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Observation of textures of nematic polymers and estimation of the elastic constants

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The texture of a copolyesteramide, Vectra® B950, has been studied by optical microscopy. At rest, the defects are typical of a biaxial nematic phase, but under the influence of a magnetic field or under shear, the nematic transforms into a uniaxial phase. The Freedericksz geometry yields a K_I elastic constant of the order of 10^{-8} N. The diffusivities K_{II}/η and K_{III}/η are obtained by measuring the light intensity transmitted through a sample during shear start-up and relaxation, and from this we estimate $K_{III} \cong 10^{-9}$ N and $K_{II} \cong 10^{-10}$ N. Since the biaxiality is small, these uniaxial constants adequately describe the phase at rest.

1. Introduction

Vectra® B950 is a copolyesteramide which is a thermotropic polymer forming a nematic phase above 290°C. Due to the ease with which well oriented and reasonably transparent samples may be obtained, its texture at rest [1], rheology [2,3] and flow-induced textures [4,5] have been extensively studied. As shown before [1], Vectra® B950 is a biaxial nematic having well-defined defects typical of such a nematic phase. The texture displayed at rest is the threaded texture. When carefully prepared by prolonged annealing at *c.* 300°C [1], it contains very few defects and their strength and character can be determined by optical microscopy. When a weak shear flow is applied, there is a sudden and large increase in the defect density. The texture developed is the so-called worm texture, characterized by half-strength disclination loops lying in the shearing plane [4,5]. These observations suggest that the biaxiality is weak and disappears under gentle flow or an applied magnetic field.

Despite the fact that thermotropic polymers have been studied for more than two decades, relatively little information is available on their structure or on the origin of field-induced changes in their textures. This is especially true when their properties are studied in the nematic phase, and not in a quenched sample. One of the most important physical properties is the elasticity originating from distortions of the director field. This

elasticity, expressed in terms of the elastic constants [6], controls the formation of textures in nematics and is a major factor in the change of texture under the influence of an external field such as a flow. Three parameters, the so-called Frank elastic constants, describe the free energy density F of a uniaxial nematic

$$F = K_I(\text{grad } \mathbf{n})^2 + K_{II}(\mathbf{n} \text{ rot } \mathbf{n})^2 + K_{III}(\mathbf{n} \times \text{rot } \mathbf{n})^2, \quad (1)$$

where K_I , K_{II} and K_{III} respectively represent the curvature elastic moduli for splay, twist and bend deformations of the director \mathbf{n} .

An ensemble of defects is called a texture. Liquid crystalline polymers have the same topologically stable defects as low molecular weight liquid crystals, but the textures are very different. The reason lies in the difference between the energetic stability of the same topological defects in low molecular weight and in polymer liquid crystals [7]. These differences generally originate from the molecular organization about the core of the defects. In order to obtain a more detailed description of defects, one needs to describe the free energy of the elastic distortion of a nematic fluid.

For liquid crystalline polymers, K_I , K_{II} and K_{III} depend on molecular weight and chain flexibility through the ratios L/d or q/d , where L is the contour length, q the persistence length for a semi-flexible model and d the chain diameter [8]. K_{III} is the largest constant for rod-like polymers, which is experimentally verified. For semi-flexible polymers in concentrated solution and

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for thermotropic polymers, K_I is the largest. K_{II} is similar to the values for small molecule nematics.

The purpose of this paper is to recall the biaxial nature of the previously studied copolyesteramide and to evaluate its elastic constants by two methods, one based on the Freedericksz transition, and the other on the creation of texture during shear and relaxation after cessation of flow.

2. Experimental

The material used is a thermotropic liquid crystalline copolyesteramide based on 60/20/20 6-hydroxy-2-naphthoic acid/hydroxybenzoic acid/aminophenol. It is supplied by Hoescht-Celanese under the trade name Vectra® B950. The melting temperature is about 290°C and its molecular weight is about 20 000 g mol⁻¹.

Two types of sample were used. One type was the peeled skin of extrudates made with a capillary rheometer. The thickness was between 10 and 20 μm. These samples were very well oriented. The other type was obtained from injection moulded plates. Their thickness was 1 mm. All samples were dried in an oven at 120°C under vacuum for 24 h to prevent hydrolytic chain scissions.

Optical studies were carried out with a Leitz microscope equipped with a Linkam hot stage. Magnetic field orientation studies were conducted by placing the thermotropic sample in a heating stage made from high-purity copper foils and positioned between the poles of a water cooled electromagnet. The field intensity was set at 2 T.

In order to study the relaxation of the worm texture, a transparent sliding-plate apparatus, described elsewhere [2], was placed in the stage of a Leitz microscope equipped with a photosensitive diode to measure the light flux ϕ_t transmitted through the sample. The shear rate could be varied from 0.1 s⁻¹ to 10 s⁻¹. At a given shear rate and at 300°C, a certain number of shear strain units were applied before the translation of the upper plate as stopped. Relaxation of the worm texture took place and was monitored with the aid of ϕ_t . The thickness of the sample was set to 50 μm.

3. Results and discussion

3.1. Textures at rest and biaxiality

Donald and Windle [9] have interpreted some discrepancies between optical and electron microscopy observations of nematic domains in thermotropic polymers in terms of biaxiality. While these results have not yet obtained complete support, it is well known that defects in uniaxial and biaxial nematics are of a very different nature, and should be the signature of the 'axiality'. Indeed, Vectra® B950 studied at rest by optical microscopy [1] shows defects which cannot be compatible with a uniaxial nematic phase. For example, a half-integer

twist disclination line can take only one configuration in a uniaxial nematic phase, while three types exist in a biaxial nematic. Figure 1 shows a schematic model of these three possible lines. Case (b) where the 'uniaxial nematic director', i.e. the chain direction, is well oriented, but where the biaxial correlations present a 90° change of orientation is interesting. The defect line is only observed under polarized light, when the polarization is along the

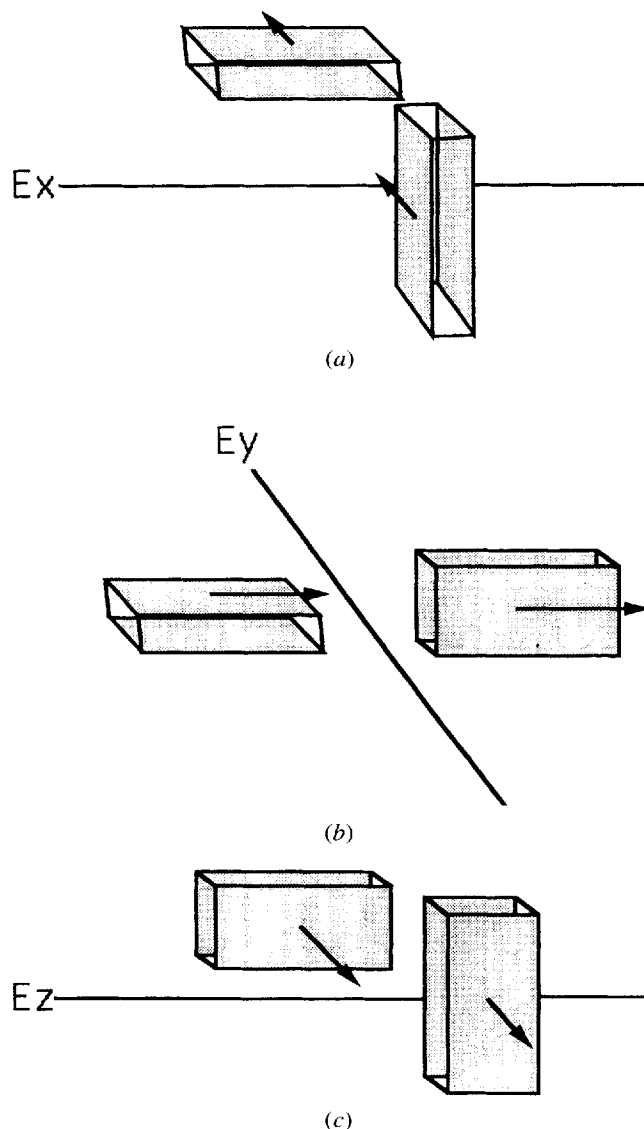


Figure 1. Model of the three possible half integer twist disclination lines in a biaxial nematic. A biaxial phase has three different directors and it can be schematically modelled by a ribbon (a uniaxial nematic would be a cylinder). The long axis of the ribbon is labelled Y, and the two others X and Z. (a) rotation around the X axis. (b) Rotation around the Y axis. (c) Rotation around the Z axis. In a uniaxial nematic, case (b) does not exist and cases (a) and (c) are identical.

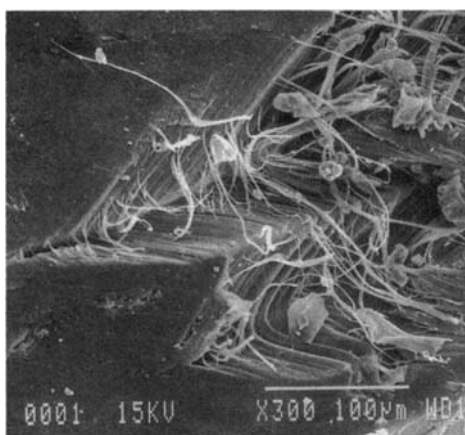


Figure 2. Scanning electron micrographs of the cut sample after 2 h in a magnetic field.

chain direction. This is indeed what is seen with Vectra® B950 [1]. However, if Vectra® B950 is biaxial at rest, it seems that an external field like a magnetic field or a flow disrupts the biaxiality and transforms the liquid crystal into a uniaxial nematic; details can be found in [1]. The measurement of elastic constants has never been reported for biaxial nematics at rest. Such a measurement is described in the following two paragraphs through the use of external fields.

3.2. Orientation under the influence of a magnetic field

The experimental configuration used was the first Freedericksz geometry [6], described earlier [1]. 1 mm thick samples placed under a magnetic field of 2 T for 2 h at 300°C were cut and microtomed. The surface observed by scanning electron microscopy is shown in figure 2. It corresponds to the sample shown in the figure 13 of [1]. It shows a sort of regular zig-zag, meaning that a reorientation of the director at 30° from the original direction occurs over a period of 90 µm. The Frank–Oseen theory related this distance to K_I/χ_a

$$H = \pi/d(K_I/\chi_a)^{1/2}, \quad (2)$$

where H is the intensity of the magnetic field, d the characteristic dimension of the distortion and χ_a the anisotropic part of the diamagnetic susceptibility. Taking $H = 20\,000$ G and $d = 90$ µm, K_I/χ_a is 3300. The value of χ_a is only weakly dependent, $3\text{--}7 \times 10^{-7}$ cgs units, on chemical structure for organic compounds [10]. Taking χ_a equal to 5×10^{-7} cgs units gives a value for K_I of about 10^{-3} dynes or 10^{-8} N.

3.3. Relaxation of the worm texture upon stopping a shear

As observed with the sliding-plate apparatus and as previously reported [2], Vectra® B950 displays the following behaviour: a few moments after starting flow, a sudden decrease of ϕ_t (a strong absorption of light), occurs

at the transition from the thread to the worm texture. Upon further shearing, damped oscillations of the light flux transmitted through the sample are observed. A similar observation has been reported for lyotropics [11]. This variation of the transmitted light is observed irrespective of the type of light. It is therefore due to the scattering of light by the core of the defects. Starting from this hypothesis, it is possible to relate the defect density ρ to the light flux ϕ_t transmitted through the sample. Assuming linear scattering, we first get

$$\frac{\phi_t}{\phi_0} = 1 - \left(\frac{S_a}{S_0}\right) \quad (3)$$

where ϕ_0 and ϕ_t are the initial and the measured light flux, respectively. ϕ_t is measured at a given shear strain. S_0 is the surface of the sample and S_a is the ‘absorbing’ surface (due to defect scattering) responsible for the decrease of the light flux.

If R_c is the lateral dimension of the optical core of the defects and L the total defect length, the following relation holds

$$S_a = R_c(L - L_0) \quad (4)$$

L_0 being the defect length before shear, i.e. the defect length of the threaded texture. As seen before by optical rheometry [2], there is a huge creation of defects during shear. It is therefore justified to assume that L_0 is small compared to L . Equation (4) then becomes

$$S_a = R_c L. \quad (5)$$

The defect density ρ is related to the total defect length l by the following relation:

$$\rho = \frac{L}{(eS_0)}, \quad (6)$$

where e is the thickness of the sample.

Taking into account the expressions for S_a and S_0 equation (6) may now be written as

$$\rho = \left[\frac{1}{eR_c}\right] \left[\frac{\phi_0 - \phi_t}{\phi_0}\right]. \quad (7)$$

This expression relating the defect density to the absorption of the light is based on one important assumption, that all defects scatter light in the same way. This is justified

Defect density ρ obtained from equation (7). ρ is expressed in cm^{-2} ; γ^* is the shear rate in s^{-1} and γ is the macroscopic shear strain defined by $\gamma = \gamma^* t$. The estimated error made on ρ is less than 10 per cent.

γ^*/s^{-1}	$\gamma = 60$	$\gamma = 150$
1	1.3×10^6	1.1×10^6
10	1.6×10^6	1.5×10^6

here, since the defects created during flow are mostly of the same kind and oriented in the same way [5]. The table gives the values of ρ , calculated from equation (7), for two different shear rates ($\dot{\gamma}^*$) and two different strains (γ) after starting the shear.

We have been able to measure directly the core dimensions R_c and the mean distance between defects in a series of SEM observations made on microtomed and etched samples obtained from quenched sheared specimens [4, 5]. We found R_c to be of the order $1 \mu\text{m}$, and the mean distance between defects of the order $7 \mu\text{m}$ after several tens of shear strain units, i.e. giving a value of ρ which is in qualitative agreement with that extracted from equation (7). The oscillation behaviour of the defect density has been investigated as follows. Shear was stopped after the application of various shear strains, and figure 3 shows a semi-logarithmic plot of the evolution of the defect density ρ , calculated from equation (7), as a function of the time t after stopping flow. Immediately after stopping the shear, the relaxation is more rapid, when the defect density is lower. The evolution of the relaxation time λ (measured from the slope of figure 3) with respect to shear strain shows oscillatory behaviour (see figure 4). Assuming that the typical relaxation of defects occurs through the rotation of the director from one orientation to another, by balancing elastic and viscous forces, one therefore expects the following scaling relation:

$$K\rho = \eta/\lambda, \quad (8)$$

where K is an effective Frank elastic constant

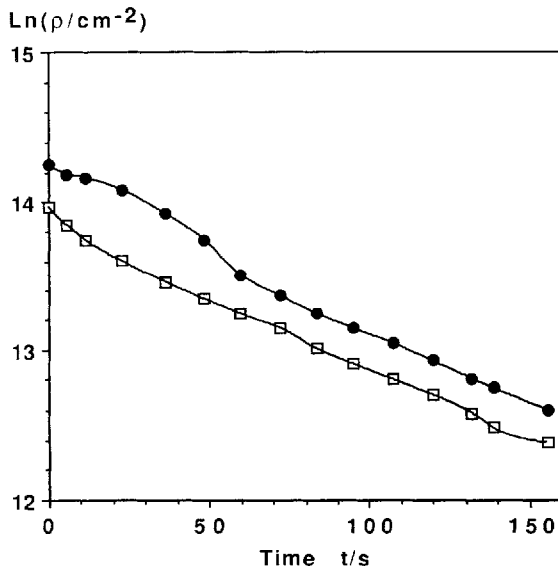


Figure 3. Naperian logarithm of the defect density ρ (in cm^{-2}) as a function of time t during the relaxation after shear at 1 s^{-1} . Two shear strains were applied before this relaxation: (●) 30 shear units and (□) 140 shear units.

Relaxation time λ/s

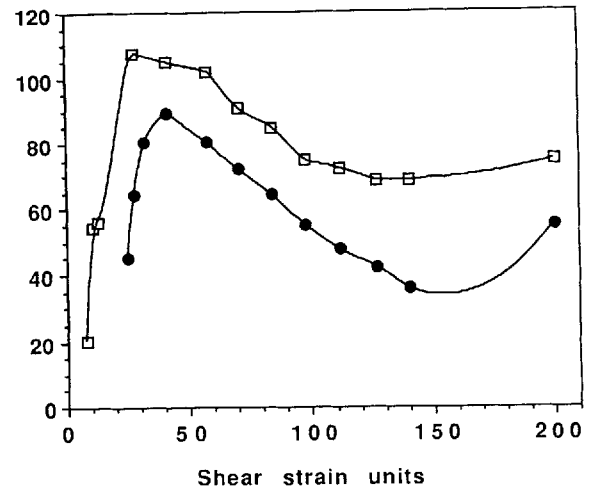


Figure 4. Relaxation time λ of the worm texture after stopping the shear as a function of shear strain. Two shear rates were applied before the relaxation: (□) 1 s^{-1} and (●) 10 s^{-1} .

(a combination of the three elastic constants), η an effective viscosity and λ the relaxation time.

Figure 5 gives the evolution of the diffusivity $D = 1/\rho\lambda$ as a function of shear strain at two different shear rates during a start-up experiment.

Clearly, D , which is not a constant, should be explained in terms of the dominant K_i term in the deformation and of the viscosity η , which in turn has a complex dependency [6] of the wavevector of the relaxation and the anisotropic

$D/m^2 \text{ s}^{-1} \cdot 10^{12}$

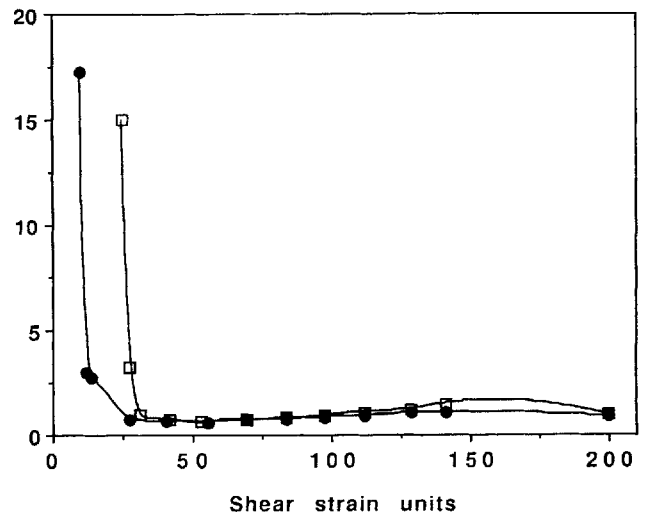


Figure 5. Variation of the diffusivity $D = 1/\rho\lambda$ as a function of shear strain for two shear rates (start-up experiment): (●) 1 s^{-1} and (□) 10 s^{-1} .

viscosity coefficients. The smallest viscosity is the rotational viscosity γ_1^* . To simplify the dependence, we shall assume η is a constant and of the same order as the shear viscosity (300 Pa s at low shear rates [2]).

In order to interpret these results, it is necessary to recall some results obtained by observing the polymer after freezing its texture [4, 5]. Defects are created during shear. They are elongated, half-strength disclination loops which have twist character with a non-planar configuration, as shown in [4]. The Frank elasticity imposed by such a configuration is the addition of bend and twist terms. Taking into account the fact that K_{II} is small compared to K_{III} , K_{III}/η is therefore of the order of $1.6 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ (see the value of K/η at the onset of the worm texture in figure 5).

During flow, after several tens of shear strain units, the configuration is planar. The Frank elasticity is purely twist and K_{II}/η is of the order of $6 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ (see also figure 5). K_{III} is therefore about 30 times K_{II} , a result which is not surprising. Assuming $\eta = 300 \text{ Pa s}$, this gives a value for K_{III} of about 10^{-9} N and a value for 10^{-10} N . These large values are comparable with the value of K_I obtained above.

4. Conclusion

The magnitude of the three elastic constants of Vectra[®] B950 is about 100 times higher than corresponding values found in the literature for other thermotropic polymers [12, 14]. To what extent these large values are related to the chemical structure of this polymer or to its biaxiality

are unclear. However, they are probably responsible for the very rapid occurrence of the threaded texture, which develops after only a few minutes at rest. This is not related to a low value of the viscosity, since the shear viscosity of this copolyesteramide is comparable to that of other copolyesters.

References

- [1] DE'NÈVE, T., KLÉMAN, M., and NAVARD, P., 1992, *J. Phys. II, France*, **2**, 187.
- [2] DE'NÈVE, T., NAVARD, P., and KLÉMAN, M., 1993, *J. Rheol.*, **37**, 515.
- [3] LEFEUVRE, P., DE'NÈVE, T., and NAVARD, P., 1994, *J. Rheol.*, **38**, 169.
- [4] DE'NÈVE, T., KLÉMAN, M., and NAVARD, P., 1993, *C. r. hebdomadaire des séances de l'Académie des Sciences, Paris*, **316**, 1037.
- [5] DE'NÈVE, T., NAVARD, P., and KLÉMAN, M., *Macromolecules* (submitted).
- [6] DE GENNES, P. G., 1974, *The Physics of Liquid Crystals* (Clarendon Press).
- [7] KLÉMAN, M., 1991, *Liquid Crystallinity in Polymers*, edited by A. Cifferi (VCM Publishers).
- [8] LEE, S. D., and MEYER, R. B., 1990, *Liq. Crystals*, **7**, 15.
- [9] DONALD, A., and WINDLE, A. H., 1983, *Coll. Polym. Sci.*, **261**, 155.
- [10] WEAST, R. C., 1983, *Handbook of Chemistry and Physics*, 64th edition (CRC Press).
- [11] MOLDENAERS, P., FULLER, G., and MEWIS, J., 1989, *Macromolecules*, **22**, 960.
- [12] ZHENG-MIN, S., and KLEMAN, M., 1984, *Molec. Crystals liq. Crystals*, **111**, 321.
- [13] GILLI, J. M., SIXOU, P., and BLUMSTEIN, A., 1985, *J. Polym. Sci., Polym. Lett.*, **23**, 379.
- [14] HAKEMI, H., and ROGGERO, A., 1990, *Polymer*, **31**, 84.