Soft Matter

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/softmatter

Chiral Dopants and the Twist-Bend Nematic Phase – Induction of Novel Mesomorphic Behaviour in an Apolar Bimesogen.

Craig T. Archbold, Edward J. Davis, Richard J. Mandle, Stephen J. Cowling, John W. Goodby

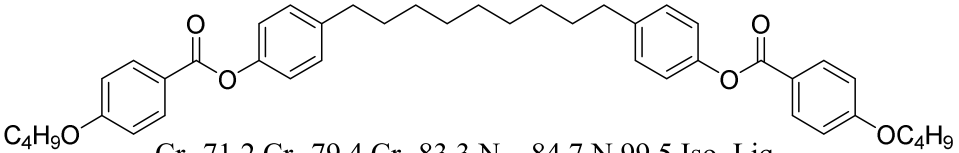
Abstract

Herein were report studies on a bimesogen that exhibits a chiral twist bend nematic phase when doped with small weight percentages of a chiral material and a partial phase diagram constructed. At low concentrations a wide temperature range blue phase is observed, whereas at higher concentrations an additional ‘nematic-like’ mesophase was discovered at a lower temperature than the twist-bend nematic phase. In addition to an apparent isotropic-"isotropic" transition, the doped materials also exhibited a weakly birefringent phase upon annealing in the isotropic liquid phase, implying pretransitional behaviour in the same vein as that seen for TGB phases. When confined in a planar aligned cell, the N_{TB} phase exhibited two domains that alternated between light and dark with rotation of the sample stage, as well as the application of an external electric field. Upon the addition of a chiral dopant one of these domains was eliminated, leading to their assignment as twist domains of opposite handedness.

Keywords: Twist-Bend Nematic, Dimer, Chiral

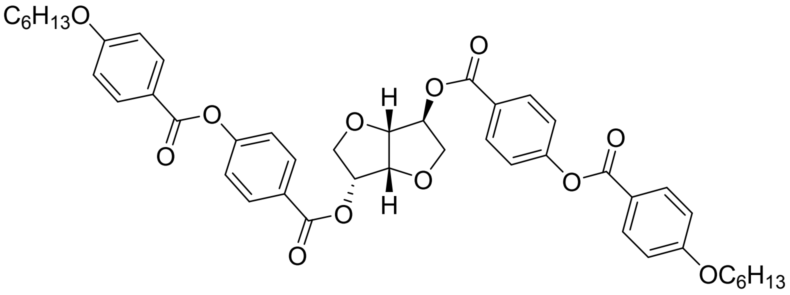
Introduction

In recent years there has been a significant quantity of research conducted into the properties of liquid crystalline materials of unusual topology, particularly bimesogens, possessing a bent molecular architecture. [1-8] This interest stems primarily from the propensity for these materials to exhibit the so-called twist bend nematic (N_{TB}) phase. The structure of this phase is still a topic of debate, however the most generally accepted model is one of a heliconical structure, as presented by Dozov in 2001. [9] In this model, upon transition into the N_{TB} phase, the nematic phase exhibits a spontaneous twist-bend deformation, making it difficult, if not impossible to fill the space within the phase while maintaining a conventional nematic structure. The packing efficiency in the phase is therefore maximised by the adoption of a helical arrangement of the molecules. The structure and properties of this phase have been probed *via* a broad range of experimental techniques including polarised optical microscopy (POM), calorimetry, X-ray diffraction, dynamic light scattering (DLS), electron spin resonance (ESR), freeze-fracture transmission electron microscopy (FFTEM), electro-optic studies, and variable temperature ^{2}H NMR spectroscopy deuterated materials. [1-8, 10-19] Furthermore the influence of molecular structure on the occurence of the N_{TB} phase has recently been an active area of study. [20-25]. Additionally, experimental evidence is at odds with the hypothetical heliconical structure of the N_{TB} phase and a number of alternative models governing either the bulk phase or local structure have been proposed. [26-29] Until now there has been limited study involving the introduction of chirality into a material exhibiting this phase. [8,21] In this work we investigate the effects of mixing a liquid crystal dimer confirmed to exhibit the N_{TB} phase (compound **1**, Figure 1), [20] with a novel chiral dopant (compound **2**, Figure 2), and the novel mesomorphic behaviour exhibited by these mixtures. Further we discuss the nature of these effects and how they serve to further our understanding of the nature of the N_{TB} phase.



Cr_1 71.2 Cr_2 79.4 Cr_3 83.3 N_{TB} 84.7 N 99.5 Iso. Liq.

Figure 1: Structure and transition temperatures (°C) of the N_{TB} material nonane-1,9-diylbis(4,1-phenylene) bis(4-butoxybenzoate) (Compound **1**).



Cr 141.66 (SmA 137.6) Iso

Figure 2: Structure and transition temperatures (°C) of the chiral dopant (Compound **2**).

Experimental

Compound **1** and 1,9-bis(4-cyanobiphenyl)nonane (CB9CB) were prepared as described previously. [20,27] Full experimental details including the synthesis of compound **2** and instrumentation used in this work are presented in the ESI to this article.

Results and Discussion

Thermal behaviour of compound 1

Compound **1** exhibits enantiotropic nematic and N_{TB} phases in addition to several crystal to crystal transitions. When examined by POM between untreated glass substrates the nematic phase of compound **1** exhibits a typical *schlieren* texture, with both 2- and 4-brush singularities (Figure 3a). Further cooling of the sample results in a transition into the lower temperature phase, which exhibited the blocky, broken-fan like texture (Figure 3b) that is typical of the N_{TB} phase.

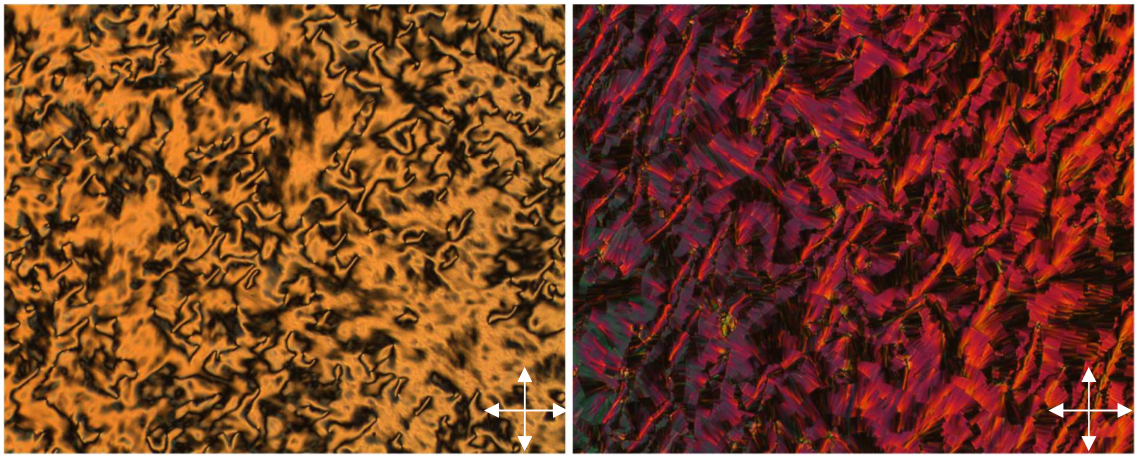

a) b)

Figure 3: Photomicrograph showing the nematic (a) and N_{TB} (b) phases of compound **1** taken at 97.4 °C and 83.0 °C respectively (x100). Both textures were obtained by cooling at 0.1 °C min^{-1}.

The assignment of the lower temperature phase was confirmed via miscibility studies with a known N_{TB} material 1,9-di-(″-cyanobiphenyl-4-yl)nonane (CB9CB). The lower temperature phase of compound **1** was found to exist for all mixtures with CB9CB, confirming the assignment of the phase as the N_{TB} phase; this is presented graphically in Figure 4.

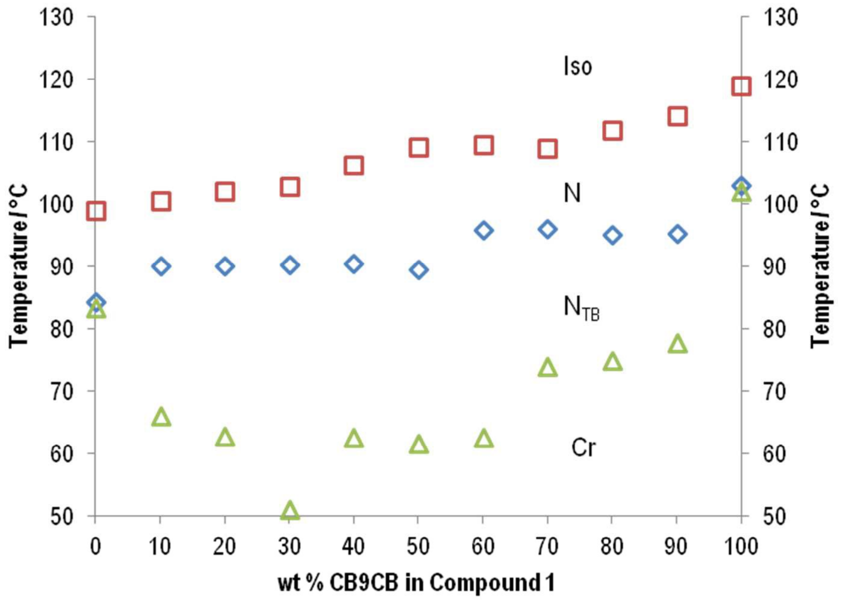


Figure 4: Gibbs phase diagram for binary mixtures (wt%) of compound **1** with CB9CB.

Mixtures of compound 1 with a chiral dopant (compound 2).

A series of mixtures of compounds **1** and **2** were prepared, ranging in concentration from 1 wt % to 10 wt % of compound **2** with compound **1** (Table 2). The thermal behaviour of the mixtures is shown schematically below in Figure 5.

Mixture	wt % compound **2** in compound **1**
M1	0.9
M2	2.1
M3	4.7
M4	5.2
M5	5.4
M6	5.5
M7	6.5
M8	7.1
M9	8.4
M10	9.8

Table 1: Concentrations of compound 2 in compound 1 for the mixtures used in this work.

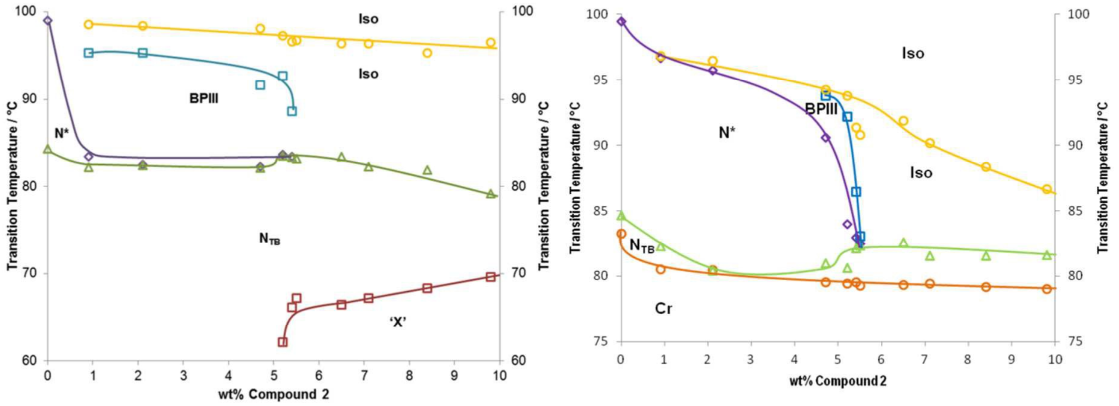


Figure 5: Partial phase diagram for binary mixtures of compounds **1** and **2**. Data obtained on both heating (right) and cooling (left). Crystal-crystal transitions have been omitted for clarity. Raw data is presented in Tables i and ii, in the supporting information to this article.

It can be seen from Figure 5 that the introduction of the chiral dopant (compound **2**) has a marked effect on the mesomorphic behaviour of compound **1**. The first and most obvious effect is the large destabilisation of the nematic phase upon the addition of even low concentrations of dopant, with the phase range decreasing by 17 °C upon the addition of just 0.9 wt % of compound **2**. The addition of this small amount of dopant is also sufficient to form a blue phase, in this case blue phase III (BPIII), persisting over a large temperature range (≈12 °C), this is consistent with results obtained by others using bent materials that do not exhibit the N_{TB} phase, wherein the introduction of chirality into the material resulted in blue phases ranging up to and in excess of 30 °C. [30-33] Due to this the clearing point of mixture is actually similar to that of the neat compound **1**, despite the significantly lower thermal stability of the nematic phase. The stability of this BPIII stays relatively constant until 4.7 wt % of compound 2 (**M3**) at which point it rapidly falls off, disappearing entirely by 5.5 wt % (**M6**). This decrease in BPIII stability occurs concurrently with the lowering of the chiral nematic range, as the presence of the chiral nematic phase below it is essential to the formation of BPIII. Supporting this is the fact that both the BPIII and the chiral nematic phase cease to be observed at the same concentration of compound **2.** Identification of this blue phase as BPIII was made *via* POM. Upon cooling from the isotropic liquid a weakly birefringent blue texture (Figure 6) was observed, even upon slow cooling (0.1 °C min^{-1}), no domain or grain boundaries, nor platelets were seen to form, confirming this as BPIII.

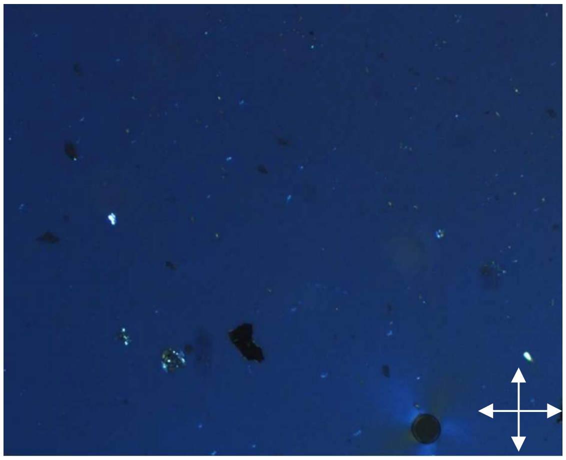


Figure 6: Photomicrograph showing the BPIII texture of mixture **M3** (5.4 wt %) at 93 °C. Sample was cooled at 0.1 °C min^{-1} (x100).

Interestingly, the thermal stability of the N_{TB} phase remains almost constant as a function of dopant concentration. Consequently, mixtures containing between 6 and 10 wt% of compound **2** exhibit a direct transition from the isotropic liquid to the N_{TB} phase without mediation by the nematic, chiral nematic phase or blue phase. This is a novel phase sequence in the field of liquid crystals and such a phase sequence allows observation of the natural texture of the N_{TB} phase which was found to separate from the isotropic liquid in the form of circularly arranged focal-conic domains (Figure 7) in a similar manner to the texture obtained when the phase is grown in from a nematic phase.

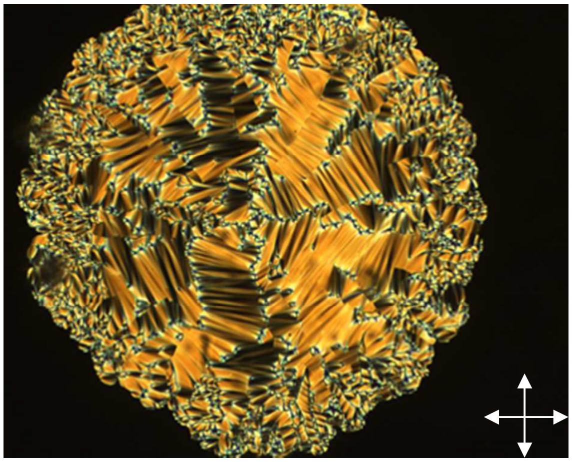


Figure 7: Photomicrograph showing the direct Iso-N_{TB} transition of mixture **M10** (9.8 wt %) at 80.3 °C. Sample was cooled at 0.1 °C min^{-1} (x100). The small optical discontinuities, shown as crosses, are diagnostic for the formation of focal-conic defects indicative of a

long range repetitive structure. The circular growth is indicative of the bend of the N_{TB} phase.

On cooling from the isotropic liquid, the mixture containing 9.8 wt% of compound **2** from the isotropic liquid appears to simply transform from the isotropic to the N_{TB} phase. However, when the mixture is held at, or slightly above the Iso-N_{TB} transition temperature weakly birefringent regions were observed to nucleate. Upon annealing the mixture slightly (≈ 0.2-0.5 °C) above the Iso-N_{TB} transition temperature, a weakly birefringent defect texture forms across the entire sample. This defect texture takes the form of large blue platelet like regions, which grow in individually before beginning to coalesce (Figure 8).

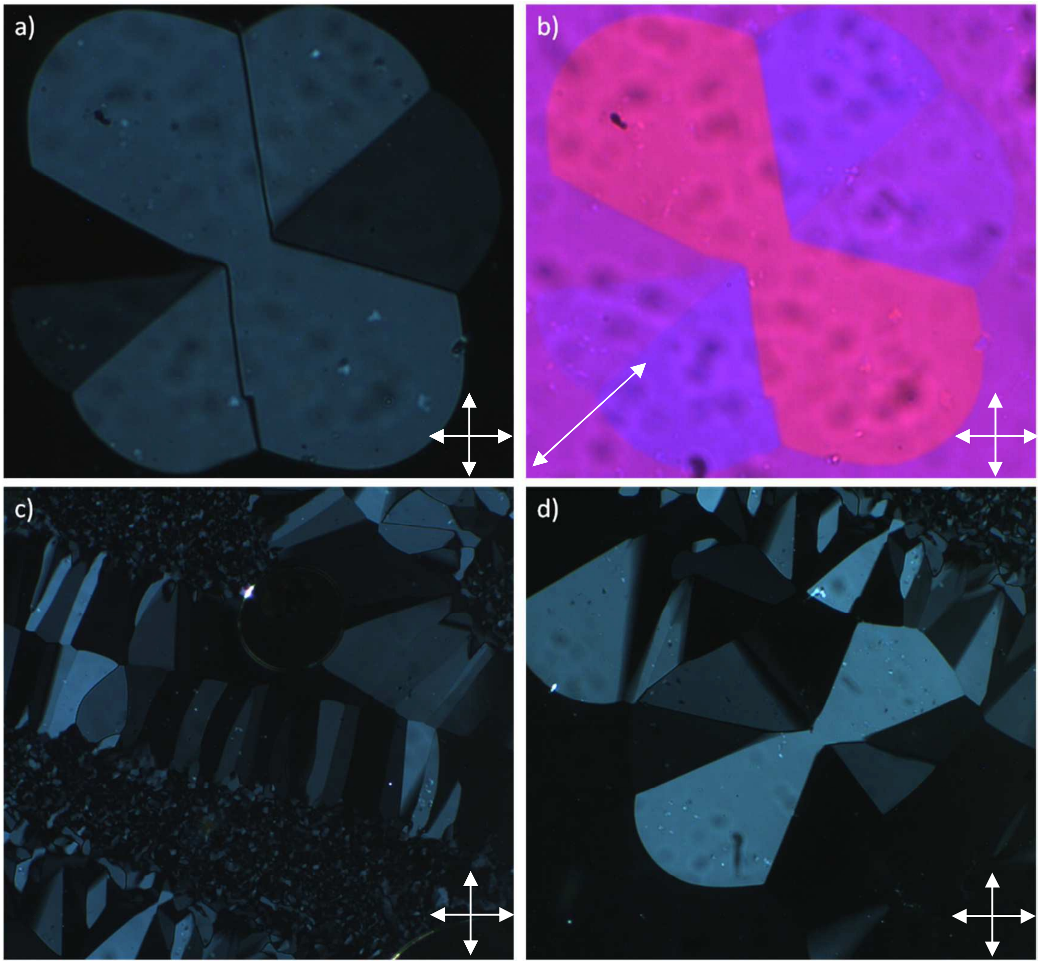


Figure 8: Photomicrographs (a-d) of the "platelet" phase observed upon annealing the mixture containing 9.8 wt% of compound **2** at 80.6 °C in the isotropic liquid. Photomicrograph (b) was taken with a quarter waveplate inserted into the microscope. All images were obtained at x100 magnification.

When the sample was cooled further a transition to the N_{TB} phase occurred at the same temperature as the Iso-N_{TB} transition temperature observed upon faster cooling, inferring a degree of kinetic control in the formation of the "platelet" phase. Upon mechanical shearing of this phase the mixture reverted to the optically extinct texture of the isotropic liquid, however upon annealing at the same temperature for another 2 hours the platelet like defect texture reformed. The textures exhibited by the "platelet" phase show a similarity to the natural texture of the smectic F phase. [37] This could be indicative of this phase possessing a hexagonal organization, and also possibly a degree of long-range order.

Calorimetric Studies

In order to further probe the thermal behaviour of the mixtures in Table 2, DSC studies were carried out. DSC traces for each of the mixtures are given in Figure 9. For mixtures **M1-M5** (0.9 – 5.4 wt %), all of which exhibited the phase series Iso-BPIII-N*-$N_{TB,}$ the nematic to N_{TB} transition is first order, the N* transition occurs nearly simultaneously with the N_{TB} transition and is thus masked by the N_{TB} peak. The thermograms obtained for **M6-M10** (5.5 – 9.8 wt%), however, were more unusual. In all mixtures a clearly defined first order transition for the Iso-N_{TB} transition was observed. Conversely there was no peak observed in the thermogram for mixture **M10** (9.8 wt%) corresponding to the emergence of the "platelet" phase shown in Figure 8, further supporting the theory that this phase transition is primarily kinetically controlled, and that the sample must be annealed in order for this phase to emerge. Such behaviour suggests that the phase could be an aggregate phase rather than a true thermodynamically stable phase of matter. Interestingly, across the entire range of mixtures (**M1-M10**) a thermally reproducible peak occurs in the region of 99-95 °C. This temperature ranges from ≈ 4 °C to over 10 °C above the clearing point observed by microscopy. At these temperatures, only an optically extinct texture is exhibited at these temperatures. Seemingly, this is a transition between two isotropic fluids as is sometimes observed for frustrated systems that exhibit TGB phases and entangled or disentangled flux phases in the liquid state. [34,35] The observation of this transition above the N_{TB} phase therefore perhaps suggests some common features between these phases.

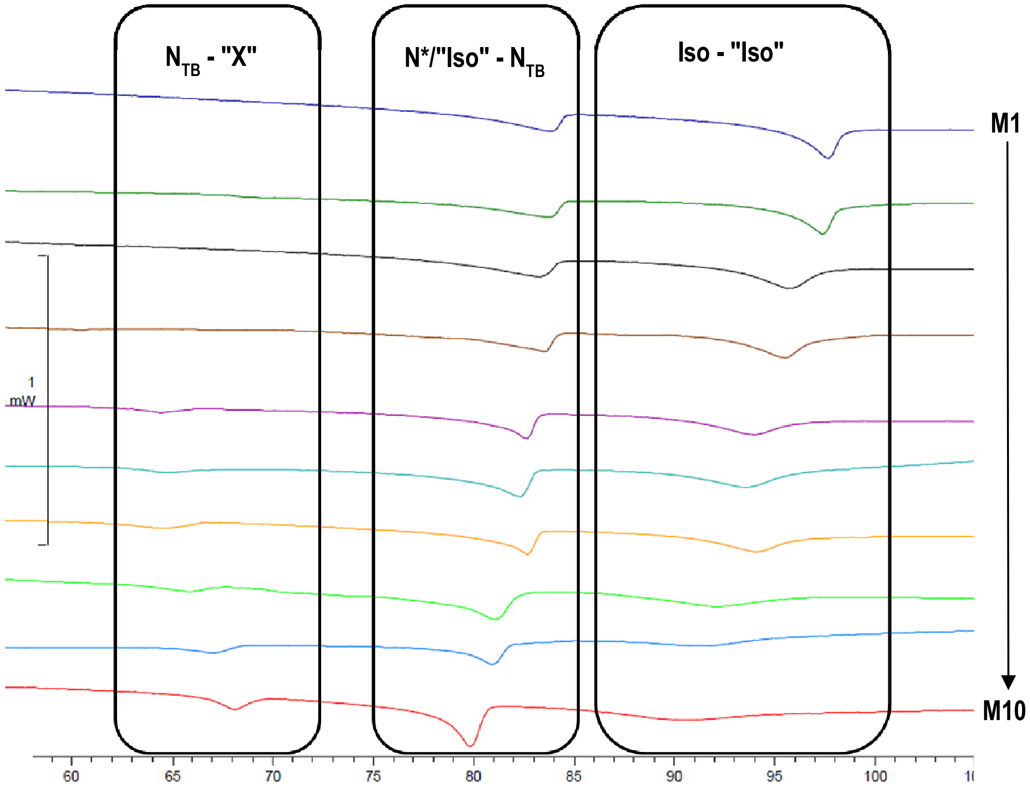


Figure 9: Plot of DSC traces (heat flow [mW] vs. temperature [°C], 10 ^{o}Cmin^{-1}) on cooling for varying concentrations of compound **2** in compound **1.**

Due to the kinetic nature of the transition to the "platelet" phase a series of calorimetric measurements were carried out on mixture **M10** at various scan rates (Figure 10The onset of the peak associated with the Iso-Iso transition was seen to shift with decreasing cooling rate, whereas the transition to the N$_{TB}$ phase, which is believed to be predominantly thermodynamically controlled, remains visible and the onset remains unchanged. This shift in the Iso-Iso onset temperature is indicative of a phase transition that is governed by kinetic processes, as would be expected for a phase composed of aggregates.

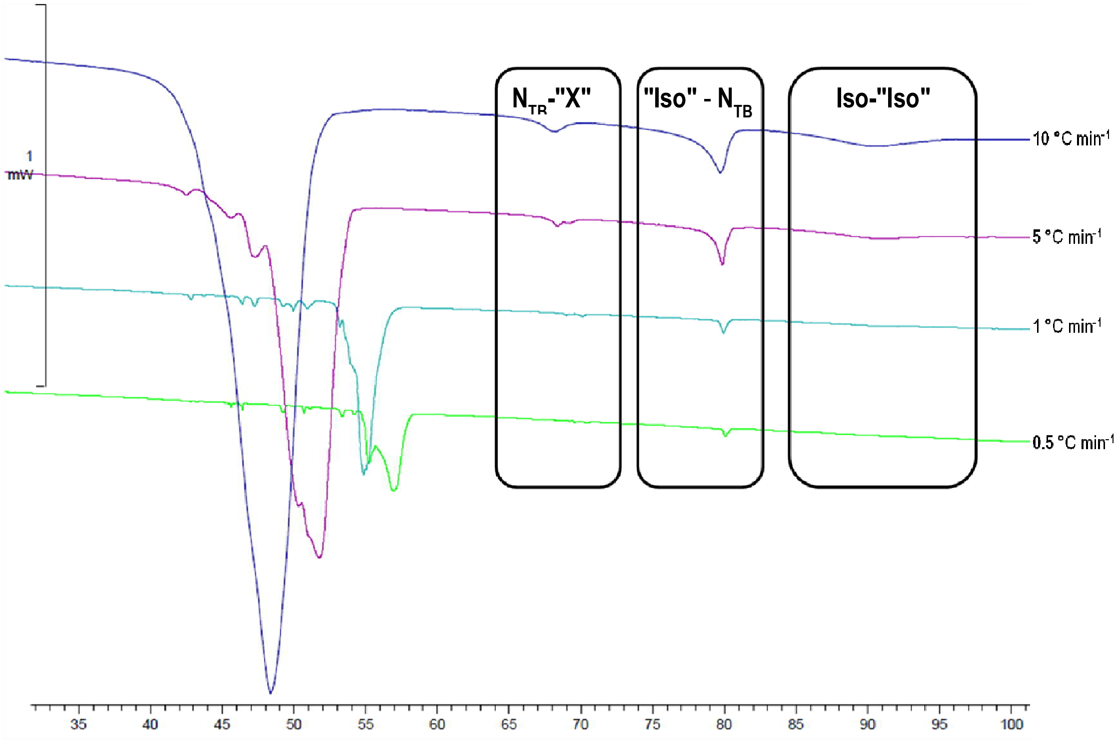


Figure 10: Plot of DSC traces (heat flow [mW] vs. temperature [°C], 10 ^{o}Cmin^{-1}) on cooling for mixture **M10** at various cooling rates.

In the thermograms of mixtures **M4-M10** a monotropic transition to a lower temperature (“X”) mesophase is observed below the N_{TB} phase. Upon investigation of this phase using POM (with rapid cooling) a transition front was clearly seen to sweep across the sample, leaving a texture for the “X” phase that is very similar to that of the N_{TB} with only a slight change in the appearance of the defects and a change in birefringence separating the two (Figure 11). On cooling from the N_{TB} phase into a smectic mesophase there is typically no paramorphosis, [20,25] therefore it seems unlikely this can account for the similarity between the textures of the N_{TB} and ‘X’ phase.

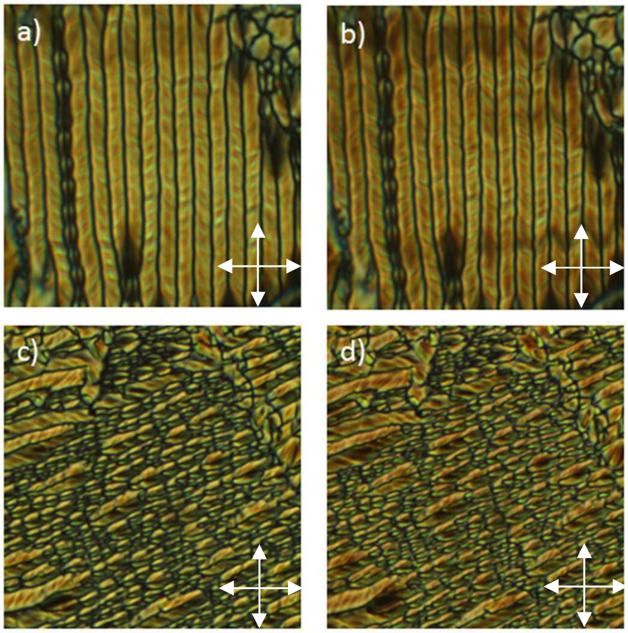
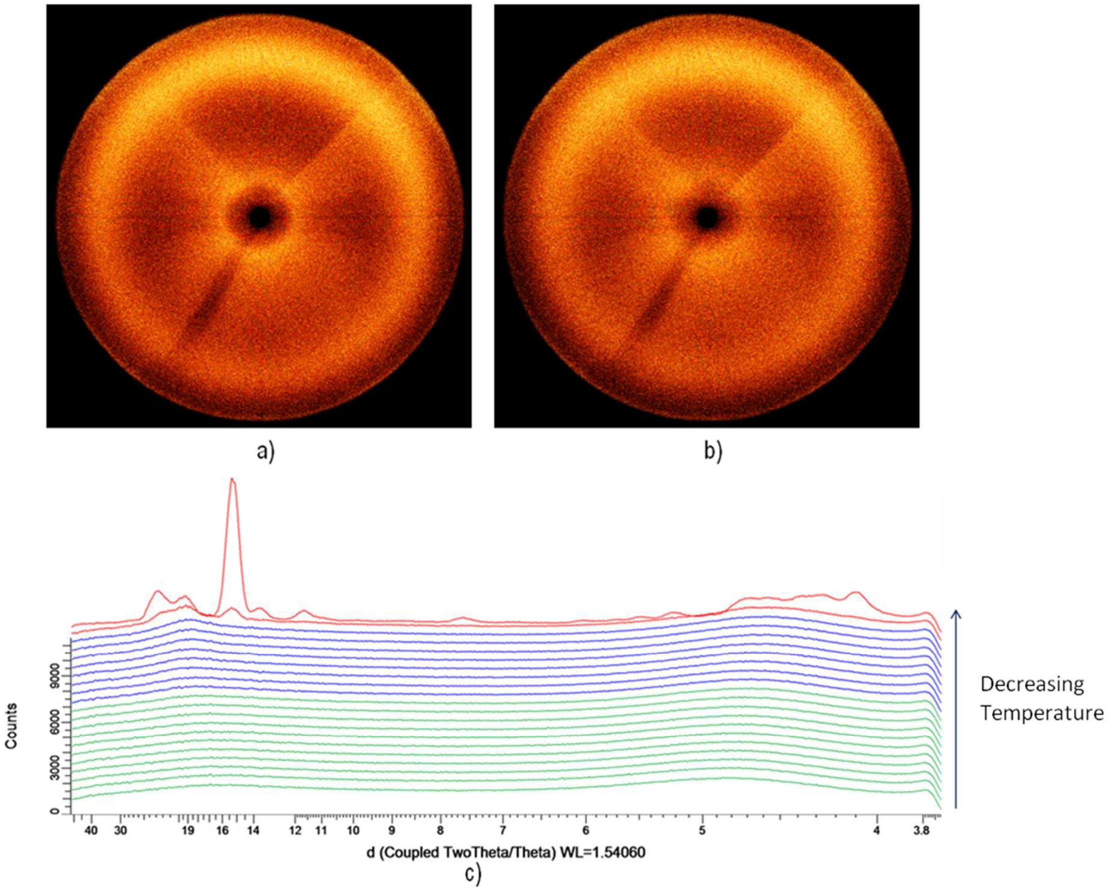


Figure 11: Photomicrographs comparing the optical texture of the N_{TB} phase of **M10** (9.8 wt%) (a, 71.1 °C and c, 70.2 °C) and the lower temperature ‘X’ phase (b, 64.9 °C, and d, 64.0 °C). (x100)

X-ray diffraction studies

Small angle X-ray scattering experiments were employed in order to study the isotropic-"isotropic" transition and lower temperature ‘X’ phase. X-ray diffraction patterns were taken across a range of temperatures from the isotropic liquid to the crystalline solid. A summary of the data obtained is presented in Figure 12.



a)

b)

c)

Figure 12: Two dimensional X-ray diffraction patterns obtained for mixture **M10** (9.8 wt% of compound **2** at; a) 71 °C in the N_{TB} phase, and b) 95 °C in the "isotropic" phase. c) A plot of d spacing as a function of temperature with measurements taken every 3 °C from 116 °C – 54 °C.

As shown by the data presented in Figure 12 - b, mixture **M10** remains isotropic when cooled to 95 °C, 1.5 °C below the temperature at which the event takes place in the DSC thermograms. This suggests that the event is indeed a transition between two isotropic phases, rather than a transition to a nematic-like mesophase. The possibility that the isotropic phase is cubic was discounted *via* XRD data obtained at larger 2θ angles. The lack of any ordering present even in these measurements lends support to the assignment of the transition as a liquid-liquid transition. The lack of any discernible change in diffraction pattern when cooling past the temperature at which the "platelet" phase occurs also serves to discount the possibility that this is the smectic F phase. When mixture **M10** is further cooled (to 71 °C) a relatively sharp scattering ring was seen to form in the small angle region of the diffraction pattern as well as a diffuse ring in the wide angle region, i.e. patterns typical of an unaligned N_{TB} phase. [4,27-28] This supports observations made by microscopy and DSC. Upon cooling to below the N_{TB}-"X" transition there is no discernible change in the diffraction pattern (Figure 13) or in the observed d spacing (18.629 Å).

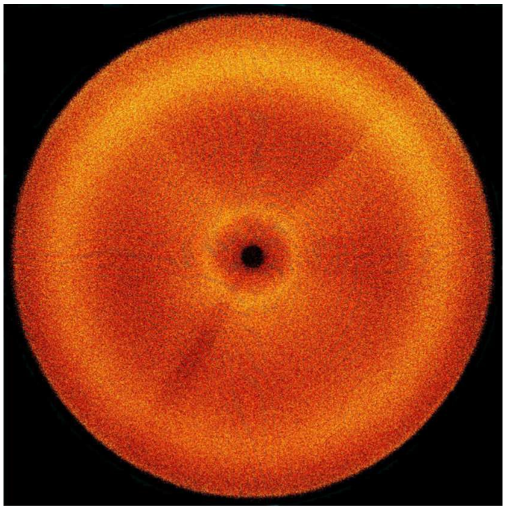


Figure 13: 2D XRD pattern of mixture **M10** (9.8 wt%) in the lower temperature "X" phase (62 °C).

When the phase series (Iso - N_{TB} - "X") is examined in more detail (Figure 14) it can clearly be seen that at 95 °C the material has not undergone transition into an ordered mesophase, further supporting the assignment of the lower "Isotropic" phase as a disordered fluid. This data also allows the difference between the N_{TB} and "X" phases to be more clearly examined, with the "X" phase giving a sharper reflection than the N_{TB} but remaining diffuse enough to discount the possibility of lamellar ordering. The absence of a layered structure indicates that the "X" phase, like the N_{TB} phase, possesses overall 'nematic-like' order leading to the possibility that this "X" phase is, in fact, another deformation of the nematic phase akin to the N_{TB}, but possibly a splay-bend deformation.

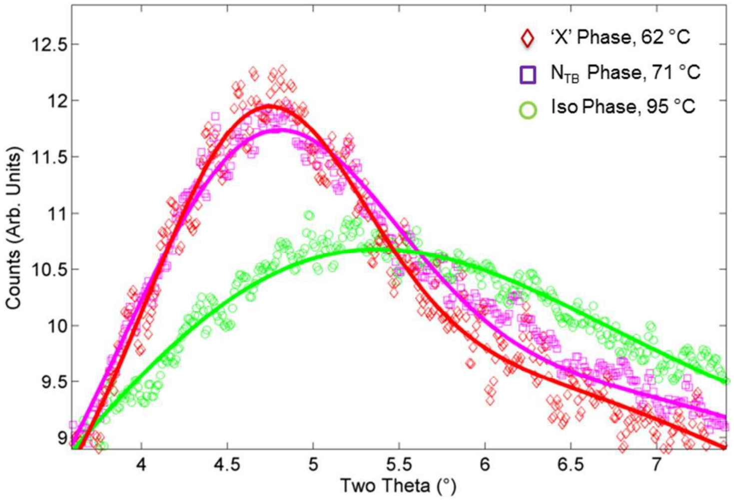


Figure 14: Plot of counts (arbitrary units) vs. two theta (°) for M10 in the lower isotropic (95 °C), N$_{TB}$ (71 °C) and "X" (62 °C) phases. Solid lines are fitted to the data using a 6-term Gaussian distribution. All fits give an R^2 value in excess of 0.99.

Electro-optic Investigations

The behaviour of both the nematic and N$_{TB}$ phases of compound **1** were examined under applied electric fields. For the nematic phase a Fréedericksz transition was observed at low frequency and voltage (< 1 Hz and < 2 V μm^{-1} respectively). Upon cooling into the N$_{TB}$ phase a rope-like texture formed and a reversible electrooptic response was observed with a low applied frequency and relatively high voltage (< 1 Hz and < 20 V μm^{-1} respectively). The angle of switching between opposite domains of the N$_{TB}$ phase was measured to be 3 °. A photomicrograph of the switching process is presented in Figure 15.

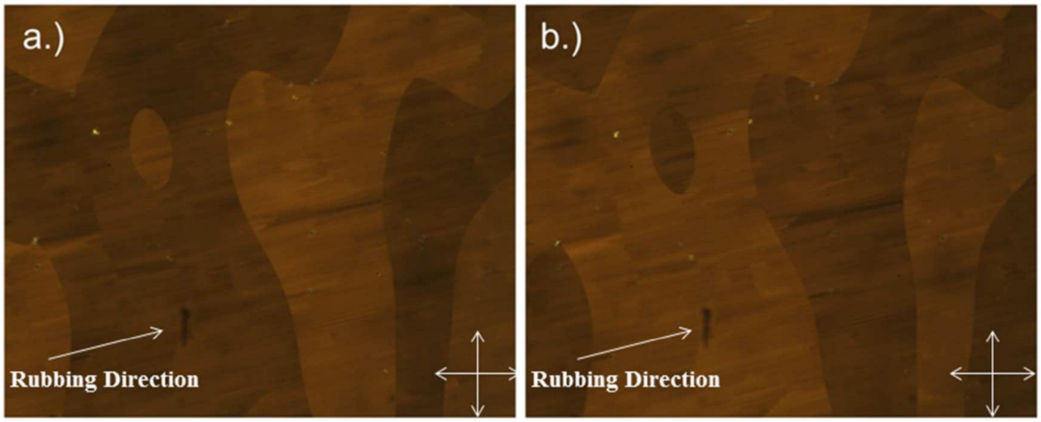


Figure 15: Evidence of opposite switching in the domains of the N_{TB} phase upon application of an electric field. Polarised optical microscope image of **1** in a 5 μm cell with a antiparallel buffed polyimide alignment layer subjected to an electric field (1 Hz, 20 V μm^{-1}, square waveform) at 81 °C. (x100)

The "platelet" phase of mixture **M10** (9.8 wt%) was also investigated *via* electro-optic methods. Under an applied square waveform (12 V μm^{-1}, 1 Hz) the domains of this phase were found to interconvert in terms of light contrast (Figure 16). The angle of switching between opposite domains of the "platelet" phase was found to be 10 ^{0}, significantly larger than that for the twist bend nematic phase, which was measured to be 3 °.

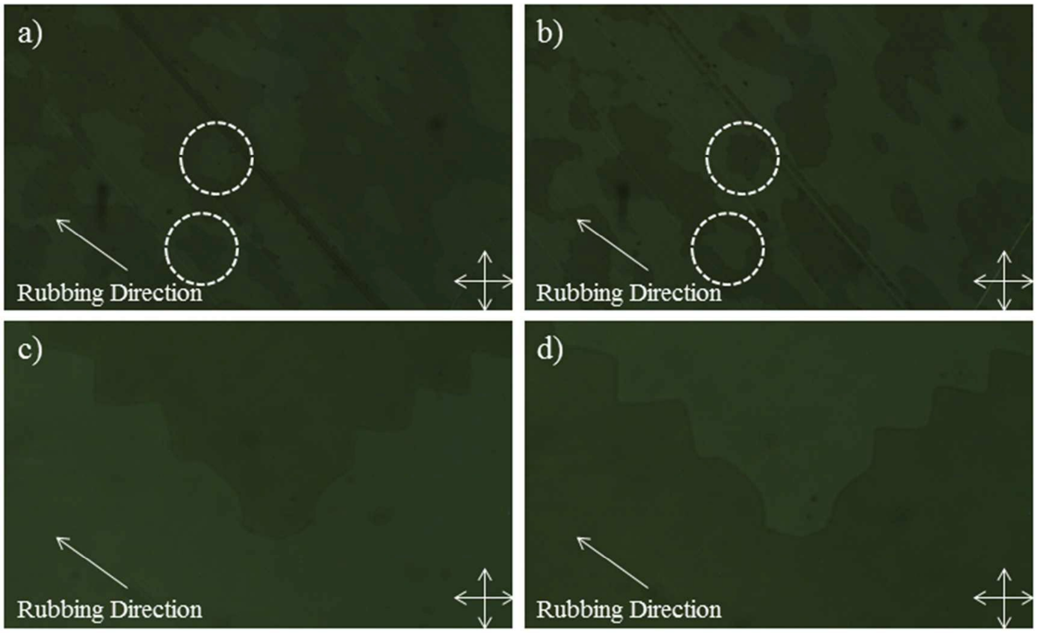


Figure 16: Evidence of opposite switching in the domains of the "platelet" phase upon application of an electric field. Polarised optical microscope images of **M10** (9.8 wt%) (x100) in a 5 μm cell with an antiparallel buffed polyimide alignment layer and subjected to an electric field (1 Hz, 12 V μm^{-1}, square waveform) at 81 °C (a and b) and 81.5 °C (c and d)

This switching process was observed even at voltages of up to, and including, 20 V μm^{-1}, however, when the frequency was increased to 33 Hz (with an applied voltage of 12 V μm^{-1}) the phase was found to undergo a reversible transition to an optically isotropic phase. Upon removal of the field the "platelet" phase was observed to reform. Photomicrographs depicting this reversible, field-induced transition to an isotropic state are given in Figure 17. Once the sample had been annealed large, weakly birefringent domains could be seen (Figure 17a). The application of an electric field (33 Hz, 12 V μm^{-1}, square waveform) to this domain phase resulted in a transition to an isotropic state (Figure 17 – b). Once removed, the domain phase began to regrow immediately (Figure 17 – c) and upon further annealing the domain texture fully regrew (Figure 17 – d). The angle of switching was found to be inversely proportional to the applied voltage, falling to 5^o at the point at which field induced isotropisation occurred.

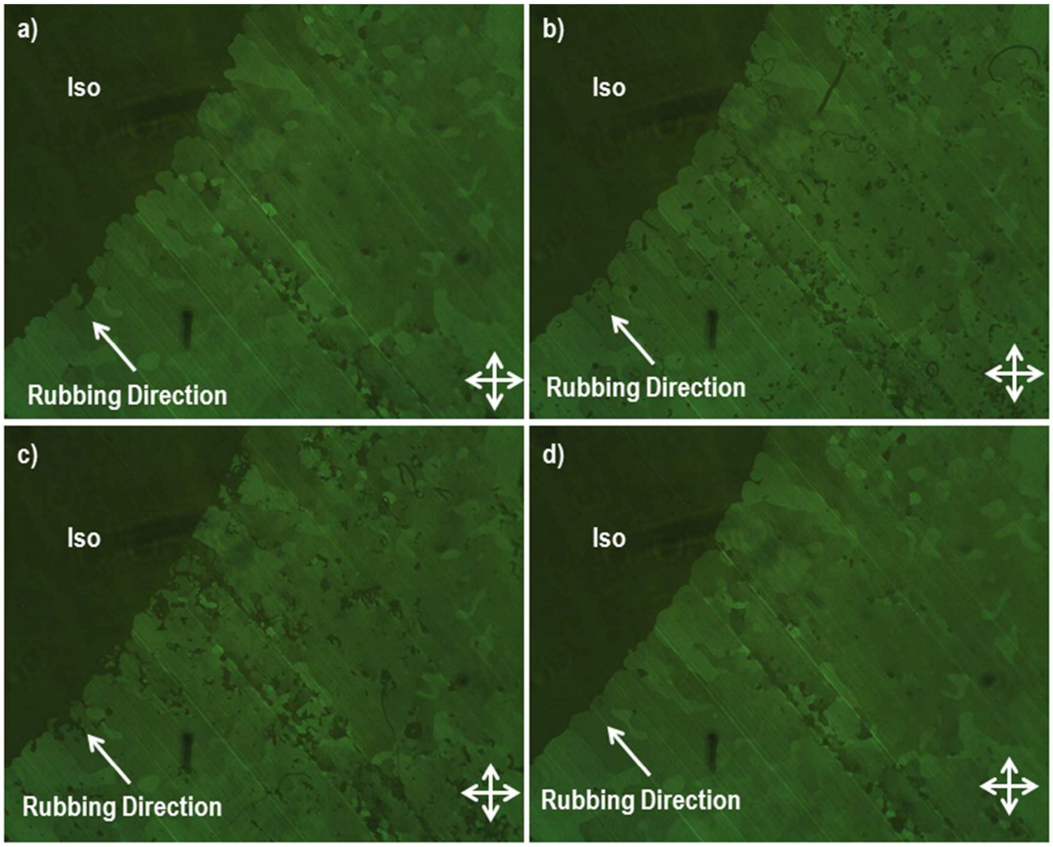


Figure 17: Domains observed (x100) upon annealing the higher temperature phase of **M10** (9.8 wt%) at 81.5 °C: a) no field, b) immediately after application of 33 Hz, 12 V μm^{-1} sq. waveform field, c) immediately upon removal of field, and d) 5 minutes after removal of field.

Conclusion

Binary mixtures between compound **1**, itself an unremarkable twist-bend material, and the chiral dopant **2** have yielded a number of new polymorphisms containing the N_{TB} phase. At all concentrations, isotropic to "isotropic" transitions, reminiscent of those found for materials that exhibit the TGB phases, were observed. This implies the possibility of the N_{TB} phase and TGB phases possessing some degree of structural similarity. It is possible that this phenomenon is not observed in the neat material due to the presence of two twist directions (Figure 15), and that it is necessary to eliminate one of these in order for the transition to occur.

At high concentrations of compound **2** a direct isotropic to N_{TB} transition exists. This observation dispels the idea that the N_{TB} phase relies on the presence of a nematic phase to form. This has allowed the natural texture (i.e. obtained from the isotropic liquid) of the N_{TB} phase to be observed for the first time. As noted previously, the fractal *schlieren* texture often seen in the twist-bend nematic phase is actually paramorphotic rather than being intrinsic to this state of matter. In its natural texture the N_{TB} phase grows in circular domains, with numerous focal conic defects.

When viewed in a planar aligned cell, the N_{TB} phase of compound **1** was seen to exhibit two types of domain that inverted with respect to one another with rotation of the microscope stage, as well as the application of an external electric field. Upon the addition of a chiral dopant one of these domains was eliminated, leading to the assignment as twist domains of opposite handedness.

For mixtures containing higher dopant concentrations annealing slightly above the clearing point (as observed by microscopy) produced large, weakly birefringent domains of a kinetically stable, as yet unknown phase referred to as the "platelet" phase. This phase undergoes a switching process upon application of an electric field at low to moderate frequencies (1V μm^{-1}, <33 Hz), however, applications of higher frequencies or voltages led to a reversible transition to an isotropic liquid. New, and as yet undiscovered, types of blue phases have been predicted to exist in phase sequences containing the twist-bend and/or splay-bend modifications of the nematic phase. [36] The "platelet" phase observed above the N_{TB} phase in mixtures containing between 6 and 10 wt% of compound **2** is possibly such an example of a twist (or perhaps splay) modified blue phase. Conversely this platelet phase also displays a defect texture similar to that of the natural texture of the smectic F phase. [37] The occurrence of the "platelet" phase above the N_{TB}, which is less ordered than the smectic F phase, discounts the possibility of definitive assignment of this phase as smectic F, however due to the similarities in optical texture it can be inferred that the "platelet" phase may exhibit some form of short-range hexagonal ordering. Measurements by DSC at variable scan rates show that the Iso-"Iso" phase transition is kinetically controlled, which implies that the "platelet" phase and the lower "isotropic" phase are, in fact, the same phase, with the texture appearing only on annealing due to the kinetically controlled nature of the phase.

Mixtures with high concentrations of compound **2** also exhibit a lower temperature phase that has, to date, eluded classification by microscopy. The optical texture of this ‘X’ phase is very similar to the N_{TB}

phase save for a small change in birefringence, and is observed only by the passing of a transition front across the sample. From X-ray diffraction we find no evidence of a lamellar structure and as such the phase would appear to have a nematic-like ordering of the constituent molecules. It is possible that this is the predicted splay-bend modification of the nematic phase, however this will require further study which itself requires materials with a superior working temperature range than that afforded by mixtures of compounds **1** and **2**.

Acknowledgements

CTA would like to thank the University of York for award of a doctoral scholarship. The authors also acknowledge the support of the Engineering and Physical Sciences Research Council (EPSRC) *via* grant codes EP/J007714/1 and EP/K039660/1.

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