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## Liquid Crystals

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Wei Wang<sup>ab</sup>

<sup>a</sup> Max-Planck-Institut für Polymerforschung, Mainz, Germany <sup>b</sup> Department of Polymer Chemistry, Kyoto University, Kyoto, Japan

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## PRELIMINARY COMMUNICATION

### Relationship between the Frank elastic constant anisotropy measured from the lamellar director and that of the molecular director around disclinations in main chain liquid crystalline polymers

by WEI WANG†

Max-Planck-Institut für Polymerforschung, Ackermann 10,  
Postfach 3148, D-55021, Mainz, Germany

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The transmission electron microscope technique enables direct visualization of disclination core structure of main chain liquid crystalline polymers. Generally, the lamellar structure, that is a function of type of polymer and molecular length, and of which the thickness is 10–200 nm, can be observed. In terms of distortions in the director field produced by a disclination, the elastic anisotropy,  $\varepsilon$ , can easily be calculated. However, the  $\varepsilon$  does not indicate the molecular distortion produced by the disclination. Continuum mechanics is used to describe the relationship between the elastic anisotropy,  $\varepsilon_a$ , measured from the lamellar director and that,  $\varepsilon_b$ , of the molecular director in main chain liquid crystalline polymers. The relationship is  $\varepsilon_a = -\varepsilon_b$ , indicating that lamellar distortion is completely different from the molecular distortion.

Recently, some investigations of the physical structure and morphology of liquid crystalline (LC) polymers by means of transmission electron microscopy (TEM) reported in the literature [1–12] have demonstrated that the defects can be imaged directly with the help of the lamellar structure formed by folded [2–5] or extended chains [7–12]. As an important experimental result, the molecular director was found to be perpendicular to the lamellar surface that was identified by electron diffraction [2, 7–9, 11]. The important features for main chain LC polymers, lyotropic or thermotropic, are long chains and large anisotropy in comparison to low molecular weight liquid crystals, resulting in a larger variation of the molecular deformation during the formation of disclinations. The physical parameter describing the variation in a disclination core is the Frank elastic constant anisotropy, indicating the bend to splay ratio in the region of the disclination core. Hudson and Thomas have shown that, according to the director variation of lamellae formed in semi-flexible and rigid LC polymers during annealing, the elastic constant anisotropy could be directly calculated from the TEM micrographs of disclination cores [4, 5]. The main result is that  $\varepsilon$  is negative in the disclination core for rigid LC polymers and positive for the semi-flexible LC polymers, indicating that the rigid polymer splays significantly more at the core, but that the semi-flexible polymer bends more at the core.

In previous studies, the fine structures of line disclination cores of P-4-BCMU (soluble polydiacetylene) lyotropic liquid crystals have been observed by means of TEM [8–12]. Typical examples of structures of  $s = \pm 1/2$  disclination cores are shown in figure 1. Owing to the formation of an extended chain lamellar structure, the liquid crystalline texture and morphology of the P-4-BCMU thin film can be easily studied by

† Address for correspondence: Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.

means of TEM. In addition, a fine striation in the micrographs which is parallel to the molecular director can be seen. An important feature, in particular for  $s = +1/2$  disclinations, is that the lamellae splay, but the fine striations bend according to their alignment. The question arises whether the directors of the lamellae or the directors of the fine striations have to be used for the determination of the elastic constant anisotropy. Obviously, the directors of the fine striations have to be used since they are parallel to the molecular directors. For normal LC polymers, however, the lamellar structure can only be seen by means of TEM. Therefore, it is necessary to understand the relationship between the Frank elastic constant anisotropies in LC polymers measured from the lamellar director and those of the molecular director around line disclinations in TEM images.

The relationship will be discussed in terms of the continuum theory that has been developed by Oseen [13], Zöcher [14] and Frank [15]. At first, it is necessary to define a dimensionless unit vector  $\mathbf{n}$  in the uniaxial liquid crystals. The distortion free energy density,  $g$ , is a quadratic function of various derivatives of the director field

$$g = \frac{1}{2} [k_{11}(\nabla \cdot \mathbf{n})^2 + k_{22}(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + k_{33}(\mathbf{n} \times \nabla \times \mathbf{n})], \quad (1)$$

where the  $k_{ii}$  are the Frank elastic constants. The first term describes the effect of the splay distortion on the free energy density, the second term the twist, and the third term the bending. Consider a planar structure in which the director is confined to the  $xy$  plane and is not a function of  $z$ , the normal to the film. Taking  $n_x = \cos \phi$ ,  $n_y = \sin \phi$  and  $n_z = 0$ , the free energy density may be written as

$$g = \frac{k}{2r^2} \left( \frac{\partial \phi}{\partial \theta} \right)^2 [1 + \varepsilon \cos 2(\phi - \theta)], \quad (2)$$

where  $r = (x^2 + y^2)^{1/2}$ ,  $\theta = \tan^{-1}(y/x)$ ,  $k = (k_{11} + k_{33})/2$  is the mean elastic constant and  $\varepsilon = (k_{11} - k_{33})/(k_{11} + k_{33})$  is the Frank elastic constant anisotropy. Minimizing the total free energy leads to the following second order non-linear differential equation

$$\frac{\partial^2 \phi}{\partial \theta^2} = -\varepsilon \left[ \frac{\partial^2 \phi}{\partial \theta^2} \cos 2(\phi - \theta) + \frac{\partial \phi}{\partial \theta} \left( 2 - \frac{\partial \phi}{\partial \theta} \right) \sin 2(\phi - \theta) \right]. \quad (3)$$

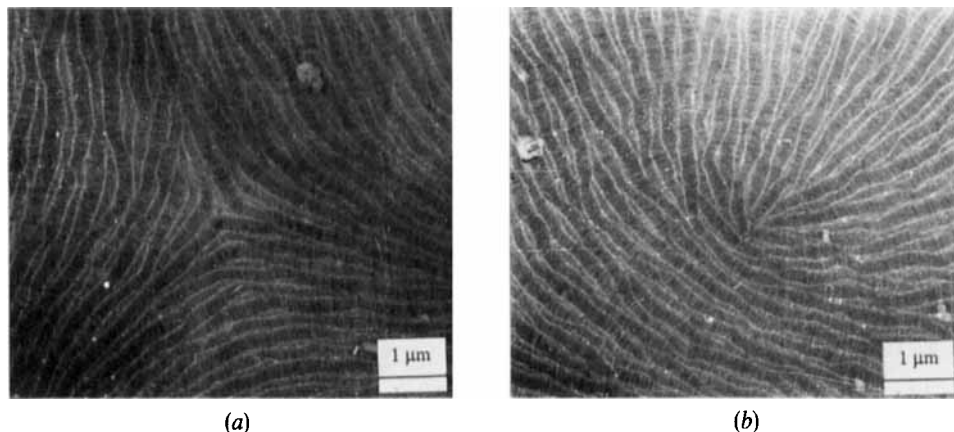


Figure 1. Two TEM micrographs of P-4-BCMU thin film showing the core structures of the line disclinations with strengths  $s = +1/2$  (a) and  $-1/2$  (b). The formation of an extended chain lamellar helps us to image the defects.

Equation (3) describes the effect of the Frank elastic constant anisotropy,  $\epsilon$ , on the distortion of the molecular direction around a line disclination. Assume that two coplanar directors  $\mathbf{n}_a$  and  $\mathbf{n}_b$  can be used to describe the same distortion produced by the same disclination. The relationship between  $\mathbf{n}_a$  and  $\mathbf{n}_b$  is orthogonal, as shown in figure 2. If the director  $\mathbf{n}_a$  is referred to as the molecular director, the director  $\mathbf{n}_b$  indicates the variation of the lamellar director. It is worthy of note that the lamellar director used in this paper is a fictitious concept, but one which is very useful for calculating the parameters of line disclinations, such as the Frank elastic constant anisotropy, from TEM micrographs of the core structure of line disclinations, since the lamellar structure is easy to observe by TEM as shown in figure 1.

In terms of continuum theory, two differential equations can be written

$$\frac{\partial^2 \phi_a}{\partial \theta_a^2} = -\epsilon_a \left[ \frac{\partial^2 \phi_a}{\partial \theta_a^2} \cos 2(\phi_a - \theta_a) + \frac{\partial \phi_a}{\partial \theta_a} \left( 2 - \frac{\partial \phi_a}{\partial \theta_a} \right) \sin 2(\phi_a - \theta_a) \right] \quad (3 a)$$

and

$$\frac{\partial^2 \phi_b}{\partial \theta_b^2} = -\epsilon_b \left[ \frac{\partial^2 \phi_b}{\partial \theta_b^2} \cos 2(\phi_b - \theta_b) + \frac{\partial \phi_b}{\partial \theta_b} \left( 2 - \frac{\partial \phi_b}{\partial \theta_b} \right) \sin 2(\phi_b - \theta_b) \right]. \quad (3 b)$$

In two orthogonal director fields, there are  $\phi_b = \phi_a + \pi/2$  and  $\theta_b = \theta_a$ , so that  $\partial \theta_b / \partial \theta_b = \partial \phi_a / \partial \theta_a$  and  $\partial^2 \phi_b / \partial \theta_b^2 = \partial^2 \phi_a / \partial \theta_a^2$ . Substituting them into equation (3 b), a new equation can be obtained

$$\frac{\partial^2 \phi_a}{\partial \theta_a^2} = \epsilon_b \left[ \frac{\partial^2 \phi_a}{\partial \theta_a^2} \cos 2(\phi_a - \theta_a) + \frac{\partial \phi_a}{\partial \theta_a} \left( 2 - \frac{\partial \phi_a}{\partial \theta_a} \right) \sin 2(\phi_a - \theta_a) \right]. \quad (3 b')$$

Comparing equation (3 b') with equation (3 a), a relationship between the elastic constant anisotropies described by two orthogonal directors  $\mathbf{n}_a$  and  $\mathbf{n}_b$  is obtained

$$\epsilon_a = -\epsilon_b. \quad (4)$$

When  $\epsilon = 0$ , equation (3) is clearly linear and was solved by Frank [15]. For the general case where  $-1 \leq \epsilon \leq +1$ , the equation (3) is non-linear and was solved by Dzytaloshinskii [16]. Hudson and Thomas have drawn the configurations of disclinations with strengths  $s = \pm 1/2$  in the case of  $\epsilon = 0, \pm 0.5$  and  $\pm 1$  [5]. On this basis a set of configurations of disclinations can be drawn after using the relationship  $\epsilon_a = -\epsilon_b$ .

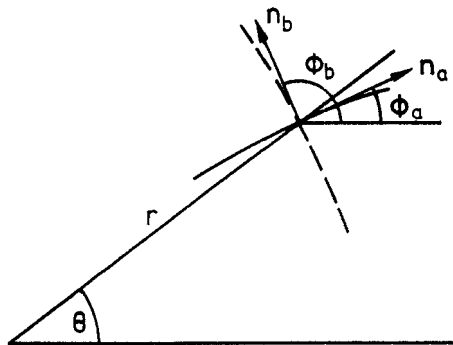


Figure 2. Schematic representation of the orthogonal directions of  $\mathbf{n}_a$  and  $\mathbf{n}_b$  in the core area of the same disclination.

In figures 3 and 4, a set of structural patterns of disclination cores with strengths  $s = +1/2$  and  $s = -1/2$  are shown.  $\mathbf{n}_a$  and  $\mathbf{n}_b$  in figures 3 and 4 are orthogonal to each other. In figure 3 (c) the solid line was drawn for the case  $\varepsilon = +1$ , indicating a bend deformation, and the dashed line for the case  $\varepsilon = -1$ , indicating a splay deformation.

This relationship has a physical significance that indicates that if in the director field  $\mathbf{n}_a$ , the function  $\phi_a(\theta)$  describes mainly bend distortions, i.e.  $\varepsilon_a$  is positive ( $k_{11} > k_{33}$ ), then in the director field  $\mathbf{n}_b$ , the function  $\phi_b(\theta)$  describes mainly splay distortions, i.e.  $\varepsilon_b$  is negative ( $k_{11} < k_{33}$ ).

The macromolecular deformation in a disclination core region can easily be determined on the basis of the TEM micrographs of the LC polymers. Generally,

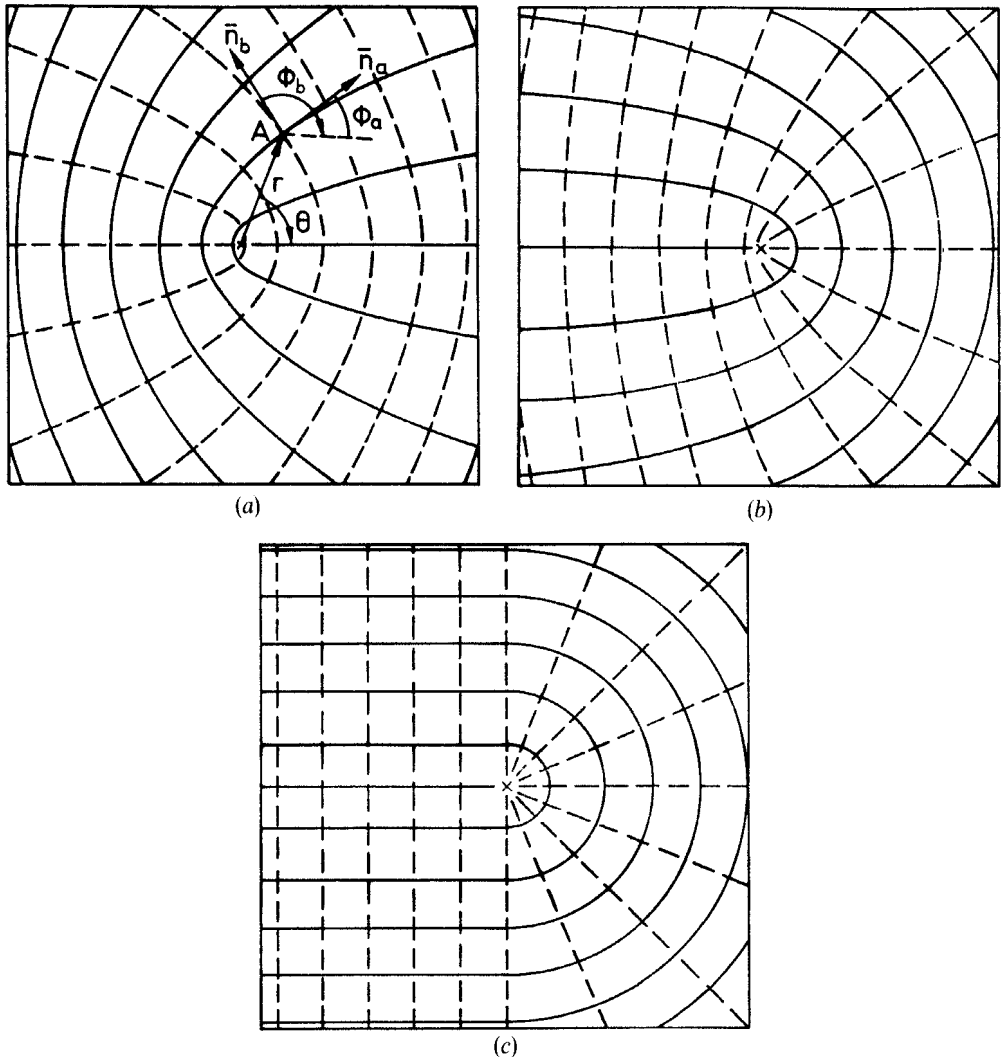


Figure 3. The  $s = +1/2$  disclination core structure patterns drawn according to continuum theory with different elastic anisotropies. In the pattern, the dashed and the solid lines are orthogonal to each other. For drawing the patterns, the  $\varepsilon_a = -\varepsilon_b$  relationship was used. (a) solid line  $\varepsilon = 0$  and dashed line  $\varepsilon = 0$ ; (b) solid line  $\varepsilon = 0.5$  and dashed line  $\varepsilon = -0.5$ ; (c) solid line  $\varepsilon = 1$  and dashed line  $\varepsilon = -1$ .

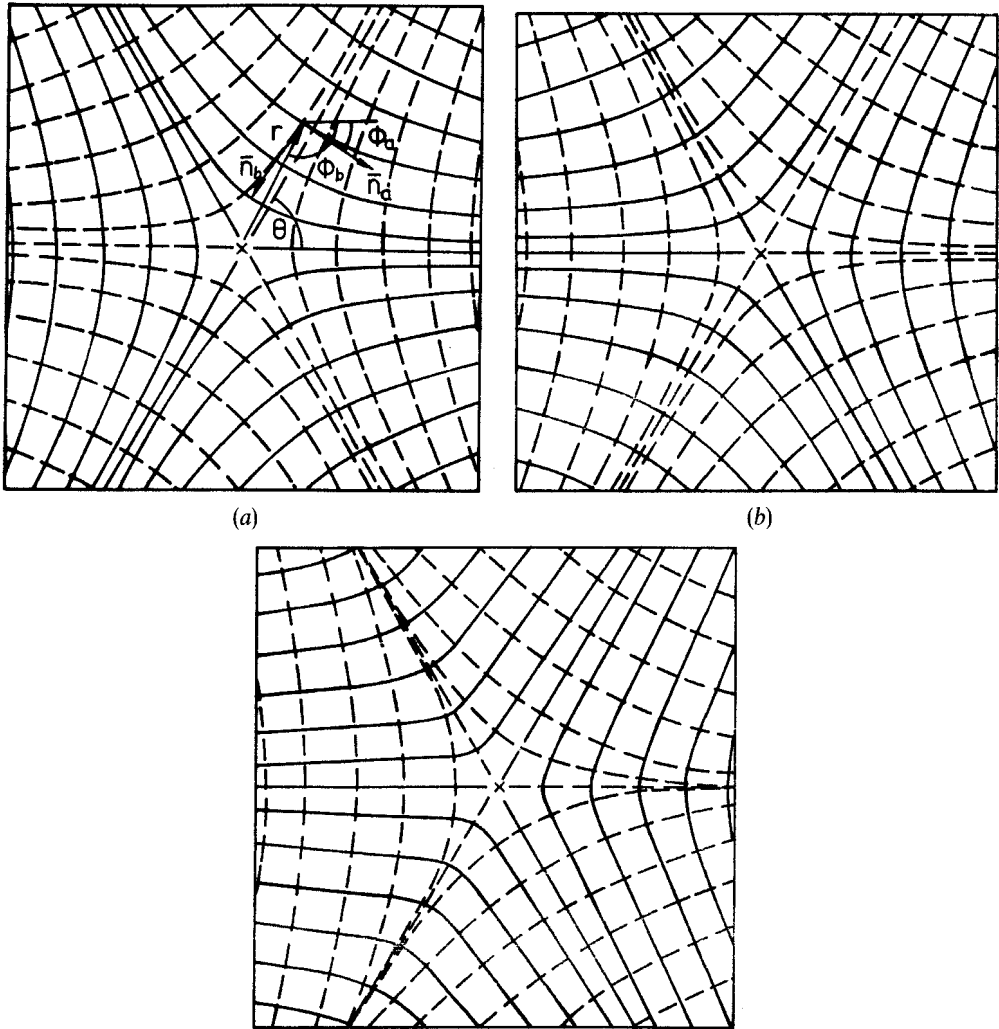


Figure 4. The  $s = -1/2$  disclination core structure patterns. The drawing conditions are the same as in figure 3.

lamellar thicknesses of about 10–20 nm for semi-rigid polymers and 10–200 nm for rigid polymers can be seen, because in the latter case lamellar thickness is a function of molecular length. The lamellar director can also be determined, and then the elastic constant anisotropy  $\varepsilon$  can be calculated according to the distortion of the lamellar director [4, 5]. The elastic constant anisotropy describes the lamellar distortion. An elastic constant anisotropy with the same value, but opposite sign,  $-\varepsilon$ , reflects the molecular distortion. In this work it is possible to calculate Frank's elastic constant anisotropy of P-4-BCMU from the TEM micrographs in figure 1. It was found, however, that the distribution of the molecular length of the polymer strongly influences the configuration of the disclinations, i.e., the elastic constant anisotropy, because the P-4-BCMU is a main chain LC polymer [11–12].

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