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Magnetic field induced instabilities in nematic solutions of polyhexylisocyanates

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Abstract

Magnetic field induced Freedericksz transition in the twist geometry of an initially well-aligned nematic solution of a rod-like polymer, polyhexylisocyanate (PHIC), is studied. For the angle α between the magnetic field and the unperturbed director $\mathbf{n}_0$, one finds a homogeneous distortion if this angle is less than 45°. For angles greater than 45°, the reorientation is inhomogeneous, and is coupled to secondary flow, giving rise to spatially periodic structures. The director deformation involves an out-of-plane tilt at short times, which manifests itself as a phase grating for transmitted polarized light. It is found that the wavelength of the instability is independent of the magnetic field strength in the experimental range, contrary to prior results for nematic solutions of polybenzylglutamate. We postulate that the insensitivity of the wavelength of the periodic structure is due to the nonflow-aligning character of PHIC solutions. © 2001 Published by Elsevier Science Ltd.

Keywords: Freedericksz transition; Rod-like polymer; Polyhexylisocyanate

1. Introduction

A variety of instabilities have been discovered when a system is driven far from equilibrium, resulting in, often times a very ordered, spatially periodic structure [1]. A well-known example of pattern formation and a paradigm for its study is a periodic structure formed by liquids due to a temperature gradient, the Rayleigh–Benard convection. Liquid crystalline polymers (LCPs), either in solution or melt, exhibit a variety of spatially periodic structures when exposed to external perturbing fields [2–7]. The most widely studied structure formation is the so-called 'banded structure' during or on cessation of shear flow. Here, we report on an instability leading to a spatially periodic structure when a nematic solution of polyhexylisocyanate (PHIC) in *p*-xylene is exposed to a magnetic field (**H**) in the twist geometry.

One of the most commonly studied phenomena in the physics of liquid crystals is the field (electric or magnetic) induced reorientation of the director in a thin liquid crystal film, termed Freedericksz transition [8]. It is frequently used to determine the elastic constants associated with curvature elasticity of the nematic phase. Fig. 1 shows various arrangements in which a nematic liquid crystal can be subjected to external fields. The application of a magnetic field (**H**) normal to the unperturbed director $\mathbf{n}_0$, but within the plane of the sample, as shown in Fig. 1(b), is expected to induce a homogeneous twist distortion. On the other hand, spatially periodic structures are found when nematic polymer solutions are studied. Such magnetic field instabilities have been found previously with other polymeric nematic solutions [2,3,9].

A nematic phase is a fluid phase, which has long-range orientational order with no positional order. In this fluid phase, the molecules comprising the nematic phase are oriented more or less parallel to one another. The average direction of the orientation or the director ($\mathbf{n}_0$) can be aligned to form a single crystal or a monodomain by surface interaction [8] as well as by an external magnetic field. The magnetic field couples to nematic phase through the anisotropy of the diamagnetic susceptibility per unit volume, $\Delta\chi_a$.

Application of a transverse magnetic field sets up a competition between the torques due to the field on one hand, and the torques due to the surface orientation manifesting as the elasticity of the liquid crystal on the other. A distortion is expected if the magnitude of the applied

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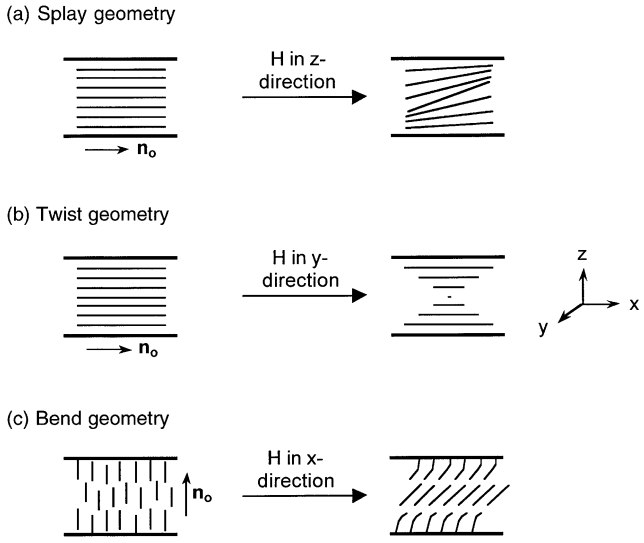

Fig. 1. A schematic showing the different geometries for the field induced transitions of nematic liquid crystals.

magnetic field exceeds a critical value, $\mathbf{H}_c$

$$\mathbf{H}_c = (\pi/d)(K_T/\Delta\chi_a)^{1/2} \quad (1)$$

where d is the separation between the bounding plates and K_T the twist elastic constant [8].

On the application of a transverse magnetic field above the critical field ($\mathbf{H} > \mathbf{H}_c$), any small perturbation in the initially uniform alignment can grow exponentially with time, and with a rate that is inversely proportional to the effective viscosity for that reorientation. In the case being considered, a simple twist distortion, the uniform rotation of the director does not involve flow [8] and hence is dependent on the rotational or twist viscosity, γ_1, of the nematic fluid. In general, the twist viscosity is quite large for nematic fluids comprising long, rod-like polymer chains in solution [2,10], thus making the rate of uniform reorientation rather slow. If there are modes that can respond faster than the homogeneous twist mode does, then the observed mode is the one with the fastest rate.

In the case of small molecule nematics, the twist viscosity, γ_1, is only slightly larger than the shear viscosity, η_{sh}. For rod-like polymers in solution, this difference can be significant, since γ_1 is usually much larger than η_{sh}. Hence, if a periodic mode can respond at a faster rate than uniform reorientation, coupling with flow, then that mode will be observed. In order for the periodic mode to have a faster response, a number of factors have to be taken into account. First, due to the equivalence of $\mathbf{n}$ to $-\mathbf{n}$, rotation of the director in either direction with respect to $\mathbf{n}_0$ (the unperturbed director) lowers the free energy of the system, and this rotation is dependent of the twist viscosity. A non-uniform distortion with a periodic pattern, such as counter rotating zones, is produced by fluid flow coupled to molecular reorientation. In such a situation, the twist viscosity of the fluid is replaced by the shear viscosity. For polymeric nematics, the twist viscosity is usually much larger than the shear viscosity, thus making periodic structures ubiquitous in polymeric materials [3,11,12].

In the case of periodic responses, these convective modes carry with them an extra penalty in terms of free energy, due to the fact that these modes involve additional elastic distortions, which are absent in the case of a uniform, continuous rotation of the director. The observed wavelength will then be determined by the balance of elastic and viscous torques. In this sense, the periodic responses are analogous to spinodal decomposition, where the fastest mode dominates the length scale observed in phase separation. Of course, shorter wavelengths (with considerably lower viscosity) involve large gradients for the director field, while long wavelengths involve considerably higher viscosities. Thus, the balance of the viscous and the elastic torques will develop an optimum wavelength for the fastest mode of response. The optimum wavelength will naturally be a function of the driving field, as has been observed for some nematic systems [3,13,14]. In the case of polybenzylglutamate (PBG) in methylene chloride solutions, the system develops a periodic pattern that is confined to the plane of the sample. Thus, the counter rotating regions are within the sample plane. Fluid flow then couples to the molecular reorientation to give a director pattern that is sinusoidal which leads to the bands that are seen under crossed polarizers.

We report here a qualitatively different type of periodic structure, where the optimum wavelength is independent of the driving field, for polymeric nematic comprising of PHIC in *p*-xylene. In this case, on the application of a magnetic field in the twist geometry, one observes that a phase grating [15,16] is created in a direction parallel to the applied magnetic field. The phase grating is the result of a spatially periodic out-of-plane tilt of the director. The optical character of this instability is thus very similar to those observed for electrohydrodynamic instability reported for small molecule nematogens [15,17], although the instability reported here is transient in nature as opposed to the steady structures in the case of electrohydrodynamic instabilities. Similar structures have been reported for another polymeric nematic system, polybenzobisthiazole (PBT) in methane sulfonic acid [2]. Such spatially periodic structures with an out-of-plane tilt of the nematic director in response to an applied magnetic field in the twist geometry has been reported for several small molecule nematogens [14]. However, in contrast to the instability reported here, the wavelength for small molecule liquid crystals were found to be a function of the applied magnetic field [14].

2. Experiment: observation of the instability and periodic structures

A 26% by weight of PHIC in *p*-xylene, exhibiting a nematic phase at room temperature, was used in this

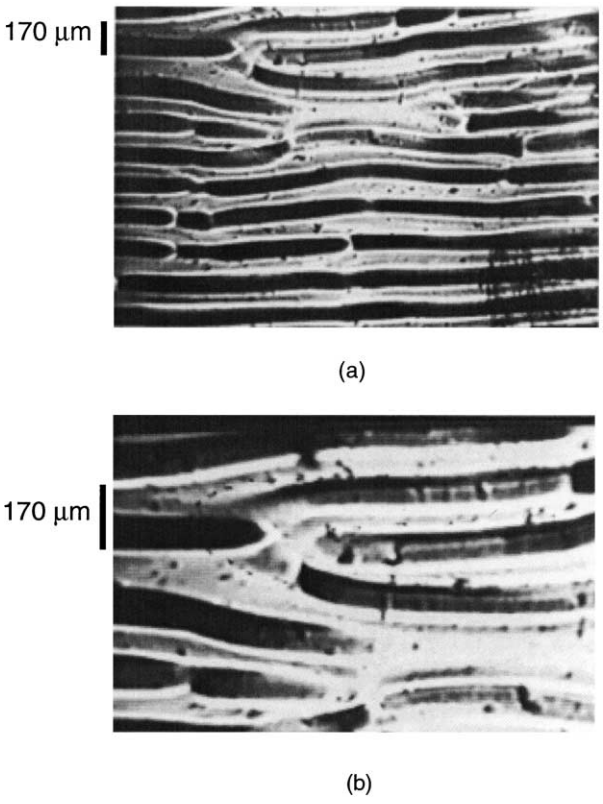

Fig. 2. Micrographs showing the phase grating formed by PHIC solutions in the twist geometry: (a) at the focal plane above the sample, and (b) at the focal plane below the sample plane. Observations were made in polarized light along $\mathbf{n}_0$.

study. PHIC was purchased from Aldrich and used as received. Monodomain samples were obtained by exposing the solutions bounded by two glass plates (coated with polyvinyl alcohol), to an external magnetic field. The field strength was varied between 1.3 and 4.7 T in intervals of 0.2 T. The sample thickness was kept at 170 μm by means of spacers between the bounding plates. Monodomains were formed in about 4 h on exposure to a 4.7 T field and remained stable for about 24 h.

The application of a magnetic field ($\mathbf{H} > \mathbf{H}_{c,T}$) in the twist geometry leads to spatially periodic structures shown in Fig. 2. The periodic structure consists of bands that are perpendicular to $\mathbf{n}_0$, and are visible in natural light or with light polarized in the direction of the unperturbed director $\mathbf{n}_0$. The structure is not visible when the incoming polarization is parallel to the applied magnetic field. Probing the structure by focusing on different planes in the thickness direction (z-direction) reveals the existence of two focal planes in which sets of bright lines could be observed, one above the midplane ($z = 0$) of the sample, and one below the midplane. The intensity modulation is displaced in each of these planes by $\lambda/2$, where λ is the wavelength of the periodic structure. No structure is discernable at other heights from the midplane. A schematic of the structure is shown in Fig. 3. The figure clearly shows the existence of two image planes one above and one below the plane of the sample. These structures are termed 'phase grating' [2,18,19]. The wavelength λ appears to be insensitive to the strength of the applied magnetic field over the entire range of field strengths used. However, the time for development of the instability was field dependent, with the instability occurring at shorter times with increasing field, thus demonstrating the rate of growth of the periodic structure is faster at higher fields.

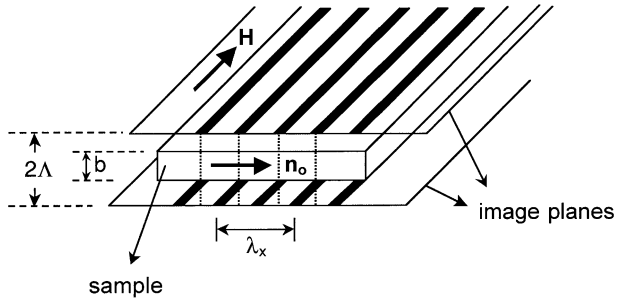

Fig. 3. A schematic of the phase grating that is formed on imposition of a magnetic field in the twist geometry.

The observations reported here have similarities to several other cases: for an electric field applied in a plane normal to the sample plane [15], in simple shear flow normal to the unperturbed director [19,20], and in Kevlar (du Pont trademark) fibers spun from solution [21]. In each of these cases, the structure acts as lattice of parallel cylindrical lenses, thus forming a phase grating to produce real and virtual images of the light source used for probing the sample.

There exists a critical angle of about $\alpha = 45°$ between the applied field and the unperturbed director, above which the periodic structures form and below which uniform reorientation occurs. This has been noted in several studies prior to the study reported here [2,22,23]. It is possible to use the growth of the uniform twist distortion to obtain a measure of the ratio of the twist viscosity to the twist elastic constant η_T/K_T, as was done elsewhere [2,24].

3. Interpretation of observations and discussion

The application of a magnetic field at angles $\alpha > 45°$ invariably produced an inhomogeneous distortion, giving rise to the transient periodic structures. Such transient structures have been observed for other polymeric systems and nonpolymeric systems. For the transient structures reported for PBG [3] in the twist geometry ($\alpha = 90°$), the director stays in the sample plane so that the distortion angle ϕ depends both on the height z from the midplane of the sample, and the position x along the axis defined by the unperturbed director. Both linear and nonlinear analyses using the Ericksen–Leslie equations have been done and the nonlinear analysis has been found to agree better with experiments. The linear analysis assumes a distortion of the

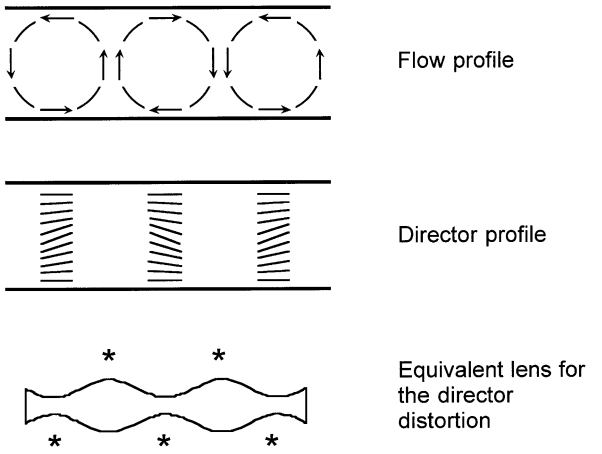

Fig. 4. Idealized schematics of the flow pattern, the director distortion, and an equivalent lens for the distortion.

type given by

$$\phi(z,x,t) = \phi_0 \exp(t/\tau_x) \cos(\pi z/d) \cos(\pi x/\lambda) \quad (2)$$

where ϕ_0 is a small initial amplitude arising from thermal fluctuations, λ and τ_x the characteristic wavelength and time constant, respectively, for the fastest growing mode. The calculated $\phi(z,x,t)$ does indeed predict the appearance of a periodic distortion observed under crossed polars [3]. The theory gives expressions for λ/d and τ_x as a function of reduced field ($h = \mathbf{H}/\mathbf{H}_{c,T}$) and several of the elastic and viscosity constants. These transients are due to a two-stage evolution: (a) the initial stage of the instability is dominated by the anisotropic viscosities (and hence flow properties can in principle provide valuable insight into the transient structure) and (b) the later stage is dominated by the anisotropic elasticities.

Experiments done on PBT systems indicate that the counter rotating flow does indeed stop after the initial stages. This was accomplished using particle tracking during the initial stages of the instability [12]. While the qualitative feature of the two stages evolution agrees with the theory [13], no other feature of the theory is seen to predict the behavior of the instabilities reported here for PHIC solutions or for PBT solutions.

The instability that we have reported here for PHIC solutions has many similarities to those found for PBT solutions [2]. Unlike the transient structure for PBG, the transient structure for PHIC has complex three-dimensional reorientation of the director, leading to the appearance of a phase grating in the initial stages. This distortion involves reorientation coupled to a circulatory flow, with adjacent vortices being antiparallel. An idealized version of the flow pattern (two-dimensional), the director distortion and an equivalent lens for the distortion is shown in Fig. 4. One can, in principle, measure the focal length of the lens to characterize the gradient of the director in the distorted sample. Such measurements were not made in the work reported here, but have been made for PBT solutions [2].

The instability with solutions of PHIC is more complicated than the one observed with PBG solutions, involving a distortion in three dimensions, and producing a phase grating. This distortion also involves reorientation coupled with a circulatory flow, with adjacent vortices being antiparallel. In the case of an electrohydrodynamic instability, which also produces a phase grating, the director tilt $\theta(z,x)$ produced by a flow induced reorientation can be expressed in the form [15,17]:

$$\theta(z,x) = \theta_o \cos(\pi x/\lambda_x) \cos(\pi z/d_{eff}) \quad (3)$$

and there is no distortion in the y-direction. Here, θ_o is the maximum tilt angle of the director out of the sample plane and d_{eff} an effective sample thickness. With this profile of the director distortion $\theta(z,x)$, the refractive index $n_E(\theta)$ for light polarized along the x-axis and propagating along the z-axis can be written as

$$n_E(\theta) = \left[\left(\frac{\cos\theta}{n_E} \right)^2 + \left(\frac{\sin\theta}{n_O} \right)^2 \right]^{-1/2} \quad (4)$$

where n_E and n_O are extraordinary and ordinary refractive indices, respectively. The optical path length can be calculated by integration of $n_E(\theta)$ through the sample, producing a diverging lens at $x = 0$ and a converging lens at $x = \pm\lambda_x/4$ [15]. The focal length f of the lenses is equal to Λ, and the calculated f-value using the refractive index profile provides a measure of θ_o given by

$$\Lambda = f = \frac{\lambda_x^2}{\pi^2 \Delta n \theta_o^2 d_{eff}} \quad (5)$$

where $d_{eff} = \lambda_x$ if $\lambda_x < d$, or $d_{eff} = d$ otherwise. In most cases, the spacing between the periodic structures is largely determined by the sample thickness.

The seeming insensitivity of the wavelength of the instability to the driving field is rather surprising, however, such behavior has been observed for at least three polymeric systems so far, PBT in methane sulfonic acid [2], PBG in *m*-cresol, and PHIC in *p*-xylene [25]. While the formation of these periodic structures is reasonably well understood, the insensitivity of the observed wavelength to the driving field is puzzling and not understood. It is tempting to attribute these peculiarities to the shear flow properties of these solutions. As already pointed out, the instability in the initial stages is dominated by the secondary flow, which is generated by the applied magnetic field. It is perhaps possible that the initial wavelength might be controlled by the secondary flow, which now is perpendicular to the unperturbed director, $\mathbf{n}_0$.

It is now well established that the above three systems are nonflow-aligning within the framework of the Ericksen–Leslie equations [20,25–27]. The Ericksen–Leslie constitutive equation provides predictions for the flow behavior of nematic fluids in terms of six viscosity coefficients α_i (i = 1–6), of which five are considered to be independent [8]. Specifically, the model predicts a homogeneous shear

deformation when the coefficients α_2 and α_3 have the same sign (i.e. $\alpha_2\alpha_3 > 0$). In such an instance, and in the absence of other constraints, shear flow of a nematic fluid is expected to tilt the director in the shear plane (the plane containing the velocity and the velocity gradient) against the shear gradient, and assumes the Leslie angle θ_0, where

$$\tan^2\theta_0 = \alpha_2/\alpha_3 \quad (6)$$

As is usual, θ_0 is the angle that the director makes relative to the flow direction and θ_0 is positive if the director tilts against the shear gradient. This corresponds to the situation where the torque on the director due to shear flow is zero. Many polymeric nematics exhibit what is termed as nonflow-aligning behavior [25,28], where the director tilts down in the shear plane, thus leading to unstable shear flow. This is because the director experiences a torque due to shear flow everywhere. In this case, a complex cascade of instabilities is observed in response to a shear flow [25].

For the PBT solutions [20,25,29,30], it is known that primary flow imposed in a direction normal to the unperturbed director does indeed create an instability that leads to the formation of a phase grating. It was also found that the wavelength of the phase grating formed was independent of the velocity of the driving primary flow. In other words, the wavelength was found to be insensitive to the magnitude of the velocity field. It would then seem logical to suggest that the wavelength selection is dominated by the flow properties of the material rather than the strength of the driving magnetic field. However, the flow in the instability observed is initiated by the applied magnetic field. A viable theory is not available, as yet, for the type of instability described here.

4. Conclusions

We have studied the field-induced transition in the twist geometry, which shows that instability is created, leading to a spatially periodic structure. The periodic structure manifests itself as a phase grating, which is coupled to a complex three-dimensional secondary flow, giving rise to a three-dimensional director pattern. The structures reported here appear to be rather unique to a class of polymeric nematics that exhibit unstable shear flow, i.e. they are nonflow-aligning in the framework of the Ericksen–Leslie equations. A theory predicting the nature of this instability is unavailable, as yet.

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