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Tolane oligomers: Model thermotropic liquid crystals

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The liquid crystalline phases of several rigid-rod, non-polar tolane oligomers are characterized by differential scanning calorimetry and transmitted polarized light microscopy. We determine that a stable nematic phase can be formed at ambient pressure if the molecular axial ratio (length-to-width ratio) is greater than 4·5. A smectic phase forms in addition to the nematic phase if the axial ratio exceeds 6·1. Symmetrical fluorination of the terminal phenyl groups reveals that the liquid crystalline phase behaviour of these rigid rods is highly sensitive to perturbations of the charge distribution along the molecules. Nematic tolane oligomers can exhibit high strength disclinations ($s = \pm 3/2$ and ± 2) in their schlieren textures, and we discuss conditions that promote the stability of these defects.

1. Introduction

Simple derivatives of tolane [Phenyl–C≡C–Phenyl] exhibit several characteristics that make them desirable as components in electro-optical [1, 2] and non-linear optical [3] materials. Furthermore, the intrinsic extended, rod-like nature of the molecules is preserved in longer sequences of *para*-linked phenyl and acetylene residues, so that such molecules resemble closely the rod-like geometry conveniently assumed in the most basic models of a liquid crystal. Unsubstituted tolane oligomers form accessible, stable thermotropic mesophases, and preliminary characterization has shown that an axial (length-to-width) ratio of approximately 4·3 is large enough to sustain nematic order at ambient pressure [4]. In the present paper, we describe the liquid crystalline transitions for a series of such non-polar tolane oligomers with axial ratios in the range 4·5 to 7·3, and we address the critical axial ratio needed to stabilize a smectic phase.

By symmetrically substituting both ends of a tolane oligomer molecule with fluorine in different ring positions, to change the intermolecular forces while not significantly altering the axial ratio, we also explore the effect of charge distribution (soft interactions) on liquid crystalline properties. We confirm that the melting point, clearing point and type(s) of liquid crystalline phase formed can be highly sensitive to the detailed charge distribution, as previously demonstrated for compounds with a terphenyl core [5, 6].

Another aspect of the liquid crystalline state that can be explored experimentally with tolanes, is the stability of microstructural defects. Disclinations in a nematic are characterized in terms of their strength [7]—a measure of the angular range through which the director orientation is perceived to rotate as one follows a closed path around the disclination. To date, the only *monodisperse, single-component* material reported to show disclinations of strength $\pm 3/2$ between homogeneous (glass) surfaces has been a tolane oligomer [8]. This paper shows that stable disclinations of strength ± 2 can also be sustained in a pure tolane oligomer confined between glass surfaces.

2. Experimental

2.1. *Synthesis*

Figure 1 shows the compounds that were characterized in this study. Syntheses for compounds **A**, **B**, **C** and **E** have been described previously [4, 8]. Reagents 4-ethynylbiphenyl and 4,4′-diethynylbiphenyl were prepared by standard techniques: organometallic coupling of the respective halides (bromides or iodides) with a mono-protected acetylene (trimethylsilyl acetylene) was followed by deprotection.

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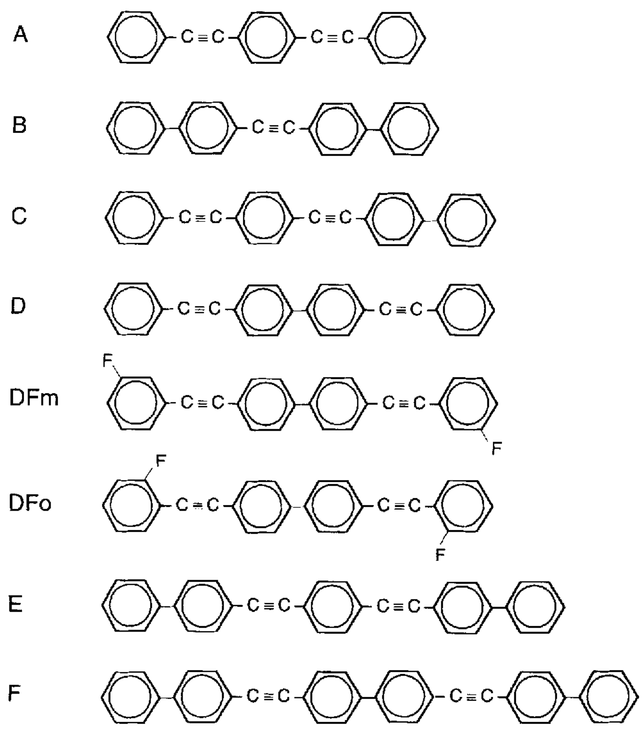

Figure 1. Schematic structures of tolane oligomers.

2.1.1. *Compound **D**: 4,4′-bis(phenylethynyl)biphenyl*

In a 500 ml round bottom flask with stirbar, reflux condenser and nitrogen bubbler was placed 4,4′-dibromobiphenyl (6·24 g, 20·0 mmol), phenylacetylene (6·12 g, 60·0 mmol), triphenylphosphine (0·40 g, 1·5 mmol) and morpholine (100 ml). The resulting solution was warmed and deoxygenated with a stream of nitrogen and then the metal catalysts palladium dichloride (0·035 g, 0·2 mmol) and cupric acetate monohydrate (0·020 g, 0·1 mmol) were added. The resulting mixture was heated at 120°C in an oil bath for six hours and, after cooling to room temperature, the solid precipitate was isolated by suction filtration, washed with morpholine and air dried. The crude product (5·50 g) was taken up in boiling toluene, hot filtered and cooled. The crystalline product was collected and crystallized again in the same fashion to give 4·08 g (57%) of pure product.

Analysis Calculated for $C_{28}H_{18}$: C, 94·88; H, 5·12. Found: C, 95·21; H, 5·20.

(The above synthesis is a variation on previous approaches reported in the literature. Melting temperatures of 253–4°C [9] and 247–9°C [10] were cited without mention of the fact that the material becomes liquid crystalline on melting; these published temperatures bracket our measured value of 251°C.)

2.1.2. *Compound **F**: 4,4′-bis(4-biphenylethynyl)biphenyl*

In a 250 ml round bottom flask with stirbar, reflux condenser and nitrogen bubbler was placed 4,4′-dibromobiphenyl (3·12 g, 10·0 mmol), 4-ethynylbiphenyl (5·35 g, 30·0 mmol), triphenylphosphine (0·40 g, 1·5 mmol) and morpholine (100 ml). The resulting solution was warmed and deoxygenated with a stream of nitrogen and then the metal catalysts palladium dichloride (0·035 g, 0·2 mmol) and cupric acetate monohydrate (0·020 g, 0·1 mmol) were added. The resulting mixture was heated at 130°C in an oil bath for three hours and after cooling to room temperature the solid precipitate was isolated by suction filtration, washed with morpholine, washed with a 1 : 1 mixture of water and ethanol and then air dried. The crude product (2·75 g) was taken up in boiling *N*-methylpyrollidinone, hot filtered and cooled. The crystalline product was collected and crystallized again in the same fashion to give 1·57 g (31%) of pure product.

Analysis Calculated for $C_{40}H_{26}$: C, 94·83; H, 5·17. Found: C, 94·85; H, 5·22.

2.1.3. *Compound **DFm**:*
4,4′-bis(3-fluorophenylethynyl)biphenyl

In a 200 ml round bottom flask with stirbar, reflux condenser and nitrogen bubbler was placed palladium dichloride (0·027 g, 0·05 mmol), cupric acetate monohydrate (0·005 g, 0·025 mmol), triphenylphosphine (0·156 g, 0·20 mmol) and di-isopropylamine (25 ml). The resulting slurry was boiled for 15 minutes and then 4,4′-diethynylbiphenyl (1·00 g, 4·95 mmol), 3-fluoroiodobenzene (4·40 g, 19·8 mmol) and more di-isopropylamine (15 ml) were added. The resulting mixture was boiled for six hours, cooled and the volatile solvent removed by rotary evaporation. The residue was stirred with a mixture of ethanol and water and filtered and the solid residue washed well with ethanol and water and air dried overnight. The residual solid was taken up in boiling toluene with some silica gel and hot filtered. As the filtrate was concentrated by boiling, methylcyclohexane was added. Upon cooling, the product was obtained as a crystalline solid (0·76 g, 39%).

Analysis Calculated for $C_{28}H_{16}F_2$: C, 86·14; H, 4·13; F, 9·73. Found: C, 85·85; H, 4·13; F, 9·41.

2.1.4. *Compound **DFo**:*
4,4′-bis(2-fluorophenylethynyl)biphenyl

This compound was prepared in a similar fashion to the *meta*-isomer in 71% yield.

Analysis Calculated for $C_{28}H_{16}F_2$: C, 86·14; H, 4·13; F, 9·73. Found: C, 85·80; H, 4·08; F, 9·47.

2.2. *Differential scanning calorimetry (DSC)*

A DuPont 1090 system was used to locate possible liquid crystal transitions. Aluminium sample and reference pans were closed with aluminium covers, using a crimper press to obtain a standard (non-hermetic) seal.

Samples with an approximate mass of 10 mg were scanned at 10°C min^{-1} in an environment of dry nitrogen. All DSC temperatures quoted below are onset temperatures.

2.3. *Transmitted polarized light microscopy*

Microscopy was performed to identify the liquid crystalline phases. Specimens were observed with a Leitz Laborlux 12 POL microscope equipped with a Linkam THM 600 heating/freezing stage and PR 600 controller. A long working distance objective (32 × ; numerical aperture 0·4) was used to view microstructures at a resolution of approximately 1·5 µm; the stage effectively restricts the incident light to a parallel beam, precluding Köhler illumination. Heating and cooling rates of 10°C min^{-1} were typical. Occasionally, slower heating rates (1°C min^{-1} to 5°C min^{-1}) were used to facilitate distinction between phases that are stable over a narrow temperature range. Specimens were maintained between glass coverslips (Corning no. 1). Unless otherwise stated, the coverslips were cleaned before use: a rinse in distilled and deionized water was followed by two rinses with acetone. They were then allowed to air dry under a dust cover.

2.4. *Molecular modelling*

Experiments suggest that relative rotation of the phenyl ring planes is associated with an energy barrier of about 2·5 kJ mol^{-1} in free tolane, with a coplanar arrangement of the two phenyl rings being least favorable [11]. The *magnitude* of this barrier is corroborated by calculation [12], though individual algorithms differ in regard to whether they predict the coplanar or perpendicular conformation as being favoured. Above the melting points of the tolane oligomers, the 2·5 kJ mol^{-1} barrier does not present a significant hindrance to internal rotation.

In a condensed phase, packing forces could have a significant effect on internal rotation, given that the energy barrier to rotation is so small. However, molecular dynamics simulations performed on *p*-sexiphenyl show that large torsional librations (±180°) can occur even in the *solid* state at 300 K, at least within molecular segments near the surface of crystals [13]. Since one component of the energy barrier to internal rotation (*ortho*-hydrogen repulsion between adjacent phenyl groups in the molecule) is insignificant in tolane oligomers compared to polyphenylenes, tolane oligomers in the *fluid* state at higher temperatures must also undergo torsional librations through a full ±180° range. Therefore, the tolane oligomer molecules are well approximated as cylinders.

Molecular dynamics calculations [14] have shown that many rigid-rod polymers can have significant flexibility due to molecular bending deformations. However, typical persistence lengths are of the order of 500 Å, i.e. well above the approximately 31 Å contour length of the largest molecule described in the present study (compound **F**). Molecular lengths and diameters for our tolane oligomers are therefore obtained from models that treat the molecules as *rigid* cylinders.

The axial ratios of molecules were measured by building models on a Macintosh IIci computer with Chem3D Plus software (version 3·0; Cambridge Scientific Computing, Cambridge, MA). Energy was minimized according to Chem3D Plus parameters. All lengths and diameters were measured between the centres of atoms.

3. Results and discussion

3.1. *Effect of axial ratio*

The table lists the phase transitions observed for each material. Compound F degrades visibly in the isotropic state, which compromises any transition data collected on subsequent cooling or heating runs. To provide the most consistent basis for comparing all the materials, transitions therefore are quoted for first heating runs performed on as-synthesized material. In addition, cooling data are quoted for compounds **A** and **B** (both of which have clearing points that lie well below the temperature at which degradation becomes apparent).

Figure 2 shows the transition temperatures for the six non-fluorinated materials. For each of these compounds, conjugation and the absence of substituents provides an approximately uniform distribution of electronic charge along the molecules. Therefore, we can expect that geometry (excluded volume, or 'hard' interactions) and not 'soft' interactions will dominate the phase behaviour. The interpolated lines in figure 2 are not intended to represent accurate phase boundaries, as the plotted data include specimens that form a monotropic liquid crystal-

Phase transition temperatures for tolane oligomers.

Material	Axial ratio	Transitions/°C
A	4·45	K 179 I microscopy reveals monotropic behaviour I 172 N 165 K (not resolved by DSC)
B	4·74	K 246 I DSC reveals monotropic behaviour I 244 N 241 K
C	5·41	K 234 N 251 I
D	5·44	K 251 N 271 I
DFm	4·66	K 208 S$_B$ 211 S$_C$ 221 S$_A$ 246 I
DFo	4·66	K 182 S$_B$ 198 N 219 I
E	6·35	K 296 S$_A$ 302 N 347 I
F	7·30	K 326 S$_A$ 338 N (344 I) degradation is significant at apparent clearing point

line phase, and also pertain to both symmetrical and asymmetrical molecules. However, we note that, for a condensed phase of rod-like molecules that are characterized by approximately uniform charge distribution along their length, an axial ratio of 4·5 is large enough to stabilize a thermotropic nematic phase at ambient pressure. A value of 4·3 was previously estimated for this critical axial ratio [4], using less accurate measurements of tolane oligomer dimensions. Figure 2 additionally shows that an axial ratio greater than approximately 6·1 will stabilize a smectic A phase in these materials. The latter observation demonstrates that, while previous theoretical [15] and experimental [16] work indicates a finite length of flexible 'tail' as being needed to enable smectic A formation by a small-molecule mesogen, this is not a universal requirement.

Several theoretical analyses (reviewed in [17]) have sought to predict the critical axial ratio needed for nematic phase formation. Such efforts include lattice models, density functional theories and Monte Carlo simulations. To test the predictions of these analyses, it is necessary to have available a homologous series of molecules that are rod-like, that form accessible liquid crystalline phases, and that are stable to temperatures above the clearing point. The poly(*p*-phenylene)s fulfil only the first of these criteria [18–20]. Advances in recombinant DNA technology (reviewed in [21]) offer the possibility of synthesizing monodisperse rods of controlled length; however, these molecules are lyotropic, and extensive intramolecular hydrogen bonding of long molecules (with correspondingly high axial ratios) is needed to stabilize rod-like conformations. The tolane oligomers described in this paper serve better than either poly(*p*-phenylene) or DNA as model compounds for studies of critical axial ratio. However, the axial ratios that we have determined as necessary for nematic and smectic formation may not be the smallest *possible* values. Smaller minimum values might be obtainable in a series of compounds with lower melting points.

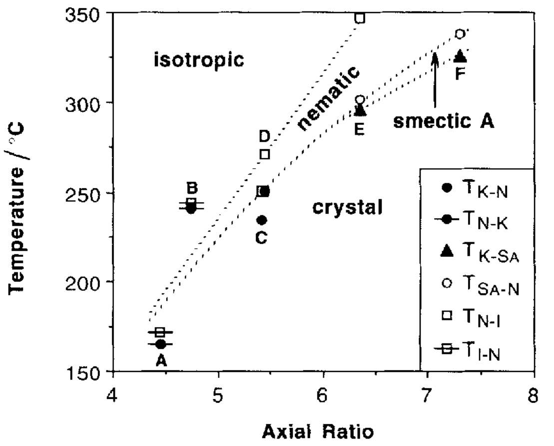

Figure 2. Phase transition temperatures of tolane oligomers. A clearing point for compound **F** is not recorded because this compound shows evidence of degradation in the isotropic state. Interpolated lines should not be regarded as accurate phase boundaries.

Monte Carlo modelling of hard spherocylinders suggests that a stable smectic phase can exist when the axial ratio is slightly greater than 3, and that formation of a nematic phase is possible if the axial ratio exceeds a critical value that lies somewhere between 3 and 4 [22]. Density functional theory of hard spherocylinders with full translational and orientational freedom [23, 24] predicts that stable nematic and smectic liquid crystalline phases can be formed by molecules that have even lower axial ratios, down to a critical value of 2·46. It is not surprising that these calculated limits differ from our values found experimentally: the Monte Carlo model and density functional theory both include density as a variable, which in turn depends on temperature *and pressure*. Simulation of various *real* liquid crystalline polymers that contain no flexible sequences, using (a) molecular mechanics (MM2) routines to assign energy profiles to each rotatable backbone bond, followed by (b) Monte Carlo techniques to assign a rotational angle to each bond at given temperatures, suggests that a critical ratio of persistence length to diameter of 5 is needed to enable a nematic to isotropic transition at ambient pressure [25].

Finally, we note from figure 2 that the rate at which T_{N-I} increases with axial ratio is an order of magnitude less than the rate predicted by a simple lattice model description of nematic phase separation in a system of rod-like particles with orientation-dependent interactions [18].

3.2. *Effect of 'soft' interactions*

It is commonly accepted [17] that 'hard' interactions are the principal cause of molecules ordering into a nematic phase. In such cases, rod axial ratio is the most significant parameter determining liquid crystalline phase formation. However, the evolution of liquid crystalline order can also be predicted for molecules that, regardless of their shape anisotropy, have a charge distribution that is anisotropic [26]. In the present investigation, the electronegativity of the fluorine substituents in **DFm** and **DFo** induces concentrations of negative charge near the ends of both types of molecule. The axial ratios of both compounds are identical (4·66). While the location of maximum negative charge in **DFm** differs only slightly from that in **DFo**, the two compounds exhibit strikingly dissimilar thermotropic phase behaviour (table and figure 3). Also, we note that compounds **DFm** and **DFo** both exhibit smectic mesophases, despite having an axial ratio that is substantially less

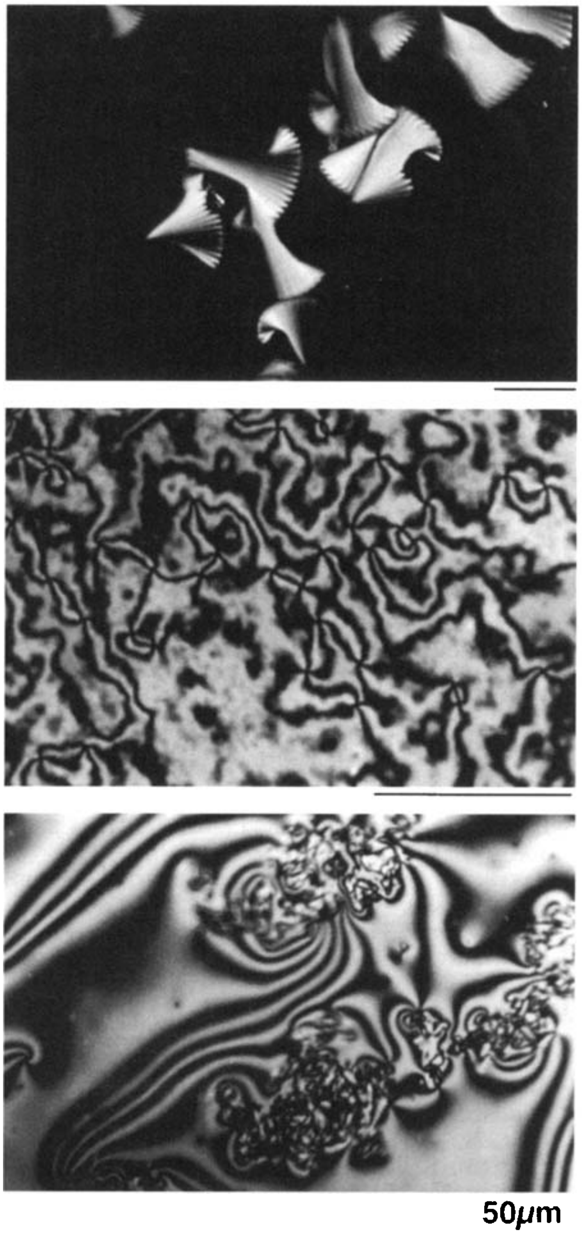

Figure 3. Top: The highest temperature liquid crystalline phase of compound **DFm** is S_A, shown here at the clearing point between cleaned glass slides. Middle: The highest temperature liquid crystalline phase of compound **DFo** is nematic, shown here between cleaned glass slides at 216°C. Bottom: The nematic phase of compound **DFo** maintained between as-received glass slides at 209°C.

than the critical value required for smectic formation by unsubstituted tolane oligomers. Furthermore, **DFm** and **DFo** are liquid crystalline over a significantly wider temperature range than compound **B**, which is the unsubstituted tolane oligomer having the closest axial ratio to **DFm** and **DFo**.

These qualitative experimental results demonstrate that 'soft' interactions can play a significant role in determining the specific *types* of liquid crystalline phases formed by tolane oligomers, in addition to modifying the intrinsic mesogenic character of rod-like molecules and their ability to crystallize. Detailed calculation of intermolecular forces in tolane oligomers is needed to quantify the relative sensitivity of phase behaviour to 'hard' and 'soft' interactions.

3.3. *High strength disclinations*

The rheology of a liquid crystalline melt, and therefore the energy required to process it, as well as the time for process-induced molecular order to relax, is a function of the time-dependent number, strength and spatial distribution of microstructural defects. Disclinations of strength 3/2 (i.e. associated with six extinction bands between crossed polarizers) have been detected in tolane oligomer specimens as the microstructure relaxes after shear [8], together with the commonly observed disclinations of strength 1/2 (two extinction bands) and 1 (four extinction bands). The high strength disclinations have also been observed in a few more complex systems: mixtures [27–30], solutions [31–33], polydisperse single component materials [34], or thin specimens subjected to hybrid boundary conditions (specifically, with air on one side of the liquid crystalline material and an isotropic organic fluid on the other) [35, 36]. However, the fact that high strength disclinations can be generated in a pure melt of simple, monodisperse rods between ordinary glass surfaces confirms that these defects can occur in nominally pure material under common experimental conditions.

Figure 4 shows a rare disclination of strength 2 (associated with eight extinction bands) in **DFo** at 174°C, in the supercooled nematic state of a specimen confined between glass slides that were used as-received. Disclinations of strength 1 and 1/2 can also be seen in figure 4. The high strength disclinations were not observed in specimens supported between slides subjected to the cleaning procedure described in the *Experimental* section above. Indeed, specimens of **DFo** confined between our cleaned slides did not even form a traditional schlieren texture in the nematic state; instead, they exhibited textures containing a preponderance of inversion walls.

It is well known that nematic microstructures are sensitive to surface anisotropy, as induced, for example, by rubbing. The present experiments demonstrate that specific textures can also be artifactually stabilized by residual impurities on isotropic, nominally clean (technically 'pre-cleaned'), as-received cover slides. In particular, high strength disclinations can be stabilized in this way. We suggest that a combination of (a) trace contaminant, such as lubricating oil from the manufacturing

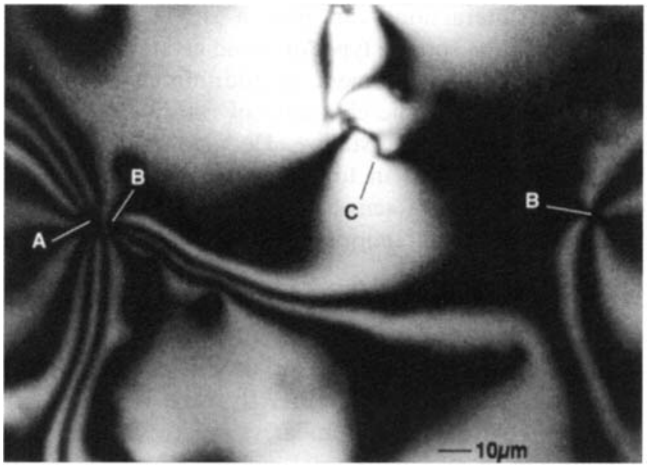

Figure 4. Disclinations in the supercooled nematic state of compound **DFo** maintained between as-received glass slides at 174°C. Examples of disclinations having strength 2 (label A), 1 (label B) and 1/2 (label C) are explicitly identified.

process, on one glass surface, and (b) a locally wider gap between surfaces, can create the hybrid boundary conditions [35, 36] that are known to promote the formation of high strength disclinations.

Studies of tolanes therefore suggest two sets of conditions under which high strength disclinations may be formed: relaxation of shear-induced molecular alignment [8], and as a result of hybrid boundary conditions promoted by limited cleanliness. Such conditions can prevail in a variety of materials processing operations, so that the possible presence of high strength disclinations should not be overlooked when modelling the evolution of microstructure in melt-processed liquid crystalline materials.

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