Observation of defects in a polyester nematic phase: 2.

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(Received 14 June 1985; revised 12 November 1985)

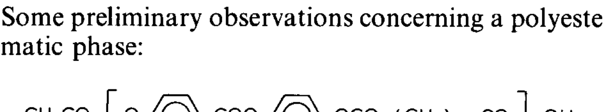
Various optical observations of defects in a free droplet of thermotropic nematic polyester are presented. These observations show a large predominance of defects of half-integer strength, and different core aspects for positive or negative strength defects. In our discussion, we take in account the very large K_1 splay constant and a model of aggregation for free ends is proposed.

(Keywords: nematic phase; polyester; disclination line; defects; core structure)

INTRODUCTION

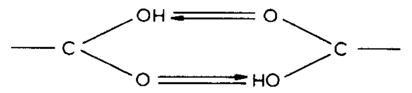
Even when it is made at a macroscopic level, the observation of defects in ordered media always brings some indirect elements to the understanding of the microstructure: the classification of possible defects in a given ordered medium is purely topological and depends on the symmetry group: the relative occurrence of a particular defect and the type of textures encountered, depend on energetic properties that take ground in the microstructure. Historical examples illustrating the interest of the study of defects in liquid crystals go back to G. Friedel[1]: more recent studies are reviewed in ref. 2.

Some preliminary observations concerning a polyester nematic phase:



with $x \approx 24$, were reported in ref. 2 (referred to below as paper 1), and clearly showed marked differences from the usual observations of defects in small-molecule liquid crystals (SMLC); although all the observations were not explained at once, a preliminary interpretation was given, which proposed that K_1, the splay constant, was much larger than K_2, the twist constant, and K_3, the bend constant. This was confirmed by further direct measurements of these constants[3].

The few existing structural models of main chain polymers agree on the prediction of a large splay constant K_1, proportional to the length L of the chain, or to L^2, according to whether entropic contributions or elastic contributions are dominant[4]. But essentially, in all models, the large magnitude of the splay constant is related to the rarity of chain ends. This is all the more true in the system we have studied where the effective length of the molecular chain can be made longer by the occurrence of opposite hydrogen bonds between similar chain ends, linking terminal carboxylic groups as follows:



Also other hydrogen bonds ($E \approx -0.1$ eV) can occur in other places along the chain although with less probability. Therefore, splay deformation, which requires free chain-ends, cannot reach a magnitude larger than 1/2L, say, without a change in the nature in the chain conformation. This could be either through the occurrence of elastic deformations, including density fluctuations, or through the aggregation of many chain ends. Elastic deformation would be in the form of hairpins, at such scales (*Figure 1a*), and this is probably not much favoured with the small flexible spacer ($n = 5$) of the polyester we have studied. Aggregation of chain ends (*Figure 1b*) would decrease the internal energy at the expense of some entropy term: such aggregation effects have already been observed in our compound (see paper 1), so that we shall assume they also play a role in the defect configuration we studied here.

Half-integral lines are predominant in C_5 polyesters of reasonable molecular weight (note that for $x \approx 5$, one recovers the texture of the SMLC's) and singular points* have never been observed, to the best of our knowledge, in this type of material.

This paper is concerned with the study of the cores of $\pm 1/2$ lines in the C_5 polyester, as they appear in free droplets; in the first section, we report on the observations, which gave evidence of a drastic difference between the $+1/2$ and $-1/2$ lines. The second section discusses the experimental results in the light of a model for aggregation of free ends.

OBSERVATIONS

Large scale observations

The samples are prepared by melting a drop of material on a clean glass plate at $\approx 180°C$ and spreading it with

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*By singular points, we mean here these point topological singularities that were first characterized in nematic liquid crystals by Meyer[5] and Williams *et al.*[6]. A typical point singularity geometry is when the molecules extend radially from a point. A general reference for topological defects including lines and points is ref. 7. It must be emphasized that there is no connection whatsoever between these singular points and the point defects (vacancies, interstitials) of physical metallurgy.

0032-3861/86/050714-07$03.00

another glass plate. We observe defects in the thin parts of the drop ($\lesssim 10$ μm) with a polarizing microscope. Lines of strength $\pm 1/2$ are clearly predominant as in paper 1. Each disclination line ends with a $+1/2$ at one end and a $-1/2$ at the other end, on the free surface, while it is stretched on the glass plate along most of its length (*Figure 2*). An interpretation of this global configuration has been given in paper 1. We confirm this model in which there is essentially a twist and bend deformation, but to this slight modification we claim that the line is attached to the bottom surface.

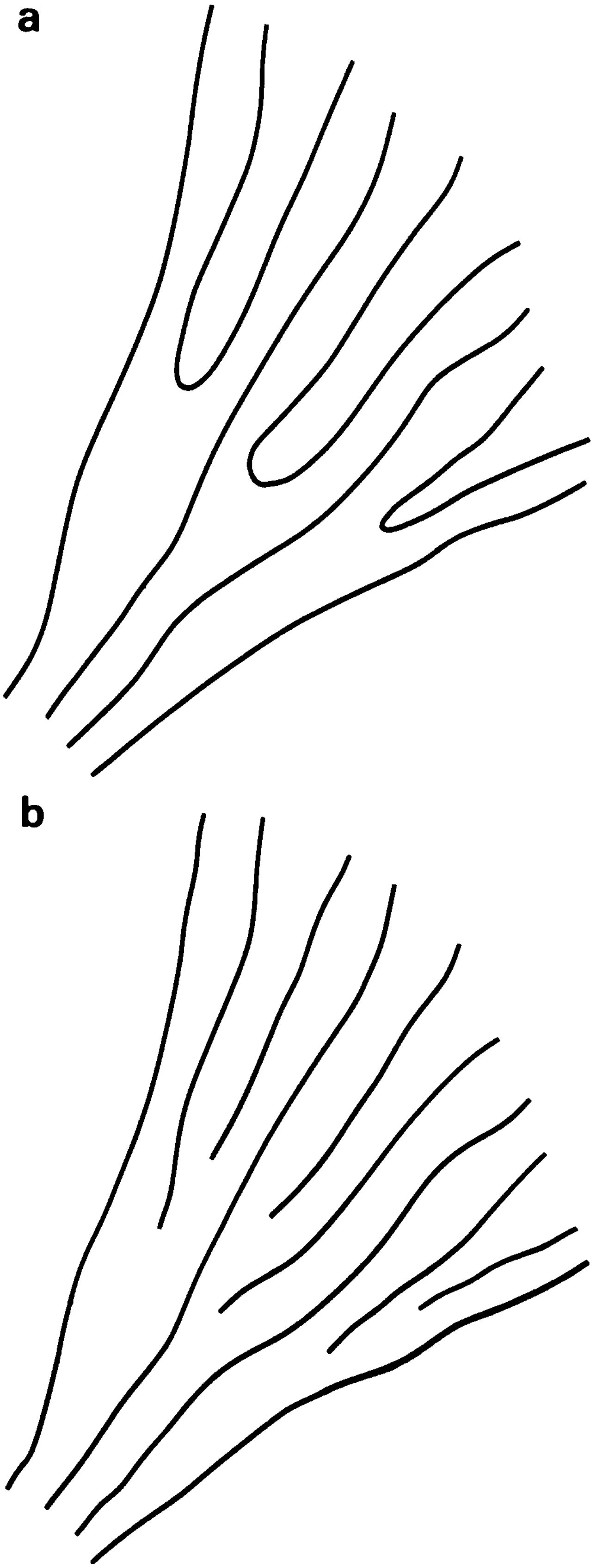


Figure 1 Accommodation of splay deformation in a nematic polymer (a) by hairpins, (b) by chain ends

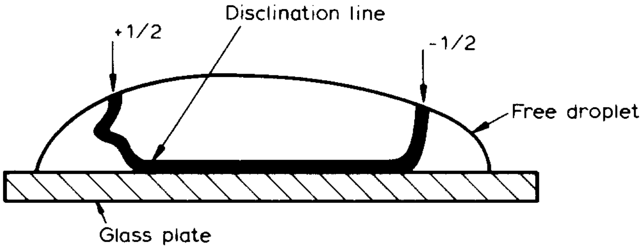


Figure 2 Geometry of half integral lines in a free droplet

The global configuration of the sample results from a balance between a planar anchoring direction on the glass plate, and anchoring at an angle at the free surface. The planar direction is induced by the shearing. The disclination lines, which are roughly parallel (along the flow) and equidistant, accommodate a three-dimensional quasi periodic distortion of the molecular directions: far from each line, the distortion involves twist (by splay–splay compensation in the manner proposed by Meyer[4], probably) and bend. Bend is predominant near the line-ends, and we shall assume, in the following, with some small error, that the configuration is in planes perpendicular to the line-ends, near these ends. There is indeed a component of the director perpendicular to the planes, but we shall assume it has a constant value.

Positive and negative defects display very different mobilities. While the $+1/2$ is practially immobile under any (gentle) blow given to the sample, the $-1/2$ moves immediately and steadily in the direction imposed by the previous shearing and drags the line along the bottom plate in the downstream direction. It is also interesting to notice that, while the $-1/2$ end is attached to the bottom plate through a quasi straight path, the $+1/2$ is attached to it through some circumvolutions containing one or two spirals. Finally, the core aspect is not the same for negative or positive defects.

Core observations

The numerical aperture of the objective lens is 0.6.

In linearly polarized light (*crossed nicols*). $+1/2$ cores are sharply defined and appear very neatly, while $-1/2$ cores are rather blurred (*Figure 3*).

In circularly polarized light (*crossed nicols*). Core regions appear as dark contrasted spots, slightly thicker for $-1/2$ than for $+1/2$. The spots are about 0.5–1 μm wide. Circularly polarized light shows the variations of the vertical component of the director. A dark spot corresponds either to a vertical configuration, or to an isotropic configuration, or to a situation where light is scattered. Three branches are visible emerging out of the $-1/2$, they are about 4–5 μm long (and four branches are even clearer out of the -1) (*Figure 4*). They appear as portions of walls where the light is scattered. We interpret them as sectors where the radius of curvature of the optical axis is quite small compared with the wavelength of light.

In unpolarized light. Core regions still appear as dark spots, but while $+1/2$ spots are dark and well contrasted, $-1/2$ spots are much clearer and weakly contrasted, and

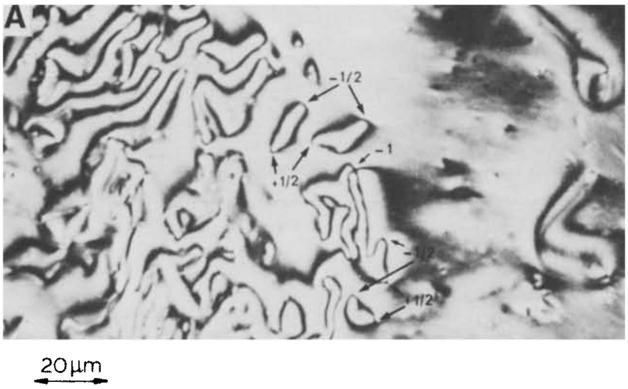
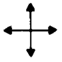


Figure 3A $-1/2$ and $+1/2$ cores at the free extremities of a half integral line in a free droplet. Linearly polarized light (crossed nicols) 

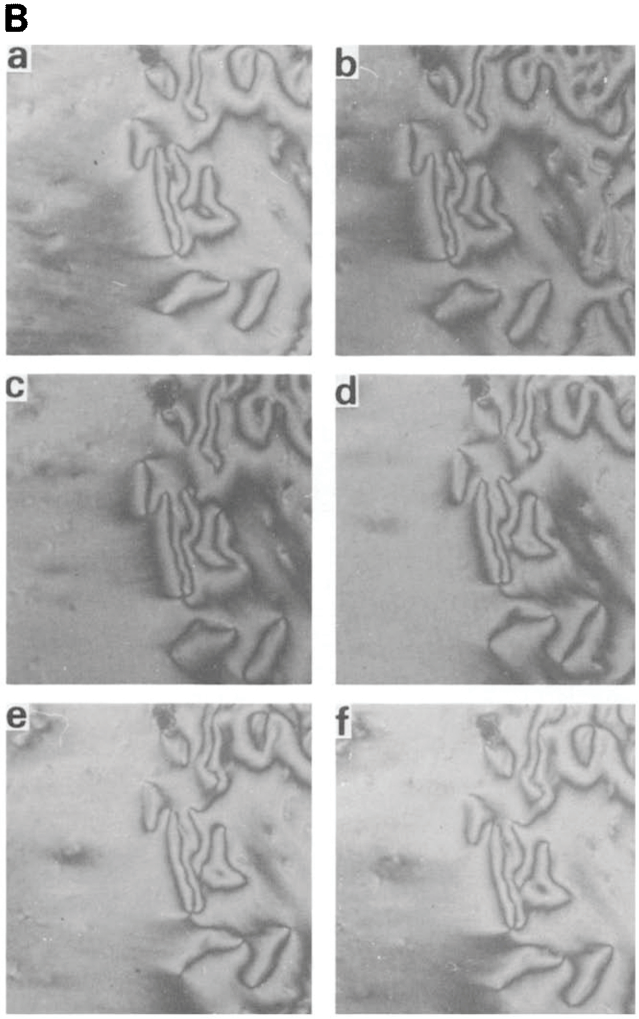
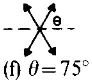


Figure 3B As for *Figure 3A* with different crossed nicols orientations 

: (a) $\theta=0°$; (b) $\theta=15°$; (c) $\theta=30°$; (d) $\theta=45°$; (e) $\theta=60°$; (f) $\theta=75°$

sometimes hardly visible (*Figure 5*). $+1/2$ cores seem to scatter light much more than the $-1/2$ cores which are rather transparent to unpolarized light.

We interpret the observations in circularly polarized light and in unpolarized light, by a high concentration of chain ends in $+1/2$ cores, which scatter light, and a vertical configuration in the $-1/2$, which are transparent to unpolarized light, but not circularly polarized light (crossed nicols). The branches out of the negative cores are still weakly visible.

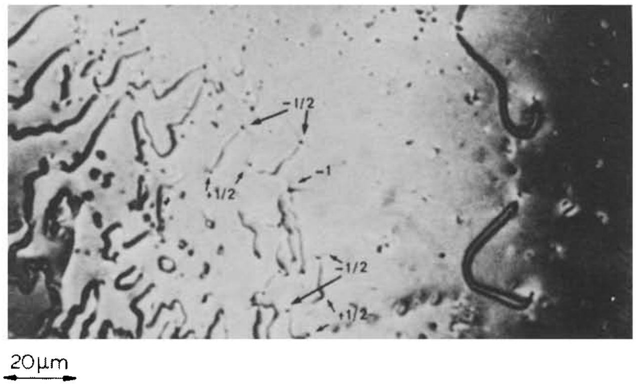


Figure 4 As for *Figure 3A* with circularly polarized light

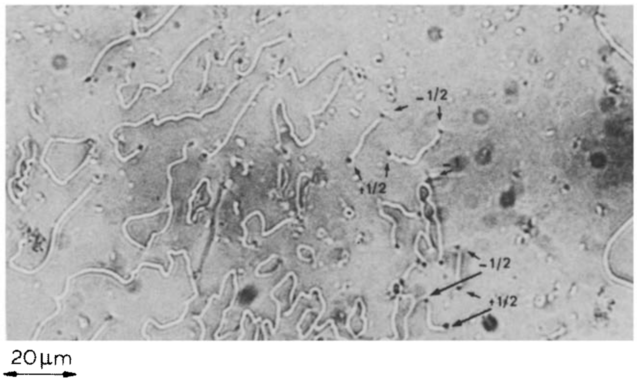


Figure 5 As for *Figure 3A* with unpolarized light

DISCUSSION

Half-integral positive lines

While the description of core microstructures can be kept at a very elementary level in SMLC's, when one is interested in obtaining an order of magnitude of core radii and core energies, the situation is much different in polymer liquid crystals. The observations reported above already indicate drastic differences, and point to the necessity of a detailed description. However, we are in trouble if we try to reach such a goal solely with optical observations. Our discussion will therefore be very tentative and will raise questions rather than give definite results.

We shall consider two types of core models: the first one liquid-like and such that the density of chain ends in the core region is the same as in the remainder of the phase: the second one, which we favour, imagines a sort of semi-liquid core state, with a density of chain ends much larger than outside the core. Finally, we shall discuss the stability of the $S=\pm 1/2$ *versus* the $S=1$ disclination.

In both models, we shall assume that there is no splay involved, but only bend, outside the core. This is akin to the model for $S=+1/2$ lines in columnar discotics, and we reproduce a part of the corresponding results obtained in ref. 8: the director lies on the evolutes of a half circle of radius R_0; $r=R_0$, the core radius is therefore larger than R_0 (*Figure 6*). The elastic energy outside the core is, per unit length of cylinder:

$$f_0=\frac{\pi K_3}{4}\ln\frac{R^2}{R_c^2-R_0^2}$$

where R is the size over which the configuration extends.

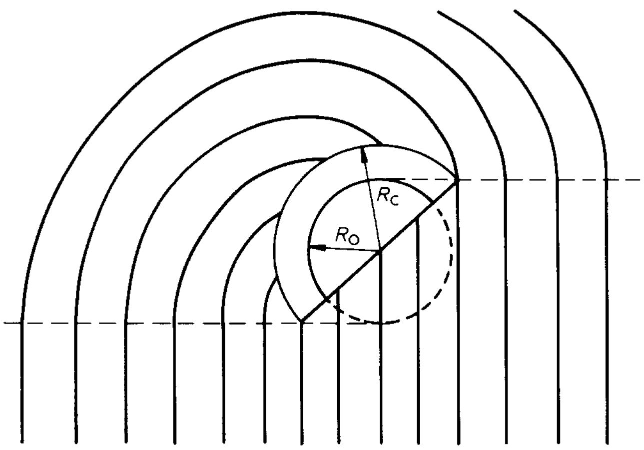


Figure 6 Pure bend geometry outside the core for a + 1/2 line. R_c: core radius; R_0: radius of the generating circle

The energy of a coreless $s = +1$ with bend and twist deformation only[9] is:

$$f(s=+1) = (2K_2 + K_3 + \frac{K_3 - K_2}{6} + O(K_3 - K_2)^2)$$

Liquid core. If the transition between the nematic and the liquid phase is second order, the boundary between the outer region and the core is smooth, and its energy, for a first approach can be included in the energy of the liquid core, which is:

$$f_i = \frac{\pi}{2} W R_c^2$$

where $W = k_B \Delta T n$ is the thermal energy per unit volume, with $\Delta T = T_c - T$, n is the number of degrees of freedom per unit volume. In a SMLC n is the number of molecules; here n is relatively small.

Minimizing $f_0 + f_i$ leads to:

$$R_0 = 0$$
$$R_c = (K_3/2W)^{1/2}$$

i.e.

$$f_{rot} = \frac{\pi K_3}{4} \ln \frac{2R^2 W}{K_3} + \frac{\pi K_3}{4} = \frac{\pi K_2}{2} \ln \frac{R}{R_c} + \frac{\pi K_3}{4}$$

A crude calculation, taking $n = N$, yields, for $T = 10$ K, $R_c \approx 30$ Å.

Assume now that the phase transition is first order, which seems to be the case for other polyesters[10]. The core boundary is now sharp, and this property implies most certainly that there is an abrupt change in the chain density there, contrary to our assumption. For, either the molecules of the outer region end at the boundary, or the boundary itself consists of a wall in which bend is transformed into splay. In the first case, a large energy of a wall of organized chain ends should be added to the core terms; in the second case, these chain ends would be spread in the wall. It is in fact reasonable to assume that the chain ends fill the whole core, as we discuss now.

Semi-liquid core. By semi-liquid, we mean here that the disorder of the core is not obtained by chain disorder, but by the introduction of a large number of chain ends. The molecules themselves would remain quite ordered and quite equidistant, if one thinks of the chain ends as playing the role of edge dislocations, all of the same sign, perturbing the parallel packing, as in *Figure 7a*. One observes that the relevant parameter is the radius of curvature r_c of the normal to the molecules, and that the density of chain ends is $1/rd$. Since the distance between molecules is kept to a constant value, there is little distortion and the energy due to the free ends is essentially proportional to their total number. However, it is not evident that such a simple geometrical arrangement can be achieved with a given number of free ends n_f fixed by the boundary conditions:

$$n_f = \frac{\pi R_0 + 2\sqrt{R_c^2 - R_0^2}}{d}$$

which have to fill a surface $\pi/2\, R_c^2$. Hence, one can expect two contributions to the core energy; the first, $f_{c1} = K n_f$ is proportional to the number of free ends; the second, f_{c2},

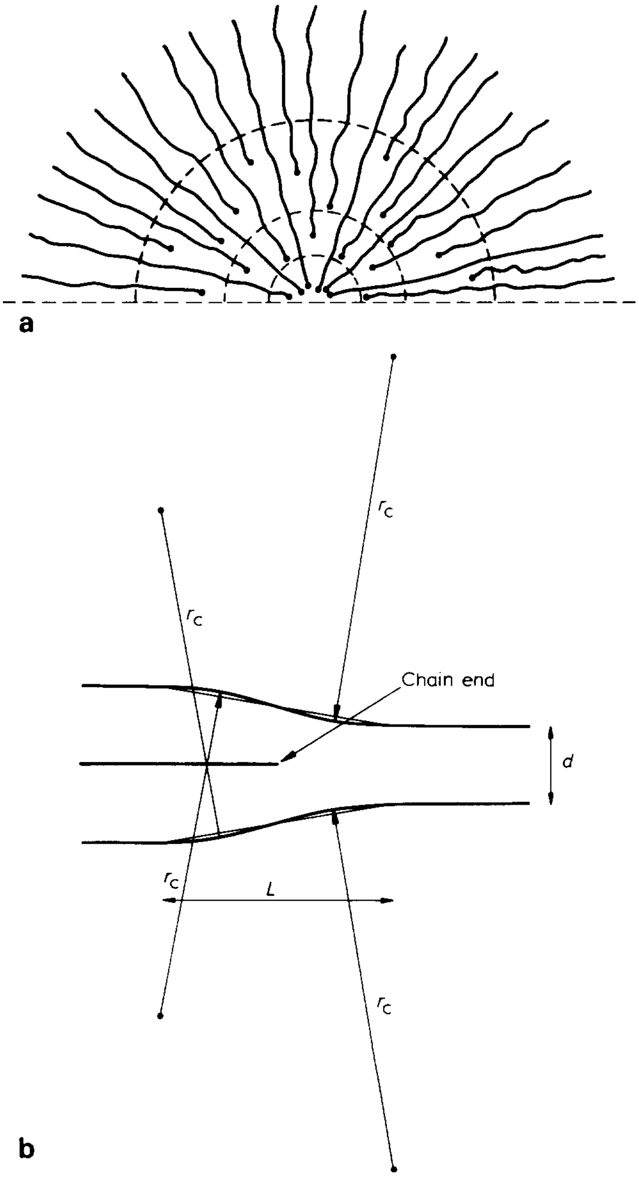


Figure 7 (a) Geometry of a high density of chain ends which minimizes elastic distortions. (b) Elastic distortion near a free chain end, considered as an edge dislocation

representing the contribution of the extra distortion. Since we have no convincing model at our disposal, and in the absence of critical experiments, we will assume $R_0=0$ (*Figure 8*), and if f_c is negligible with respect to f_{c1} let us try to find the elastic energy of a chain end considered as an edge dislocation (*Figure 7b*). We shall assume that the chemical energy of a chain end is negligible with respect to the elastic energy of the induced distortion. The radius of curvature is:

$$r_c=\frac{L^2}{2d}+\frac{d}{8}$$

If L is about a few monomers' length the bend energy inside the core is then (per unit length):

$$f_b=Ld\frac{K_3}{r_c^2}\times\frac{2R_c}{d}=\frac{2K_3LR_c}{r_c^2}$$

the total energy is

$$F_{tot}=\frac{\pi K_3}{2}\ln\frac{B}{R_c}+2K\frac{R_c}{d}$$

where $$K=\frac{K_3Ld}{r_c^2}$$

and it is minimized for $R_c=\frac{\pi}{4}\frac{K_3}{K}d$

The equilibrium value is

$$F_{tot}=\frac{\pi}{2}K_3\ln\frac{R}{R_c}+\frac{\pi}{2}K_3$$

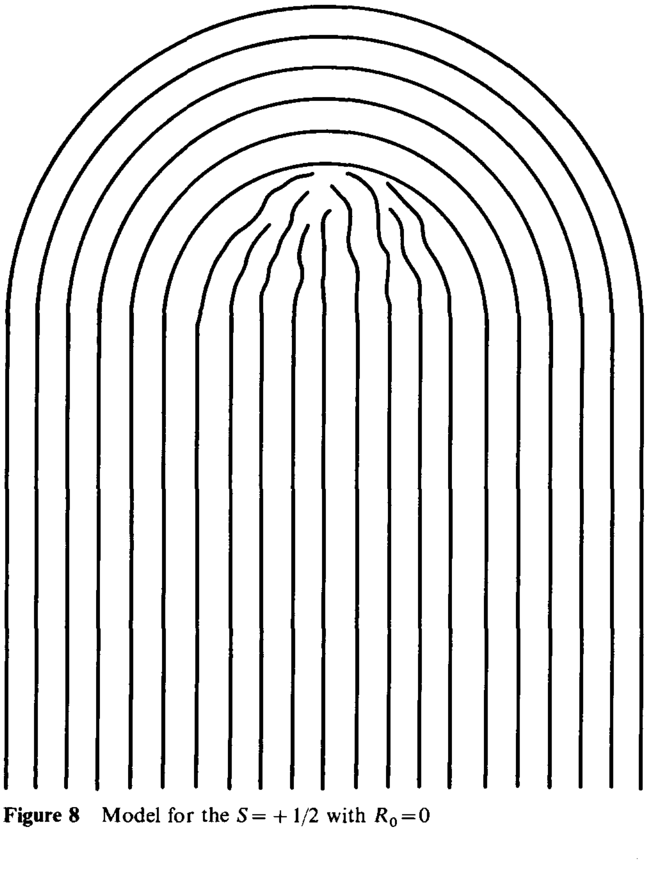


Figure 8 Model for the $S=+1/2$ with $R_0=0$

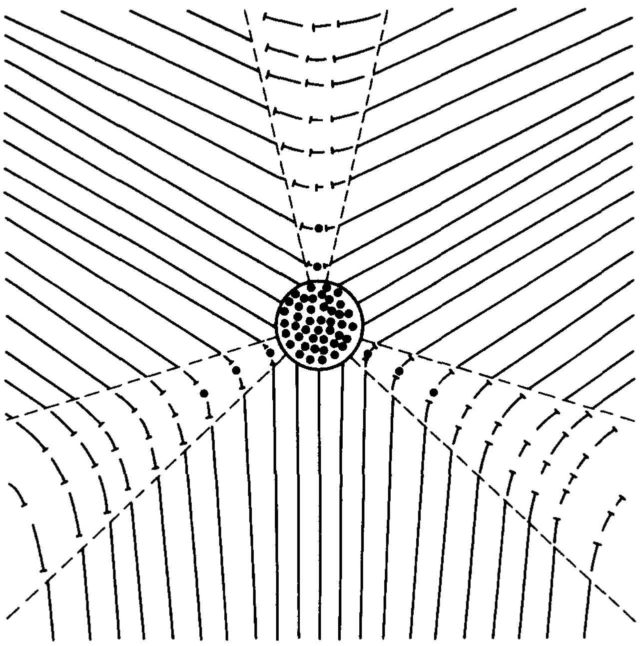


Figure 9 Model for the $S=-1/2$

For $d=5$ Å and $L\approx 80$ Å (2 monomers' length) we get:

$$r_c=640\text{ Å}\qquad K=\frac{K_3}{1024}$$

and

$$R_c\approx 540\text{ Å}$$

The total energy is

$$F_{tot}=\frac{\pi K_3}{2}\ln\frac{R}{R_c}+\frac{\pi}{2}K_3$$

R_c is larger than in the liquid core model; therefore, the energy of the semiliquid core model is lower.

It is probable that the non-occurrence of the $S=+1$ line is related to the precise model of the core, which clearly cannot be just 'twice' the model of the $S=+1/2$.

Mobility. The model with a variable chain end density fits better with the property of immobility being of the order $s=+1/2$. Any motion of such a line would necessarily be 'non conservative' in the sense that chain ends should diffuse in any motion of the line; this process is akin to the process of the climbing of a dislocation in normal crystals, which necessitates the motion of vacancies and interstitials[11]. It is interesting to note that it is just a characteristic of the core which leads us to distinguish for disclinations in liquid crystals between climbing (as here) and glide motion (as we shall see for the $S=-1/2$).

Half-integral negative lines

For $S=-1/2$ we can propose a model which minimizes elastic energy by concentrating it in some angular sectors outside the core (*Figure 9*). Inside the core, the configuration is vertical. In this model, the energy balance between splay and bend, which are the only contributions, leads to a subtle geometry where most of the bend energy is concentrated in a manner that avoids too much splay energy. Remember that in our samples $K_1 \gg K_3$.

In such a model, a radius of curvature of the lines of force of the director decreases near the core and when it is small enough, compared with the wavelength, light is scattered: those angular sectors appear as portions of wall. The following calculation, suggested by Nityananda and Ranganath[12], assumes an essentially two-dimensional model, even in the angular sectors. However, we cannot reject the possibility of some vertical component of n in these sectors. This vertical component, which creates splay deformation, partly relaxes the bend deformation, which is very large. In their model, the director's orientation ϕ depends on the polar angle θ and $u=\phi-\theta$ obeys the differential equation:

$$u_\theta^2=1+\frac{E}{1+\varepsilon\cos 2u}$$

where

$$\varepsilon=\frac{K_1-K_3}{K_1+K_3}$$

and E must be fixed by the strength of the defect.

For $\varepsilon=1$ ($K_3=0$ or K_1 infinite) this equation has a simple solution:

$$u=-\sin^{-1}\left[\left(\frac{2+E}{2}\right)^{1/2}\sin\theta\right]$$

$$E=2/3 \text{ for } S=-1/2 \qquad E=2 \text{ for } S=-1$$

and the elastic energy is

$$F=\frac{1}{2}K\ln\frac{R}{R_\mathrm{c}}\left[2\sin^{-1}\left(\frac{2}{2+E}\right)^{1/2}+(2E)^{1/2}-\pi\right]4|S-1|$$

where $$K=\frac{K_1+K_3}{2}$$

R_c is the core radius and R is the size of the sample.

The case $\varepsilon=1$ corresponds to an ideal situation. In our case we have $\varepsilon\approx 0.83$ and corrections must be made to the model. Let us first consider, as in ref. 12, corrections which preserve the two-dimensional character of the model. The additional free energy is

for $S=-1/2$

$$\Delta F=\frac{K}{2}(-1.5444\delta-1.7321\delta\ln\delta)\ln\frac{R}{R_\mathrm{c}}$$

for $S=-1$

$$\Delta F=\frac{K}{2}(-2.4548-4\delta\ln\delta)\ln\frac{R}{R_\mathrm{c}}$$

where $\delta=1-\varepsilon$

The curvature is maximal for $\theta_0=-\pi/3, \pi/3, \pi$, for $-1/2$. Let us find the radius of curvature at a point (π, θ). If we suppose that for any value of ε, we still have $u(\theta_0)=-\pi/2$ (this condition preserves the continuity of the director), we get:

$$\rho=\frac{r}{|1+u_\theta|} \quad \text{and} \quad u_\theta=-\sqrt{1+\frac{E}{1-\varepsilon}} \quad \text{for} \quad \theta=\theta_0$$

Let us suppose that light is scattered for $\rho<5\lambda$, $\lambda\approx 0.5\ \mu$m. $\rho=5\lambda$ for $\pi=5\lambda|(1-\sqrt{(1-E)/(1-\varepsilon)}|\approx 3\ \mu$m which is approximately the length of the branches emerging from the $-1/2$ cores. In fact, the branches are not perfectly symmetrical, the $+1/2$ core and the $-1/2$ core are at both ends of a disclination line, and they influence each other.

We have also:

$$\operatorname{div}\vec{n}=\frac{\phi_\theta}{r}\cos\theta-\phi=\frac{u_\theta+1}{r}\cos u$$

$$\operatorname{div}\vec{n}=\frac{\cos u}{r}\left[1-\sqrt{1+\frac{E}{(1-\varepsilon)+2\varepsilon\cos^2 u}}\right]$$

(i) for $u=-\pi/2(\theta=\theta_0)\operatorname{div}\vec{n}=0$ for $\varepsilon\neq 1$;

(ii) for a fixed value or r, $|\operatorname{div}\vec{n}|$ is maximal for $u\approx\pm 1.15$ rad; we expect some density of free chain ends in these regions. However, some escape of the chains along the third dimension could lead to splay–splay compensation.

We must add a core energy term to the elastic energy of the defect. We suppose, for the $-1/2$ case, a nematic core, with the director parallel to the core axis. A cylinder of radius R_c can be made by twisting and bending the molecules on a distance $\approx L$ which is about a correlation length. The energy to create a unit length of such a cylinder, ΔF, is approximately equal to $R_\mathrm{c}K_2/L$.

The total energy of the defect becomes, per unit length:

$$F_\mathrm{rot}=A\ln\frac{R}{R_\mathrm{c}}+R_\mathrm{c}\frac{K_2}{L} \qquad A\approx 8.10^{-7}\ \text{(cgs)}$$

Minimizing this energy, we find: $R_\mathrm{c}\approx 3L$. For our polyester if $L\approx 500$ Å, $R_\mathrm{c}\approx 1500$ Å. The same model can be used for the -1 core, where we then find: $R_\mathrm{c}\approx 15L$.

Let us compare free energies for $S=\pm 1$ and $S=\pm 1/2$, in the case of our polyester, and in the case of an ordinary nematic.

For the polyester:

$$F(-1)=3.69\times 10^{-6}\ln R/R_\mathrm{c}+K_2R_\mathrm{c}/L\ \text{(dynes)}\ R_\mathrm{c}\approx 15L$$
$$=3.69\times 10^{-11}\ln R/R_\mathrm{c}+K_2R_\mathrm{c}/L\ (\mathrm{J\ m^{-1}})$$

$$F(-1/2)=8\times 10^{-7}\ln R/R_\mathrm{c}+K_2R_\mathrm{c}/L\ \text{(dynes)}R_\mathrm{c}\approx 3L$$
$$=8\times 10^{-12}\ln R/R_\mathrm{c}+K_2/L\ (\mathrm{J\ m^{-1}})$$

$$F(+1/2)=\frac{\pi K_3}{2}\ln R/R_\mathrm{c}+\pi K_3 \quad R_\mathrm{c}\approx 5400\ \text{Å}\simeq 0.54\ \mu\text{m}$$

$$F(+1)=\pi(2K_2+K_3+\frac{K_2-K_3}{6}+\mathrm{O}(K_3-K_2)^2)$$

$$K_1=32\times 10^{-7}\ \text{(dynes)}=3.2\times 10^{-12}\ (\mathrm{J\ m^{-1}})$$

$$K_2=2.5\times 10^{-7}\ \text{(dynes)}=2.5\times 10^{-12}\ (\mathrm{J\ m^{-1}})$$

$$K_3=3\times 10^{-7}\ \text{(dynes)}=3\times 10^{-12}\ (\mathrm{J\ m^{-1}})$$

We have plotted these energies as a function of R, the area over which the configuration extends (*Figure 10*). For $R>1\ \mu$m $S=-1/2$ is more stable than the $S=-1$. For $R<30\ \mu$m $S=+1/2$ is more stable than the $S=+1$.

In an ordinary nematic (isotropic elasticity $K_1=K_2=K_3=K$):

$S=-1$ escaped core model $F-1=\pi K$

$S=+1$ escaped core model $F+1=3\pi K$

$S=\pm 1/2 \qquad F\pm 1/2=\pi K/4\ln R/R_\mathrm{c}+E_\mathrm{c}$

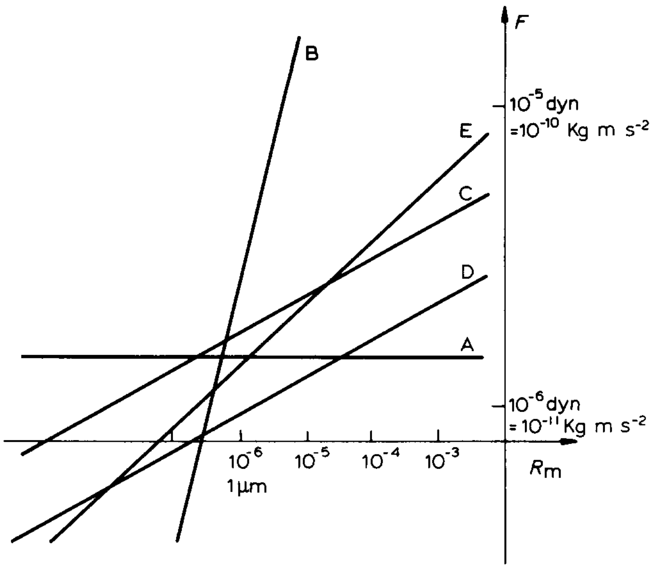


Figure 10 Energy of the $S=\pm 1$ and $S=\pm 1/2$ as a function of R. (A) $S=+1$; (B) $S=-1$; (C) $S=+1/2$ liquid core; (D) $S=+1/2$ semiliquid core; (E) $S=-1/2$

For a large enough value of R, half integral lines are less stable than integral lines.

These models also explain the difference of mobility between $S=-1/2$ and the $S=+1/2$. To move a $S=-1/2$ core we only have to change the molecular direction, n, as it is a conservative motion; while in motion, $S=+1/2$ has to drag with it all the chain ends gathered inside the core and it is considered a non-conservative motion.

CONCLUSION

Our observations on this nematic polyester have pointed out a clear difference between $-1/2$ and $+1/2$ cores, especially in the core aspect.

For $S=-1/2$, a model minimizes elastic energy, but involves a lot of bend energy which can explain the three dark branches emerging from the core. The weak contrast displayed by the core in natural light compared with circularly polarized light, suggests to us a vertical configuration inside it. This model can be extended to the -1 lines, but their energy is much larger.

For $S=1/2$, we suppose a large concentration of chain ends inside the core, which scatters light. Outside the core, we can find a configuration with no splay distortion.

This study has been made on a single member of this family of polyesters. Other investigations, involving the molecular length and the length of the flexible part, would bring more information, as also would other techniques, such as electron microscopy, which would give a more detailed description of the molecular arrangement around the lines.

ACKNOWLEDGEMENTS

We thank Dr L. Strzelecki for the provision of samples and for useful discussions.

REFERENCES

1 Friedel, G. *Ann. Phys. (Paris)* 1922, **18**, 273
2 Kléman, M., Liébert, L. and Strzelecki, L. *Polymer* 1983, **25**, 295
3 Sun, Z. M. and Kléman, M. *Mol. Cryst. Liq. Cryst.* 1984, **111**, 321
4 Meyer, R. B. in 'Polymer Liquid Crystals', (Eds. A. Ciferri, W. R. Krigbaum and R. B. Meyer), Academic Press, New York, 1982
5 Meyer, R. B. *Mol. Cryst. Liq. Cryst.* 1972, **6**, 255
6 Williams, C. F., Piéranski, P. and Cladis, P. E. *Phys. Rev. Lett.* 1972, **29**, 90
7 Kléman, M. 'Points, Lines and Walls', John Wiley, Chichester, UK, 1983
8 Kléman, M. *J. de Phys.* 1980, **41**, 737; Oswald, P. and Kléman, M. *J. de Phys.* 1981, **42**, 1461
9 Cladis, P. E. and Kléman, M. *J. de Phys.* 1972, **33**, 591
10 Maret, G. in 'Polymer Preprints of the A.C.S. Meeting, Washington, DC, August 1983', p. 249; de Gennes, P. G. *Mol. Cryst. Liq. Cryst.* 1984, **102**, 95
11 Friedel, J. 'Dislocations', Pergamon Press, London, 1964
12 Nityananda, R. and Ranganath, G. S. in Proceed. Int. Conf., Bangalore, 1979, p. 205, (Ed. S. Chandrasekhar), Heyden, London, 1980