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High strength disclinations in a rigid rod nematic polytolane

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Transient disclinations of strength ±3/2 were observed in the nematic phase of a single-component, thermotropic, rigid rod polytolane. These disclinations were characterized by 6 extinction brushes in textures observed by hot stage transmitted polarized light microscopy. The small number and short lifetime of these disclinations is discussed in terms of their energy per unit line length, and in terms of the force that causes them to be attracted to and annihilated at other disclinations.

1. Introduction

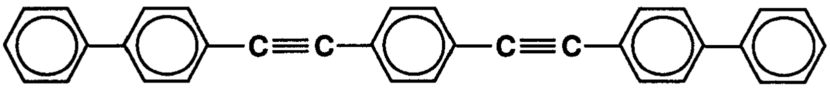
According to the textbook literature on liquid crystals, the only experimentally observed disclinations in nematics have been those with strengths $\pm\frac{1}{2}$ and ± 1. The research literature contains some isolated references to observations of higher strength disclinations in two-component materials: in a lyotropic liquid crystal [1–3], in mixtures of a lyotropic and a thermotropic liquid crystal [4], and in nematogens mixed with plate-like non-mesogenic molecules [5, 6]. A solvent or diluent is present in all these cases; it has been suggested that the high strength singularities are stabilized by the surface tension gradient at the interface with submicroscopic droplets [4], or by concentration gradients [5, 6].

This paper presents evidence that disclinations of strength $\pm\frac{3}{2}$ can exist in a single-component nematic material.

2. Experimental

2.1. *Material*

Microstructural studies were conducted on 1,4-bis(4-biphenylethynyl)benzene, a polytolane:



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The bonds linking the phenyl and acetylene units are collinear. Therefore, each molecule of this compound resembles a rigid rod. The axial (length-to-width) ratio of the rods is 6·3, as determined by using Chem3D Plus software (version 3.0; Cambridge Scientific Computing, Cambridge, MA) to construct an energy-minimized model of the molecule. Similar (though shorter) polytolanes have been shown to form nematic liquid-crystalline phases [7].

2.2. *Synthesis*

In a 250 ml round bottom flask equipped with stirbar, reflux condenser and nitrogen inlet was placed 4-ethynylbiphenyl (5·35 g, 30 mmol), 1,4-diiodobenzene (3·30 g, 10 mmol), morpholine (75 ml) and triphenylphosphine (400 mg). The solution was warmed and degassed with nitrogen, and then palladium chloride (35 mg) and cupric acetate monohydrate (20 mg) was added. The resulting solution was heated in a 125°C oil bath for 5 hours and then cooled to room temperature. The resulting slurry was filtered and the solid washed first with morpholine and then ethanol and finally air dried to give the crude product (4·35 g). This material was taken up in hot *N*-methyl pyrrolidinone (100 ml) and allowed to cool and crystallize. The solid was isolated by suction filtration and washed with ethanol and then recrystallized again in the same fashion to give the pure product (3·72 g, 86 per cent).

Analysis: calculated for $C_{34}H_{22}$: C, 94·85 per cent, H, 5·15 per cent; found: C, 95·20 per cent, H, 5·21 per cent.

2.3. *Characterization*

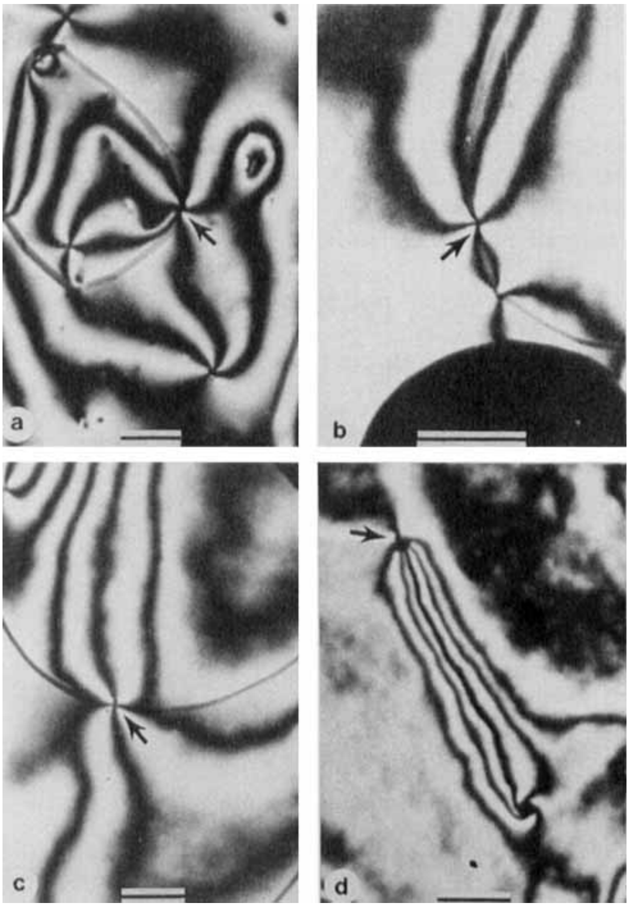
Phase transitions were initially detected by differential scanning calorimetry (DSC), on a DuPont 1090 system. Specimens with an approximate mass of 10 mg were scanned at $10^{\circ}\mathrm{C\,min^{-1}}$ in an atomosphere of dry nitrogen. Phases were identified by transmitted polarized light microscopy. A Leitz Laborlux 12 POL microscope equipped with a Linkam THM 600 heating/freezing stage and PR 600 controller was used to examine the textures of samples confined between two glass cover slides. Microstructures were recorded on Fuji Neopan 1600 Professional black and white film, using a Canon T90 camera.

3. Results

The material exhibits the following phase transitions on heating

$$\mathrm{C}\ 293{\cdot}8^{\circ}\mathrm{C}\ \mathrm{S_A}\ 299{\cdot}1^{\circ}\mathrm{C}\ \mathrm{N}\ 343{\cdot}5^{\circ}\mathrm{C}\ \mathrm{I}.$$

Undisturbed nematic samples exhibit disclinations of strength $\pm\frac{1}{2}$ and ± 1, characterized by either 2 or 4 extinction brushes between crossed polars. However, if nematic samples are stirred by vigorously agitating the top cover slide for a few seconds, occasional transient singularities of strength $\pm\frac{3}{2}$, characterized by 6 extinction brushes, can subsequently be found in the textures (see the figure). These disclinations are more frequently found at temperatures close to the clearing point, and they have only a short lifetime. In experiments on 50 samples, these disclinations were never seen for more than 34 s after samples were stirred. The disclinations do not remain stationary in the field of view. They move erratically towards another disclination or a sample/air interface, where they are annihilated. It was necessary to use high speed film (1600 ASA) to freeze this motion sufficiently to record textures with minimal blurring. However, use of such high speed film introduces significant 'grain' into the recorded images. Because



Sample microstructures at 340°C observed between crossed polars. The scale bar represents 10 μm in each case. Views (*a*)–(*c*) each contain a singularity of strength $\pm\frac{3}{2}$, characterized by 6 extinction brushes. View (*d*) shows a strength $\pm\frac{3}{2}$ singularity with a wider, isotropic core; observations with the analyser removed confirmed that isotropy was not due to the presence of air bubbles. A sharp line discontinuity passing through the singularity is clearly visible in (*a*) and (*c*), and faintly visible in (*b*).

of the mobility and short lifetime of the microstructure, it was not possible to rotate the crossed polars and reliably distinguish between disclinations of strength $+\frac{3}{2}$ and $-\frac{3}{2}$.

4. Discussion

For disclinations that have a distinct core, i.e. those with half-integral strength, the energy per unit line length is [8]

$$W = W_c + \pi K s^2 \ln \frac{R}{r_c}. \qquad (1)$$

(The simplifying assumption is made that the elastic properties of the nematic can be described by the single elastic constant K, s is the strength of the disclination, R is its radius, r_c is the radius of the core, and W_c is the core energy.)

The core energy can be approximated by [9]

$$W_c = k_B \Delta T \pi r_c^2 \frac{\rho N}{M}. \tag{2}$$

(Here k_B is Boltzmann's constant, ΔT is the difference between the specimen temperature and the clearing point, ρ is the density of the nematic, N is Avogadro's number, and M is the molar mass.)

If m is the mass of a single molecule, this simplifies to

$$W_c = k_B \Delta T \pi r_c^2 \frac{\rho}{m}. \tag{3}$$

Therefore

$$W = k_B \Delta T \pi r_c^2 \frac{\rho}{m} + \pi K s^2 \ln \frac{R}{r_c}. \tag{4}$$

By differentiating, the value of r_c that minimizes the overall energy of the disclination can be found

$$r_c^2 = \frac{mKs^2}{2\rho k_B \Delta T}. \tag{5}$$

By substituting in equation (4) we obtain

$$W = \pi K s^2 \left[\frac{1}{2} + \ln\left(\frac{R}{s}\sqrt{\left(\frac{2\rho k_B \Delta T}{mK}\right)}\right)\right]. \tag{6}$$

Thus, for disclinations with half-integral strength:

The overall energy increases with increasing strength, consistent with the fact that higher strength is accompanied by more complex director field distortions. Therefore, the number of $s = \pm\frac{1}{2}$ disclinations should always exceed the number of $s = \pm\frac{3}{2}$ disclinations.

The energy of a disclination of given strength is decreased by a combination of high molecular weight and small undercooling, though the dependence is not a sensitive one. This is qualitatively consistent with our observation that the $\pm\frac{3}{2}$ strength disclinations are more common at temperatures close to the clearing point of the nematic, and may also help to account for the fact that we have not found these disclinations in the textures of shorter polytolanes.

If we substitute equation (5) into only the first term of equation (4) we obtain another useful expression for the energy of disclinations with half-integral strength:

$$W = \pi K s^2 \left[\frac{1}{2} + \ln \frac{R}{r_c}\right]. \tag{7}$$

This shows that the overall energy is higher for disclinations with narrow cores, which is consistent with the fact that narrow cores require more severe director field distortions.

If a disclination has integral strength, its core is expected to be diffuse, i.e. there is no line singularity associated with the disclination. The energy is then simply given by [9]

$$W = 2\pi K |s|. \tag{8}$$

We are now in a position to estimate and compare the relative energies of different disclinations. Dimensionless data for this comparison can be obtained from rearrangements of equations (7) and (8):

$$\frac{W}{\pi K}=s^2\left[\frac{1}{2}+\ln\frac{R}{r_c}\right], \tag{9}$$

$$\frac{W}{\pi K}=2|s|. \tag{10}$$

We assume a reference value of $R\sim 10\,\mu\mathrm{m}$, based on the scale of typical microstructures. The calculation for $\pm\frac{1}{2}$ strength disclinations is performed for several values of R/r_c, ranging from 5000 to 10. These values correspond to a core radius that ranges from being 1 molecule long to 500 molecules long; the actual value will depend on the (unknown) elastic constants of the material, and on the specimen temperature, as expressed in equation (5). The R/r_c values used to obtain the corresponding reduced energies for $\pm\frac{3}{2}$ strength disclinations must be normalized to take account of the fact that r_c is proportional to s (if all other parameters remain constant), again as expressed in equation (5). Values of reduced energy $W/\pi K$ are shown in the table.

We can now point to two reasons why the $\pm\frac{3}{2}$ strength disclinations are seen so much less frequently than $\pm\frac{1}{2}$ strength disclinations:

> If the relative probability of forming a disclination is assumed to follow a Boltzmann-type distribution (i.e. if probability is inversely proportional to the exponential of reduced energy), the data in the table imply that $\pm\frac{1}{2}$ strength disclinations are 200–2000 times more likely to occur than $\pm\frac{3}{2}$ strength disclinations.
>
> Because the force between disclinations is proportional to the product of their strengths [9], the higher strength disclinations should anneal out of the microstructure more rapidly.

The latter consideration may also contribute to explaining why ± 2 strength disclinations were not observed. On the basis of the reduced energies in the table, and the assumption of a Boltzmann-type relationship between energy and probability, we might expect to observe more ± 2 strength disclinations than $\pm\frac{3}{2}$ strength disclinations—unless the latter have very wide cores. However, regardless of core size, any ± 2 strength disclinations would be attracted to other disclinations and annihilated more rapidly than disclinations of lower strength. In addition, observations

Dimensionless reduced energies $W/\pi K$ for disclinations in a nematic, calculated from equations (9) and (10).

	R/r_c for disclination with distinct core						
s	5000	1000	500	100	50	10	Diffuse core
0·5	2·3	1·9	1·7	1·3	1·1	0·7	
1							2·0
1·5	17·8	14·2	12·6	9·0	7·5	3·8	
2							4·0

of ± 2 strength disclinations in nematogens mixed with plate-like non-mesogenic molecules [6] suggest that the director does not necessarily collapse in the third dimension near ± 2 strength defects. These disclinations therefore can have finite cores, in which case equation (9) would predict a higher reduced energy and a lower probability of formation, compared to $\pm \frac{3}{2}$ strength disclinations.

5. Conclusions

Transient disclinations of strength $\pm \frac{3}{2}$ can be generated during deformation or flow of the nematic phase of a single-component liquid crystal consisting of rigid rod-like molecules. Formation of these high strength disclinations is promoted by a combination of mechanical agitation, smaller undercooling below the clearing point, and higher molecular weight.

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