting that they provide an appropriate transition substrate. As noted above, the fact that the layer edges of filaments of pure NOBOW are visible in the FFTEM image but not in those of filaments of a NOBOW/8CB mixture (inset, Figure 5a) may indicate that the prealignment is occurring on the layer edges, a mode that would be consistent with the strong adsorption of 8CB on aromatic graphite¹⁷ and polyimide¹⁸ surfaces. On the other hand, it is well-known that smectic layers at interfaces are molecularly smooth and exhibit a wide variety of surface induced phase transitions, including the formation of smectic layers at the isotropic–air and isotropic–solid interfaces. At this point, however, the precise molecular adsorption mechanism in the prealigned layer is not known. The prealigned 8CB sheath might resemble liquid crystal films at the air–water interface^{19–22} or prewetting films of 8CB on silicon substrates,^{23,24} where a smectic-like trilayer organization, comprising a tilted, polar monolayer of 8CB with a thickness of 8 Å, covered by a 32 Å bilayer, is energetically favored, even in the isotropic phase.

Alternatively, the nanofilament layer edges, clearly visible in the FFTEM images of pure NOBOW, should present a highly anisotropic organic surface to the surrounding 8CB molecules, similar to that found on rubbed polymer surfaces commonly used to align liquid crystals. Such surfaces impose planar alignment of the liquid crystals and induce nanometer thick aligned surface layers in the isotropic phase.^{25,26}

Conclusion

In summary, binary mixtures of 8CB and NOBOW can be well understood in terms of nanophase separation, with the 8CB filling the interstitial volume in the dilute networks of NOBOW B4 helical nanofilaments. Pretransitional orientational ordering of 8CB far above its bulk Iso-N transition has been unambiguously verified by NMR spectroscopy. Due to the relatively large surface area of the NOBOW filaments, a large fraction of 8CB is prealigned at elevated temperature. The short-range interactions between the 8CB molecules and the B4 filament surface leads to the formation of a thin film of orientationally ordered 8CB adsorbed to each helical nanofilament.

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Supporting Information Available: Additional figures showing DSC results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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