RHEOLOGY AND CHANGES IN STRUCTURE
OF
THERMOTROPIC LIQUID CRYSTALLINE POLYMERS

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CHAPTER 1

INTRODUCTION

Thermotropic liquid crystalline polymers (LCPs) owe their technological importance to the relative ease of manufacturing products with outstanding mechanical properties and high dimensional precision using ordinary processing techniques, such as injection moulding. This ease of processing is the result of the liquid crystalline structure of the melt in a temperature region between the semi-crystalline state and the isotropic-melt state, resulting in relatively low viscosities, to low shrinkage, and to easy molecular orientation. The liquid crystalline state is the consequence of the rigidity of the molecules, which are spontaneously ordered along a mean direction, called the director \( n \). This order persists over domains of micrometer size. Domains with different director orientations are separated by defects, called disclinations. This intrinsic multi-length scale structure of the liquid crystalline melt undergoes changes during flow, which are thought to be responsible for the complicated rheological behaviour of LCPs. Hence, prediction of processing behaviour of LCPs is much more complex than for flexible polymers.

The objective of this thesis is to determine key features of the rheology of thermotropic main-chain LCPs and to relate these to the underlying structural changes. Since the development of orientation and structure in these materials during flow is responsible for their rheological responses, in-situ optical (rheo-optical) experiments are necessary in addition to rheological measurements to understand their flow behaviour. Until present most experimental data of the rheology and rheo-optics of liquid crystalline polymers have been obtained from solutions (lyotropes). The most widely investigated thermotropic LCP, Vectra® A900, is highly turbid and, therefore, unsuitable for rheo-optical experiments. Optical investigations on this material have been performed only on quenched samples. In this thesis the results from rheological and rheo-optical experiments on a liquid crystalline copolyesteramide (Vectra® B950) are reported and analyzed. Studies like these should provide a basis for further improvement of rheological models, which at present do not account for all experimental features and for the difference between melts and solutions.

1.1 Liquid crystalline polymers

Liquid crystallinity was first discovered in low molecular weight systems some 100 years ago and later also in polymers. Many books and review articles have appeared on this
subject ever since to which the reader is referred for details [e.g., de Gennes (1974), Ciferri et al. (1982), Gray (1987), Kwolek et al. (1987), Ciferri (1991), Chandrasekhar (1992), Collyer (1992), and Donald and Windle (1992)].

Liquid crystals comprise an intermediate phase between the crystalline phase, that shows long-range correlations in both the position and orientation of the constituent molecules, and the (isotropic) liquid phase, that only shows short-range correlations. The liquid crystalline or mesophase refers to the situation in which the molecules exhibit an orientational order but no positional order (nematic) or an orientational order and a long-range positional order in one or two directions (smectic) (see Fig. 1.1). Liquid crystals have flow properties like ordinary liquids, while they exhibit anisotropic properties, such as birefringence, that are characteristic of crystals.

A requirement for the formation of a liquid crystalline phase is a strong asymmetry in shape at the molecular level, that frustrates the ability of the molecules to adopt a random orientation in the liquid state even in the absence of flow. This requirement is met by rod-, plate- or disclike molecular groups, called mesogenic units. In the case of main-chain liquid crystalline polymers (LCPs) the rodlike units are incorporated in the polymer chain. This class of materials is mainly used in constructional applications, because of their excellent mechanical properties and processing behaviour. On the other hand, in side-chain LCPs the mesogenic units are attached to the flexible polymer chain with a (flexible) spacer group. This class of materials exhibits no superior mechanical properties, but owes its importance to the special electrical and optical properties.
A major subdivision of liquid crystals is made on the basis of whether the formation of the liquid crystalline phase is induced by changes in temperature or concentration in a solvent. The former type is referred to as thermotropic, while the second is known as lyotropic. Some materials can exhibit both thermotropic and lyotropic phases and are referred to as amphotropic.

The materials studied in this work are thermotropic main-chain LCPs. The synthesis of these type of polymers is not straightforward. Simply increasing the length of liquid crystalline molecules by polymerization soon results in a system that does not melt, since the crystal melting point of these rigid chain crystals increases substantially with increasing chain length to exceed the decomposition temperature [Donald and Windle (1992)]. Such rigid chain polymers may exhibit lyotropic liquid crystalline behaviour and a well-known example is poly(para-phenyleneterephthalamide) (PPTA) from which high modulus fibres are spun by Dupont (Kevlar®) and Akzo (Twaron®). These extremely stiff and strong materials are used in, e.g., protective clothing (bullet proof vests, helmets), high strength fabrics (sails), and plastic reinforcement (aircraft) [Jansson (1992)].

To obtain melt processable LCPs the regularity of the polymer chain has to be disrupted or the flexibility of the chain increased so that the crystal/liquid-crystal transition is suppressed to a point below the decomposition temperature of the polymer. Basically three methods are used to achieve this [see, e.g., MacDonald (1992)]: frustrated chain packing, flexible spacers, and non-linear links. The thermotropic main-chain LCPs studied most are aromatic random copolyesters or copolyesteramides. They have the advantage over lyotropic LCPs of being melt-processable. Usually, they display a good processability due to a low melt viscosity, a very high dimensional stability and tight tolerances (due to a low coefficient of thermal expansion), very good mechanical properties in the orientation direction, and a high chemical and heat resistance [Römer (1993)]. Applications are found mostly in precision injection moulding parts, such as electronic connectors, lens holders for CD players, etc., and also in lamp housings, parts of pumps in chemical processes etc. [Jansson (1992)].

Two thermotropic LCPs are studied in this thesis. The rheological and rheo-optical studies are conducted on the random copolyesteramide Vectra B950 (manufactured by Hoechst Celanese), consisting of 60% 2,6-hydroxynaphthoic acid, 20% terephthalic acid, and 20% aminophenol. This material exhibits a glass transition temperature of 142 °C and a melting point at about 284 °C. The choice of this material was based on its better suitability for rheo-optical experiments in contrast to that of the more widely used LCP Vectra A900 (a
random copolyester consisting of 73\% para-hydroxy benzoic acid (HBA) and 27\% 2-hydroxy, 6-naphthoic acid (HNA)), which is highly turbid. Moreover, during the course of this investigation other groups published rheological and (rheo-)optical data on the same material, making comparison possible. Static optical experiments are conducted on drawn films the random copolyester Ultrax KR4002\textsuperscript{®} (manufactured by BASF), consisting of 1,4-hydroxybenzoic acid, terephthalic acid and 2,7-dihydroxy-naphthalene, unfortunately, in an unknown composition. This LCP shows a glass transition at 128 °C and a melting point in the range of 272-298 °C. The choice of this material was based on its good drawability, resulting in smooth regular films in contrast to drawing of both Vectra’s, which resulted in irregular surfaces. Both used LCPs show a nematic phase above the melting point, but no further transition is observed to an isotropic phase at higher temperatures.

1.2 Morphology of nematic liquid crystalline polymers

Nematic phases are characterized by a uniaxial symmetry of the molecular orientation distribution function \( f(\theta) \), describing the probability density of finding a rod with its orientation between \( \theta \) and \( \theta + d\theta \) around a preferred direction, called the director \( n \) (see Fig. 1.2). A direct observable and important characteristic of the nematic phase is the scalar order parameter \( S \) or \( \langle P_2^r \rangle \), also called Hermans orientation factor \( f \) [Saupe and Maier (1961)]. This is the value of the second order Legendre polynomial \( P_2 \) of \( \cos \theta \),

\[
S = \frac{1}{2} \left( 1 + \frac{1}{2} \langle P_2^r \rangle \right)
\]

where \( \langle P_2^r \rangle \) is the average value of the second Legendre polynomial over the distribution of orientations.

\[
P_2(\cos \theta) = \frac{1}{2} \left( 3 \cos^2 \theta - 1 \right)
\]

This represents the average cosine squared of the angle between the director and a given orientation, weighted by the probability density of that orientation.

\[
\langle P_2^r \rangle = \int_{-1}^{1} P_2(\cos \theta) f(\theta) \, d\cos \theta
\]

The order parameter \( S \) ranges from 0 for a completely isotropic state to 1 for a perfectly aligned nematic phase.
Figure 1.3: Basic deformation modes for the director field and the associated Frank elastic constants.

\[ S = \langle P_2 \rangle = \frac{1}{2} (3 \langle \cos^2 \theta \rangle - 1) = 1 - \frac{3}{2} \langle \sin^2 \theta \rangle \]  \hspace{1cm} (1.1)

where \( \theta \) is the angle between an individual molecule (described by the unit vector \( \mathbf{u} \) and the director \( \mathbf{n} \) and the brackets indicate the averaging process:

\[ \langle P_2 \rangle = \int_0^\pi f(\theta) P_2(\cos \theta) \sin \theta \, d\theta \]  \hspace{1cm} (1.2)

The order parameter is zero for isotropic systems, -1/2 for fully perpendicular alignment and 1 for perfect parallel alignment. Several models describing the phase transitions from isotropic to nematic result in different predictions regarding the order parameter in the nematic phase [Larson (1988), Marrucci and Greco (1993)]. In the Maier-Saupe theory the order parameter jumps from zero to \( S = 0.44 \) at this transition, while for the Onsager theory it jumps to \( S = 0.84 \).

The description of the nematic phase above is a simplification of the real systems. Only when substrates with uniform boundary conditions are used and/or when large magnetic fields are applied, the orientation may be uniform over macroscopic distances to result in a monodomain. Usually, the orientation of nematics varies in space on the submicron (0.5 \( \mu \)m) to micron scale (10 \( \mu \)m) due to non-uniform boundary conditions or external (electric or magnetic) fields or forces. A continuous deformation of the oriented material, small enough that the change in \( \mathbf{n} \) over the length of the molecule is insignificant, can be decomposed into three basic distortions: splay, twist and bend distortions (see Fig. 1.3).
Therefore, three elastic (material) constants, known as the Frank elastic constants \((K_1, K_2, \text{ and } K_3)\), are required to describe the resistance offered by the nematic phase to these orientational distortions [Frank (1958), De Gennes (1974)]. If the deformation of the director field is discontinuous, defects are introduced in the material [Frank (1958), de Gennes (1974), Kléman (1991), Chandrasekhar (1992)]. These defects usually take the form of line disclinations (see Fig. 1.4). The strength \(s\) of a disclination is defined as the amount of director rotations \(2\pi s\) around the defect. Since the energy associated with the disclination line is proportional to \(s^2\), the half integer lines are more stable. However, the stability of a defect also depends strongly on the anisotropy of the Frank elastic constants.

The disclinations are mostly responsible for the texture observed in the microscope, which is often referred to as a polydomain texture. Here a domain is defined as a region of
length scale $a$ in which the molecular orientation is uniform (see Fig. 1.2). Different disclinations have different appearances in the microscopic picture. *Wedge* lines (Fig. 1.4 a-f), which are parallel to the rotation vector, are visible in the typical schlieren textures (in which the disclination lines are perpendicular to the sample boundaries). On the other hand, *twist* lines (Fig. 1.4 g), which are orthogonal to the rotation vector, show up as a threaded texture (in which the lines are parallel to the sample boundaries).

On the molecular scale, i.e. within one domain, the order parameter is defined by equation (1.1). The experimentally measurable mesoscopic order parameter ($P_2^{exp}$), i.e. the orientation of an ensemble of domains, is however, determined by both this molecular order parameter ($P_2^{mol}$) and the distribution of director orientations over the domains ($P_2^{dom}$):

$$P_2^{exp} = P_2^{mol} \cdot P_2^{dom}$$  \hspace{1cm} (1.3)

At the macroscopic level, in e.g., injection moulded products, the orientation is the result of local shear and elongational flow. Often a layered structure is found parallel to the flow direction, in which the orientation differs from one layer to another. The processing conditions highly influence the number of layers, the thickness of the layers and the orientation inside the layers, which in turn influence the (anisotropy of the) mechanical properties, the coefficient of expansion and the form stability [see, e.g., Merckx (1992), Hsiung et al. (1993), Hsiung and Cakmak (1993), Jansen et al. (1994)].

### 1.3 Optical investigations of LCPs

Since LCPs exhibit a complex microstructure, the use of various techniques probing the different length scales has been reported in literature. Techniques that are in principle suitable for assessing structures at the molecular level are birefringence, infrared, ultraviolet, and Raman spectroscopy, wide-angle X-ray scattering (WAXS), small-angle neutron scattering (SANS), and nuclear magnetic resonance (nmr). Techniques able to obtain information at the domain or mesoscopic level include polarized optical microscopy (POM), small-angle X-ray scattering (SAXS), small-angle light scattering (SALS), and (visible light) dichroism.

Most of the above techniques have been applied to stationary or quenched samples, because of experimental limitations. Only some have been used successfully in measurements during rheological experiments (the so-called *rheo-optical* experiments) to
obtain information on the evolution of the structure of LCPs during flow. These include birefringence, WAXS, SANS, POM, SALS and dichroism. For birefringence, dichroism and POM the samples have to be fairly translucent to be able to obtain sufficient information. This condition is, however, only met by some LCP systems, in particular the lyotropes. In general, the domain sizes of thermotropic systems are smaller than those of lyotropes, resulting in highly scattering samples. This has obstructed quantitative measurements on thermotropic materials until present.

In this thesis birefringence, dichroism, POM, SALS and WAXS have been used either during flow or after quenching. For the theoretical background and experimental procedures of most of these techniques the reader is referred to the appropriate chapter. In particular, in chapter 6 a literature review is presented on rheo-optical investigations of LCPs. In the present section only definitions of some quantities, that are used throughout this thesis, are presented.

In the quantitative rheo-optical measurements a well-defined light beam is sent through a sample and collected at a detector. Information about the microstructure of the material during flow is obtained from the change of the initial beam on its way through the sample. The effect of the sample on the light beam can be twofold: it can change both the phase and the amplitude of the electric vector [see, e.g., Fuller (1995)]. These effects are reflected in the changes of, respectively, the real part \( n' \) and imaginary part \( n'' \) of the refractive index tensor:

\[
n = n' - i n''
\]  

(1.4)

For isotropic materials, the phase shift and attenuation of the light is equal in all directions. On the other hand, for (uniaxial) anisotropic materials, such as LCPs, these quantities may be direction dependent, resulting in birefringence \( (\Delta n') \) and dichroism \( (\Delta n'') \):

\[
\Delta n' = n'_1 - n'_2
\]  

(1.5)

\[
\Delta n'' = n''_1 - n''_2
\]  

(1.6)

where the subscripts 1 and 2 refer to the values along the principal axes of both the real and imaginary part of refractive index. The frames of the real and imaginary part do not necessarily have to be coaxial. The birefringence is directly related to the anisotropy in the polarizability (electron distribution) of the material and, therefore, reflects the degree of
molecular orientation [see, e.g., Burghardt et al. (1995)]. The dichroism may be caused by anisotropic absorption (intrinsic or consumptive dichroism) or scattering (conservative dichroism) of light and is a strong function of the wavelength. For LCPs a range of wavelengths can be used where no absorption occurs, but where the polydomain texture scatters light. Hence, the dichroism is a measure of the anisotropy at the mesoscopic level [see, e.g., Moldenaers et al. (1989)].

Usually, in optical experiments (see chapters 5 and 6) the birefringence and the dichroism are extracted from an intensity signal through, respectively, a function of the retardation $\delta'$ or the extinction $\delta'':$

$$\delta' = \frac{2 \pi \Delta n' d}{\lambda}$$

$$\delta'' = \frac{2 \pi \Delta n'' d}{\lambda}$$

where $d$ is the sample thickness, and $\lambda$ is the wavelength of light.

1.4 Nematic main-chain LCPs in flow

The rheology of main-chain LCPs has been studied extensively for lyotropic systems but to a much lesser extent for thermotropic systems. This is mainly the consequence of the experimental problems associated with the thermotropes, such as the high measuring temperatures. At these temperatures physical and chemical changes may take place, resulting in a sensitivity of the sample to the thermal history and a time dependence of the measured properties. Moreover, compared to the thermotropes the experimentally "easier" lyotropes show a much more ideal behaviour, following the predictions of the current theories for rodlike molecules better.

Starting with the description of the steady state behaviour immediately demonstrates the complexity of the rheology of LCPs. A feature found for many LCPs is a viscosity versus shear rate curve showing two shear thinning regions at low and high shear rates, separated by a region of constant viscosity (see Fig. 1.5). This flow curve is often referred to as a "three region flow curve" [Onogi and Asada (1980)] and is quite common for many lyotropic systems. For some low concentration nematics, however, no region I has been found or the flow curve is shear thinning throughout, exhibiting three different power law indices [e.g., Mortier et al. (1996)]. For some thermotropic systems a three region flow
Figure 1.5: Schematic representation of the bulk texture of an LCP during shear flow in the respective regions of the three region flow curve, as proposed by Onogi and Asada (1980).

Figure 1.6: Viscosity (O) and first normal stress difference \( N_1 \) (\( \star \), \( \triangle \)) for a solution of 12% poly-\( \gamma \)-benzyl-L-glutamate in m-cresol as a function of the shear rate. The filled symbols indicate the area where \( N_1 \) is negative. (Data kindly provided by prof. Moldenaers).
curve has been found, but also here region II is not always horizontal [see, e.g., Wissbrun (1981), Cocchini et al. (1991), Giles and Denn (1994), Langelaan and Gotsis (1996)], while for others shear thinning with a single power law is encountered throughout [Wissbrun (1981), Kalika et al. (1990)]. At the transition from region II to III a kink is sometimes observed [Moldenaers and Mewis (1986)].

Onogi and Asada (1980) suggested a phenomenological model to relate the texture to the three region flow curve (see Fig. 1.5). In region I the flow is not strong enough to introduce considerable changes in the existing random polydomain texture. Application of a stress results in yield and plastic flow of piled domains there. In region II the flow disturbs the polydomain texture, resulting in a flow of randomly oriented domains dispersed in an oriented nematic. At still higher shear rates this texture evolves to a uniformly aligned sample in region III. Based on many optical observations these descriptions for regions I and III are still supported at present. However, the contemporary vision on region II has changed: Instead of a gradual texture enlargement into a monodomain, a texture refinement is observed at these shear rates as seen using, e.g., POM [Vermant et al. (1994)], dichroism [Burghardt and Fuller (1991)] or SALS [Walker (1995)]. This texture refinement is described well with the current theories (see chapter 2).

An even more striking feature of LCPs is the evolution of their steady state first normal stress difference \( N_{1} \) as a function of shear rate. For isotropic polymers \( N_{1} \) is an all positive, steadily increasing function of the shear rate. During flow the flexible polymer molecules orient in the flow direction. As a result of their tendency to return to the random coil configuration they exert a force perpendicular to the flow direction. However, both positive and negative values of \( N_{1} \) are measured for many lyotropes (Fig. 1.6) [e.g., Kiss and Porter (1978) and (1980), Moldenaers et al. (1989), Grizzuti et al. (1993), Baek et al. (1993)]. For densely packed lyotropes and most, if not all, thermotropes only positive values are found [see, e.g., Baek et al. (1994), Langelaan and Gotsis (1996)]. The behaviour of the first normal stress difference is closely related to the molecular dynamics of rodlike polymers and the explanation of the negative values will be discussed in chapter 2.

The transient behaviour of LCPs, i.e., the response after a sudden change of shear rate or stress, also exhibits remarkable features that depend strongly on the history of the sample. For isotropic polymers in transient experiments at high shear rates (shear thinning regime) a single overshoot in the shear and normal stress is observed before reaching steady state.
Figure 1.7: Example of strain scaling oscillations during transient experiments of a solution of 12% poly-γ-benzyl-L-glutamate in m-cresol: stepwise increase of the shear rate from 0.05 s\(^{-1}\) to 0.2 s\(^{-1}\) (●), 0.5 s\(^{-1}\) (○) and 1 s\(^{-1}\) (☆) (Data kindly provided by prof. Moldenaers).

Figure 1.8: Example of strain scaling oscillations of the reduced shear stress (i.e. stress divided by steady state value) during start up of flow of the thermotropic LCP Vectra A900. (Data kindly provided by dr. Langelaan).
At low shear rates (Newtonian plateau) only a monotonic growth is observed towards the steady-state value. Further, the steady state is always reached within a few strain units (defined as shear rate multiplied by time: $\dot{\gamma} \cdot t$). On the other hand, for LCPs in the plateau regime at intermediate shear rates the steady state may be reached only after 100 strain units or more. Pronounced oscillations in the shear and normal stress are observed for lyotropic LCPs in start-up of flow, reversal of flow, and a stepwise increase or decrease of the shear rate (Fig. 1.7) [see, e.g., Moldenaers and Mewis (1989), Moldenaers et al. (1991), Picken et al. (1991), Mortier et al. (1996)]. Similar oscillations have been observed in the dichroism [Moldenaers et al. (1989)] and the birefringence [Hongladarom and Burghardt (1993)], indicating that the microstructure is responsible for the stress responses. These oscillations do not scale with time, as would be expected for isotropic polymers, but they scale with strain ($\dot{\gamma} \cdot t$). For thermotropic LCPs the oscillations are less pronounced but, nevertheless, the strain scaling and the long times required to reach steady state also hold for these materials (see Fig. 1.8) [Cocchini et al. (1991), Guskey and Winter (1991), and Langelaan and Gotsis (1996)].

Also during relaxation after cessation of shear flow LCPs exhibit some peculiarities. Firstly, the shear and normal stress of both lyotropes and thermotropes relax over long times when compared to flexible chain polymers [Moldenaers and Mewis (1990), Burghardt and Fuller (1991), Han and Kim (1994), Langelaan and Gotsis (1996), and Mortier et al. (1996)]. These long relaxation tails again scale with strain, in this case defined as the previously applied shear rate multiplied by time: $\dot{\gamma} \cdot t$. Secondly, in recoil measurements for both lyotropes and thermotropes a similar scaling holds and the recovered strain may be considerably larger (300-400%) than for flexible chain polymers (10-100%) [Larson and Mead (1989), Mortier (1995)]. Thirdly, a part of the evolution of the dynamic moduli after cessation of shear flow scales with the previously applied shear rate [Larson and Mead (1989), Mortier (1995), Mortier et al. (1996), and Walker et al. (1995)]. Further, at least for one LCP, the poly-$\gamma$-benzylglutamate (PBG) solutions, the dynamic moduli decrease, while for all other reported lyotropes and thermotropes the moduli increase after flow [see, e.g., Moldenaers and Mewis (1986), Grizzuti et al. (1993), Mortier et al. (1996), Langelaan and Gotsis (1996)]. Using birefringence, it has been confirmed that an increase in dynamic moduli indicates a decrease in average orientation with respect to the flow direction and vice versa [Burghardt et al. (1995)]. Hence, the orientation of PBG increases after cessation of shear flow, whereas for all other LCPs the orientation decreases.
1.5 Outline

As stated earlier, the objective of this thesis is to obtain key features of the rheology of thermotropic main-chain LCPs and to relate them to the underlying changes in the structure. The first goal was to characterize the material under investigation, Vectra B950, by measuring its steady-state and transient rheological responses. The second goal was to obtain indirect indications of the changes in structure during flow through investigation of the stresses in response to different flow histories. Obtaining direct information on the structure changes during flow by setting up rheo-optical experiments was the third goal of this thesis.

The outline of this thesis is as follows. In chapter 2 theoretical models for the flow dynamics of rodlike nematics are summarized. In chapter 3 the steady state rheology of Vectra B950 is described as measured with both a cone and plate and a capillary rheometer. This is followed by a treatment of transient cone and plate experiments that include start-up measurements after a well-defined preshear protocol, immediate reversal of shear flow, a sudden increase or decrease of the shear rate, and the relaxation after steady shear flow. Chapter 4 treats the influence of the flow history on the subsequent transients. An attempt is made to relate the shape of the stress growth curves to the underlying structural changes. Further, the dynamic moduli during relaxation after cessation of shear flow are monitored. In chapter 5 a spectrographic birefringence technique is applied to drawn films of Ultrax KR4002 to measure the development of orientation as a function of draw ratio. The results are compared to those of infrared dichroism and wide-angle X-ray scattering to demonstrate the feasibility of the method for measurements of orientation of highly scattering thermotropic LCPs. Chapter 6 starts with a review of the available literature on rheo-optical investigations on LCPs. The rheo-optical experiments on Vectra B950 are then presented and discussed. They consist of polarized optical microscopy, spectrographic birefringence, dichroism, and small-angle light scattering measurements. Finally, chapter 7 contains some general conclusions.

1.6 References


Larson, R.G., Constitutive equations for polymer melts and solutions, (Butterworths, Boston, 1988).


CHAPTER 2

THEORY

2.1 Introduction

Nowadays, the flow dynamics of isotropic flexible polymers is reasonably well understood [see, e.g., Astarita and Marrucci (1974), Doi and Edwards (1986), Bird et al. (1987), Larson (1988)]. The flow behaviour of low molecular weight liquid crystals (LMLCs) is well understood too [e.g., de Gennes (1974)]. The flow of liquid crystalline polymers, that in some ways resembles the flow of LMLCs, but in other ways that of flexible polymers, can, however, not be described easily by any of the respective theories, nor by any trivial combinations of them. In this chapter some currently accepted theories, describing the rheology of rodlike LCPs, are summarized. For more detailed reviews the reader is referred to, e.g., Larson (1988) and Marrucci and Greco (1993). Only a two-dimensional situation is considered here, in which the director is located in the shearing plane, i.e., the plane made-up of the shear flow direction and the gradient direction. Instabilities that drive the director out of the shearing plane into the vorticity direction, the out-of-plane motions, are not considered, although they have been treated theoretically [Larson and Öttinger (1991), Larson (1993)] and have been observed experimentally [see, e.g., Larson and Mead (1992), Vermant et al. (1994)].

2.2 Components to the total stress

As discussed in the chapter 1, LCPs exhibit structural features at different length scales. All these features are expected to contribute in various amounts to the total stress response in rheological experiments. The total stress is represented by [Larson (1996)]:

$$\sigma = \sigma_s + \sigma_v + \sigma_e + \sigma_f + \sigma_{tex}$$  \hspace{1cm} (2.1)

$\sigma_s$ is the small viscous contribution of solvent-solvent frictional forces present in LCP solutions. The viscous stress $\sigma_v$ is caused by the frictional forces between a rod and its surrounding medium. $\sigma_e$ is the elastic stress associated with the flow-induced deviation of the molecular orientation distribution from equilibrium. The spatial gradients of the director associated with the polydomain texture result in the direct $\sigma_f$ and indirect $\sigma_{tex}$ elastic textural contributions. Equations describing the above mentioned contributions to the total stress are generated in theories below.
2.3 The Leslie-Ericksen theory

The Leslie-Ericksen (LE) theory [see, e.g., Ericksen (1960) and (1976), Leslie (1968) and (1979), de Gennes (1974)] has been developed for the description of the dynamic behaviour of low molecular weight liquid crystals (LMLC). It was derived from a continuum mechanics approach and couples the director and the velocity fields via an appropriate choice of the expression for the stress tensor. Other external fields, such as magnetic and electric fields, are capable of changing the director field, but they are omitted here.

In contrast to the viscous stress in ordinary polymers, which is proportional to the strain rate, the viscous stress in anisotropic fluids also depends on the orientation of the director \( n \) with respect to the velocity field \( v \). The viscous Leslie-Ericksen stress (\( \sigma_{LE}^v \)) looks as follows:

\[
\sigma_{LE}^v = \alpha_1 A : nn nn + \alpha_2 nN + \alpha_3 N n + \alpha_4 A + \alpha_5 n \cdot A + \alpha_6 A \cdot nn
\]  

(2.2)

where the vector \( N \) represents the rate of change of the director with respect to the background fluid, which is given by:

\[
N = \dot{n} - W \cdot n
\]

(2.3)

The time derivative \( \dot{n} \) is a convected derivative, i.e., it describes the rate of change of \( n \) as it is observed while following the particle in its motion. The tensors \( A \) and \( W \) are the symmetric and antisymmetric part of the velocity gradient, respectively the rate of deformation and the vorticity tensor. The parameters \( \alpha_i \) to \( \alpha_6 \) are known as the Leslie coefficients and have the dimension of viscosity. The description of the viscous stress of anisotropic fluids thus requires 6 viscosity coefficients in comparison to only 1 for isotropic fluids. Only five coefficients are, however, independent, since \( \alpha_2 + \alpha_3 = \alpha_6 - \alpha_5 \), which is known as the Parodi relationship [Parodi (1970)].

Due to orientational distortions in the director field, an elastic term should be added to the viscous stress. The energy resulting from a small gradient in the director is described as [Frank (1958), de Gennes (1974)] (see section 1.2):

\[
E_r = \frac{1}{2} K_s (\nabla \cdot n)^2 + \frac{1}{2} K_t (n \cdot \nabla \times n)^2 + \frac{1}{2} K_3 (n \times \nabla \times n)^2
\]

(2.4)

where \( K_s, K_t \) and \( K_3 \) are the Frank elastic constants for splay, twist and bend distortions,
respectively. The elastic Frank stress is derived from $E_F$ through the following operation:

$$
\sigma_F = \frac{\partial E_F}{\partial \nabla n} \cdot (\nabla n)^T
$$

(2.5)

The total stress in this theory then follows from the sum of the viscous ($\sigma_{LE}$, eq. (2.2)) and the elastic ($\sigma_F$, eq. (2.5)) stresses.

When the LE equations are applied to simple shear flow, two distinct types of dynamic behaviour can be distinguished, depending on the values of the coefficients $\alpha_2$ en $\alpha_3$. Since $\alpha_2$ is always negative, the sign of $\alpha_3$ is decisive. We start off omitting the elastic contribution. If $\alpha_3 / \alpha_2$ is positive, i.e., $\alpha_3$ is negative as well, the nematic is flow aligning. The director aligns in the plane of shear at a fixed angle (known as the Leslie angle), determined by:

$$
\tan^2 \theta_L = \frac{\alpha_3}{\alpha_2}
$$

(2.6)

The value of the Leslie angle is solely determined by the value of the Leslie coefficients, and it is independent of the shear rate or the initial orientation of the director. Even when the director is forced to adjust to a different angle at the wall of the sample (boundary condition), the Leslie angle will prevail throughout the bulk when the applied shear stress is large enough. This introduces, however, a (Frank) elastic distortion between the bulk and the wall layer. When the applied shear stress gets vanishing small, the orientation at the wall will be able to persist through the entire sample. Hence, the nematic appears to be non-Newtonian, since the viscosity depends on the orientation of the director.

On the other hand, if $\alpha_3 / \alpha_2$ is negative (while omitting elastic contributions) the director undergoes a continuous rotation in the plane of shear, known as tumbling. It can be derived from the angular momentum equation that the change of director orientation depends only on the amount of shear strain $\gamma$, by which the sample has been deformed. This result even holds for initial director orientations that do not lie in the plane of shear. Introduction of elastic contributions has a remarkable influence on the tumbling behaviour of the nematic. The orientational elasticity can in fact arrest the tumbling of an intrinsically tumbling nematic. The effect of the director winding up along the gradient direction is the occurrence of orientational distortions throughout the bulk, and not just in the boundary layers as in the flow aligning case. Since $\alpha_3$ is predicted to be positive for LCPs [Marrucci (1985), Marrucci and Maffettone (1989), Larson (1990), Burghardt and Fuller (1991), Marrucci and Greco (1993)], it is expected that these materials show
tumbling behaviour in shear flow.

Although the LE theory is very useful for describing phenomena, such as tumbling and flow alignment, it has some limitations. The viscous part of the theory is limited to the linear case, i.e., it is only applicable to small molecules or slow flows. Further, nematics described by the LE theory cannot be considered normal viscoelastic, since their relaxation times are not intrinsic to the material, but they depend on external variables (e.g., apparatus dimensions). Moreover, the theory is fundamentally incapable of dealing with defects, and consequently it only holds for monodomains. The theory should, however, be considered as a ground-state theory, i.e., non-linear theories should have the LE theory as a limiting case.

2.4 The Doi theory

A molecular model, derived by Doi will now be considered. This model is in fact capable of predicting and describing many of the unusual phenomena reported for LCPs. It is based on the Smoluchowski equation for rigid rods at concentration $c$ with uniform length $L$ and diameter $b$ in the concentrated regime ($c > 1/bL^2$), where the excluded volume interactions dominate. It gives the time evolution of the orientation distribution function $\psi$ of a monodomain in a flow field [Doi (1981), Kuzu and Doi (1983) and (1984), Doi and Edwards (1986), Larson (1988)]:

$$\frac{\partial \psi}{\partial t} + \frac{\partial}{\partial u} \left[ (u \cdot \nabla v - uu u : A) \psi \right] - \tilde{D}_r \frac{\partial}{\partial u} \left[ \frac{\partial \psi}{\partial u} + \psi \frac{\partial}{\partial u} \left( \frac{V_i}{k_BT} \right) \right] = 0 \quad (2.7)$$

$u$ is the unit vector describing the orientation of an individual rod, $k_B$ the Boltzmann constant, and $T$ the temperature. $\tilde{D}_r$ (dimension $s^{-1}$) is the average rotational diffusion coefficient, that represents the Brownian motion of the rod. This coefficient depends on the average orientation of the surrounding rods, but not on the orientation of the individual rod with respect to the surrounding rods. The rotational diffusion coefficient is related to the time required for a rod to become totally disoriented by a mechanism of translation along the molecular axis and subsequent small rotations. Increasing the degree of orientation leads to less molecular hindrance of the rotary diffusion process and, therefore, to a higher $\tilde{D}_r$. The potential $V_i$ describes the interactions between the rods in the nematic phase. Usually, in calculations the term $V_i$ is given either by the Onsager theory (only entropic excluded volume interactions) or by the Maier-Saupe theory (excluded volume and energetic interactions, like orientation dependent van der Waals forces between the
molecules). The pressure and temperature dependence of the Maier-Saupe theory makes it especially suitable for describing thermotropic LCPs.

The orientation distribution function $\psi$, obtained by solving equation (2.7), is used to calculate averages that correspond to macroscopic measurable quantities. As mentioned in the introduction, a very important quantity is the scalar order parameter $S$, which can be determined by, e.g., birefringence. It is related to the order parameter tensor $\mathbf{S}$, defined by:

$$
\mathbf{S} = \langle uu \rangle - \frac{1}{3} \delta = S(nn - \frac{1}{3} \delta)
$$

(2.8)

where the right hand side holds for uniaxial symmetry around the director $n$; $\langle \cdot \rangle$ indicates an averaging over the distribution function (as defined in eq. (1.2)) and $\delta$ is the unit tensor. Equation (2.8) can also be rewritten as:

$$
S = \frac{3}{2} \mathbf{S}: nn
$$

(2.9)

Substituting $\mathbf{S}$ with the centre part of equation (2.8) results in the order parameter, as defined in the introduction.

A second, for rheological studies important quantity is the stress tensor $\sigma$. Using the Maier-Saupe potential the (elastic part of the) stress tensor reads:

$$
\sigma = 3ck_sT \left[ \mathbf{S} - V (\mathbf{S} \mathbf{S} - \mathbf{S} \langle uuuu \rangle) \right]
$$

(2.10)

where $V$ is a constant proportional to $cbL^2$. This equation contains both second and fourth moment terms and Doi used the following decoupling approximation to close it:

$$
\langle uuuu \rangle \approx \langle uu \rangle \langle uu \rangle
$$

(2.11)

This closure approximation unfortunately fails to predict tumbling and related features, such as negative normal stresses in a range of shear rates. Therefore, more accurate expressions should be used to predict the experimentally observed phenomena. Marrucci and Maffettone (1989), (1990a), and (1990b) tackled this problem by solving equation (2.7) for shear flow in two dimensions, using a Maier-Saupe potential. Larson (1990), on the other hand, solved the dynamical equation numerically in three dimensions by an expansion of the orientation distribution function in spherical harmonics, using an Onsager potential. Moreover, he used another closure approximation, which enables the Doi theory
Figure 2.1: Schematic representation of the predictions of the Doi theory for the viscosity and the first normal stress difference as function of the steady shear rate.

to predict tumbling. Despite the differences in approach, the calculations confirm each other on the essential parts. Also another approach, based on molecular dynamics, agrees quite well with these calculations [Ding and Yang (1994), (1995)].

At low values of the potential (isotropic and first part of nematic regime) only stationary solutions of $\psi(\mathbf{u})$ are found for all shear rates, i.e., the polymer behaves in a flow aligning way. Both the shear and the normal stress reach a steady value through damped oscillations. At a potential higher than a critical value (fully nematic) and at low shear rates no stationary but a periodic solution is found: The LCP tumble. The molecules all rotate collectively or, in other words, the director, which is associated with the maximum in $\psi(\mathbf{u})$, rotates continuously. The shear and normal stress never reach a steady value, but keep oscillating. At high shear rates the theory predicts a dynamic transition from tumbling to flow aligning. This transition occurs through a state called wagging [Larson (1990)], in which the director oscillates up and down between two limiting orientations, instead of going through all angles as in the tumbling regime. The stresses oscillate correspondingly. In the flow-aligning situation the molecules still rotate individually but the global orientation distribution becomes stationary.
The steady-state predictions of the Doi theory are shown in figure 2.1. Predictions for the first normal stress difference show a value that is positive at low shear rates, where \(N_1\) is proportional to \(\dot{\gamma}^2\). At intermediate shear rates, at the transition from tumbling to flow aligning, \(N_1\) goes through a negative minimum, and eventually it becomes positive again at high shear rates. The negative sign in \(N_1\) can be explained by the tendency of the rods to align towards the equilibrium orientation distribution, that by the tumbling motion is more spread [Marrucci and Maffettone (1989)]. The sign of \(N_2\) is opposite to the sign of \(N_1\) and the values of the shear rate, where the sign inversions take place are close to the positions of the sign change in \(N_1\), although not quite coincident [Larson (1990)]. These results have been confirmed by Maffettone (1992), who performed calculations leaving the fourth moment untouched and using an approximation for the higher moments.

The viscosity curve predicted by the Doi theory shows a plateau at low shear rates, followed by a shear thinning region at higher shear rates (Fig. 2.1). The onset of shear thinning is located just before the shear rate where \(N_1\) is expected to become negative. In the same shear rate range a kink is observed in the viscosity curve. Region I is not predicted by the Doi theory. It has been suggested that the introduction of an additional viscous term associated with the domain texture is necessary to explain region I behaviour [Marrucci and Greco (1993), Smyth and Mackay (1994)].

Some important intrinsic properties of polymers, such as polydispersity and chain flexibility, are not accounted for in the Doi theory. It is not fully clear what the influence of these properties is on the state of flow of LCPs, i.e tumbling or flow aligning. Probably the most important shortcoming of the Doi theory is the inability to deal with spatial inhomogeneity of the director field and the accompanying defects. The theory was derived only for a monodomain. In order to account for spatial inhomogeneities, it is assumed that, although there is a polydomain system, each of the domains behaves independently. Or in other words, the individual domains evolve in time according to the predictions of an isolated monodomain. Interactions between the domains, in the form of Frank elasticity, are at first neglected, because it is supposed that they are much smaller than the viscous forces. As a consequence, the stationary overall (space averaged) stress of a polydomain is taken to be equivalent to calculating a time average over one period of the tumbling cycle of the monodomain stress. This results, however, in an indefinite oscillation of the transient stresses, whereas the experimentally observed ones are damped eventually. Therefore, the influence of the polydomain texture should be taken into account.
2.5 Scaling laws

From the experimental observations that the texture becomes finer under the act of shear flow, as described in chapter 1, in combination with the increased understanding of the flow behaviour at the molecular level as described in the preceding section, it becomes clear that tumbling should be responsible for the texture refinement. The characteristic length scale (domain size) is determined by the balance between the elastic forces associated with the distortions of the director field and the local hydrodynamic forces imposed by the shear flow [Marrucci (1985), Wissbrun (1985), Burghardt and Fuller (1990)]. This balance can be represented by the Eriksen number:

$$Er = \frac{\dot{\gamma} \eta}{K/a^2}$$  \hfill (2.12)

where $a$ refers to the characteristic length scale or domain size (see Fig. 1.2), $K$ represents the elastic (Frank) constants, $\eta$ is the viscosity and $\dot{\gamma}$ is the shear rate. Burghardt and Fuller (1990) showed that the Eriksen number is independent of the shear rate in region II. Any attempt to raise this number by increasing the shear rate results in a decrease of the texture length scale with $\dot{\gamma}^{0.5}$ through a winding of the director. In transient experiments the hydrodynamic torque can rotate the director through several revolutions before the elastic force can balance it. Hence, the transient stresses show damped oscillatory patterns. Further, the accumulated Frank elasticity is responsible for the strain recovery, which should be independent of the previously applied shear rate. This had indeed been observed in experiments on poly-$\gamma$-benzyl-L-glutamate (PBLG) and hydroxypropylcellulose (HPC) solutions [Larson and Mead (1989)]. The analysis by Burghardt and Fuller (1990) also predicted scaling of the stresses in transient shear flow and relaxation experiments via the deformation $\gamma = \dot{\gamma} \tau$, in accordance with the experimental results summarized in section 1.4:

2.6 Polydomain modelling

Based on the scaling laws above together with the notion that tumbling can in fact be halted by the introduction of Frank elasticity, Larson and Doi (1991) proposed a mesoscopic domain theory. In this theory the LE equations are assumed to apply to each domain, but the stresses are averaged over a spatial region larger than the domain size, yet smaller than the macroscopic dimensions. The averaging of the LE equations results in equations describing the evolution of the mesoscopic order parameter $\vec{S}$ and the stress tensor $\vec{\sigma}$:
\[
\bar{\sigma} = 2\mu \mathbf{A} + 2\mu_1 \mathbf{A} : \mathbf{S} (\mathbf{S} + \frac{1}{3}\mathbf{\hat{S}}) + \frac{2}{3}\mu_2 \mathbf{A} + \\
\mu_2 (\mathbf{S} : \mathbf{A} + \mathbf{A} : \mathbf{S}) - \frac{1}{2} (\alpha_2 + \alpha_3)(\varepsilon + \phi) I \mathbf{S}
\]
(2.13)

\[
\frac{d\mathbf{S}}{dt} = \mathbf{W}^T \mathbf{S} + \mathbf{S} : \mathbf{W} + \lambda \left(\frac{2}{3} \mathbf{A} + \mathbf{A} : \mathbf{S} + \mathbf{S} : \mathbf{A} - 2 \mathbf{S} : \mathbf{A} (\mathbf{S} + \frac{1}{3}\mathbf{\hat{S}})\right) - \varepsilon I \mathbf{S}
\]
(2.14)

where \(\mathbf{A}\) and \(\mathbf{W}\) are the symmetric and antisymmetric parts of the velocity gradient, and \(\mathbf{\hat{S}}\) is the unit tensor. \(\mu, \mu,\) and \(\lambda\) are based on the LE viscosities (\(\alpha_i\)) and are obtained from the Doi theory. The terms including the unknown adjustable parameters \(\varepsilon\) and \(\phi\) represent the indirect and direct contribution of the texture to the stress tensor. The evolution of the domain size is incorporated through the evolution of the defect density:

\[
\frac{dl}{dt} = \alpha \dot{\gamma} l - l^2
\]
(2.15)

where \(\alpha\) is an unknown parameter, determining the rate of the defect density evolution. \(l\) is defined as the disclination annihilation rate:

\[
l = \frac{\zeta K}{\eta a^2}
\]
(2.16)

where \(\zeta\) is a phenomenological constant, and the other quantities have their usual meaning.

With the constitutive equations above, correct scaling behaviour is found for transient experiments, such as flow reversal, stepwise increase or decrease of the shear rate, and strain recovery. The theory cannot properly predict the transient stresses after a start up of shear flow, since no quiescent domain state is defined. Incorporation of an initial domain size enables one to calculate the start-up transients but a precise description of the initial polydomain texture is required to approach a more realistic prediction [Kim and Chung (1996)]. Further, the above equations predict that the steady-state first normal stress difference depends linearly on the shear rate in region II, which is in agreement with the observations.

2.7 Concluding remarks

In the recent years a considerable progress has been made in the modelling of the flow of
LCPs. It has been shown that the evolution of the stresses during shear flow of many experimental systems can be explained by the concept of tumbling. Through the tumbling motion a flow-induced defect texture is introduced in the material, as is often observed in experimental systems. This defect texture disables the application of the Leslie-Ericksen theory, derived for low molecular weight liquid crystals. Also the molecular model of Doi, derived basically for a monodomain, is able to predict only some of the experimental phenomena, such as the negative first normal stress difference. A combination of both theories in the Larson-Doi mesoscopic domain model, which incorporates the interaction between the domains, comes much closer to the description of the experimentally observed phenomena and is able to describe the damped oscillations in the transient experiments quite well. It must be noted, however, that convenient assumptions (e.g., about the domain size evolution) were used in the derivation, and the model is, therefore, not expected to be applicable in general [Larson and Doi (1991), Marrucci and Greco (1993)]. None of the theories explain the shear-thinning region I. More detailed information on the polydomain texture is thus required to adequately describe the flow of LCPs for all shear rates.

The theories mentioned in this chapter have all been derived for moderately concentrated solutions of rodlike polymer molecules. It is, therefore, not surprising that these theories do not fully describe the behaviour of the more flexible (100% concentrated) thermotropic melts. Baek and coworkers (1994) addressed this problem by performing experiments on both lyotropic solutions of increasing concentrations and thermotropic melts of hydroxypropylcellulose (HPC) and by comparing their results to predictions from the Doi theory. The disappearance of negative $N_1$ values on increasing the concentration was mainly attributed to the increased polymer-polymer frictional interactions, which cause a rapid decrease of the rotational diffusivity. Also a higher flexibility of the molecules at elevated temperatures may be an explanation for the suppression of tumbling. However, flexibility alone cannot explain the disappearance of negative $N_1$ values, since highly rigid LMLCs in general do not tumble, but show flow-aligning behaviour instead. It is not clear whether thermotropic LCPs show tumbling behaviour despite the absence of negative $N_1$ values.

2.8 References


CHAPTER 3

TRANSIENT AND STEADY STATE RHEOLOGICAL BEHAVIOUR OF THE THERMOTROPIC LIQUID CRYSTALLINE POLYMER VECTRA B950

3.1 Introduction

Thermotropic liquid crystalline polymers (LCPs) are known for their ease of being manufactured into products with outstanding mechanical properties and high dimensional precision using ordinary processing techniques like injection moulding. The ease of production stems from the intrinsic highly oriented structure in the liquid phase of these types of polymers. This structure is, however, a complicating factor in their rheological characterization and makes the prediction of their processing behaviour more difficult compared to flexible polymers. In investigating the rheology of LCPs this structure may be responsible for the quite unusual phenomena that have been observed. One of the most striking may be the behaviour of the first normal stress difference (N1) in shear flow. In a certain shear rate regime some lyotropic liquid crystalline systems, such as poly-γ-benzyl-glutamate (PBG) and hydroxypropylcellulose (HPC) solutions, exhibit negative steady state values for N1. Furthermore, in start up, stepwise increase or decrease of the shear rate and in flow-reversal experiments several lyotropic LCPs show oscillatory shear and normal stresses. These oscillations scale with strain for a range of shear rates.

Many of the above phenomena can be explained using the rodlike molecular model of Doi [Doi (1981), and Doi and Edwards (1986)]. The analysis of the basic theory in two dimensions by Marrucci and Maffettone (1989), (1990a) and (1990b), and in three dimensions by Larson (1990) contributed substantially to the understanding of the flow behaviour of LCPs. The picture is, however, not complete yet. Based on a phenomenological model, Onogi and Asada (1980) proposed a "three region flow curve" for the steady state viscosity of LCPs. At low (Region I) and high (Region III) shear rates the viscosity is shear thinning, while the intermediate region shows a Newtonian plateau (Region II). The existence of this three region flow curve has been experimentally verified for several LCP systems. The theory of Doi indeed shows a plateau at low shear rates followed by shear thinning behaviour at higher shear rates. Region I, however, is not accounted for by this theory. According to Marrucci and Greco (1993) the missing link

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could be found in the behaviour of the defects of the nematic phase at slow flows.

It is now well established that the damped oscillatory stress response of LCPs in transient shear flows in Region II is associated with the tumbling of the molecules in the domains. The periods of the oscillations do not scale with time, as would be expected for materials with an intrinsic time constant, but they scale with the accumulated deformation. The general scaling law for LCPs can be written as: \( \sigma_{\text{red}} = f(\dot{\gamma} \cdot t) \), where \( \sigma_{\text{red}} \) is the instantaneous value of the stress divided by the steady state value, \( \dot{\gamma} \) is the shear rate, and \( t \) the time. Models describing the flow of LCPs require an external length scale to define a time scale [Marrucci and Greco (1993)]. Burghardt and Fuller (1990) demonstrated that the domain size is the appropriate length scale of the LCP system. At higher shear rates the tumbling changes into flow aligning behaviour (Region III). The damping of the oscillations accelerates there and mostly a single overshoot is found. Around the change from Region II to Region III the Doi theory predicts the often observed reversals of the sign of \( N_1 \).

The current theories assume that the stress tensor consists of an elastic and a viscous part [Doi (1981), Marrucci and Maffettone (1989), Larson (1990), Marrucci and Maffettone (1990a) and (1990b), and Larson and Doi (1991)]. Both parts can be sub-divided in different contributions. The elastic part of the stress tensor consists of a contribution associated with the deviation of the molecular orientation distribution from the equilibrium, one associated with the free volume (interaction potential), and one with the texture. The viscous part consists of a purely hydrodynamic dissipation but an additional viscous term arising from the texture contribution is required to adequately describe the flow in Region I [Marrucci and Greco (1993), Smyth and Mackay (1994)]. When applying the Doi theory, usually the viscous contribution has been neglected, because the flow was thought to be dominated by elastic effects. Only recently, some reports demonstrated that the viscous contribution cannot be neglected in all cases [Smyth and Mackay (1994), Maffettone et al. (1994)].

The theory does not account for any differences between lyotropic and thermotropic LCPs (TLCPs). Experiments on TLCPs have so far been inconclusive on this matter. Some of the phenomena, like, e.g., the oscillatory stress behaviour in transient experiments, have also been encountered in TLCPs, but they are less pronounced. The presence of a negative \( N_1 \) is, however, controversial for TLCPs. Most reports of rheological experiments on thermotropes are based on the commercial LCP Vectra® A900 of Hoechst Celanese and less on some self synthesized materials. This presents the danger that peculiarities
Transient and steady-state rheology of Vectra B950

connected to a specific material may be ascribed to the general behaviour of TLCPs. Rheological measurements on other LCPs are needed to extract the common trends and to verify the rheological properties which are due to the LC character of thermotropic polymers.

In this article the results are reported of an investigation of steady and transient shear flow experiments on the commercial thermotropic LCP Vectra® B950 (manufactured by Hoechst Celanese). The choice of this material was based on its better potential accessibility for rheo-optical experiments because it is fairly translucent at rest. Only a limited amount of reports have appeared on this polymer until now. Most reports are concerned with steady state rheology in slit and capillary dies [La Mantia and Valenza (1989), Zaldua et al. (1992), Izu et al. (1993), Geiger and De'Nève (1994), Lefèuvre et al. (1994)], with the nature of the defects [De'Nève et al. (1992), (1994), and (1995)] or with rheo-optical investigations [De'Nève et al. (1993)]. A conference abstract and an article by Izu and coworkers (1994, 1996) are briefly concerned with transient measurements. There is only one article on the processing of Vectra B950 [Bastida et al. (1995)].

3.2 Experimental

**Material.** Vectra B950 is a random copolyesteramide, consisting of 60% 2,6-hydroxynaphthoic acid, 20% terephthalic acid and 20% aminophenol. The as-received material was characterized thermally by DSC-measurements, and showed a glass-transition at 142°C and a melting point at about 284°C. Annealing at temperatures below this melting point resulted in recrystallization of the material. Melting points as high as 320°C could then be found. No sign of additional melting peaks besides the one at 284°C was found, however, after several hours at 300°C, the temperature used here for the rheological measurements. The as-received material was dried for 4 hours at 190°C in a nitrogen atmosphere and the samples were kept in a vacuum oven at 60-80°C.

**Cone and plate experiments.** The rheological experiments were conducted under nitrogen atmosphere in a Rheometrics® RMS 800 equipped with a cone and plate geometry. The cone angle was 0.1 rad and the diameter was 25 mm. Measurements were conducted at shear rates between 0.1 and 50 s⁻¹ at 300°C and no noticeable problems with edge fracture were present. Because of the well known dependence of the rheology of LCPs on the thermal and flow history, care was taken to keep the following filling procedure of the instrument identical for all experiments. Circular samples with a thickness of approximately 1.5 mm were compression moulded at 300°C. The diameter of these
samples was based on the desired volume to precisely fill the gap between the cone and the plate in the rheometer when squeezed to the appropriate thickness. The sample was placed between the pre-heated cone and plate. The temperature was raised again to 300°C, and was kept there for 5 minutes. Then the sample was squeezed with a speed of 2.5 \( \mu \text{m/s} \) to the desired gap (truncated cone 50 \( \mu \text{m} \) above the plate). This procedure was similar to the one used by Langelaan and Gotsis (1996) for their measurements on Vectra A900. After squeezing, the sample was let to relax for 400 seconds, which resulted to a more or less steady residual normal force of about 0.02 N. This value is in the order of the sensitivity of the normal force transducer and no conclusions can be drawn from it about the existence of a yield stress.

After loading, the sample was presheared for 500 strain units (s.u.), where strain is defined as \( \dot{\gamma} \cdot t \). The preshear was followed by a period of relaxation and a subsequent start up, or by an immediate flow reversal, a stepwise increase or a stepwise decrease of the shear rate. By applying this fixed preshear protocol a well defined initial state for the measurements was obtained. Preshear has a profound effect on the subsequent shear measurements. The study of this effect falls outside the scope of the present report and is discussed in a following article [Beekmans et al. (1996)].

**Capillary experiments.** A Rosand\textsuperscript{c} twin-bore capillary rheometer (RH7-8/2) equipped with two capillaries (D = 0.5 mm, L = 20 mm and l = 2 mm, entrance angle = 90\(^\circ\)) was used to measure the steady shear viscosity at high shear rates (32-4096 s\(^{-1}\)). The results were both Bagley and Rabinowitsch corrected. In every experiment the plunger speed was kept constant until the pressures above both capillaries were steady before doing a measurement. The presented values have been averaged over several experiments from different fillings.

**Optical experiments.** Polarized optical microscopy and transmitted light intensity measurements during flow were performed using a Mettler PH80 HT hot stage, modified into a sliding plate flow cell. The top plate was moved by a motor. The maximum attainable deformation was 400 s.u. The shear rate could be varied from 0.1 to 20 s\(^{-1}\). The thickness of the sample was controlled by 25 \( \mu \text{m} \) stainless steel spacers between the glass plates. The samples for the rheo-optical measurements were made from compression moulded sheets or melt drawn films with thicknesses slightly larger than the gap-size, so that upon melting good contact was obtained between the molten sample and the glass plates. After melting, the sample was left to equilibrate for 15 minutes at 300°C before the test was started. The transmitted light intensity of red laser light (632.8 nm), with a beam
diameter of 1 mm, was measured using a photodiode.

3.3 Results and discussion

3.3.1 Steady shear flow

Vectra B950 was not stable in the air for a long time at 300°C and the use of nitrogen atmosphere was necessary. Even then, the viscosity and the first normal stress difference of the sample were found to increase slowly with time (after the initial transients) at very long times (figure 3.1). Moreover, it was found that more than 400 strain units were needed to achieve steady state during each measurement. At low shear rates (≤ 0.5 s⁻¹) this is equivalent to measuring times of 1000 seconds or more. For these shear rates the effect of time on the viscosity and N₁ becomes important, as can be seen in figure 3.1.

It is not clear what causes this increase with time in the properties of Vectra B950. Recrystallization of the melt at 300°C could not be detected by DSC. Further, the changes were irreversible and the values of the viscosity and the normal stress did not decrease
Figure 3.2: Steady state viscosity and first normal stress difference as a function of shear rate at 300°C (Δ, □ = cone and plate data, ○ = capillary data).

when the sample was heated at 330°C and then remeasured at 300°C. It seems, therefore, that the increase is the result of further polymerization of the material. Further, this change is independent of accumulated strain. The same increase was found in continuous measurements and in measurements where the flow was interrupted for part of the experiment time.

In order to account for the effect of time on the viscosity and the normal stress, the growth of $\eta$ and $N_1$ in Figure 3.1 was approximated by the linear expressions: $\eta = \eta^0 [1 + \alpha \cdot (t-750)]$ and $N_1 = N_1^0 [1 + \beta \cdot (t-750)]$, where $\eta^0$ and $N_1^0$ are the values at 750 s. The coefficients $\alpha$ and $\beta$ are independent of shear rate in the range of 1 to 5 s⁻¹, where we could measure them and have the values $\alpha = 8.63 \cdot 10^{-5}$ s⁻¹ and $\beta = 7.56 \cdot 10^{-5}$ s⁻¹. The corrected values $\eta^0$ and $N_1^0$ for shear rates ≤ 0.5 s⁻¹ could be obtained from the raw data using these expressions and coefficients.

Figure 3.2 shows the (corrected) steady shear viscosity and the primary normal stress difference as a function of the shear rate. At high shear rates the viscosity curve has been complemented with the capillary data. The viscosity values of Vectra B950 measured in the cone and plate rheometer agree very well with the values from the capillary rheometer;
there is even an overlap of data points. Despite some experimental scatter, the shape of the viscosity curve resembles the classical three region flow curve that has been suggested by Onogi and Asada (1980) for LCPs. This shape is quite common for many lyotropic systems. For some low concentration nematics, however, no Region I has been found or the flow curve is shear thinning throughout, exhibiting three different power law indices [e.g., Mortier et al. (1996)]. For some thermotropic systems a three region flow curve has been found, but also here Region II is not always horizontal [see, e.g., Wissbrun (1981), Cocchini et al. (1991), Giles and Denn (1994), Langelaan and Gotsis (1996)], while for others shear thinning with a single power law is encountered throughout [Wissbrun (1981), Kalika et al. (1990)].

The level of the plateau of the viscosity curve is of the same order as the results of measurements by De'Nève and coworkers (1993) in similar geometries. No Region I is reported in that reference, however, and the capillary data are much lower than in Fig. 3.2. On the other hand, our capillary results are in good agreement with the reports of La Mantia and Valenza (1989) and Izu and coworkers (1993). The latter authors also found a three region flow curve [Izu et al. (1996)]. Their viscosity values were even higher both in the Newtonian plateau and in Region I, where, however, no correction for the time effect on the viscosity was reported.

The first normal stress difference N\textsubscript{1} of Vectra B950 is found to be everywhere positive. Its steady state value increases linearly with the shear rate. A similar dependence on the shear rate with a slope close or equal to one has been observed in several other LCPs [e.g., Baek et al. (1994), Mortier et al. (1996)]. No saturation was found in the present study at high shear rates, as reported for Vectra B950 by De'Nève and coworkers (1993). Moreover, the present results show higher values than their data.

A linear relationship between N\textsubscript{1} and \dot{\gamma} is predicted in region II by both the molecular theory of Doi [Doi (1981)] and the mesoscopic domain theory of Larson and Doi [Larson and Doi (1991)]. At higher shear rates the Doi theory predicts a negative N\textsubscript{1}. This has been experimentally found for several lyotropes. De'Nève and coworkers (1993) speculated that the saturation of N\textsubscript{1} they found at the high shear rate end of the curve of Vectra B950 was the onset of the decrease towards a negative region. They supported this idea by an ordered texture they observed in strands made at high shear rates in a capillary.

It is not clear whether there is a region of negative N\textsubscript{1} values in thermotropic LCPs as a rule. For Vectra A900 negative values have been measured [Guskey and Winter (1991)]
Figure 3.3: Traces of a) the reduced shear stress and b) the reduced first normal stress difference of Vectra B950 at 300°C as a function of strain during start-up flow, after a fixed pre-shear of 500 strain units at 2 s⁻¹ and a waiting period of 250 s. c) Stress path constructed from the reduced normal stress versus the reduced shear stress for start-up at 1 s⁻¹.
but they were probably influenced by the neglect of the residual stress present after the squeezing of the sample [Cocchini et al. (1992), Han and Kim (1994)]. When these stresses were subtracted, \( N_1 \) became everywhere positive [Langelaan and Gotsis (1996)]. For the PHB/PET 80/20 copolyester the negative values of \( N_1 \) that were measured also became positive when no more crystallites were present in the melt [Gotsis and Baird (1985)]. Baek and coworkers (1994) found no negative \( N_1 \) values for HPC melts at all shear rates they used. Neither did they expect a negative region outside their measuring window. The absence of negative \( N_1 \) values may be associated with the disappearance of tumbling or wagging due to the greater chain flexibility of the thermotropic LCPs, or with the higher polymer-polymer friction interactions.

### 3.3.2 Start-up flow

**Figures 3.3a and b** show the reduced shear and normal stress growth curves versus strain for start-up experiments at different shear rates after a fixed preshear of 500 s.u. at 2 s\(^{-1}\) and a relaxation period of 250 s (i.e. 500 s.u. when calculated with the previous shear rate). All the shear rates fall within Region II (Fig. 3.2), except for 0.25 s\(^{-1}\), which is in Region I. A first observation from figure 3.3 is the relatively good strain scaling of the transient curves for the shear rates in Region II. The scaling of the height of the peaks is, however, not as good as expected on account of the experience with lyotropic systems in Region II. Even the curve at 0.25 s\(^{-1}\) shows a reasonable scaling for \( N_1 \), but less for the shear stress.

If plot logarithmically, a small but well reproducible overshoot is observed early in the shear stress curve (see insert in figure 3.3a). It does not scale well with strain but appears at a time of around 0.06 s. Hence, it might be identified with some molecular disentanglement process of the semi-flexible chains. However, due to reported limitations of the instrument electronics the signal from the force transducer may only be reliable after 0.1 s [Liang and Mackay (1993), and Mortier (1995)]. Nevertheless, similar start-up measurements on PP and PS do not show any overshoot at short times in the shear or normal stress response. These are strong indications that the peak may be real.

The stress growth curves of different shear rates scale with strain and reduced height. The shear stress (Fig. 3.3a) shows some clear reproducible shoulders at approximately 10 and 70 s.u., after which the curves increase gradually to a maximum at 182 s.u. The height of this peak is about 20% higher than the steady state value. One may discern an oscillation superimposed on the curve, with a period of approximately 110 strain units.
The first normal stress difference (Fig. 3.3b) increases immediately upon inception of flow and shows a clear shoulder at about 17 s.u., after which the curves show two oscillations with peaks at 90 and at 176 s.u. The heights of these peaks are approximately 40-50% higher than the steady state value. Also in this case one may superimpose an oscillation on the total curve that starts out of phase with the shear stress oscillation. The period is about 80 strain units, which is somewhat smaller than the period for the shear stress.

Some remarks can be made about these stress growth curves. Similar curves have been briefly reported by Izu and coworkers (1994, 1996). Firstly, it is remarkable that Vectra B950 shows several oscillations before reaching steady state. This has been found in lyotropic LCPs, while for thermotropic LCPs after a preshear and a relaxation period before starting up, usually only a single overshoot is reported at low amounts of strain [Cocchini et al. (1991), Driscoll et al. (1991), Han and Kim (1994), and Langelaan and Gotsis (1996)]. The start-up traces of the shear stress of Vectra B950 bear some resemblance with the interrupted stress growth curves of 60% HBA/PET as reported by Viola and Baird (1986). An overshoot at about 70 strain units was reported there, without an earlier peak even after a long relaxation period between the preshear and the subsequent start up. They also reported stress growth curves of 12% poly-( paraphenyleneterephthalamide) (PPTA) in H₂SO₄, for which only one overshoot at small strain and no peak at higher strain is found. They concluded that the second peak at high strain is not associated with liquid crystallinity but that it may be related to the copolymeric nature of the system. However, Mortier and coworkers (1996) reported start-up transients on 19.4% and 19.7% PPTA in H₂SO₄ that did show a peak at higher amounts of strain. An overshoot in the shear stress was reported at 1 s.u., followed by a more pronounced peak at approximately 60-70 s.u. An explanation was not given.

Secondly, the shape of the initial part of the stress growth curves of both the shear stress and the normal stress is rather unusual. A common feature of both thermotropes (see first remark) and lyotropes [Mortier (1995)] in the start-up transients after a preshear is a considerable initial overshoot in the stresses at low strain. Here, apart from the small initial peak in the shear stress, the stresses increase gradually. Only start-up experiments of presheared lyotropic PBG or PBDG [poly(y-benzyl-D-glutamate)] solutions [Moldenaers et al. (1991), Vermant et al. (1994) and Mortier (1995)] show similar stress growth curves.

Thirdly, although the start-up curves of Vectra B950 show several oscillations, a feature common for transients of lyotropic LCPs, there are some obvious differences with the latter systems. The first difference is that the magnitude of the periods of the oscillations
here is much larger than the ones reported for lyotropes. Moldenaers and coworkers (1991) reported shear stress transients of PBDG solutions in intermittent start-up flow for different waiting times. They found a fixed period of approximately 33 s.u. for relatively short waiting times. Similar magnitudes for the period were reported for PBG, HPC and PPTA solutions [Mortier (1995)]. For Vectra B950, the periods of oscillations reported above were 80-110 s.u. An explanation for the large difference in the periods between the thermotropes and the lyotropes could be found by extrapolating the dependence of the tumbling period on concentration predicted by the Doi theory [Kuzu and Doi (1984), Mortier (1995)]. A larger period again indicates a reduced tendency to tumble. The apparent oscillations in the shear and normal stress growth curves, however, may also originate from a process other than tumbling (see the discussion on the optical microscopy).

A second difference with lyotropes is that the periods for the shear and normal stress are not identical. Comparing the shear and normal stress curves of the intermittent experiments reported by Mortier (1995), it appears that the periods of the shear and normal stress are the same in the lyotropic systems. This is what Mortier also explicitly mentioned for the oscillations in the transients during flow. Although we do not have an
Figure 3.5: Evolution of the reduced transmitted light intensity of unpolarized laser light during start-up in the sliding plate shear flow cell as a function of strain for Vectra B950 at 300°C.

Explanation for this discrepancy, it is tempting to couple this observation to the difference in the steady state behavior of $N_1$ between thermotropic and lyotropic systems, i.e. the absence of negative $N_1$ in the former.

A convenient way to directly see the differences between the growth of the shear and the normal stress is to plot one stress versus the other in a stress path. Figure 3.3c shows such a plot of a start-up experiment at 1 s⁻¹. After an initial hesitation, the stress path develops to end in a clockwise loop, indicating that the flow at large strains is dominated by elastic processes [Maffettone and Marrucci (1994), and Maffettone et al. (1994)]. One can clearly see that $N_1$ reaches its maximum just before the shear stress does. Increasing the shear rate does not change the general shape of the curve. Only the size of the loop increases slightly. The curves bare some similarity with the stress paths of intermittent shear flow experiments on PPTA [Mortier et al. (1996)].

Optical microscopy (figure 3.4) shows a threaded texture in the material at rest, in which black lines are clearly visible against a birefringent background. Upon starting up of shear flow of Vectra B950 at low shear rates (0.1 s⁻¹) this threaded texture becomes deformed and denser, without an appreciable generation of new defects, reminiscent of a "line
Figure 3.6: Traces of a) the reduced shear stress and b) the reduced first normal stress difference of Vectra B950 at 300°C as a function of strain, after flow reversal.
texture” [see, e.g., Graziano and Mackley (1984)]. Upon inception of flow in Region II an "explosion" of shear induced defects takes place [see also De’Nève et al. (1993)]. Besides the black lines, new types of defects occur, resulting in a texture that is often referred to as wormlike. The fast formation of defects leads us to suspect that the LCP is in the tumbling regime. The broad peak present in the stress growth curves of both the shear stress and \( \eta \), seems to be associated with the formation of a steady defect network.

Although the picture starts darkening at approximately 10 to 20 strain units, it only seems to be evenly filled with defects after 150 s.u., which is close to the location of the peak in the shear stress. In contrast, Vectra A900 exhibits no threaded texture at rest but shows a steady wormlike texture of a minimum density. Upon inception of shear flow this texture rapidly multiplies to form a dense defect network comparable to the one found for Vectra B950.

Measurements of the transmitted light intensity during start up of shear flow using either no polarizer, one polarizer or crossed polarizers do not confirm the existence of a critical strain, above which the intensity drops, as it was found by De’Nève and coworkers (1993). Nor do our measurements confirm the reported oscillations in the transmitted light intensity. Figure 3.5 shows the evolution of the transmitted light intensity (reduced over the initial value) during start up at different shear rates. A fast monotonic drop of the light intensity is recorded upon inception of flow. The decrease scales with strain for shear rates inside Region II, indicating that the formation of defects does not depend on the shear rate but on the total deformation. At shear rates in Region I the scaling breaks down, as expected, and more strain is required for the defects to form. The transmitted light intensity therefore never reduces to such low levels as in Region II.

3.3.3 Transients during flow

For these sets of experiments the sample was sheared for 500 s.u. at different shear rates and then the flow was either directly reversed at the opposite shear rate, or the shear rate was suddenly raised or lowered by a factor of 5. Figures 3.6a and b show the shear stress and \( \eta \), respectively, plotted versus strain after flow reversal at different shear rates. The stresses have been reduced by dividing by the steady state value. The zero in the time is the reversal point. Figures 3.7 and 3.8 show the stress responses after step-up and step-down, respectively. These stresses have also been reduced between 0 and 1. For the step-up \( \sigma_i = (\sigma - \sigma_f)/(\sigma_f - \sigma_i) \), and for the step-down \( \sigma_i = (\sigma - \sigma_f)/(\sigma_f - \sigma_i) \) are used [Moldenaers et al. (1994b)], where \( \sigma \) is the reduced stress, \( \sigma_i \) is the initial stress and \( \sigma_f \) is the final stress (both steady state values).
Figure 3.7: Traces of a) the reduced shear stress and b) the reduced first normal stress difference of Vectra B950 at 300°C as a function of strain, after a stepwise increase ($\dot{\gamma}_f/\dot{\gamma}_i = 5$) of the shear rate.
Figure 3.8: Traces of a) the reduced shear stress and b) the reduced first normal stress difference of Vectra B950 at 300°C as a function of strain, after a stepwise decrease ($\dot{\gamma}/\dot{\gamma}_i = 1/5$) of the shear rate.
Apart from a change in sign, the shear stress seems hardly influenced by the abrupt flow reversal (Fig 3.6a). Very small oscillations (if any) may be observed. A larger oscillatory response is found in $N_1$ (Fig. 3.6b): after an initial dip at 3 s.u., a clear overshoot is visible at 56 s.u., followed by an undershoot at 120 s.u., giving an oscillation period of approximately 120 s.u. The extrema scale very well with strain and reasonably well with height, as is expected for the shear rates in Region II. Even the transient curves for 0.25 and 0.5 s$^{-1}$ (both probably in Region I) scale quite well. Figures 3.7 and 3.8 show similar trends for the step-up/step-down experiments: the shear stress exhibits no oscillations, while $N_1$ shows oscillations that scale with strain. An overshoot in $N_1$ is found for the step-up experiments (figure 3.7b) at 26 s.u., followed by a weak undershoot at 90-100 s.u., leading to an oscillation period of about 138 s.u. After the shear rate is decreased to one fifth in the step-down experiments (figure 3.8b) the extrema of $N_1$ are located at 11 and 57 s.u., giving an oscillation period of 92 s.u. The good scaling with strain in these experiments is again expected since the step-up and step-down ratios were kept constant [Marrucci and Greco (1993)].

Both the flow reversal experiments and the step-up/step-down experiments show stronger transients in the normal than in the shear stress. For Vectra A900 equally low response was observed for both stresses on abrupt reversal of flow, and only if a certain amount of relaxation time was allowed before restarting the flow, an overshoot for both stresses was regained [Langelaan and Gotsis (1996)]. In contrast, a very clear response in the shear stress was found for the lyotropic systems in such experiments and an even more pronounced one in the normal force [see, e.g., Moldenaers et al. (1994b), Mortier et al. (1995)]. The explanation of the stronger damping in the oscillatory pattern of the thermotropic LCPS could be found in the effect of the molecular flexibility on the anisotropy of the viscosity, together with the higher defect density, which provides more anchoring points for the oscillating directors [Mortier (1995)]. In that respect the rheology of Vectra B950 seems to be closer to the behaviour of the lyotropes than to the other TLCPs studied. This material, then, seems either to be stiffer than Vectra A900, or to have a lower defect density, or to have a higher mobility of the defects. No sufficient information is available at present to give a solid explanation. As far as we know, no data exist on the flexibility of Vectra B950 or on the nature of the defects in Vectra A900 during flow. From optical microscopy it has been found that at least the rest-state defect textures of the two Vectras differ.

A phase difference of 180° between the oscillations in the flow reversal experiment and in the step-up/step-down experiments, reported for lyotropic systems [e.g., Moldenaers and
Figure 3.9: Comparison of the reduced first normal stress difference of the three transient experiments during shear flow (flow reversal at 2 s⁻¹, stepwise increase from 1 to 5 s⁻¹, and stepwise decrease from 10 to 2 s⁻¹) of Vectra B950 at 300°C as a function of strain.

Mewis (1990), Moldenaers et al. (1991), Moldenaers et al. (1994b) can not be found in the present study. The flow reversal, step-up, and step-down transients in figure 3.9 do not show a simple phase difference. The transient curve for flow reversal and step-down (shifted to the same level for comparison) are almost in phase, whereas the transient curve for the step-up experiment is further out of phase. The periods of oscillations seem to be different for the three experiments. According to Moldenaers and coworkers (1994b) a phase difference of 180° between the oscillations from the flow reversal and the step-up transient indicates that the average orientation coincides more or less with the flow direction. Extending this explanation to our results, this would imply that the orientation may not coincide with the flow direction in the case of Vectra B950. DeNève and coworkers (1995) found that the defects associated with the worm texture consist of loops in the shearing plane. Inside the loops the director orientation is mainly in the flow direction, while outside the loops the director orientation is along the vorticity direction. Since, during shear in Region II a high defect density exists, it is expected that a mixture of director orientations is present in the sample, including along the vorticity direction. On the other hand, a higher viscous contribution of the defect texture may also distort the phase difference between the various transient experiments and explain figure 3.9.
Figure 3.10: Stress path constructed from the reduced normal stress (Fig. 3.6b) versus the reduced shear stress (Fig. 3.6a) of flow reversal at 1 s⁻¹.

Despite the absence of oscillations in the shear stress, the stress path for the flow reversal (figure 3.10) nicely resembles the stress paths reported in literature for PBG [Moldenaers et al. (1994a) and (1994b)] and PPTA [Mortier et al. (1996)] in the flow aligning and tumbling regime: i.e. the curve rotates mainly in the counterclockwise direction. Increasing the shear rate does not change the general evolution of the curve. According to Maffettone and Marrucci [Maffettone and Marrucci (1994), and Maffettone et al. (1994)] such a counterclockwise evolution indicates mainly viscous flow. This is in contradiction with the clockwise stress path of start-up flow (figure 3.3c), which indicated the domination of elastic processes. This difference, as well as the different values of the periods of oscillations of the stresses in the three transient experiments above indicate that the establishment of the equilibrium state of the defect network during flow is different in the various cases. On the contrary, for lyotropic systems more or less the same period is found for the oscillations in different experiments on one material [Mortier (1995)]. Apparently, the development of the wormlike texture during start up of shear flow of Vectra B950 is attended by the introduction of considerable (Frank) elastic energy (figure 3.3c). On the other hand, before the flow reversal, steady state has been obtained in the experiment and, with it, a fully developed defect network exists. This structure shows a mainly viscous response in changes of the flow (Fig. 3.10).
Figure 3.11: Traces of a) the reduced shear stress and b) the reduced first normal stress difference of Vectra B950 at 300°C during relaxation after cessation of shear flow, as a function of strain (calculated using the previous shear rate: $\dot{\gamma}_p \cdot t$).
3.3.4 Relaxation

The relaxation of the elastic part of the stress in LCPs is known to evolve in two steps: a fast initial drop and a slowly decreasing tail [e.g., Moldenaers and Mewis (1990), Burghardt and Fuller (1991)]. The first part is ascribed to the local molecular rearrangements and is independent of the previous shear rate. The slow process is due to the relaxation of elastic stresses associated mainly with the relaxation of the shear induced texture.

Figure 3.11 shows the relaxation of the reduced shear stress and the reduced $N_1$ versus strain after flow at different shear rates. Here the strain is calculated with the previous shear rate ($\dot{\gamma}_p \cdot t$). There is indeed a first non-strain scaling part, which, however, does not scale well with time, something that would be expected for a molecular relaxation. As already mentioned, the results of these experiments are reliable only after 0.1 s. In figure 3.11, this time coincides more or less with the onset of the strain scaling part for all shear rates. Data presented before 0.1 s should, therefore, be regarded with caution.

The strain scaling of the shear stress is very good for the shear rates in Region II, but also for 0.25 s$^{-1}$, which seems to be in Region I (see figure 3.2). After the initial drop, the relaxation curve seems to start off at a plateau (seen in a semilog plot in figure 3.11), the height of which is an indication of the textural contribution to the total stress. By extrapolating the curve towards $\dot{\gamma}_p \cdot t = 0$, a textural contribution to the total shear stress of approximately 46% is found. The strain scaling for $N_1$ is worse, although a general curve can be clearly discerned. The textural contribution to the total normal stress determined by the extrapolation procedure is approximately 57%.

The abrupt drop in shear stress is quite large compared to reports on other LCPs in region II. This indicates that the textural contribution to the elastic stress is rather small compared to the molecular (nematic) elastic and/or viscous contribution. For the lyotropic systems PBLG (poly(γ-benzyl-L-glutamate)), HPC, and PPTA plateau values of respectively 50%, 90%, and 80% have been reported [Moldenaers and Mewis (1990), Mortier (1995), and Mortier et al. (1996)]. Mortier (1995) also reported the shear stress relaxation of two thermotropic LCPs (Victrix and Rhodester). Both polymers seem to possess a texture contribution to the stress of 80% or more. A similar result was found for Vectra A900 [Langelaan and Gotsis (1996)]. Mortier (1995) also reported plateau values in the normal stress relaxation of 80% for PPTA and HPC and 80-90% for PBG solutions. Hardly any data on $N_1$ relaxation of thermotropic LCPs are available. Langelaan and Gotsis (1996)
reported a totally different behaviour for Vectra A900, i.e. an initial decrease and then a gradual increase of $N_1$ on cessation of shear flow.

Based on the differences among the various lyotropic polymers investigated in her thesis, Mortier (1995) concluded that the textural stress contribution increases with the molecular flexibility. However, this is not the only factor responsible for a high textural contribution to the stress. This contribution may also depend on the kind and the amount of defects that are created during flow and the viscous forces that are associated with them [Marrucci and Greco (1993)]. Keeping in mind the similarity between the start-up transients of Vectra B950 and PBG solutions, it is striking that also the textural contributions (revealed by the shear stress relaxation) of these two polymers are in the same order of magnitude. From the flat first part of the relaxation curve we could not discriminate between viscous and elastic molecular contributions to the total stress for Vectra B950. Little is also known about its molecular stiffness. Hence, it is not possible to determine whether the lower textural contribution is the result of the higher viscous or elastic properties of the more flexible polymer chains, or of an additional viscous contribution from the defects.

The period for the shear stress to reach the zero level is approximately 150 s.u. Such long periods for the stress relaxation have been reported also for other thermotropes (in Region II and III) [Han and Kim (1994), and Langelaan and Gotsis (1996)]. The shear stress relaxation is much slower than the one for lyotropic systems, which reaches zero after 20 s.u. The relaxation of the first normal stress difference of Vectra B950 shows an undershoot at approximately 90 s.u., which seems to be negative (figure 3.11b). The actual stress levels are, however, very small there and in the order of the residual stress after squeezing. Nevertheless, the undershoot is found for all shear rates. A similar trend has been found for lyotropic systems, where the stresses reach a real negative minimum after 25 (PBG), 40 (PPTA), or 100 s.u. (HPC), and then they slowly relax back to zero [Mortier (1995)].

Optical microscopy shows that the dense shear-induced defect texture of Vectra B950 relaxes back to the threaded texture within a few minutes after cessation of flow [see also DeNève et al. (1994) and Izu et al (1994)], but a full relaxation to a more or less defect free sample takes about 20 minutes. Although the shear stress relaxation of Vectra A900 is comparable to that of Vectra B950, no threaded texture has been found for the former polymer after relaxation. A steady defect network remains in this case. The fact that Vectra B950 relaxes further to a steady threaded texture is, according to DeNève and coworkers (1994), due to the high elastic constants of its defects compared to other
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thermotropes. This last step in the texture relaxation does not show up in the stress relaxation.

3.4 Conclusion

The use of only one polymer for the study of the rheological behaviour of thermotropic liquid crystalline polymers presents the danger of considering responses particular to that material as the general behaviour of the whole class of these materials. This has been done to some degree with the study of Vectra A900 as a representative of all TLCPs. We have shown in this article that another thermotropic polymer may show behaviour that approaches the rheology of lyotropes and agrees with the existing theories better than Vectra A900 does.

The thermotropic polymer, Vectra B950, exhibits a three region flow curve. Even though Region II apparently corresponds to tumbling of the director, the normal force is everywhere positive and increases linearly with the shear rate. The transients of the shear stress show strain scaling oscillations in start-up flow, while the normal stress exhibits oscillations in start up, flow reversal, and step-up/step-down experiments that scale with strain in agreement with the theory of Larson and Doi. The oscillations start generally out of phase and their periods are not identical for the normal and the shear stress in start-up flow, and for the various transient experiments for N₁.

A threaded texture is observed in the material at rest. A shear-induced wormlike texture develops during the start-up flow (from a relaxed sample) in Region II, attended by the storage of elastic energy and results in a higher elastic contribution to the stress tensor. The reversal of the direction of flow does not change the texture drastically and the stresses are then mostly viscous. However, the total textural contribution to the stress is lower than in other TLCPs and some relatively flexible lyotropes. This may indicate either that Vectra B950 is a relatively stiff thermotrope or that besides the elastic contribution, its defect texture introduces an additional viscous contribution.

3.5 References


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CHAPTER 4

INFLUENCE OF THE FLOW HISTORY ON STRESS GROWTH AND STRUCTURE CHANGES IN THE THERMOTROPIC LIQUID CRYSTALLINE POLYMER VECTRA B950

4.1 Introduction

Rheological experiments on main-chain liquid crystalline polymers (LCPs) have indicated that these materials show a much more complex behaviour than that of flexible-chain polymers. This complexity is attributed to the existence of different structural entities in the melt and solutions of these materials. At the molecular level there is a spontaneous ordering along a mean direction, called the director. This alignment is, however, not homogeneous at the mesoscopic level, where the molecules are clustered in domains with different director orientations to form a polydomain texture. The discontinuous change in preferred orientation between the domains results in defects of (sub-) micron dimensions.

From several rheo-optical investigations it is known that the structure of LCPs is strongly modified by shear flow. Many LCP systems show structural changes that can be associated with the "three region flow curve" for the steady state viscosity, proposed by Onogi and Asada (1980). At low shear rates (region I), where the viscosity is shear thinning, hardly any change in molecular orientation or defect texture is observed (piled domain flow). At intermediate shear rates (region II), where the viscosity is constant, a strong generation of defects is observed, while the molecular orientation is (although low) on average in the flow direction. At high shear rates (region III), where the viscosity is shear thinning again, the defects gradually disappear to form a monodomain exhibiting a high average molecular orientation.

The generation of defects in region II is caused by tumbling of the molecules in the domains. This tumbling gives rise to a damped oscillatory stress response often observed in transient shear flow experiments. Constitutive equations based on the rod-like molecular model of Doi have been used successfully to qualitatively describe these transient responses for both monodomain and polydomain samples [Doi (1981), Marrucci and

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Maffettone (1989), (1990a), (1990b), Larson (1990), Larson and Doi (1991)]. The periods of the oscillations do not scale with time, as would be expected for materials with an intrinsic time constant, but they scale with total deformation. The general scaling law for LCPs can be written as: \( \sigma_{rel} = f(\dot{\gamma} t) \), where \( \sigma_{rel} \) is the instantaneous value of the stress divided by the steady state value, \( \dot{\gamma} \) is the shear rate, and \( t \) the time. Models describing the flow of LCPs require an external length scale to define a time scale [Marrucci and Greco (1993)]. Burghardt and Fuller (1990) demonstrated that the domain size is the appropriate length scale. At higher shear rates the tumbling changes into flow aligning behaviour (region III). The damping of the oscillations in the transients accelerates there and mostly a single overshoot is found. The shear thinning region I is not accounted for by the above theories.

The success of the theories is based mainly on comparisons with experimental data of lyotropic LCPs. The most widely studied thermotropic LCP is the commercial copolyester Vectra A900 or A950. Its behaviour has shown some deviations from the predictions of the theories. It is not clear yet if this is typical for thermotropic LCPs or specific for this material. Further, Vectra A900/A950 is totally opaque and unsuited for optical experiments. Another commercial thermotropic LCP, better suited for rheo-optical experiments, is Vectra B950. Steady state and transient shear flow experiments of this material, including start-up flow, reversal of flow, and stepwise increase and decrease of shear rate have been reported by Beekmans and coworkers (1996). The material shows a three region flow curve and a positive steady state first normal stress difference linearly increasing with the shear rate. Further, its transient shear flows show better strain scaling than other thermotropic LCPs, sometimes approaching the behaviour of the lyotropic systems. Finally, the relaxation after cessation of flow indicates a lower elastic contribution to the total stress compared to other semi-flexible systems. In the present article the effect of the initial orientation and texture on transient flows of the same material is studied in order to gain more insight on the structures that develop during flow and their effect on the rheological behaviour of thermotropic LCPs.

4.2 Experimental

Sample preparation. The random thermotropic copolyesteramide Vectra B950 (Hoechst Celanese), consisting of 60% 2,6 hydroxynaphthoic acid, 20% terephthalic acid and 20% aminophenol, was used in this work. DSC-measurements (Perkin Elmer DSC-7) showed that the as-received material exhibited a glass-transition at 142°C and a crystal-nematic transition at about 284°C. No problems of recrystallization were detected in the present
rheological measurements at 300 °C.

The as-received pellets were dried in a nitrogen atmosphere for 4 hours at 190°C and stored in a vacuum oven at 60-80°C. Circular samples with a thickness of approximately 1.5 mm were compression moulded at 300 °C. The initial diameter of these samples was based on the volume to precisely fill the gap between the cone and the plate in the rheometer by squeezing, so that no additional sample handling was required. The circular samples were also kept in the vacuum oven before use.

**Cone and plate experiments** A Rheometrics® RMS 800 equipped with a cone and plate geometry (cone angle 0.1 rad, plate diameter 25 mm) was used under nitrogen atmosphere to perform the transient and dynamic rheological experiments at 300 °C. The filling procedure was kept identical for all samples because of the well known dependence of the rheology of LCPs on the thermal and flow history. After the circular sample had been placed between the preheated cone and the plate, the temperature was raised again to 300 °C and was kept there for 5 min. The sample was then squeezed with a speed of 2.5 μm/s until the truncated cone was 50 μm above the plate. After squeezing, the sample was left to relax for 400 s, which was sufficient to obtain a more or less steady residual normal force of 0.02 N. This value is lower than the reliability of the normal force transducer and no conclusions can be drawn from it about the existence in this material of a yield normal stress that has been reported for Vectra A900 [Langelaan and Gotsis (1996)].

The transient experiments described in this article include start-up measurements following different flow histories, i.e. immediately following the filling procedure (first start up), after preshearing for varying periods, and after a well defined preshear followed by a varying relaxation period. Further, the evolution of the dynamic moduli during stress relaxation after different flow histories was analyzed. Because this evolution has been found to be independent of the applied frequency [Moldenaers and Mewis (1986), Mortier (1995)], in the present set of experiments the dynamic moduli were recorded as a function of time at an arbitrarily chosen frequency of 62.8 rad/s, and at 2.5% strain amplitude, which was found to lie well within the linear viscoelastic region of the material. The reproducibility of all reported curves was good, and the steady state values of the stress in all experiments at the same shear rate were independent of preshearing conditions. No significant degradation of the samples was noticed during the measurements, as observed in the unchanged colour of the sample.
Figure 4.1: Traces of a) the reduced shear stress and b) the reduced first normal stress difference of Vectra B950 at 300 °C as a function of strain, during start-up flow following the filling procedure described in the text.
**WAXS experiments** To obtain a qualitative indication of the molecular orientation during the different stages in the transient flow of Vectra B950 wide-angle X-ray scattering photographs were taken of quenched samples. For this purpose the rheometer was equipped with a fixed cone and a disposable aluminum plate or two disposable plates (25 mm diameter). The samples were treated identically to the ones for the stress measurements, and it was confirmed that measurements in these configurations showed stress growth curves comparable to the original cone and plate geometry. All shear experiments were performed at an (apparent) shear rate of 2 s⁻¹. After the flow experiment, the oven of the rheometer was opened and the sample was quenched with a flow of cold nitrogen gas from a liquid nitrogen reservoir. The sample was carefully removed from the rheometer and put in a Kiessig camera connected to a Philips PW 1130 generator that produces Ni-filtered CuKα radiation. The X-ray beam was 1 mm in diameter and the distance from the sample to the photographic film was 100 mm. The exposure times were 2 to 2½ hours.

### 4.3 Results

#### 4.3.1 Start-up flow after different flow histories

Stress growth experiments from unpresheared LCP samples are usually avoided because of the ill-defined initial texture. In the present experiments, however, reproducible results could be obtained by applying a well prescribed filling procedure of the cone and plate apparatus. Figures 4.1a and 4.1b respectively show such shear and normal stress growth curves versus strain (defined as shear rate multiplied by time: \(\dot{\gamma}\cdot t\)) at various shear rates. The stresses have been reduced, i.e. divided by their steady shear values. The actual values of the steady state viscosity can be found in the article by Beekmans et al. (1996).

The curve of the shear stress growth (Fig. 4.1a) shows a reproducible peak at 2-3 strain units (s.u.), an undershoot at 37 s.u. and a second peak between 203 and 217 s.u.. For clarity we will call these two peaks α and β respectively. It is clear that the oscillations scale well with accumulated strain, and slightly less with (reduced) height. Scaling both with strain and height is expected because most shear rates in figure 4.1 are located in region II [Beekmans et al. (1996)]. But even the curve of 0.25 s⁻¹, which is in region I, scales rather well. The reduced height of peak α has a value of around 0.75 to 1, while peak β is around 1.25 and the undershoot reaches 50% to 60% of the steady state value.

The primary normal stress difference shows a similar trend (Fig. 4.1b). The extrema also
Figure 4.2: Traces of a) the reduced shear stress and b) the reduced first normal stress difference of Vectra B950 at 300 °C as a function of strain, during start-up flow at 2 s⁻¹ after various amounts of preshear strain and a fixed relaxation period of 500 s.u. c) Reduced height of peak $\alpha$ versus the amount of preshear strain. $\Delta$ = shear stress, $+$ = normal stress.
scale with strain but they occur at strains different from the shear stress. The first peak (\( \alpha \)) is located at 3-4 s.u. and the undershoot at 45 s.u. The second overshoot of \( N_1 \) appears as a double peak (\( \delta, \varepsilon \)) with a first maximum at approximately 140 s.u. and a second maximum at 206 s.u. The reduced value of peak \( \alpha \) varies from 1 to 1.4, while the second overshoot (\( \delta, \varepsilon \)) is about 1.5. The undershoot is about 60 to 70% of the steady state value, at least for the shear rates in region II.

The shape of the stress growth curve of Vectra B950 depends on the flow history. If the sample is presheared long enough, peak \( \alpha \) disappears. In order to examine this effect, some well defined shearing protocols were applied before the actual measurement. One series of measurements used 500 s.u. at different preshearing rates. In a second series the sample was presheared at 2 s\(^{-1}\) for various strains, i.e. the flow was interrupted on top of peak \( \alpha \) (4 s.u.), in the undershoot (14 and 38 s.u), and before (100 s.u.), at (150 and 200 s.u.) and after (250 and 500 s.u.) the second broad overshoot (\( \beta \) or \( \delta, \varepsilon \)) in Figure 4.1. A relaxation period of 500 s.u. (calculated based on the preshearing rate) was maintained between the preshear and all subsequent flow measurements. It was found that the preshearing rate had no influence on the shape of the subsequent transient; it was the amount of preshear strain that counted.

Figure 4.2a shows the reduced shear stress transients after preshearing for varying total strain. Almost the original start-up transient is regained after interruptions at 4 and 14 s.u., except for the height of peak \( \alpha \). This peak decreases with increasing amounts of preshear strain and it fully disappears for 38 s.u. (which is preshearing till the undershoot in Fig. 4.1a). After this, the height of peak \( \alpha \) increases again exceeding its original value. The position of this overshoot shifts from 2 s.u. to approximately 6 s.u. after preshearing for 100 strain units or more. Then the peak starts decreasing and it changes into a shoulder after 250 or more strain units preshear, which is past the second broad overshoot of both the shear stress (\( \beta \)) and \( N_1 \) (\( \delta, \varepsilon \)). The position of the undershoot does not change much, but the level changes more or less in the same way as the height of the first peak. The position of peak \( \beta \) shifts to lower strain with increasing preshear strain and settles down at approximately 70 s.u., while the height decreases only a little.

Figure 4.2b shows the transient first normal stress difference for these experiments. The first overshoot (\( \alpha \)) exhibits a similar trend as in the shear stress, the behaviour being more pronounced for both the height and the position (which shifts from 4 s.u. to about 15 s.u.). The undershoot is more or less fixed in position. Peaks \( \delta \) and \( \varepsilon \) fuse into one (\( \beta \)) after preshearing for 100 s.u. or more. Similar to the shear stress, the position of peak \( \beta \) shifts
Figure 4.3: Wide-angle X-ray scattering photographs from samples quenched after various amounts of strain. The sample-film distance was 100 mm. The arcs are the result of reflections from planes with d-spacings of 4.7 Å.
towards lower strain.

Every time the shear flow is resumed after a varying preshear and a relaxation period of 500 s.u. peak α reaches a magnitude that seems to be proportional to the level that the stress had when the preshear was interrupted. Only after more than 250 s.u. of preshear, which is past the second overshoot for both the shear stress (β) and N₁ (δ, ε), peak α disappears permanently when the flow is resumed. The plot of the height of peak α for the shear stress and N₁ versus the amount of preshear strain at interruption shows a curve with a similar shape as the transient itself (figure 4.2c).

Similar transient flow experiments were performed in a plate-plate geometry. Start-up experiments on squeezed samples (i.e. without preshear) showed stress growth curves comparable to the ones measured in the cone and plate geometry, although the peaks were found at slightly higher (apparent) strains. To avoid a radial flow that distorts the random initial orientation, a few runs were done with samples that were not squeezed. Compression moulded or cold pressed samples from ground as-received pellets were used and the gap was continuously adjusted during melting to keep the normal force zero. The stress growth curves of these samples exhibited a similar shape as the squeezed samples, i.e. they also showed peak α. However, the position of this peak in the normal stress had shifted from about 4 s.u. to 15 s.u. Stress growth curves of starting up after a preshear of 500 s.u. did not show this peak for any of the samples in the plate-plate geometry. Hence, starting up from a random as well as a squeezed sample results in a stress growth curve that commences with a large stress overshoot in both the shear and normal stress. On the other hand, starting up from a presheared sample results in a gradually increasing stress growth.

To investigate if the difference in the molecular orientation between squeezed and presheared samples is responsible for the difference in the stress responses, X-ray measurements were performed on samples taken after different flow histories. Figure 4.3 shows three X-ray photographs taken after respectively squeezing, shearing for 38 s.u., and shearing for 500 s.u. Also drawn in this figure is the place where the X-ray beam hit the samples. From these photographs it is clear that the orientation of Vectra B950 is more or less along the vorticity direction (perpendicular to the shear plane) after the squeezing procedure, but it turns into the flow direction (parallel to the shear plane) after the preshear procedure. In fact, the orientation already tends to the flow direction after 38 s.u. of shear. Hence, these experiments qualitatively indicate that the first peak in the start-up flow after squeezing is associated with the initial molecular re-orientation from the
Figure 4.4: Stress paths constructed from the reduced normal stress versus the reduced shear stress in figure 4.2 with the amount of preshear strain as a parameter.

vorticity direction into the shear plane.

The above results indicate that Vectra B950 is capable of maintaining a shear induced orientation for a long time after cessation of flow since for all flow histories a resting period of a few minutes passed before the flow restarted. Indeed, even a resting period of more than 20 min between squeezing and starting up the flow did not influence the height of the first peak noticeably.

Another way of presenting the stress growth data is to plot the reduced first normal stress difference versus the reduced shear stress for different amounts of preshear strain (Fig. 4.4). A common feature for all experiments is the clockwise turn (cw in figure 4.4) at the end of the curve with a maximum for both the shear and the normal stress at a more or less fixed position. This corresponds to the stress growth around and after peaks $\beta$ and $\delta$, $\varepsilon$. Apparently, the underlying process responsible for the stress growth there is independent of the history of the sample. Figure 4.4a (after 4 s.u. preshear) resembles the stress path of an experiment without preshearing. The curve goes first through a counterclockwise loop (ccw in figure 4.4a) before entering the final clockwise (cw) turn. Increasing the preshear strain results in the decrease and disappearance (for 38 s.u.)
preshear) of the ccw1 loop. Another counterclockwise loop (ccw2) starts then increasing and at some point overrules the clockwise loop (Fig. 4.4c). Eventually, this large loop disappears after sufficiently long preshear strains and only the cw-loop remains in the stress path (Fig. 4.4d).

According to the Doi theory a counterclockwise loop results from the viscous stress contribution, while a clockwise loop results from the elastic contribution to the total stress [Maffettone et al. (1994), and Maffettone and Marrucci (1994)]. In the flow aligning regime, where the viscous stresses play an important role, the stress path of the total stress is, therefore, predicted to evolve in a counterclockwise direction. However, counterclockwise stress paths have also been observed in the tumbling regime, where the viscous stresses are usually negligible [Moldenaers et al. (1994), Mortier (1995), and Mortier et al. (1996)]. Recent calculations based on the mesoscopic domain theory of Larson and Doi (1981) indicate that the elastic stress contribution may evolve also in a counterclockwise direction and no viscous contribution is required [Larson (1996)]. The clockwise evolution at the end of the stress paths in figure 4.4, therefore, remains unexplained by the current theories. A more adequate description should probably include the stresses that were neglected in the above references, such as the direct contribution of the defect texture to the total stress.

4.3.2 Effect of relaxation period

The effect of the relaxation period between the preshear flow and the following start-up experiment of Vectra B950 was investigated by performing intermittent measurements, in which the LCP was sheared for 500 strain units and then let to relax for periods ranging from 50 to 1200 s.u. (calculated with the previously applied shear rate: $\dot{\gamma}_{p,r}$). After this rest period, the flow was resumed at the same shear rate for another 500 s.u. Measurements were performed at 2 and 5 s$^{-1}$ and good scaling with both reduced height and accumulated strain was found. We checked for reversibility by applying a short relaxation period (100 s.u.) after a measurement with a long relaxation period (1200 s.u.). The transient curve after this procedure reproduced the transient of a fresh sample (that had relaxed for 100 s.u.) very well. Hence, the significant changes in the curve after long relaxation periods are not due to irreversible changes in the sample. Figure 4.5 shows the evolution of the transient curves at 2 s$^{-1}$ of the shear stress and $N_i$ as a function of the rest period.

The general trend for the shear stress (figure 4.5a) is an instant jump to a starting value
Figure 4.5: Traces of: a) the reduced shear stress and b) the reduced first normal stress difference of Vectra B950 at 300 °C as a function of strain during start-up flow, with the relaxation period between the fixed preshear flow and the actual measurement as a parameter.
that decreases with increasing relaxation period. All curves show then a shoulder at approximately 20 s.u., after which a peak (A in figure 4.5a) is observed that shifts linearly with waiting period to higher amounts of strain (from 60 to 100 s.u.). The height of this peak (A) goes over a maximum and is eventually transformed into another shoulder (after 600 s.u.). For relaxation periods of more than 500 s.u. a second peak (B) becomes visible at about 180 s.u. No large changes can be observed in the shape of the shear stress transient after waiting for more than 600 s.u., except for a shift of the full curve to higher amounts of strain and a slight increase of peak B.

The first normal stress difference (figure 4.5b) shows a more gradual increase (through a faint shoulder) to a first peak (A). Similar to the shear stress, this peak shifts linearly to higher amounts of strain (from 48 to 97 s.u.) for longer waiting periods, and its height goes over a maximum to turn into a shoulder eventually. Already at short relaxation times a second peak (B) is observed at 170 s.u. After a waiting period of 600 s.u. (when peak A has almost disappeared) peak B also shifts to higher strain. In contrast to the dramatic changes in the stress growth curves of both the shear and the normal stress, hardly any change is observed in the corresponding shape of the stress paths. All stress paths more or less resemble figure 4.4d, showing only the clockwise turn at the end of the curve. The shape of the stress path is determined only by the amount of preshear strain and not by the length of the relaxation period.

Comparing these results to other LCPs shows that the evolution of the stress growth after a variable relaxation period is very system dependent. The present shear stress transients (Fig. 4.5a) bare strong resemblance with similar flow results of poly-γ-benzyl-glutamate (PBG) solutions [Moldenaers et al. (1991), and Mortier (1995)]. The decrease in the magnitude of the initial instant jump in the shear stress growth curve with increasing relaxation period was also found for the latter material. Further, the curve showed several peaks, some of which were fixed and others shifted in position. However, PBG showed more stress peaks after 300 s of relaxation, that Vectra B950 did not. Moreover, the resemblance disappears upon comparing the growth curves of their normal stresses. On the other hand, the evolution of the normal stress of the Vectra B950 melt (Fig. 4.5b) shows some similarities to the one of poly(paraphenyleneterephthalamide) (PPTA) solutions, while the shear stress growth curves of the latter changed very little with increasing rest periods [compare with Doppert and Picken (1987), Mortier (1995), and Mortier et al. (1996)]. Both peaks of the growth curve of N, for PPTA grew in magnitude and shifted in position with increasing waiting period. The position of peak B for Vectra B950 remained temporarily constant. For Vectra A900 the initial single overshoot in the shear and normal
stress was absent after short relaxation times but reappeared after sufficient rest time, its magnitude being proportional to the relaxation period. No further oscillations in the shear and normal stress growth were encountered for this material [Cocchini et al (1991), Guskey and Winter (1991), and Langelan and Gotsis (1996)]. A similar behaviour was reported for hydroxypropylcellulose (HPC) solutions [Grizzuti et al. (1990), and Mortier (1995)]. Viola and Baird (1986) reported the disappearance of a first overshoot for the shear stress even after a long relaxation for HBA/PET melts. They also observed a second broad overshoot that was mainly unaffected by the rest period.

4.3.3 Dynamic moduli after cessation of flow

A non-destructive way to monitor the relaxation of the flow-induced orientation of LCPs after cessation of flow is to impose a small amplitude oscillatory shear flow on the sample [Moldenaers and Mewis (1986)]. Burghardt and coworkers (1995) confirmed the long suspected relation between the average molecular orientation and the dynamic moduli for LCPs. An increase in $G''$ with time indicates a decrease of the molecular orientation and vice versa. Figure 4.6 shows the evolution of the dynamic moduli (for $\omega = 62.8$ rad/s and
Figure 4.7: Traces of the loss modulus of Vectra B950 at 300 °C as a function of time after cessation of preshear flow (at 2 s⁻¹) for various amounts of strain. Measurement at ω = 62.8 rad/s and γ = 2.5 %. The curves have been shifted along the G''-axis for clarity. The actual initial (O) and final (□) values of G'' as a function of preshear strain are shown in the insert.

γ = 2.5 %) as a function of reduced relaxation time (scaled with the previously applied shear rate) after cessation of 500 s.u. of shear flow at three shear rates in region II. Some interesting features can be observed in this figure. Firstly, there is a reasonable strain scaling for the evolution of the moduli. Such a strain scaling has been reported also for PBG [Larson and Mead (1989), Mortier (1995), Walker et al. (1995)] and PPTA solutions [Mortier et al. (1996)]. Secondly, G' and G'' decrease significantly after cessation of steady shear flow. This indicates that the orientation of Vectra B950 increases after cessation of flow. Thirdly, the magnitudes of the moduli depend systematically on the previously applied shear rate. And finally, the period for the dynamic moduli to reach a stable value is rather long (over 2000 s.u.), indicating that the relaxation of the orientation evolves over a much longer time scale than the relaxation of the stresses, which reach zero level after 90 (Nₚ) and 150 s.u. (shear stress) [Beekmans et al. (1996)].
Figure 4.7 shows the loss modulus for the relaxation after various amounts of preshear strain at 2 s\(^{-1}\). The curves have been shifted along the G\(\''\)-axis to obtain an overview of the evolution of the shape as a function of preshear strain. For the sample that was not presheared G\(\''\) is more or less constant in time. The sheared samples show a continuous change in shape as a function of preshear strain. The sample that was presheared for 63 s.u. (in the undershoot between peak \(\alpha\) and \(\beta\) in figure 4.1) shows only a slight asymptotic increase after cessation of flow. Increasing the preshear strain results in curves with a more pronounced increase followed by a clear decrease. The sample that was presheared for 500 s.u. shows a clear maximum of G\(\''\) at approximately 140 s. The actual values of G\(\''\) immediately (initial value) and at 1000 s (final value) after cessation of flow are shown in the insert of figure 4.7 as a function of preshear strain. They exhibit an evolution similar to peak \(\alpha\) of the shear and normal stress transients for the interrupted shear flow experiments (see Fig. 4.2c).

Until now, an initial increase followed by a continuous decrease of the dynamic moduli after cessation of shear flow, and, therefore, an eventual increase of the molecular orientation in LCPs during relaxation, has only been reported for highly concentrated PBG solutions [Moldenaers et al. (1990), Mortier (1995), and Walker et al. (1995)]. Less concentrated solutions show a continuous decrease [Moldenaers and Mewis (1986) and (1993), Larson and Mead (1989), Hongladarom and Burghardt (1993), and Burghardt et al. (1995)]. Other lyotropic systems, like HPC [Grizzuti et al. (1990) and (1993), Burghardt et al. (1995), and Mortier (1995)] and PPTA [Mortier et al. (1996)], and thermotropic systems [Cocchini et al. (1991), Guskey and Winter (1991), Han and Kim (1994), Mortier (1995) and Langelaan and Gotsis (1996)] show a continuous increase of the dynamic moduli after cessation of shear flow, indicating that the degree of orientation decreases as the material relaxes.

The thermotropic LCP under investigation seems to possess a memory of the deformation history even after long relaxation periods. Although similar shapes for the strain scaling relaxations of the dynamic moduli after cessation of shear flow at different shear rates are observed, the overall values of the dynamic moduli become higher when the previously applied shear rate increases. Following the argumentation described above this would indicate that the orientation of Vectra B950 is lower at higher shear rates in region II and that this difference remains for a long time after cessation of flow. Similar but more pronounced memory effects have been reported for HPC solutions, where particularly the final values of the dynamic moduli after long relaxation depend on the previously applied shear rate [Grizzuti et al. (1993), Hongladarom et al. (1994), Burghardt et al. (1995)].
Since direct measurements indicated that the final orientation of HPC solutions was independent of the preshearing rate, it was put forward that some mechanism other than the molecular orientation should also provide a direct contribution to the dynamic moduli. Hongladarom and coworkers (1994) suggested that distortional elasticity associated with differences in the mesoscopic texture following shear flow at various rates could provide the explanation. For the present results this could indicate that for increasing shear rates in region II, where an increasing defect density is observed, an additional contribution from the defect network should be responsible for the difference in the values of the dynamic moduli.

4.4 Discussion

A complex picture of the transient flow of Vectra B950 emerges from the present results. There seems to be a complicated interplay between the orientation of the molecules and the creation and the evolution of defects. The first overshoot ($\alpha$ in Fig. 4.1) in a start-up transient is usually associated in the literature with the distortion of the initial polydomain texture, i.e. either with the change of the macroscopically isotropic orientation distribution into a flow generated distribution (tumbling or flow aligning), or with the break-up of the defect texture into smaller domains. This first peak is also predicted by the mesoscopic domain theory of Larson and Doi (1991), when the initial texture is modelled by a random polydomain texture with a minimum defect density [Kim and Chung (1996)]. The amplitude of the first overshoot is, then, associated with the reduction in the domain size upon inception of flow. We have shown experimentally that this is not the case here. The first overshoot ($\alpha$), which was present for squeezed and isotropic samples, disappeared from the start-up transient if a (sufficiently long) preshear was applied and the director was on average in the shearing plane. Moreover, optical measurements showed no difference in the decrease of light intensity upon inception of shear flow for samples with an initially random orientation (from compression moulded sheets), or with orientations parallel or perpendicular to the shear flow direction (from melt drawn films) [Beekmans et al. (1996), Beekmans (1997)]. The rate of reduction in domain size for the three initial orientations is of the same order. Hence, the first peak in the stress growth curves is caused by a change in the macroscopic orientation distribution and not by a sudden decrease in the defect size or an increase of the density. This is confirmed by the WAXS photographs (in Fig. 4.3) and is also in agreement with the predictions of the Leslie-Ericksen theory where an overshoot at low strain is expected due to the reorientation of fluid particles, while no overshoot is to be found for an already oriented fluid [Viola and Baird (1986)].
The evolution of the stress paths in the interrupted shear flow experiments (Fig. 4.4) reveals two processes that take place during the start-up flow of a non sheared sample: The initial rotation of the director into the flow direction (peak $\alpha$ in Fig. 4.1, corresponding to loop ccw1 in Fig. 4.4a) and the development of a defect structure due to tumbling (peaks $\beta$ or $\delta$, $\epsilon$ in Fig. 4.1, corresponding to loop cw in Fig. 4.4a). Figure 4.4 also shows that interrupting the transient during the development of the defect network (e.g., at 150 s.u. in Fig. 4.4e) may result in another process upon resumption of shear flow. In the stress growth curves this process appears as a shifted peak $\alpha$ (Fig. 4.2a and 4.2b). The evolution of the stress paths now show another, more pronounced loop ccw2. Apparently, for preshear strains less than 38 s.u. peak $\alpha$ is caused by the rotation of the director from the vorticity direction into the flow plane. This rotation cannot occur homogeneously and is accompanied by the formation of a polydomain texture through the introduction of defects. With more than 38 s.u. preshear the flow then restarts from a partially developed polydomain texture with an average, albeit low orientation in the flow direction, corresponding to the point of interruption. The growth curves now resemble the curves of non-squeezed or isotropic samples. Starting the flow from this texture involves a combined motion of a (continued) rotation of the director into the flow plane and a tumbling motion, introducing defects in different planes. This is now responsible for peak $\alpha$ and the shift in its position.

To check if the shifted peak $\alpha$ is indeed caused by a partially developed polydomain texture, the following experiment was conducted (see Fig. 4.8). The sample was presheared for 500 s.u. at 2 s$^{-1}$, it was allowed to relax for another 500 s.u. and then it was sheared for 150 s.u. at 2 s$^{-1}$. No peak $\alpha$ could be found in the latter flow. The sample was then allowed again to relax for 500 s.u. and resheared at 2 s$^{-1}$. An overshoot, although less pronounced, was now found for both the shear and the normal stresses at respectively 6 and 15 s.u. This indicates that the shifted peak $\alpha$ may indeed be caused by starting the flow from a partially developed polydomain texture.

The difference in the development of the defects for the various initial conditions may also be observed with optical microscopy [Beekmans et al. (1996), Beekmans (1997)]. The relaxed sample shows a threaded texture of low density. Starting the flow from a randomly oriented sample (from a compression moulded sheet) or a parallel to the flow direction oriented sample (from a melt drawn film) generates dense clouds of defects spread irregularly over the picture. On the other hand, if the flow starts from a sample oriented along the vorticity direction, a more homogeneous distribution of initially large defects is observed. These defects decrease rapidly in size as flow progresses. The strain of 38 s.u. is
Figure 4.8: Traces of the reduced shear and normal stress of Vectra B950 at 300 °C as a function of strain at 2 s⁻¹. The sample was presheared for 500 s.u. and allowed to relax for another 500 s.u. It was then sheared for 150 s.u., allowed again to relax for 500 s.u. and resheared for a third time.

then presumably the point where the generation of the defects due to tumbling (in the shear plane) starts interfering with the defect generation due to the rotation of the director into the shearing plane. Eventually, after shearing for more than 250 s.u. (i.e. over the broad peak β or δ, ε) an equilibrium between the hydrodynamic and the elastic forces halts the tumbling motion and, hence, the generation of new defects. A steady defect network emerges, which is independent of the initial texture. Larson and Mead (1992) also found that the initial orientation affected the transient textures, but not the final one.

In spite of a dense defect network, the final orientation (although not very high) is on average in the flow direction. This is supported by the work of DeNève and coworkers (1995), who studied the nature of the defects in detail. They observed loops of disclinations in the shearing plane, which they associated with the often observed wormlike texture. The most common defects in this texture have a twist character. The molecular orientation is parallel to the flow direction inside the observed loops, whereas, outside, the molecular orientation is perpendicular to the flow direction. The shear rates used in the present study generate a very dense defect network, so that in the fully developed state the orientation is indeed on average in the flow direction. Stopping the flow during the transients interrupts the formation of these defects, and a global average is expected between the parallel and the perpendicular orientation.
Figure 4.2c shows that upon resumption of flow after waiting for 500 s.u. the material exhibits a stress peak related to the level at which the flow was stopped. Further, there is a striking similarity between the curve in figure 4.2c and the height of the loss modulus as a function of preshear strain in the insert of Fig. 4.7. This indicates that the orientation distribution that was introduced by the preshear influences both the stresses and the moduli in a similar way. Comparable results have been reported for HPC solutions, where it was found that when the flow was resumed from a high modulus state, the shear stress showed a dramatic overshoot [Hongladarom et al. (1994)]. On the other hand, restarting from a low modulus state resulted in only weak stress oscillations. In the present stress transients (Fig. 4.2a and 4.2b) peak α, although shifted in position, returns when reshearing until the preshear applied strain is over the second broad peak of figure 4.1 (β or δ, ε, at around 250 s.u.). The same preshear strain is required for the orientation to start increasing during relaxation after the cessation of flow (i.e. for the final value of G" in Fig. 4.7 to be lower than the initial value), indicating that if the flow stops after the completion of the defect network, then the molecules tend to enhance their orientation along the flow direction during relaxation.

X-ray photographs (Fig. 4.3) show that the average orientation already tends to the shear direction after 38 s.u. This observation was also reported by Larson and Mead (1992), who found that the strain required to reorient the director was typically less than that required for the texture to achieve a steady state length scale, which in the case of Vectra B950 is more than 250 s.u.

An interesting feature that should be mentioned in this context is the time for complete relaxation of the defect texture of Vectra B950 after stopping the flow at different preshear strains [De'Nève et al. (1994)]. The shape of the graph of these relaxation times versus the preshear strain is the inverse of figure 4.2c. For about 38 s.u. preshear the relaxation time of the defect texture is the longest, whereas before and after this point the relaxation time is much shorter. Hence, the fact that no peak is found upon restarting the flow after the interruption of preshearing at 38 s.u. may also be related to the slow relaxation of the texture at this point.

From the intermittent shear flow experiments it is evident that the relaxation of the fully developed texture takes place by two processes (Fig. 4.5): one process is responsible for the shifting peak A, and a second process is responsible for the temporarily fixed peak B. It appears that the first process has to be completed before peak B is able to shift and the two processes may overlap at longer relaxation times. Peak B is similar to peak β or δ, ε in figure 4.1 and is associated with the generation of a defect network in an ordered
sample, caused by the tumbling of the molecules. During relaxation from the fully developed defect network, the defect density decreases, i.e. the domains grow with relaxation period. The rebuilding of the partially relaxed defect texture upon reshearing is manifested by peak A, the position of which scales with the relaxation strain. Peak B in this case is smaller and corresponds to the already relaxed material. Apparently, the relaxation of the steady state defect texture is not accompanied by a randomization of the orientation, since this would cause the appearance of peak \( \alpha \) upon reshearing.

The tendency towards better alignment during the relaxation after cessation of the shear flow in region II may be related to the results of the intermittent flow experiments (Fig. 4.5). Moldenaers and coworkers (1991) have related the shape of the shear stress growth curves at start up after a preshear and a relaxation period (and the effect on it of the length of the relaxation period) to the evolution of the dynamic moduli during the relaxation step and the increase or decrease of the orientation that this indicates. For PBG solutions, where \( G' \) and \( G'' \) decrease during relaxation, the shear stress grows by an instant jump upon reshearing, the jump decreasing for longer relaxation periods. The normal force shows a negative undershoot for longer relaxation periods [Mortier (1995)]. On the other hand, the shear stress and \( N_\tau \) for HPC and PPTA solutions grow immediately upon reshearing, while the dynamic moduli increase during the relaxation step. Mortier (1995) has pointed out the apparent relation between the decrease of the dynamic moduli during relaxation of PBG and the negative undershoot of the normal force upon reshearing. The present results do not support this relation, however. The growth of the normal force upon reshearing of Vectra B950 resembles the one of PPTA solutions, while the growth of the shear stress upon reshearing and the evolution of the dynamic moduli upon cessation of flow are similar to those of PBG solutions. It seems, therefore, that the shape of the normal stress growth in the intermittent experiments is not a good indication for an increasing orientation after cessation of flow but the shape of the shear stress growth curve is. The values that the moduli have reached after a relaxation period is reflected by the initial value that the shear stress will reach upon reshearing after a corresponding rest period. If the moduli increase, then the jump (or initial peak) in the stress will also increase after longer relaxation periods. If they decrease, as in the case of PBG and Vectra B950 (Fig. 4.6), the initial jump of the shear stress upon reshearing will also decrease with the relaxation period.

No clear picture is obtained in trying to compare the different relaxation phenomena. A relatively fast relaxation for the shear (150 s.u.) and normal stress (90 s.u) after cessation of flow has been reported [Beekmans et al. (1996)], which is related to the relaxation of
the elastic contribution of the defect texture to the total stress. The dynamic moduli reach a maximum at about 280 s.u. after cessation of flow, which may indicate that the molecular re-orientation induced by the relaxation of the defect network is then complete. The orientation then increases monotonically for about 2500 s.u. Peak A in the intermittent shear flow experiments remains visible until 500-600 s.u. of relaxation, indicating that the shear-induced texture has only then relaxed. However, until 1200 s.u. of relaxation in the intermittent flow experiments, restarting the flow still results in different stress growth curves. It seems, therefore, that not the defects themselves but the orientation distribution that comes with them is responsible for the stress growth curve in a following start-up experiment.

4.5 Conclusion

In conclusion one may say that the thermotropic LCP Vectra B950 exhibits some features that are usually found only in lyotropes. The increase of the orientation after cessation of steady shear flow is unexpected for a semi-flexible polymer. It may open new possibilities in the processing of this thermotrope. Besides the already known evolution of the dynamic moduli as an indication of an increasing orientation after cessation of flow, the shear stress growth curves of the intermittent shear experiments may also be used for this purpose.

The shape of the stress growth curve of this material depends considerably on the flow history. Samples that are not presheared show an initial overshoot at low strains, whereas a long enough preshearing results in a more gradual stress growth curve upon restarting the flow. Also experiments that are interrupted during the preshear procedure show an initial overshoot in the stress growth curve upon resumption of flow, similar to the one found for randomly oriented samples. The initial overshoot is, therefore, associated with the re-orientation of the director in the shearing plane. The effect of a varying relaxation period after a fixed preshear is reflected in the appearance of two peaks in the subsequent stress growth curves. One peak is related to the rebuilding of the steady defect texture after a partial relaxation and the other with the generation of a new defect texture after a longer relaxation.

The present results show a complex interplay between the molecular orientation and the generation of defects. Beyond the initial rotation of the director into the flow plane, it appears that the start-up and relaxation stress transients are fully determined by the generation and disappearance of a macroscopic director orientation distribution and the associated defect texture. The orientation of the molecules during steady shear flow is on
Stress growth and structure changes of Vectra B950

average in the flow direction. During the transients, intermediate orientation levels may exist depending on the amount of strain. The material is able to maintain this flow-induced orientation distribution for a long time after cessation of flow. This is reflected in a similar fashion in the initial magnitudes of the stresses and the dynamic moduli after various preshear strains. The stress levels and the texture inside an article manufactured from this material will, therefore, depend on the amount of shear strain that each part has received.

4.6 References


CHAPTER 5

DETERMINATION OF ORIENTATION IN THERMOTROPIC LIQUID
CRYSTALLINE POLYMER FILMS BY SPECTROGRAPHIC MEASUREMENT
OF THE BIREFRINGENCE

5.1 Introduction

Liquid crystalline polymers (LCPs) owe their name to the duality of their liquid state. They show liquid-like behaviour in the solution or in the melt retaining, however, a high degree of local molecular orientation reminiscent of the solid state. The local molecular ordering is the consequence of the chemical structure of these polymers, having rigid anisometric parts in their main chain or side chains. A general feature of the liquid crystalline state of polymers is the relative ease of obtaining flow-induced orientation on a mesoscopic or macroscopic scale. This enables manufacturing products with unique properties because of the high degree of anisotropy. The relative ease of introducing orientation is especially exploited in main-chain LCPs, which are mainly used in mechanical or structural applications. Well-known examples are aramids, from which high modulus fibres are obtained by spinning from a liquid crystalline solution, and aromatic ester/ester or ester/amide copolymers, which can be melt-processed due to their thermotropic nature.

Knowledge of the degree of orientation of LCPs, on the molecular, mesoscopic and macroscopic scales, is crucial to understanding the behaviour of LCPs and to correlating properties and processing conditions. This holds especially for thermotropic liquid crystalline polymers, which are usually subjected to complex flows during processing by extrusion or injection moulding. The degree of orientation in the final product is highly dependent on a combination of the flow type (elongation or shear), the flow rate, the duration of flow and relaxation effects. More than with flexible polymers, the processing conditions determine the microstructure and, therefore, the properties of the final product.

Many reports are concerned with the characterization of the molecular orientation in final products of thermotropic LCPs, like injection moulded parts. Techniques commonly used

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are polarized optical microscopy, X-ray scattering and (reflection or photoacoustic) infrared dichroism [see, e.g., Barres et al. (1991), Bensaad et al. (1993), Blundell et al. (1988), Dreher et al. (1995), Heynderickx and Paridaans (1993), Hsiung and Cakmak (1993), Jansen et al. (1994), Kaito et al. (1991, 1993), Turek and Simon (1993), Voyiatzis et al. (1996)]. Often a layered structure is found parallel to the flow direction, in which the orientation differs from one layer to another. The processing conditions highly influence the number of layers, the thickness of the layers and the orientation inside the layers, which in turn influence the (anisotropy of the) mechanical properties, the coefficient of expansion and the form stability [Mercx (1992)]. Far fewer reports have appeared concerning the structure evolution during flow of thermotropic LCPs, describing mainly qualitative measurements [Alderman and Mackley (1985), DeNève et al. (1993), Graziano and Mackley (1984), Hsiao et al. (1990), Navard and Zachariades (1987), Nicholson et al. (1992), Srinivasarao et al. (1992)]. Yet, detailed understanding of the interrelation between rheological behaviour and structure development in the liquid crystalline state is crucial, just as for lyotropic LCPs, for which a substantial number of both qualitative and quantitative rheo-optical investigations have been reported [Burghardt et al. (1995), Burghardt and Fuller (1991), Hongladarom et al. (1993, 1994), Hongladarom and Burghardt (1993), Larson and Mead (1992), Mortier (1995), Picken et al. (1991), Vermant et al. (1994)].

Techniques that are in principle suitable for assessing changes in polymer structures are X-ray diffraction and optical analysis including birefringence and light scattering. A requirement for such measurements is that the flow cell used is transparent to the waves applied. High intensities and sensitive detectors are required for sufficient time-resolution of the measurements. For X-ray measurements this results in the necessity of using synchrotron radiation [Nicholson et al. (1992), Picken et al. (1991)]. For optical studies an additional problem is the high level of light scattering caused by the fine polydomain texture, which makes small gapsizes ($\lesssim 25$ $\mu$m) in the flow cell necessary. Further, for thermotropic LCPs a flow cell is required that is able to operate at temperatures of approximately 300$^\circ$C. Therefore, rheo-optical studies of thermotropic LCPs have not received much attention, in contrast to lyotropic LCPs.

In this paper we describe a spectrographic birefringence technique for the determination of orientation in thermotropic LCPs. This technique has been designed for rheo-optical experiments on highly birefringent materials. It is based on the same principles as techniques used for lyotropic LCPs under shear flow [Burghardt et al. (1995), Hongladarom et al. (1993), Hongladarom and Burghardt (1993)]. Results are reported for
drawn solid films of the thermotropic LCP Ultrax KR4002. The aim of this research is to demonstrate the feasibility of this method for measurement of orientation of highly scattering thermotropic LCPs, and to optimize the technique for future quantitative rheo-optical experiments. Therefore, the results are compared to data obtained by techniques well-established for solid samples, i.e. infrared dichroism and wide-angle X-ray scattering (WAXS).

5.2 Experimental

5.2.1 Sample preparation

The liquid crystalline polymer investigated in this work was the commercially available thermotropic LCP Ultrax KR4002 from BASF. Its main constituents, according to the supplier, were 1,4-hydroxybenzoic acid, terephthalic acid and 2,7-dihydroxy-naphthalene, unfortunately, in an unknown composition. The LCP was thermally characterized with DSC measurements (Perkin Elmer, DSC-7). It exhibited a glass transition temperature of 128°C and a crystal-nematic transition in the range of 272-298°C, which was sometimes difficult to detect. Annealing of the polymer for one hour at 270°C resulted in a melting point of about 310°C. A similar annealing effect has been reported in literature for HBA/HNA random copolyesters [Langelaan and Posthuma de Boer (1996)]. The as-received pellets were dried at 150°C for 4 hours in nitrogen atmosphere and stored in a vacuum oven at 60-80°C. The thermotropic LCP was extruded in a Collin single screw extruder equipped with a slit die. Three slit-heights, 0.2, 0.5 and 1 mm, were used to obtain sufficiently thin samples to be able to do the birefringence measurements over a wide range of draw ratios. The width of the die was 100 mm and the temperature of the extruder and the die were 300 and 280°C, respectively. After leaving the die, the polymer film was stretched by a winding mechanism and quenched by an air flow within 100 mm from the die exit. Draw ratios between 1.5 and 65 could be obtained by changing the take-up speed, where the draw ratio was calculated as the quotient of the surface of the cross-section at the die outlet and of the solid film. The orientation measurements were all performed at ambient temperatures.

5.2.2 Spectrographic birefringence technique

The spectrographic birefringence technique was first introduced and treated in much detail by Hongladarom et al. (1993). In figure 5.1 a schematic illustration of our set-up is shown. The optical train starts at a 400W Xenon white light source (Oriel) that provides
Figure 5.1: Schematic illustration of the optical set-up for spectrographic birefringence measurements.

an intensity high enough to obtain a sufficient signal at the detector over a wide wavelength range despite the extreme turbidity of the samples. Using a lens and collimation system a parallel beam is created with a spot size of about 4 mm. The polymer film is placed perpendicular to the propagation direction of the light beam between two parallel or crossed polarizers, the directions of polarization of which are set at ± 45° with reference to the stretch direction of the sample. Both spectra for parallel and crossed polarizers were recorded. The detector system consists of a quartz optical fibre that leads to a grating spectrograph (Oriel Multispec), which in turn splits the beam and projects the spectrum (300-800 nm) onto a diode array (1024 pixels) with a resolution of 1.8 nm. The collection of one spectrum requires 40 or 80 ms depending on the turbidity of the sample and for one measurement the data are averaged 16 times.

Mueller matrix analysis of the optical train, neglecting any dichroism, yields the following equations for the light intensity transmitted through a pair of crossed (⊥) or parallel (∥) polarizers and the sample:

\[ I^\perp = \frac{I_0}{2} e^{-2\alpha} \sin^2\left(\frac{\pi \Delta n d}{\lambda}\right) \]  

\[ I^\parallel = \frac{I_0}{2} e^{-2\alpha} \left[1-\sin^2\left(\frac{\pi \Delta n d}{\lambda}\right)\right] \]  

(5.1)  

(5.2)
In these equations $I_0$ is the intensity of the incident beam with wavelength $\lambda$, $\Delta n$ is the birefringence, $d$ is the sample thickness and $e^{-2a}$ a term that accounts for the attenuation of light due to isotropic absorption or scattering. Normalized these equations give:

\[ N^\perp = \frac{I^\perp}{I^\perp + I^\parallel} = \sin^2\left(\frac{\pi \Delta n d}{\lambda}\right) \]  

(5.3)

\[ N^\parallel = \frac{I^\parallel}{I^\perp + I^\parallel} = \cos^2\left(\frac{\pi \Delta n d}{\lambda}\right) \]  

(5.4)

and:

\[ N^\perp - N^\parallel = \cos\left(\frac{2\pi \Delta n d}{\lambda}\right) \]  

(5.5)

Equations (5.3), (5.4) and (5.5) are independent of $I_0$ and the attenuation term $e^{-2a}$. Thus, fitting the normalized intensity versus wavelength curve easily leads to the birefringence.

The birefringence is for a nematic directly related to the order parameter $S$ or $<P_2>$ [Saupe and Maier (1961)], which is the degree of orientation of the molecular main chains around the director $n$ and is defined by the second order Legendre polynomial:

\[ \frac{\Delta n}{\Delta n_{\max}} = S = <P_2> = \frac{1}{2} (3 <\cos^2 \theta > - 1) = 1 - \frac{3}{2} <\sin^2 \theta > \]  

(5.6)

where $<..>$ represents an average over the orientation distribution function and $\theta$ is the angle between an individual molecule and the director (the angular brackets around $P_2$ are omitted in the remaining text). $\Delta n_{\max}$ is the maximum birefringence determined by the values of the refractive indices parallel and perpendicular to the polymer chain. Equation (5.6) holds for a monodomain only, i.e. in case there is no additional spatial inhomogeneity. Larson and Doi (1991) proposed the concept of a mesoscopic order parameter $P_2^{dom}$ that accounts for the existence of a polydomain texture. $P_2^{dom}$ is the degree of director orientation averaged over the domain orientation distribution function. Hence the experimentally measured order parameter is composed of contributions from the molecular level ($P_2^{mol}$) and from the domain level ($P_2^{dom}$):

\[ P_2^{exp} = P_2^{mol} \cdot P_2^{dom} \]  

(5.7)

With birefringence, where the spotsize of the light is usually much larger than the domain size, only this overall order parameter can be obtained. Determination of the molecular
order parameter requires either a monodomain sample or a special technique like solid-state nmr.

5.2.3 Wide-angle X-ray scattering (WAXS)

X-ray photographs were taken of the stretched thermotropic LCP films in our laboratory, using a Kiessig camera connected to a Philips PW 1130 generator that produces Ni-filtered CuKα radiation. The X-ray beam was 1 mm in diameter and the distance from the sample to the photographic film was mostly 100 mm and for some measurements 50 mm. The exposure times were between 16 and 24 hours (for the 100 mm sample-film distance) depending on the sample thickness. A few photographs were made of a stack of drawn samples with the X-ray beam parallel to the film surface to see if there is any biaxiality in the films. The strong equatorial reflections of photographs with a sample-film distance of 100 mm were scanned at Akzo-Nobel research laboratories with a Joyce Loebl Microdensitometer Mk III cs, that was able to perform the azimuthal scan. From the digitized data the order parameter was determined by averaging the $\sin^2\alpha$ over the distribution function, where $\alpha$ is the angle between the equator and the normal to a crystal plane. The distribution function was either the intensity curve of the raw data or a fit with a Pearson VII function [Hall et al. (1977)]. Because an averaging of the equatorial reflection was used instead of the meridional reflection the so obtained $<\sin^2\alpha>$ had to be multiplied by two in order to get $<\sin^2\theta>$, the average required for determination of the order parameter with equation (5.6) [Northolt (1994), Sack (1961), Willems (1995)].

5.2.4 Infrared dichroism

Diffuse reflectance infrared spectroscopy (DRIFT) was used to determine the orientation, since even for the thin films (20 μm) the absorption of infrared light in transmission experiments was too high. The spectra were collected with a Mattson Polaris High Resolution FTIR spectrometer equipped with a wire grid polarizer (1200 Aluminum l/mm on a Zinc Selenide substrate, range: 500-5000 cm⁻¹, Specac) and a DTGS detector. The resolution was 8 cm⁻¹ and the spotsize was comparable to the birefringence measurements, i.e. 4-5 mm. The influence of the absorption on the amplitudes of the spectral features of the specular reflectance scan was eliminated by using light polarized perpendicularly to the plane of reflection (s-polarization) [Korte (1990)]. Reflectances parallel and perpendicular to the draw direction were measured twice by turning the sample fully around on a flat turntable. Results of opposite measurements were averaged to eliminate nonplanarity of the sample. The specular reflectance spectra were differentiated to obtain spectra suitable
Figure 5.2: Coordinate system including relevant angles for infrared dichroism measurements of a monodomain sample. In case of a polydomain sample the director \( \mathbf{n} \) can also have an angle with the \( z \)-axis.

for interpretation [Jansen (1992), Jansen et al. (1994)]. No difference was found between simple differentiation and the more correct Kramers-Kronig transformation.

The dichroic ratio \( R \) is defined as:

\[
R = \frac{A_p}{A_{\perp}}
\]

(5.8)

\( A_p \) and \( A_{\perp} \) being the absorptions parallel and perpendicular to the draw direction (\( z \)-direction in Figure 5.2). The order parameter was calculated from the dichroic ratio by [Fraser (1960)]:

\[
P_2 = \frac{R - 1}{R + 2} \frac{R_0 + 2}{R_0 - 1}
\]

(5.9)

where \( R_0 \) is the dichroic ratio for the case of perfect molecular alignment. \( R_0 \) is directly related to the inclination angle \( \alpha \) of the transition moment (see Figure 5.2):

\[
R_0 = 2 \cot^2 \alpha
\]

(5.10)
Figure 5.3: Normalized intensity versus wavelength using equations (5.3) and (5.4).

For uniaxial systems assuming that the sample is transversely isotropic equation (5.9) can also be expressed as:

$$P_2 = \frac{P_2^{IR}}{P_2^\alpha}$$  \hspace{1cm} (5.11)

where $P_2^{IR}$ is the measured quantity $(R-1)/(R+2)$ in equation (5.9), which is the overall misalignment. $P_2^\alpha$ is the value of the second-order Legendre polynomial for angle $\alpha$, which is a correction factor that is required because of the inclination of the transition moment to the molecular axis. Because the spot size of the infrared beam is much larger than the average domain size the order parameter determined with this technique is comparable to the experimental order parameter $P_2^{exp}$ in equation (5.7).

Although the effective penetration depth of the infrared light with this technique was estimated to be a few microns only, special care was taken to remove the minor reflections from the back of the sample by mounting the films on a polyethylene substrate with an immersion oil in between [Jansen (1992)]. Due to the small penetration depth the orientation measured on the surface of the sample did not reflect the average orientation that was measured with birefringence and X-ray diffraction. Therefore, layers were removed by careful grinding to obtain a depth profile of $P_2$. From the depth profile an average order parameter was calculated that could be compared to the values obtained from the other techniques used.
5.3 Results

5.3.1 Spectrographic birefringence

Figure 5.3 shows the intensity versus wavelength curves normalized according to equations (5.3) and (5.4). They are shown in the range from 550 to 800 nm only, because below 550 nm the signal is too weak. Obviously, the amplitude of the measured oscillations is very small and not constant, and the period varies locally. This variation in amplitude and period is not systematically related to the sample thickness but is sample-dependent. The fact that an oscillation is observed at all can, however, only be attributed to the existing birefringence in the sample. The reason that the normalized intensity curves do not resemble a true \( \cos^2 \) or a \( \sin^2 \) with amplitudes between 0 and 1 originates from depolarization and polarization mixing due to the polydomain texture not accounted for in equations (5.1) and (5.2) [Hongladarom et al. (1993), Hongladarom and Burghardt (1993)].

A more adequate description of the transmission intensity should include an extra term accounting for depolarization effects. The transmission equations (5.1) and (5.2) can be modified as follows [Hsiao et al. (1990), Kumar and Stein (1987)]:

\[
I^+ = F \sin^2\left(\frac{\pi \Delta n d}{\lambda}\right) + T_s 
\]  
\[
I^- = F \left[1-\sin^2\left(\frac{\pi \Delta n d}{\lambda}\right)\right] + T_s 
\]

where \( F \) is the attenuation of light resulting from absorption, scattering or reflection (comparable to the term \( e^{-2a} \) in eq. (5.1) and (5.2)), and \( T_s \) the transmittance of the sample arising from depolarization or leakage from the polarizers. Normalization of equations (5.12) and (5.13) similar to equations (5.3) and (5.4) results in equations with a reduced amplitude and an additional term. Both this reduced amplitude and additional term depend on the amplitude term \( F \) and the depolarization term \( T_s \). For large depolarization this normalization results in a curve with a much reduced amplitude, superimposed on the additional term of approximately 0.5, as observed in Figure 5.3. When equation (5.5) is used to normalize the intensity equations (5.12) and (5.13) the additional term drops out and a cosine curve with a reduced amplitude is obtained oscillating around 0. Figure 5.4 shows three examples for different draw ratios.

Hongladarom et al. (1993) fitted their curves directly with a \( \sin^2 \) or \( \cos^2 \) function including a wavelength dispersion function to obtain the correct fit. The present curves are not as
Figure 5.4: Normalized intensity versus wavelength for three films with different draw ratios. The curves have been obtained from the raw data by normalization with equation (5.5).
Figure 5.5: Scaling of the normalized intensity curve for the film with DR = 8.3 of figure 5.4.

neat as theirs and, therefore, we circumvent the difficult fitting procedure by determining the periods of oscillations from which the birefringence is calculated at various wavelengths. This is done by determining all zero-crossings, \( \lambda_i \), and the midpoints between these crossings, \( \lambda_m = 1/2 (\lambda_{i+1} + \lambda_i) \). Assuming that the birefringence does not change much between two subsequent zero-crossings, it can be approximated by:

\[
\Delta n \approx \frac{\lambda_{i+1} - \lambda_i}{2d(\lambda_{i+1} - \lambda_i)} = \frac{\lambda_m^2}{2d(\lambda_{i+1} - \lambda_i)}
\]  

(5.14)

This approach, of course, works only if the observed zero-crossings are closely spaced, like in our results.

In order to determine the zero-crossings in those cases where the normalized intensity curves are not symmetrical with reference to the zero-value, as is the case in figure 5.4 for DR = 17, the normalized curves are scaled to maximum values of \( \pm 1 \), from which the zero-crossings can unambiguously be determined. An example of a normalized intensity curve and its associated scaled version is shown in figure 5.5. All birefringence values reported in this article have been calculated from these scaled normalized intensity curves.

The birefringences calculated accordingly refer to the mid-points \( \lambda_m \), which are the wavelengths used in figure 5.6 for plotting \( \Delta n \) versus the wavelength, showing immediately the (experimentally obtained) wavelength dispersion for this system. Hongladarom et al. suggested a cubic relationship as a general approximation for this
Figure 5.6: Birefringence versus wavelength for the three examples of figure 5.4.

dispersion and calculated the coefficients for this relationship from monodomain birefringence measurements. The present results can over the relevant part of the spectrum well be represented by a straight line with a slightly negative slope, that turned out to be approximately equal for all experiments. One single slope was, therefore, used to fit the experimental data and the birefringence was calculated at 633 nm. In figure 5.6 the three
Figure 5.7: Birefringence versus draw ratio: O experimental data, --- pseudo-affine deformation.

examples of figure 5.4 are shown again.

Optical microscopy shows that the samples consist of an elongated polydomain texture. The width of the domains is of the order of 1 or 2 microns, the length (which is difficult to determine) is of the order of 10 microns or more. No monodomain was observed for any draw ratio. Sampling with a beam of 4 mm diameter, therefore, leads to an average birefringence over many domains and to an overall order parameter $P_z^{exp}$ as defined in equation (5.7).

The existence of an elongated domain texture suggests that the samples should exhibit a considerable dichroism due to anisotropic scattering. Dichroism values ranging from $10^{-4}$ to $10^{-3}$ have been measured, depending on the draw ratio. Neglecting the dichroism in deriving equations (5.1) to (5.5), therefore, results in an error in the birefringence of about 2.5 to 5%. This value is within the accuracy of our experiments and of no great influence on the purpose of our work.

All birefringence data calculated for $\lambda_m = 633$ nm are plotted versus the draw ratio (DR) in figure 5.7. Every point shown is a single measurement and the trend is obvious,
although there is a considerable amount of experimental scatter. The scatter is most probably caused by differences in local draw ratios, because the films were not homogeneous in thickness. Duplicate measurements of the same samples at the same spot show that the individual values are correct. No birefringence has been detected for an isotropic sample. Between draw ratio values of 1 and 2.2 we have not been able to perform valid birefringence measurements because of the thickness of these samples.

**Figure 5.7** therefore, shows an empty part. The first measurable point (DR=2.2) already has quite a high birefringence and the value starts to level off at a draw ratio between 10 and 15. The drawn curve is the Kuhn and Grün equation for pseudo-affine deformation, with a limiting birefringence value of 0.415 [Kuhn and Grün (1942), Ward (1960)]:

\[
\Pi_2 = \frac{1}{2} \left[ \frac{3}{1-k^2} - \frac{3k\cos^{-1}k - 1}{(1-k^2)^{3/2}} \right]
\]  

(5.15)

where \( k \) is \((DR)^{3/2}\). The very high limiting birefringence value is in accordance with values reported for LCP fibres [Hamza and Sikorski (1978)]. The experimental data follow the affine deformation curve quite well.
Figure 5.9: Azimuthal scan of the equatorial reflection at 4.54 Ångstrom with the Pearson VII fit for a film with DR = 2.5. + raw intensity scan, ———— Pearson VII fit.

From these results a preliminary conclusion can be drawn that the spectrographic birefringence technique is able to measure orientation in solid thermotropic liquid crystalline polymers despite the huge turbidity of the samples. To test if the measured values are in the right order of magnitude the data are now compared to infrared dichroism and WAXS results.

5.3.2 Wide angle X-ray scattering

Figure 5.8 shows a WAXS photograph taken with a sample-film distance of 50 mm together with its radial scan along the equator. The photograph exhibits only a few reflections on the equator and hardly any on the meridian. The strongest peak located on the equator is caused by planes with a d-spacing of 4.54 Ångstrom. From the radial scan (more clearly visible for a sample-film distance of 100 mm) a shoulder can be observed at slightly higher angles originating from a second peak hidden underneath the large peak. This peak is caused by planes with a d-spacing of 4.29 Ångstrom and might indicate an orthorhombic unit cell with almost equal a and b distances [Wilson et al. (1993)]. No significant difference is found between azimuthal scans of both peaks. Hence, the larger peak (at 4.54 Ångstrom) is used to obtain the order parameter. The same peak has also
been used by Hsiung and Cakmak (1993) to investigate the structural layering phenomena in injection moulded Ultrax samples by using a microbeam X-ray diffraction technique. This peak, however, consists of contributions from the crystalline phase but also from the quenched nematic phase, since the "amorphous" scattering is spread over an area containing this crystalline peak. Nevertheless, the azimuthal scans can accurately be described by a Pearson VII function (see Fig. 5.9): correlation coefficients of 0.98-0.99 are obtained. No attempt is, therefore, made to improve this fit by using two distribution functions, a sharp one for the crystalline and a broad one for the "amorphous" part, as reported for semi-crystalline polymers [Voice et al. (1993)]. Hence, the order parameter deduced from WAXS, reported in this article, is mainly determined by the crystalline phase, but partly reflects the order of the quenched nematic phase as well.

<table>
<thead>
<tr>
<th>Draw Ratio</th>
<th>P₂ raw curve</th>
<th>P₂ P-VII fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>0.71</td>
<td>0.70</td>
</tr>
<tr>
<td>2.6</td>
<td>0.77</td>
<td>0.75</td>
</tr>
<tr>
<td>4.5</td>
<td>0.79</td>
<td>0.77</td>
</tr>
<tr>
<td>6.1</td>
<td>0.8</td>
<td>0.78</td>
</tr>
<tr>
<td>12</td>
<td>0.81</td>
<td>0.78</td>
</tr>
<tr>
<td>17</td>
<td>0.82</td>
<td>0.79</td>
</tr>
<tr>
<td>24</td>
<td>0.82</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Table 5.1: Order parameter obtained from WAXS as a function of the draw ratio

In table 5.1 the order parameter determined from the raw intensity curves itself and from the Pearson VII fit are shown for various draw ratios. There is only a small difference between the two methods. In further comparison with other techniques the results obtained from the Pearson VII fits will be used, because the raw curves sometimes show problems with the baseline resulting in an erroneous order parameter. No significant difference could be observed between the azimuthal densitometer scans of WAXS photographs perpendicular and parallel (of a stack of drawn samples) to the surface of the samples and, therefore, the films are believed to be transversely isotropic.

Assuming that at high draw ratios the order parameter for birefringence and WAXS
become equal, a scaled order parameter from the birefringence data can be deduced using the highest value for the order parameter from WAXS ($P_2 = 0.79$). Using equation (5.6) the maximum birefringence is calculated to be $\Delta n_{\text{max}} = 0.50$. This in turn is used to calculate an order parameter for the other birefringence data. The results from both techniques are shown in Figure 5.10. The drawn curve is again the pseudo-affine deformation (eq. (5.15)) with a limiting value of $P_2$ of 0.83. It is clearly seen that at low draw ratios the order parameters from WAXS are much higher than the birefringence results, while at high draw ratios the values (of course) become similar.

**5.3.3 Infrared dichroism**

Figure 5.11 shows examples of the differentiated infrared spectra of the absorption parallel and perpendicular to the film stretch direction. It is clearly seen that there is a considerable amount of dichroism, i.e. several absorption bands show orientation dependent intensities. Although the dichroic ratio can be determined for many bands, the one at 1745 cm$^{-1}$ proved to be most reliable for the determination of the order parameter with equation (5.9). This band can be interpreted as the transition moment of the C=O stretching, which absorbs more in the perpendicular direction than in the parallel direction.
\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.11.png}
\caption{Differentiated infrared reflectance spectra for a film parallel and perpendicular to the infrared polarization.}
\end{figure}

Unfortunately, the angle of the carbonyl group with the main chain is unknown. Hence, the absolute value for the order parameter can not be determined directly. Only the trend of the changing uncorrected order parameter with increasing draw ratio is obtained. However, if one again assumes that at high draw ratios the order parameter for infrared dichroism is comparable to the order parameter obtained from WAXS, an angle $\alpha$ can be calculated from the maximum values of both techniques. With a maximum $P_2$ of 0.79 for WAXS and a maximum $P_2^{IR}$ of -0.24 for infrared dichroism an angle of 69° between the C=O stretch direction and the main chain is found using equations (5.10) and (5.11). Now the infrared dichroism data can be scaled on the WAXS and birefringence results.

In figure 5.12 three depth profiles of the scaled order parameter are shown of films with different draw ratios. The orientation at the surface is of the same order of magnitude for every draw ratio. However, removing surface layers by careful grinding shows a draw ratio dependent decrease of the order parameter. The symmetry of the depth profile indicates that the measured decrease of orientation is not just an effect of the grinding. For the high draw ratios $P_2$ is less thickness dependent as for the lower draw ratios. This observation agrees with the results of Kaito et al. (1991,1993), who found that the orientation function of extruded strands and sheets of a thermotropic copolyester increased...
Figure 5.12: Depth profiles of the order parameter for three films with different draw ratios. The lines are drawn to guide the eye.

with increasing draw ratio and with decreasing diameter of the die outlet. Figure 5.12 shows that the flow profile looks like a parabola. Averaging the order parameter over the thickness using either the parabola or a simple linear function does not differ much. Therefore, an average order parameter has been calculated by taking the mean of the values at the surface and at the centre. These averages are shown in figure 5.10. It is clear that the results of the infrared dichroism measurements correspond with the birefringence data better than the WAXS results, although there is still a considerable amount of scatter in the data (each point is a single measurement).

5.4 Discussion

The present results demonstrate the possibility of determining birefringence of highly scattering solid films of thermotropic LCPs by means of the spectrographic method. Due to depolarization and polarization mixing effects the amplitude of the measured
oscillations is very small as compared to results obtained for lyotropic systems
[Hongladarom et al. (1993), Hongladarom and Burghardt (1993)]. Nevertheless,
meaningful values for $\Delta n$ can easily be obtained by counting the numbers of zero
crossings per unit wavelength. This spectrographic method can, therefore, be expected to
be a new tool for investigations of the rheological behaviour of thermotropic LCPs,
provided the scattering of flowing systems is not very much larger than that of the solid
films. Flow birefringence measurements showing the potential and limitations of this
technique will be reported later.

The interpretation of the birefringence results of the drawn solid films in terms of an order
parameter is not straightforward, as the comparison with the WAXS and infrared results
shows. This is partly due to the lack of knowledge of the structure of the material and of
the consequences of the preparation method and partly due to the different meanings of
the results of different techniques.

The structure of drawn films of thermotropic LCPs is complicated. From polarized optical
microscopy it is clearly visible that all our samples, even at the highest draw ratios, are
built up of domains. No monodomain structures were seen. Scanning electron microscopy
showed that the films are made up of discrete layers (thickness of the order of 1 $\mu$m)
parallel to the film surface. A similar layered structure is proposed as an explanation for
the residual normal stresses in the absence of shear stresses in the LCP Vectra A900
[Langelaan and Gotsis (1996)]. The present infrared dichroism results indicate that
different layers possess a different degree of orientation. Furthermore, differences in
degree of orientation may exist between the crystalline and quenched nematic parts of the
material within the layers, differences which vary between the layers.

The distribution of orientations over the thickness of the samples is the result of the
preparation process: extrusion and subsequent drawing and cooling. It is difficult to
describe the deformation distribution over the sample thickness because the flow profile is
not sufficiently known. Within the die shear flow is predominant and most of the
deformation will be near the wall because of the shear thinning behaviour of the melt.
Outside the die extensional flow and solidification compete. At low draw ratios the
material in the centre of the film is not much extended after it has left the die, at high
draw ratios it is.

The birefringence results represent an average over all textural entities throughout the
thickness of the sample and, therefore, represent an average orientation of the entire
sample. In comparing these results with WAXS results, which also entail a thickness averaging, one should keep in mind that this latter technique mainly samples the orientation of the crystalline parts (see below). Comparison of the birefringence measurements with measurements of dichroism by DRIFT is straightforward provided a complete thickness profile of the dichroism has been measured.

**Figure 5.10** shows that the birefringence data follow the Kuhn and Grün equation for affine deformation quite well, although it could also be said that this equation is the lower bound of the experimental data. Adjusting the exponent of the draw ratio in the Kuhn and Grün equation from -3/2 to -2 yields the upper bound of the data. This suggests that the coefficient is somewhere between the two, indicating in a slightly overaffine deformation process. Usually, the deformation process for flexible polymers in the molten state is described quite well by the affine function. It is not clear whether the small deviation from the affine behaviour is caused by the liquid crystalline nature of the material or by the preparation method, i.e. drawing of films having an initial orientation due to the flow through the die. Of course, it would have been better to prepare oriented films by drawing isotropic films, because in that way the orientation introduced in the extruder would have been avoided. Unfortunately, drawing of compression moulded (isotropic) samples was found impossible.

The thickness averaged infrared dichroism data show an affine behaviour as well (**Fig. 5.10**), although less data are available. As stated in the results, we calculated the average order parameter taking a linear decrease of orientation from the skin to the centre of the film. Using a square relationship did not improve the agreement between the infrared dichroism data and the Kuhn and Grün curve.

From the data gathered in **figure 5.10** it can be concluded that the orientation of the crystalline part develops differently from the orientation of the entire sample as a function of the draw ratio. The orientation process of the crystalline part appears to be highly overaffine contrary to the remaining part of the material. This has also been reported for several other LCPs [Bruggeman and Buijs (1996), Dibenedetto et al. (1989), Kaito et al. (1993), Radler et al. (1994), Voyiatzis et al. (1996)]. One explanation put forward in literature for this discrepancy between the WAXS data and the results from other techniques invokes the easy rotation of the already existing domains [Bruggeman and Buijs (1996), Voyiatzis et al. (1996)]. Another explanation takes into account the non-isotropic orientation distribution at the capillary exit [Dibenedetto et al. (1989), Radler et al. (1994)]. However, these explanations would predict overaffine behaviour for results of
all measurement techniques considered because neither explanation distinguishes between crystalline and non-crystalline (in our case quenched nematic) parts of the material. A possible alternative explanation should take into account the process of crystallization, which is usually very much accelerated by orientation of the melt. If this is the case for thermotropic LCPs as well [see, e.g., Nicholson et al. (1992), Langelaan (1995)], crystallites will preferentially be formed in the regions of the highest orientation of the elongating films. Hence, at low draw ratios the orientation of the crystallites is higher than the average orientation. When the draw ratio increases, the differences even out. Therefore, at high draw ratios the crystalline orientation may be assumed to reflect the average orientation, which justifies the scaling of the results of the birefringence and the infrared measurements to the maximum order parameter as obtained from WAXS measurements.

5.5 Conclusion

We have demonstrated in this article that the birefringence of highly scattering solid films of thermotropic LCPs can be determined by the spectrographic method. The amplitude of the intensity oscillations as a function of the wavelength, although small, is sufficiently large for quantitative determination of birefringence. The spectrographic birefringence technique is, therefore, expected to be suitable for rheo-optical studies of thermotropic LCPs.

The interpretation of the degree of orientation as determined from measurements of birefringence, infrared dichroism, and WAXS is different for each of these techniques and is dependent on the techniques themselves and on the nature and preparation of the samples. The average orientation in the solid drawn films as determined from birefringence and infrared dichroism measurements follows the Kuhn and Grün equation for pseudo-affine deformation. Infrared dichroism results show that the orientation varies through the thickness of the film. The orientation derived from WAXS measurements is distinctly overaffine, which may be the consequence of orientation-induced crystallization.
5.6 Appendix: A simple model of depolarization and polarization mixing

![Diagram showing light source, polarizer, sample, and detector with polarization states](image)

**Figure 5A.1** A light beam traversing a parallel or crossed polarizer set-up containing an oriented polydomain sample. Every arrow indicates a part of the beam that passes the sample via a pile of independent domains. The resultant intensity at the detector is an average of many of these independent parts.

The spectrographic birefringence results of the drawn LCP films used in this chapter show irregular oscillatory intensity versus wavelength curves with both locally varying periods and amplitudes. A simple model is described in this appendix to gain some insight in the origin of these irregularities. For this purpose the polydomain LCP film can be depicted by a pile of birefringent elements, that are on average but non-uniformly oriented in the draw direction (see Fig. 5A.1). A similar presentation has been used for textured block copolymer systems [Amundson et al. (1992), Balsara et al. (1992), Garett et al. (1993), and Milner (1993)]. Depending on the retardations and the orientation angles of the domains, a small part of the light beam traversing through one pile of domains (one arrow in figure 5A.1) can be depolarized to various magnitudes. Moreover, since the light beam is in reality much larger than the domain size, the resulting polarization state at the
detector is an average of many of these depolarized beams, called polarization mixing.

In the present calculations of the intensity versus wavelength curves, every single domain is represented by a Mueller matrix $M_{\text{domain}}$ for a birefringent element (Fuller (1995)):

$$M_{\text{domain}} = \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & (c_{2\beta}^2 + s_{2\beta}^2) c_{\delta'} & s_{2\beta} c_{2\beta} (1 - c_{\delta'}) & -s_{2\beta} s_{\delta'} \\
0 & s_{2\beta} c_{2\beta} (1 - c_{\delta'}) & (s_{2\beta}^2 + c_{2\beta}^2) c_{\delta'} & c_{2\beta} s_{\delta'} \\
0 & s_{2\beta} s_{\delta'} & -c_{2\beta} s_{\delta'} & c_{\delta'}
\end{bmatrix} \quad (5A.1)$$

where $c_{2\beta} = \cos 2\beta$, $s_{2\beta} = \sin 2\beta$, and $\beta$ is the orientation angle of the domain. $c_{\delta'} = \cos \delta'$, $s_{\delta'} = \sin \delta'$, with $\delta'$ is the retardation defined as:

$$\delta' = \frac{2 \pi \Delta n' d}{\lambda} \quad (5A.2)$$

where $\Delta n'$ is the birefringence and $d$ the thickness of a domain, and $\lambda$ the wavelength of the light. The properties of every individual domain can be varied by adjusting the orientation angle $\beta$ and the optical path difference ($\Delta n'd$).

Neglecting (multiple) scattering, the transmitted intensity of a small part of the beam (one arrow in figure 5A.1) through a pile of these independent domains is then simply obtained by a multiplication of the impinging light beam, represented by a fourth order vector $S_0$, with the consecutive Mueller matrices [see Fuller (1995)]:

$$S_n = \mathbf{M}_{\text{pol}} \cdot \mathbf{M}_{\text{sample}} \cdots \mathbf{M}_{\text{pol}} \cdot S_0$$

$$S_n = \mathbf{M}_{\text{pol}} \cdot \mathbf{M}_{n} \cdot \mathbf{M}_{n-1} \cdots \mathbf{M}_{2} \cdot \mathbf{M}_{1} \cdot \mathbf{M}_{\text{pol}} \cdot S_0 \quad (5A.3)$$

The fourth order vector $S$ is called the Stokes vector, which describes the intensity and the phase of the beam; for unpolarized light $S_0 = [I_0, 0, 0, 0]^T$. $M_{\text{pol}}$ is the Mueller matrix of a polarizer, given by:
Figure 5A.2  Calculated intensity (-----) and $\sin^2$ fit (------) for a crossed polarizer set-up of a single beam traversing 20 domains with various optical path differences and orientation angles.

$$M_{pol} = \frac{1}{2} \begin{bmatrix} 1 & C_{2\beta} & S_{2\beta} & 0 \\ C_{2\beta} & C_{2\beta}^2 & S_{2\beta}C_{2\beta} & 0 \\ S_{2\beta} & S_{2\beta}C_{2\beta} & S_{2\beta}^2 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$  \hspace{1cm} (5A.4)

Figure 5A.2 shows the calculated intensity versus wavelength (crossed polarizers) for a single light beam through 20 domains with various optical path differences and orientation angles. Clearly, some anomalies are observed in the calculated $\sin^2$ curve but the periods are quite regular and the amplitudes are still rather large. These anomalies depend mostly on the variation in orientation angle per domain. For small off-zero angles (up to about $\pm 10^\circ$, as used in Fig. 5A.2) the fit with a $\sin^2$ results in a curve that follows the calculated one closely. The optical path difference obtained from it is close to the sum of all path differences of the individual domains. Hence, the average orientation is almost as high as a fully oriented sample. At larger off-zero angles the intensity curve becomes highly irregular and quasi wavelength dependent. This curve can no longer be fitted properly by a $\sin^2$. However, the period clearly increases, indicative of a decrease of the birefringence,
Figure 5A.3 Calculated intensity (----) and sin² fit (-----) for a crossed polarizer set-up averaged over 10 independent light beams with different total optical path difference per beam. Each beam traversing 20 domains with various optical path differences and orientation angles.

and hence the average orientation.

To account for polarization mixing two steps are performed. First, a number of beams with not too large off-zero angles, as described above, are calculated. Each beam going through 20 domains, having various optical path differences and orientation angles per domain. This results in similar curves as shown in figure 5A.2, although the anomalies in the amplitudes can be shifted along the wavelength axis. Second, a resultant intensity versus wavelength curve is calculated by simply averaging the intensity of the individual light beams. Of course, this is a simplification of reality and a more rigorous model should include an averaging over a domain distribution function.

Performing this calculation for 10 light beams, each going through 20 domains with different total optical path difference, results in a highly irregular curve (Fig. 5A.3). The amplitudes have decreased to values comparable to the experimental ones and the periods are even more irregular than those of the experimental curves. This curve cannot be fitted properly with a sin² function. This may be related to the small number of light beams used for the calculations as compared to the experimental system [see also Hongladarom et al.
Figure 5A.4 Calculated intensities for a crossed polarizer set-up. Starting from the curve of figure 5A.3 each subsequently lower curve represents an addition of two light beams with a fixed total optical path difference. The curves have been moved downwards along the intensity axis for clarity reasons, but the ticks at the intensity axis represent a scale equal to that in figure 5A.3 (1993)]. Nevertheless, the fit of this worst case calculation over a large wavelength range results in an average optical path difference that is close to the average input value. Fitting over smaller wavelength ranges can, however, lead to erroneous birefringence values. If the same calculation is performed by mixing a number of beams with equal total optical path difference a result comparable to figure 5A.2 is obtained.

Adding an increasing number of intensity curves with an equal total optical path difference per beam to the polarization mixed situation results in a shift of the resultant intensity curve. Figure 5A.4 shows such shift. The successive curves have been moved (manually) downwards along the intensity axis to obtain a more clear view on the wavelength shift. Eventually, a curve evolves with a more regular period and no shift is observed any more. This curve can be easily fit with a \( \sin^2 \).

In conclusion one can say that using this simple description of a polydomain sample many of the experimentally observed anomalies in the intensity versus wavelength curves can be modelled, without including scattering, which is evidently present in LCPs. In particular
the polarization mixing of light beams with a varying total optical path difference per beam results in an irregular curve with many deviations from a real sin². Nevertheless, fitting this "worst case" calculation over a wide wavelength range still results in the right value of the average birefringence. Hence, these calculations validate the use of the spectrographic birefringence method for measurements on highly irregular and strongly scattering systems. In general, real oriented samples will show less irregular curves, since the polarization mixing is averaged over much more domains in comparison to the present calculations. The irregularities diminish upon adding light beams with a fixed optical path difference per beam or, equivalently, by creating a better average optical path difference of the polydomain system.

5.7 References


Orientation in thermotropic LCP films


CHAPTER 6

RHEO-OPTICAL INVESTIGATIONS OF LIQUID CRYSTALLINE POLYMERS

From the preceding chapters a complicated picture of the structure of thermotropic LCPs emerges, that is thought to be responsible for the unusual rheological behaviour. Both the evolution of the molecular orientation and the defect or domain texture seem to play an important role in the stress growth and relaxation in shear flow. In this chapter attempts will be reported to elucidate the evolution at both structural levels during flow of thermotropic LCPs by using various rheo-optical techniques, including polarized optical microscopy, spectrographic birefringence, dichroism, and small-angle light scattering. First, a literature review on the rheo-optical investigations of LCPs will be presented below.

6.1 Literature

Until present quite an extensive piece of work has been published including various rheo-optical techniques to assess changes of LCPs at different structure levels. Most reports have, however, been concerned with the investigation of lyotropic systems, while only limited attention has been paid to thermotropes due to the experimental problems (see also the introduction of chapter 5). Techniques commonly used to elucidate changes at the domain or defect level are (polarized) optical microscopy (POM), small-angle light scattering (SALS), and (visible-light) dichroism. Techniques used to obtain information at the molecular level include birefringence, wide-angle X-ray scattering (WAXS), and small-angle neutron scattering (SANS). Most rheo-optical experimental set-ups were equipped with transparent parallel plates, plate-plate or cone and plate geometries incorporated in a suitable optical train. For the experiments reviewed in this section the incident light was in general perpendicular to the plates, describing the structure development in the flow-vorticity plane.

6.1.1 Optical microscopy

Polarized optical microscopy is a straightforward and convenient way to monitor the structural evolution of LCPs on the domain scale during flow. Consequently, it has been used by many research groups in trying to relate the unusual rheological phenomena to the underlying textures. Because there seems to be a general agreement on the appearance for both lyotropes and thermotropes, a universal description of the textures will be presented
below. It is based on the reports of Graziano (1982), Graziano and Mackley (1984), Alderman and Mackley (1985) on various thermotropic LCPs and on the report of Vermant and coworkers (1994a) on poly-γ-benzyl-glutamate (PBG) solutions. These thorough reports describe most of the textures encountered ever in LCPs, while in other articles usually only a part of the possible textures is reported depending on the materials used, the molecular weight, the concentration, and the temperature.

**Steady state textures** At very low shear rates the flow causes only a small perturbation of the initial defect texture, reminiscent of the plastic flow of a "piled domain system" [Onogi and Asada (1980)]. Disclinations not pinned to the surface flow with the bulk. Those pinned to the surface or flowing around pieces of debris break up into dark lines with free floating ends, elongating in the flow direction. Eventually, the entire field is dominated by the presence of these dark lines and this texture is called "line texture" [Graziano and Mackley (1984)]. The density of the lines is not homogeneous and is highest in the vicinity of debris. The lines can also be observed in bright field and are thus the result of light scattering. The background light is not extinguished for any position of the crossed polarizers, so no preferred orientation exists in this shear rate regime.

At higher shear rates a homogeneous speckled grainy texture is observed, which is generally referred to as the "worm texture" [Graziano and Mackley (1984)]. The size of the worms is typically of the order of microns and decreases (or, equivalently, the density increases) with increasing shear rate. The creation of large amounts of defects suggests that the LCP is in the tumbling regime. The worms can be observed in bright field, but are more clearly visible between crossed polarizers. Although observations of the basic entities of this texture are difficult because of the small size and the high density, quenched samples reveal that the worms consist of loops in the shearing plane [DeNève et al. (1995)] or inclined at an angle to it [Graziano (1982)]. The background is heavily obscured by the dense defect texture and the LCP seems to be poorly oriented. However, sometimes an average orientation in the flow direction has been reported for samples exhibiting a worm texture [Alderman and Mackley (1985), Picken et al. (1991), Vermant et al. (1994a)].

As the shear rate is increased further a "striated texture" [Vermant et al. (1994a)] gradually develops, with stripes (possibly consisting of stretched disclination loops) running parallel to the flow direction. This texture has the appearance of a series of parallel dashed lines separated from each other by a constant spacing, the size of which depends on the system. The stripes seem to be the result of a periodic misalignment at an angle of 35°-45° with
the flow direction [Larson and Mead (1992), Vermant et al. (1994a)]. The transition from the worm to the striated texture does not clearly correspond to a rheological transition. It may be related to the transition from tumbling to wagging, which is located at the transition from positive to negative Nij. However, for PBG the transition from the worm to the striated texture takes place at the positive maximum in Nij, while for hydroxypropylcellulose (HPC) it happens even earlier [Vermant et al. (1994a)].

At still higher shear rates a gradual transition takes place to an "ordered texture". The defects more or less disappear and a clear birefringent picture remains that transmits maximum light with the crossed polarizers at ±45° (or equivalently, that extinguishes light for polarizers at 0 and 90°), indicating a uniformly aligned sample. The transition to this aligned state takes place at approximately the negative minimum in Nij [Kiss and Porter (1980), Vermant et al. (1994a)] and is related to the onset of flow aligning behaviour.

Increasing the molecular weight lowers the mobility of the molecules and causes the transitions from one texture to the other to shift to lower shear rates and in some cases the disappearance of certain textures from the list above [Graziano (1982), Graziano and Mackley (1984), Alderman and Mackley (1985)]. On the other hand, increasing the temperature or the concentration causes a shift of the transitions to higher shear rates due to a decrease in viscosity [Graziano and Mackley (1984), Alderman and Mackley (1985), Vermant et al. (1994a)].

For poly(para-phenylene-terephthalamide) (PPTA) only one shear-induced texture has been found: the worm texture [Picken et al. (1991), Vermant et al. (1994a)]. Increasing the shear rate causes only a texture refinement. At very high shear rates the picture between crossed polarizers (at 0 and 90°) becomes darker without going through a striated texture, suggesting an average alignment in the flow direction. However, no defect free sample is obtained. A similar texture evolution has been reported for Vectra B950 [De'Nève et al. (1993)]. An ordered texture is never reached for this thermotropic LCP in the optical flow cell, although quenched extrudates from a capillary suggest that an ordered texture may be found at very high shear rates.

For solutions of the rigid poly(1,4-phenylene-2,6 benzobisthiazole) (PBZT) only two textures have been encountered [Chow et al. (1992)]. At rest and at low shear rates a speckled grainy texture is observed that is not perturbed by the shear flow. However, above a threshold shear rate (and relatively high concentrations) a defect free flow aligning sample appears quite fast. Hence, this LCP distinguishes itself from the others in
that it shows no region II behaviour, but instantly changes from region I to III, the flow aligning regime. No sufficient literature is yet available to extract a general behaviour for this type of LCP [Chow et al. (1992), Odell et al. (1993)].

**Transient textures** The steady state textures have been found not to depend on the initial condition of the sample, i.e. irrespective of the initial orientation or quiescent state defects, the final texture that evolves is caused solely by the flow. The transient textures through which steady state is reached may, however, depend on the initial orientation or textures and hence on the sample loading and the preshearing procedure. Further, the amount of strain required to reach steady state depends on the initial orientation [Larson and Mead (1992)]. For PBG and HPC it has been reported that in start-up transients at specific shear rates all possible steady state textures (described above) may appear consecutively, while at other shear rates only some of the possible textures appear. Additional textures can appear as well, when starting from a monodomain. At inception of shear flow at intermediate shear rates and above a critical strain, which depends on the angle between the director and the flow direction, a transient banded texture develops perpendicular to the initial alignment of the monodomain [Kiss and Porter (1980), Larson and Mead (1992), Vermant et al. (1994a), Müller et al. (1996)]. This periodic banded texture gives way to the worm or the striated texture when shearing is continued.

At first sight the transitions from one texture to another during the start up of shear flow seem to be linked directly to the oscillations in the shear stress transients [Vermant et al. (1994a)]. However, it is more likely that the instantaneous stress levels are mainly determined by the average molecular arrangements on which the defect texture will have an influence.

For PPTA no change in transient textures has been observed in start-up flow [Picken et al. (1991), Vermant et al. (1994a)]. From an initially homogeneous sample containing only some disclination loops, a grainy speckled texture evolves by massive multiplication of the defects after 20-25 strain units. The grainy texture remains visible during the transient, while its density is increased. A similar evolution has been reported for the thermotropic LCP Vectra B950 [DeNève et al. (1993)]. The initial threaded texture is strongly changed after a critical strain, where, due to a sharp increase of the defect density, a sudden decrease in the transmitted light intensity is observed (see Fig. 6.1). No influence of the initial orientation on the transient texture evolution has been reported for both PPTA and Vectra B950.
Figure 6.1: Evolution of the unpolarized light intensity transmitted through a Vectra B950 sample as a function of strain at three different shear rates at 300 °C. \( \gamma_{TW} \) is the critical shear strain corresponding to the transition from the initial thread texture to the worm texture. (Reprinted with kind permission from De'Nève et al. (1993). Copyright (1993) The Society of Rheology.)

An exception to the general picture described above is the report of Hsiao and coworkers (1990) on a thermotropic LCP. In region II they observed an elongation of the domains in the shear flow direction, while the size in the perpendicular direction remained relatively constant, indicating an increase of defect size or, equivalently, a reduction in defect density.

Relaxation textures Some of the steady state textures can reappear during the relaxation after cessation of shear flow. Graziano and Mackley (1984) reported a shear rate dependent initial change of the steady state texture to the threaded texture, followed by a slower stage in which the density of the threads decreases. This is in agreement with the general observation that the initial part of the relaxation is faster as the previous shear rate increases. Sometimes even an inverse proportionality with the previous shear rate has been reported. The ordered texture relaxes through the worm texture to the threaded texture without showing a line texture [Graziano and Mackley (1984)]. For the higher molecular weight version of their LCP a transient banded texture occurs perpendicular to the previous flow direction. It shows a periodic misalignment similar to the striated texture
during flow, except that the stripes during the flow are running parallel to the flow direction. This banded texture has been observed by many other researchers. A thorough study on the kinetics of the band formation for PBG and HPC solutions, including many references, has been reported by Vermant and coworkers (1994b). The observation that a banded texture not always appears during the relaxation may be related to the absence of a negative $N_1$ (Kiss and Porter (1980)) or attributed to the fact that this texture is only found in a specific shear rate window [Vermant et al. (1994b)]. The lower critical shear rate of this window does not correspond to any transition of texture in steady state, while the upper critical shear rate may be associated with the onset of flow aligning behaviour. Below the lower critical shear rate only a coarsening of the texture is observed during relaxation, while above the upper limit the alignment persists for a long time. After the disappearance of the banded texture the LCP can either relax to a well aligned state (PBG) or to a macroscopically isotropic (polydomain) state (HPC).

6.1.2 Small-angle light scattering

From the previous section it is clear that LCPs exhibit a polydomain texture with domains of the order of microns separated by defects with sub-micron dimensions. These structural entities give rise to light scattering and two techniques have been used in literature to obtain information about the domain and defect dynamics: small-angle light scattering (SALS) and (conservative) dichroism [Fuller (1995)].

With SALS a scattering pattern is recorded with a particular shape and intensity distribution that yields information on the size, anisotropy and the distribution of the scattering entities. Direct interpretation of the scattering patterns is, however, not possible and indirect methods have to be employed to determine the structure responsible for the scattering. There are basically two approaches to interpret the scattering pattern [Fuller (1995), Søndergaard (1995)]. The first one is to assume a specific model of the scattering entity and to make a summation of the scattered amplitudes arising from a collection of these entities. The second one is the statistical approach, in which the system is defined in terms of correlation functions describing fluctuations in density and orientation. From the comparison of the calculated intensity distribution with the observed one a final interpretation is possible. Both approaches have been used in interpreting the scattering patterns arising from LCPs and since both have their limitations, they should be used complementarily.

Quiescent state SALS patterns Several research groups have reported the same SALS
patterns for various thin solution cast thermotropic LCP films, indicating that some universal structure is responsible for the scattering [Rojstaczer and Stein (1988), Hashimoto et al. (1989), Shiwaku et al. (1990), Silvestri and Chapoy (1992)]. The depolarized or $H_V$ pattern (i.e. the polarizer horizontal and parallel to the flow direction, the analyzer vertical) shows a four-leaf clover pattern with lobes oriented along the directions of the polarizer and the analyzer, having a maximum intensity at a scattering angle $\theta_{\text{max}}$. In contrast the $V_V$ pattern shows a four-leaf clover with lobes at 45° with the polarizers. Hashimoto and coworkers (1989) made an attempt to describe these experimental patterns theoretically by considering isolated disclination lines contained in a disk. This simple presentation of the structure was not able to describe the observed patterns adequately and they suggested that a better description of the structure should include many-body interactions of the disclinations and the resulting fluctuations of the director field. Greco (1989) used these suggestions to derive a simple model containing two-body interactions between the disclinations, which was indeed able to explain all the essential features of the experimental $H_V$ patterns, such as the orientation of the lobes and the position of the intensity maxima.

**Steady shear flow SALS patterns** In contrast to the above mentioned four-lobes pattern the initial scattering pattern reported before flow or after a long relaxation is usually a featureless circular one. The explanation for this contradiction may be multiple scattering or a change in structure along the depth axis [Silvestri and Chapoy (1992)], since the measurements in the quiescent state are conducted on solution cast films with a small thickness, while experiments on flowing LCPs are usually performed on thicker samples.

From the reports on SALS a more or less universal picture has arisen for LCPs in steady state shear flow [Ernst and Navard (1989), Ernst et al. (1990), Takebe et al. (1990), Picken et al. (1991), Vermant et al. (1994a), Navard (1995), Patlazhan et al. (1995), Patlazhan et al. (1996)] and in transient shear flow [Hsiao et al. (1990), Picken et al. (1991), Vermant et al. (1994a)]. Figure 6.2 shows an example of $H_V$ SALS patterns as a function of shear rate and shear strain. For HPC, PBG, and aramid (PPTA and poly(4-4'-benzanalidylene-terephthalamide) DABT) solutions at low shear rates an elliptical scattering pattern is observed with its main axis perpendicular to the flow direction. Similar patterns are reported for the $V_V$ and $H_H$ patterns. These patterns indicate a larger orientation correlation distance parallel than perpendicular to the flow direction, caused by a small distortion of the spatial distribution of the defects.

At higher shear rates (region II) $H_V$ patterns have been observed that consist of a sharp
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**Figure 6.2:** Conoscopic SALS H₂ image of a 19.8% DABT sample at 80 °C as a function of strain (vertical axis) and shear rate (horizontal axis). The direction of flow was from left to right. (Reprinted with kind permission from Picken et al. (1991). Copyright (1991) American Chemical Society.)

streak perpendicular to the flow direction and four lobes at an angle with the flow direction (Fig. 6.2). Walker and Wagner (1994) have reported this pattern for a wide range of shear rates starting at low values but they discriminate two regimes that seem to coincide with regions I and II. In both regimes two processes take place of which one may prevail [Walker and Wagner (1994), Walker (1995), Walker et al. (1996)]. In region I the asymmetry of the pattern seems to be changing more than the position of the intensity maximum, indicating a stretching of the existing defect texture. On the other hand, in region II the position of the intensity maximum changes more while the asymmetry is
almost constant, indicative of a texture refinement. Hsiao and coworkers (1990) found a deviating trend like for their direct texture observations. In region II they reported an increase of the aspect ratio of an elliptical pattern but at the same time an increase in correlation area, indicative of a decrease of the defect density.

Usually, at shear rates in region II the $H_h$ and $V_v$ patterns are more or less similar to each other but differ largely from the $H_v$ pattern, indicating that in addition to orientation fluctuations also density fluctuations play a role. Ernst and coworkers (1990) and Takebe and coworkers (1990) explained this pattern using a qualitative model comparable to Asada and Onogi's description of region II [see, e.g., Asada (1982)]. The defects are supposed to be localized in elongated regions that float in a medium with a more or less uniform orientation and less defects, rendering effective density fluctuations. Two different orientation correlations within the regions of localized defects should then be responsible for the full pattern of the streak and the lobes. This model does not seem to be in agreement with the optical observations of section 6.1.1, and Vermant et al. (1994a) associated the streak in the scattering pattern to the striations parallel to the flow direction. Based on comparison with a low molecular weight liquid crystal, Pickcn et al. (1991) suggested that the streak could be attributed to scattering from stretched one-dimensional line disclinations. This last suggestion has recently been extended into a model by Patlazhan and coworkers (1996), who used only the aligned (horizontal) parts of the twist defect loops observed in the thermotropic LCP Vectra B950 [De'Nève et al. (1995)] as a basic scattering unit. By considering the scattering from a collection of these rod-like particles, assuming the angle of the optical axis in the core of the disclination to be at 60° with the flow direction, they were able to predict the streak perpendicular to the flow direction, including the sometimes observed oscillatory intensity as a function of the scattering angle. Also a texture refinement was predicted, but the four lobes were not explained by this model. Hence, Patlazhan and coworkers put forward that this feature must be caused by a different physical mechanism, such as the vertical parts of the disclination loops not accounted for in their model. Vermant (1996) suggested that orientation fluctuations due to out-of-plane components accompanying the tumbling motion may be responsible for the four lobes in the pattern.

At still higher shear rates some reports have mentioned the disappearance of the typical features of the high shear rate scattering pattern, indicating that the LCP is either forming a monodomain or that the defects become too small to scatter light [Vermant et al. (1994a), Navard (1995)].
Relaxation SALS patterns After cessation of flow in the low shear rate regime an equal monotonic relaxation from the elliptical to a circular scattering pattern occurs for all three polarization geometries ($H_v$, $V_v$, and $H_h$) [Takebe et al. (1990)]. On the other hand, a dramatic change of the scattering patterns is observed after cessation of flow in the high shear rate regime, which is different for the three polarization geometries [Navard (1986), Takebe et al. (1990)]. The streak perpendicular to the flow direction disappears rapidly, after which a $H_v$ pattern evolves with two intense dots along the flow direction. These dots are due to the Bragg scattering from the periodic band texture, that only appears after shear above a critical shear rate (see also section 6.1.1). After long relaxation the three patterns become equally circular again, indicating that the shear-induced texture has fully relaxed.

6.1.3 Dichroism

Polarization dependent attenuation of the intensity of the primary beam due to absorption or scattering gives rise to dichroism, which is described by the imaginary part of the refractive index. Hence, for LCPs, which strongly scatter light but hardly absorb light in the visible wavelength regime, dichroism yields information on the anisotropy of the defect or domain texture. Since light scattering is wavelength dependent a study of the dichroism versus wavelength yields additional information on the dominant length scale in the LCP during shear flow.

Steady shear dichroism The steady state dichroism of PBG and HPC solutions is a monotonically decreasing function of shear rate in region II and III (see, e.g., figure 6 of Moldenaers et al. (1989)). These dichroism experiments performed at a single wavelength can, however, not discriminate between changes in orientation or shape of the scattering entity and changes in density or domain size. Burghardt and Fuller (1991), therefore, performed steady state dichroism measurements at different shear rates as a function of wavelength. They found that the maximum in the dichroism shifted to lower wavelengths with increasing shear rate, indicating a texture refinement.

Transient shear dichroism Transient rheo-optical experiments similar to the mechanical ones reported in chapter 3 have been performed measuring dichroism of PBG and HPC solutions. At first sight there is a remarkable resemblance in the response of the optical rheometry experiments and that of the mechanical experiments. They also show strain scaling damped oscillations after a reversal of shear flow or a stepwise increase of the shear rate with a $180^\circ$ phase difference between the oscillations in the reversal and
stepwise increase experiments (see Fig. 6.3) [Moldenaers et al. (1989), Burghardt and Fuller (1991), Mortier (1995), Vermant (1996)]. Using different wavelengths it was determined that all length scales within the polydomain texture exhibit oscillations with the same period.

The similarities between the optical and rheological responses strongly suggest that a fundamental structural unit is responsible for the oscillations. The rheo-optical experiments do, however, show somewhat more oscillations than the rheological experiments, and depending on the concentration the oscillations of the stress and the dichroism can be out of phase [Vermant (1996)]. Hence, there does not seem to be a one-to-one relationship between the evolution of the texture and the stress. By comparing the evolution of the dichroism and the SALS pattern upon flow reversal, Vermant showed that both the orientation fluctuations (lobes in the SALS pattern) and the defect texture (streak in the SALS pattern) contribute to the dichroism signal.

**Dichroism during relaxation** The dichroism of HPC solutions hardly changes after cessation of slow flows [Mortier (1995)]. However, increasing the preshear rate results in a complex oscillatory response of the dichroism upon cessation of flow with increasing amplitudes. This complex behaviour is even more pronounced in the relaxation of PBG solutions, where no real oscillations are observed but a more or less noisy, irreproducible
signal is obtained. This behaviour is most probably connected to the formation of the banded texture.

6.1.4 Molecular orientation during flow

Until present only a limited amount of reports have appeared on the determination of the molecular orientation during flow. On one hand this is not surprising because of the experimental difficulties, as discussed in the introduction of chapter 5. On the other hand it is, since the most successful predictions of the rheological phenomena are based on the molecular model of Doi (1981). So knowledge about the evolution of the molecular orientation during flow is crucial for testing these molecular models.

Techniques that have been used successfully in determining changes at the molecular level during flow are birefringence, and X-ray and neutron scattering. Other techniques that are in principle suitable for assessing changes at the molecular level, such as infrared, ultraviolet and Raman spectroscopy, and nmr have not yet proven to be practically applicable to flowing LCPs. In the early eighties Asada and coworkers [Onogi and Asada (1980), Asada (1982), Asada et al. (1984)] studied the orientation of PBG and HPC solutions during flow using the light transmission method. This method is similar to the spectrographic method described in chapter 5 and the same equations are applicable. However, the light source in their case was a He-Ne laser and the detector they used was a photomultiplier. Hence, they studied the transmitted light intensity at a single wavelength as a function of the (steady state) shear rate. Oscillations in the intensity should then be attributed to changes in the birefringence. Asada and coworkers also reported a depolarization intensity, measured with the polarizer parallel to the flow direction and the analyzer perpendicular to it. About ten years later the effort to elucidate the evolution of the molecular orientation during shear flow using optical techniques was revived by Hongladarom, Burghardt and coworkers [Hongladarom et al. (1993), Hongladarom and Burghardt (1993), Hongladarom et al. (1994), Burghardt et al. (1995), Hongladarom et al. (1996)]. They used the spectrographic technique as described in chapter 5 to study the orientation of PBG and HPC solutions. The advantage of this technique is that it unambiguously determines a quantitative value of the birefringence. Hongladarom, Burghardt and coworkers used the amplitude of the oscillations of the intensity-wavelength curves as a measure of depolarization: a small amplitude indicates a large depolarization or polarization mixing. The same group recently reported results of synchrotron X-ray scattering and small-angle neutron scattering on PBG and HPC solutions [Hongladarom et al. (1996)]. Other groups reported orientation measurements on aramid solutions (PPTA
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and DABT) [Picken et al. (1990, 1991)] and PBZT [Odell et al. (1993)] using synchrotron X-ray radiation and HPC solutions [Keates et al. (1993), (1996)] using both a conventional laboratory X-ray set-up and a synchrotron set-up equipped with a 2-D detector. Also a neutron scattering study on PBLG solutions appeared [Dadmun and Han (1994)].

**Tumbling or flow-aligning** Throughout this thesis the terms "tumbling" and "flow-aligning" have been used to discuss the flow phenomena that have been encountered in the rheological experiments, such as strain scaling oscillations in the shear and normal stress. In addition to the theoretical predictions and the strong indications in the rheological experiments a direct evidence for director tumbling could only be provided by rheo-optical experiments. Two reports with such experiments on lyotropic systems supplying the evidence have appeared, describing the change of director orientation of a well-aligned monodomain in response to shear flow. Both reports were based on the prediction that applying a small shear deformation to a monodomain aligned in the flow direction would rotate the director orientation of a tumbling nematic in the same sense as the shear flow vorticity to become unstable eventually, while a flow-aligning nematic would rotate the director in the opposite direction towards the (stable) Leslie angle.

The sense of director rotation has been determined by Srinivasarao and Berry (1991) through monitoring the displacement of the conoscopic interference pattern of poly(1,4-phenylene-2,6-benzobisthiazole) (PBZT) as a function of shear rate and shear strain. Except for small strains, no homogeneous shear flow was obtained with a rotation of the director, which is consistent with tumbling. However, using the same technique it has also been reported that one LCP could exhibit both tumbling and flow-aligning behaviour in different temperature regimes [Srinivasarao et al. (1992)]. Burghardt and Fuller (1991) applied a single-wavelength transmission method with a beam tilted (in the shear plane) at an angle with the normal incidence. In their case a rotation of the director in the same sense as the flow vorticity (tumbling) would decrease the optical anisotropy, while a rotation in the opposite sense (flow-aligning) would increase the anisotropy. Their experiments on PBG solutions were consistent with director tumbling. For both techniques the changes were reversible for small strains, whereas at higher strains the monodomain broke up into a polydomain structure that did not relax back to the monodomain state.

**Steady shear flow** For shear rates at the intermediate Newtonian plateau, i.e. in the tumbling regime, Asada and coworkers obtained a more or less constant intensity for the crossed and parallel polarizer set-up (see Fig. 6.4). Therefore, they concluded that for PBG solutions in this shear rate regime hardly any orientation existed in the flow direction.
Figure 6.4: Effect of sample thickness for a 20% solution of PBG in m-cresol. (a) Intensity between crossed polarizers (O) and parallel polarizers (●) plotted against shear rate. (b) Intensity with crossed polarizers at the extinction position plotted against shear rate. (Reprinted with kind permission from Asada et al. Macromolecules 13, 867 (1980). Copyright (1980) American Chemical Society.)

However, Hongladarom, Burghardt and coworkers revealed the danger of the single-wavelength technique, in that it was only able to monitor relative changes in the birefringence. A constant intensity does not indicate the absence of orientation but
Figure 6.5: Viscosity (●) and birefringence (+) as a function of steady shear rate in (a) PBG/cresol, (b) HPC/water, and (c) HPC/cresol. Filled arrow indicates shear rate at which N₁ changes sign from positive to negative. (Reprinted with kind permission from Burghardt et al. (1995). Copyright (1995) American Chemical Society.)

indicates that no changes in orientation occur as the shear rate is increased. Hongladarom, Burghardt and coworkers reported a low and constant birefringence of approximately 53-63% of the perfectly oriented monodomain value (see Fig. 6.5). This value was significantly lower than the predictions from the mesoscopic model of Larson and Doi (1991), but the trend, i.e. a constant average orientation in the tumbling regime, was consistent with this model. By measuring the full refractive index tensor, Hongladarom
and Burghardt (1994) showed that at low shear rates a large portion of the molecules was out of the shearing plane, i.e. in the vorticity direction, resulting in a biaxial state.

At higher shear rates Asada and coworkers observed a wavy pattern for the PBG solutions (see Fig. 6.4), indicative of a change of the birefringence or equivalently the molecular orientation. This is in agreement with the observations of Hongladarom, Burghardt and coworkers (see Fig. 6.5). They found that increasing the shear rate resulted in a stepwise increase of the birefringence to a higher plateau value of about 90% of the monodomain value, which is in reasonable agreement with the theoretical predictions. The position of this transition shifted to higher shear rates for lower molecular weights and higher concentrations. The stepwise increase of the birefringence seemed to coincide with the transition from positive to negative first normal stress difference, indicative of the transition from tumbling to flow aligning. The birefringence results agree very well with the SANS and synchrotron X-ray scattering results of Hongladarom et al. (1996). However, they only agree partly with the report by Dadmun and Han (1994), who studied the orientation of PBLG in deuterated benzyl alcohol (DBA) using neutron scattering. They found an initial increase in the orientation at low shear rates, followed by a plateau and a subsequent second (indefinite) increase at higher shear rates. Hence, only in the centre part of their curve there is agreement with the results of Hongladarom, Burghardt and coworkers. Two explanations were given for this discrepancy. The first is the difference in techniques: the neutron scattering experiments require a larger scattering window and a longer scattering time than the optical experiments. Therefore, the molecular orientation from neutron scattering is a time and domain averaged quantity on another scale than the optical quantity. A second explanation could be the nature of the solution: PBLG in DBA is known to show a strong aggregation in contrast to the usual PBLG in m-cresol solutions.

Hongladarom, Burghardt and coworkers also performed measurements on HPC/water and HPC/cresol solutions (see Fig. 6.5). Compared to PBG both solutions showed an additional transition for decreasing shear rates to an even lower orientation, which may be associated with the existence of a region I for these solutions. The plateau value in region II is, however, very difficult to discern, and the transition from tumbling to flow-aligning (positive to negative $N_1$) is not clearly associated with a transition in the orientation. The general trace of the steady state orientation of HPC/water solutions as a function of shear rate is in agreement with the optical results of Asada and in very good agreement with the X-ray scattering measurements of Keates and coworkers (1993, 1996).
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Synchrotron X-ray scattering results of aramid solutions disagree completely with the above mentioned results. Picken and coworkers (1990, 1991) reported a more or less constant steady state order parameter over a large (shear thinning) shear rate regime. From earlier depolarization measurements they had concluded that the alignment increased as a function of shear rate [Doppert and Picken (1987)]. The explanation for this apparent contradiction between the optical and X-ray scattering results was thought to originate from the influence of the defects on the optical results in contrast to the X-ray data. This is, however, in contradiction with the above mentioned results on PBG and HPC solutions, where both optical and X-ray experiments yield comparable results. Although many researchers refer to this work, it has not been confirmed yet with other techniques and it is not clear if the results are system or technique dependent.

Both Asada and coworkers and Hongladarom, Burghardt and coworkers reported a high depolarization at low shear rates because of the piled domains. The depolarization decreased with increasing shear rate, which according to Asada and coworkers indicated that many depolarizing domains get dispersed in an increasingly flow aligning sample. However, according to Burghardt and coworkers the decreasing depolarization could be explained by the often observed decrease of the texture length scale: smaller domains result in less polarization mixing between different light paths due to more effective averaging of optical properties. At high shear rates an overall flow aligning sample was obtained, showing very little depolarization.

**Transient shear flow** Hongladarom, Burghardt and coworkers also extensively studied the molecular orientation during transient experiments of PBG and HPC solutions using the spectrographic technique. The birefringence in response to a reversal of shear flow (see Fig. 6.6) or a stepwise increase of the shear rate in the tumbling regime showed a damped oscillatory behaviour, where the oscillations in the flow reversal experiment were clearly more pronounced. Also Onogi and coworkers reported oscillations for HPC solutions, although less pronounced. For PBG the oscillations scaled with strain reminiscent of the earlier reported oscillations in the shear and normal stress (see chapters 3 and 4). For HPC poor strain scaling was observed, probably due to distortional elastic effects that play a more important role in HPC rheology. Although the oscillations were predicted by the mesoscopic domain model of Larson and Doi (1991) the direction in which they commence and the subsequent evolution did not completely agree with this theory. According to Hongladarom, Burghardt and coworkers this discrepancy is due to inaccuracy of the theory in the description of the detailed structure at low shear rates.
Figure 6.6: Response of 20% PBG solution to flow reversal. (a) Birefringence vs shear strain following reversal at a shear rate of 1 s\(^{-1}\). (b) Same data corrected for variation in sample thickness. (c) Corrected birefringence vs shear strain following reversals at 0.2 (---), 0.4 (•), and 1 s\(^{-1}\) (——). (d) Amplitude of oscillations in normalized spectra vs shear strain; same symbols as in (c). (Reprinted with kind permission from Hongladarom and Burghardt (1993). Copyright (1993) American Chemical Society.)
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The depolarization also showed a strain scaling oscillation on reversal of shear flow, indicating that the redistribution of orientation was associated with a temporary change of texture. An overshoot in the depolarization was also reported by Hsiao and coworkers (1990) on inception of shear flow for a thermotropic copolyester. However, in stead of oscillations in the birefringence they found a more or less linear increase with strain after inception of shear flow.

Similar to the steady-state results, the transient results for aramid solutions at first sight did not agree with the results from other LCPs. Picken and coworkers (1990, 1991) did not report any oscillations in the X-ray measurements for start up of shear flow. However, an exposure time of 30 seconds was required for the X-ray measurements, averaging out every detailed variation in the order parameter. Their data seemed to be described reasonably well by an affine deformation.

**Relaxation** The relaxation of the birefringence for PBG solutions after cessation of shear flow is shown in **figure 6.7**. As discussed in **chapter 4** the expected relation between the decreasing dynamic moduli and the increasing orientation, as measured with birefringence, for PBG solutions after cessation of shear flow was demonstrated for preshear rates in the tumbling regime [Hongladarom and Burghardt (1993, 1994)]. The birefringence during relaxation scaled with strain, like for most transient responses. Recently, Hongladarom and coworkers (1996) reported synchrotron X-ray scattering data that agree with the birefringence data only at low concentrations of PBG. At higher concentrations the X-ray results indicate a decrease of orientation after cessation of flow, while the birefringence continues to increase. This discrepancy was attributed to the coarsening of the texture during relaxation, resulting in a birefringence determination of the local orientation (monodomain), rather than an averaging of the domain distribution along the light paths. The depolarization deduced from the amplitude of the oscillations showed a strong peak at 100 strain units after cessation of flow, which was associated with the occurrence of a banded texture [see, e.g., Vermant et al. (1994b)].

The orientation during relaxation of HPC after shear flow showed a decrease upon cessation of flow [Onogi et al. (1980), Hongladarom and Burghardt (1993, 1994), Hongladarom et al. (1996), Keates et al. (1996)]. A decreasing orientation after cessation of shear flow was also reported for aramid solutions [Picken et al. (1990, 1991)], which is in accordance with the observed increasing dynamic moduli [Mortier (1995)], and for PBZT solutions [Odell et al. (1993)]. Hongladarom, Burghardt and coworkers suggested that the disruption of orientation in HPC solutions resulted from a transition back to the
Figure 6.7: Relaxation following cessation of shear flow of PBG solutions. (a) Birefringence vs scaled time (symbols refer to previous shear rate: 0.2 (●), 0.4 (——), and 1 s⁻¹ (★)). (b) Magnitude of complex modulus, |G*| vs scaled time (2 Hz). (Reprinted with kind permission from Hongladarom and Burghardt (1993). Copyright (1993) American Chemical Society.)

cholesteric phase. The behaviour was, however, much more complicated than for PBG. It showed no strain scaling and the final equilibrium moduli and orientation depended on the previously applied shear rate. An explanation may be that the texture found after relaxation differs from the initial texture and keeps an equilibrium degree of orientation that was "remembered" from the steady state orientation [Keates et al. (1996)]. In describing the orientation relaxation of HPC three types could be discriminated [Keates et al. (1996)]. A first type, found at low shear rates, was represented by a simple exponential decay, independent of the previous shear rate. It was associated with a slightly distorted defect texture, which relaxed back to its initial distribution (see section 6.1.2). The other two types showed more stages in the relaxation of the orientation and were associated with the build-up and break down of a banded texture and a subsequent further orientation.

6.1.5 Concluding remarks

In reviewing the literature on rheo-optical investigations of model LCP systems a general
picture of the structure evolution during flow emerges. Many systems, however, do not comply with this general picture and do not show all the features reported for the model systems. In particular, for thermotropes too little data is available to be able to compare their behaviour to the general one. Further, even for the model lyotropic systems the changes in defect texture and molecular orientation do not always coincide with rheological changes. Moreover, there seems to be a discrepancy between the results from different measurement techniques. Nevertheless, a summary of the general picture obtained from the observations of the (lyotropic) model systems is presented below.

For the steady state experiments at low shear rates (region I) only a small perturbation of the initial defect texture occurs. This is consistent with the light scattering results, which indicate only a small anisotropic distortion of the spatial distribution of the defect texture without changing the defect density very much. In this regime there is very little (if any) average molecular orientation. At intermediate shear rates (region II) a shear-induced defect texture, usually referred to as worm-texture, evolves, increasing in density with increasing shear rate. The $H_\nu$ SALS pattern now exhibits some typical features, such as an intense streak perpendicular to the flow direction, indicating a much enhanced orientation of defects or orientation fluctuations in the flow direction. The other feature of this pattern, the four-leaf clover, has not yet been explained satisfactory. For PBG the orientation is constant throughout region II at an intermediate level, while for HPC no clear plateau but only a decrease in slope is observed. At the high shear rate end of region II the texture transforms into a striated texture, that finally, at still higher shear rates, gives way to a more or less clear background that does not show a scattering pattern any more. At the same time the orientation of PBG increases to reach a final plateau of about 90% of the monodomain value. This transformation to region III, the flow aligning regime, seems for PBG to be associated with the change from positive to negative $N_\nu$. However, the transitions of the molecular orientation and the texture for HPC are not clearly associated with this transition in $N_\nu$.

Strain-scaling oscillations are the key observations of the transient experiments (reversal of shear flow and stepwise increase of the shear rate). The oscillations of the dichroism are found to be in phase with the mechanical rheometry experiments. The oscillations in the birefringence start out of phase with the ones in dichroism and stress, and they have a slightly smaller period. The parallelism between these results suggest that one particular structural unit should be responsible for the oscillations. The oscillations in the dichroism in response to a reversal of shear flow and a stepwise increase of the shear rate are comparable in strength, while for birefringence the oscillations for the flow reversal are
Figure 6.8: Schematic presentation of the sliding plate flow cell, consisting of a fixed lower glass plate (3) and a moving upper glass plate (4), separated by two 25 μm stainless steel spacers (2). The upper glass plate is confined in a metal holder (5), which is connected to the microstepper motor. A linear displacement of the upper plate is ensured by two metal clamps (1) that keep the metal holder in position.

significantly larger than the ones for the step-up experiment. This indicates that both the defect texture and the molecular orientation distribution undergo considerable changes upon flow reversal. On the other hand, upon a step-up of shear rate a texture refinement takes place, while there is only a minor adjustment necessary for the molecular orientation distribution function.

The relaxation of LCPs is still a very difficult subject from the structural point of view. The evolution of orientation after cessation of shear flow either increases or decreases, depending on the system and within one system on the concentration. The evolution of the defect texture is even more complex. Besides the well-known banded texture the relaxation evolves in a chaotic way, as described by, e.g., the dichroism results. There is a irreproducible change in defect size and shape.

6.2 Experimental

High temperature flow cell A Mettler PH80 HT hot stage was modified into a sliding plate flow cell for the rheo-optical experiments on thermotropic LCPs (see Fig. 6.8). It consists of a fixed lower plate and a moving upper plate, that is driven by a Time and Precision microstepper motor (12800 steps = 0.5 mm displacement per revolution), so that
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even at low shear rates no distinct steps can be observed under the microscope. The shear rate can be varied from 0.1 to 20 s\(^{-1}\). The maximum attainable deformation is 400 s.u., which is sufficient to reach a rheological steady state (see chapter 3). The thickness of the samples is controlled by 25 μm stainless steel spacers between the glass plates. With this flow cell changes in LCP samples are monitored in the plane made up by the shear flow direction and the vorticity direction.

Sample preparation Vectra B950 was used for the rheo-optical experiments, just as for the rheological experiments described previously. For the composition and the characterization the reader is referred to chapters 3 and 4. The samples for the rheo-optical experiments were made from either macroscopically isotropic compression-moulded sheets or from oriented melt-drawn films. The preparation method of these oriented films was similar to the one of the Ultrax KR4002 films, described in chapter 5, and the order parameter versus draw ratio showed a more or less similar trend. The initial thickness of these samples was slightly larger than the gap size, so that upon melting good contact was obtained between the glass plates and the molten polymer. After melting the sample was left to equilibrate for 15 minutes at 300°C.

Optical microscopy A Jenapol polarizing optical microscope was used to observe the textural changes during the start-up and the reversal of shear flow, and during the relaxation after shear flow. The polarizers were placed at ±45° with the flow direction. Usually, a long-distance objective lens with a magnification of 16 times was used. The evolution of the texture was recorded on video tape and videoprints were made from it afterwards.

Dichroism Linear dichroism during start-up and reversal of shear flow and during the relaxation after flow was measured using a Rheometrics Rheo-Optical Analyzer (ROA) at the Catholic University of Leuven, Belgium. This apparatus is based on the polarization modulation technique that enables fast and accurate determination of dichroism (or birefringence), which makes it especially suitable for transient experiments. A very clear introduction into the modulation technique and its application is given by Fuller (1995).

For dichroism measurements the optical train (see Fig. 6.9) consists of successively a HeNe laser (632.8 nm), a polarizer at 0° with the flow direction, a rotating half-wave plate (spinner), the high temperature flow cell, and the detector (photodiode). The modulation of the polarization in this optical train is introduced by the spinner, that rotates with a frequency of 2 kHz. The signal at the detector can be calculated using Mueller matrices
Figure 6.9: Optical train for dichroism measurements. See main text for explanation.

(see Fuller (1995)):

$$ I = \frac{I_0}{2} \left[ \cosh \delta'' - (\cos 2\theta \sinh \delta'') \cos 4\omega t - (\sin 2\theta \sinh \delta'') \sin 4\omega t \right] $$  \hspace{1cm} (6.1)

where $I$ is the intensity at the detector, $I_0$ is the incident intensity of the laser, $\theta$ the orientation angle of the dichroic element in the flow cell, $\omega$ is the frequency of the rotating half-wave plate, and $t$ is time. $\delta''$ is the extinction defined as:

$$ \delta'' = \frac{2\pi \Delta n''d}{\lambda} $$  \hspace{1cm} (6.2)

where $\Delta n''$ is the dichroism, $d$ is the sample thickness, and $\lambda$ the wavelength of the light. To extract information from the measured intensity $I$, the harmonic content of the signal ($I_{\cos \omega t}$ and $I_{\sin \omega t}$) must be analyzed. Therefore, the signal is sent to two lock-in amplifiers (phase sensitive detectors). The "dc" component ($I_{dc}$) can be extracted using a low-pass filter; it represents a magnitude of the transmitted light intensity. This analysis results in:
\[ I_{dc} = \frac{I_0}{2} \cosh\delta'' \] 

(6.3)

\[ I_{\text{cos}2\theta} = -\frac{I_0}{2} \cos2\theta \sinh\delta'' \] 

(6.4)

\[ I_{\text{sin}2\theta} = -\frac{I_0}{2} \sin2\theta \sinh\delta'' \] 

(6.5)

Normalization of the harmonic signals by dividing by the "dc" component results in two signals \( R_1 \) and \( R_2 \), that are independent of the initial intensity:

\[ R_1 = \frac{I_{\text{sin}2\theta}}{I_{dc}} = -\sin2\theta \tanh\delta'' \] 

(6.6)

\[ R_2 = \frac{I_{\text{cos}2\theta}}{I_{dc}} = -\cos2\theta \tanh\delta'' \] 

(6.7)

These signals can be used for further calculation to obtain the angle \( \theta \) and the extinction \( \delta'' \):

\[ \theta = \frac{1}{2} \arctan \left( \frac{R_1}{R_2} \right) \] 

(6.8)

\[ \delta'' = -\text{sgn}(R_2) \text{ arctanh} \sqrt{\frac{R_1^2}{R_2^2} + \frac{R_2^2}{R_1^2}} \] 

(6.9)

With the above definition the dichroism is positive for an anisotropic (scattering) entity oriented in the flow direction and negative when this entity is oriented perpendicular to it. The turnover point is located at ± 45°.

**Spectrographic birefringence** The basic technique has been described extensively in chapter 5, where it was demonstrated that with this technique a quantitative value of the birefringence of solid drawn films could be determined. To obtain a stronger signal at the detector for the experiments on flowing LCPs the set-up was slightly modified. In stead of using a quartz optical fibre the Oriel Multispec was placed directly under the optical train and the signal was collected with a lens system. The absolute value of the light intensity
1° or I° (at 632.8 nm) represented a measure of the transmitted light, but in this case between parallel or crossed polarizers at angles ± 45° with the flow direction.

**Transmitted light intensity measurements** In addition to the information on transmitted light intensity obtained during measurements of flow dichroism (one polarizer) and birefringence (two parallel or crossed polarizers) a series of direct light intensity measurements were performed, using a HeNe laser and a photodiode detector without any polarizers. No significant differences were detected between the various ways of detecting transmittance through the sample during or after flow and in the presentation of the results they will be discussed as one.

**Flow small-angle light scattering** The optical train for the H\text{v} SALS measurements is a vertically oriented set-up in which the flow cell is placed between two crossed polarizers. The light source consists of a HeNe laser, which is followed by a polarizer with its orientation in the flow direction (indicated with the capital H). The analyzer beneath the flow cell is oriented perpendicular to the flow direction (indicated with the capital subscript \text{v}). The detector consists of a semi-transparent paper screen on which the scattering pattern is projected. This pattern is recorded by a videocamera that is positioned right below the screen and the videoframes are collected by a pc using a frame grabber.

6.3 Experimental results and discussions

6.3.1 Optical microscopy

To follow the evolution of the texture of Vectra B950 during start up and reversal of shear flow and during relaxation after shear flow various shear rates, 0.1, 0.5, 1, 2 and 5 \text{s}^{-1}, have been used. Figure 3.2 shows that 0.1 \text{s}^{-1} is in region I, that 0.5 \text{s}^{-1} is at the onset of region II, and that 1, 2, and 5 \text{s}^{-1} are in region II. Shear rates in region III are not attainable with the flow cell used. All start-up experiments depart from a thread texture [DeNève et al. (1993)], that consists of a clear birefringent background in which black disclination loops are clearly visible. No significant differences in optical appearance are observed when the polarizers are taken out during the experiments.

**Start-up of shear flow** For shear rates in region II (1, 2, and 5 \text{s}^{-1}) all texture changes seem to scale with strain, which is not surprising since all stress responses also scale very well with strain in this regime for the LCP under investigation (see chapters 3 and 4). At inception of shear flow of isotropic compression-moulded films the loops are dragged by
Figure 6.10: Optical microscopy pictures of the start up of shear flow at 1 s$^{-1}$ of a compression-moulded (macroscopically isotropic) Vectra B950 sample at 300 °C as a function of strain.
the flow but they do not multiply. Sometimes the loops pass one another and they may even grow when one side of the loop is attached to the wall or a piece of debris. Very soon the visibility of the loops decreases because at the same time new flow-induced defects appear creating a worm texture (see Fig. 6.10). As soon as the flow starts elongated clouds of these defects appear heterogeneously spread over the picture with their long axis more or less perpendicular to the flow direction. These clouds exhibit a kind of rolling motion in which their visibility varies and eventually they cannot be observed any more as separate clouds. As the flow continues the defect density increases and the picture becomes progressively dark. From approximately 30 s.u. on no details can be observed in the microscopic picture. It is, however, not homogeneously black until about 150 s.u. This value is slightly below the values of the second broad peaks in the shear and normal stress responses for start-up experiments reported in chapters 3 and 4 and it is, therefore, tempting to associate these stress peaks with the full accomplishment of a homogeneous defect network.

Melt-drawn films (see chapter 5) have been used to perform start-up experiments on samples with the initial alignment parallel or perpendicular to the flow direction. At ambient temperatures the films exhibit a highly oriented polydomain texture and partly extinguish light when oriented parallel to one of the polarizers in the microscope. Upon melting the oriented polydomain texture first rapidly relaxes to a random polydomain texture reminiscent of the worm texture. After a few minutes of relaxation the worm texture disappears and a thread texture emerges oriented preferentially parallel to the former direction of the films. The melts still partly extinguish light parallel to one of the polarizers, indicating that they have retained an average molecular orientation. The texture evolution during start-up flow in region II of melt-drawn films oriented parallel to the flow direction shows no large differences as compared to the texture evolution starting from an isotropic sample. For this orientation too a generation of irregular defects is observed that eventually leads to a homogeneously dark picture. On the other hand, starting-up the flow in region II from a melt-drawn film oriented initially perpendicular to the flow direction results in a different texture (see Fig. 6.11). After inception of shear flow a much more homogeneous defect texture evolves, that very gradually increases in density. This difference in texture between the three initial orientations seems to be associated with the difference in stress response, reported in chapter 4. There is, however, no clear relation between the creation of defects and peaks in the stress, since the timescale over which the defects appear and the picture turns black is comparable for the three initial orientations.
Figure 6.11: Optical microscopy pictures of the start up of shear flow at 2 s\(^{-1}\) of a melt-drawn Vectra B950 film with its preferred direction perpendicular to the flow direction as a function of strain.
Figure 6.12: Optical microscopy pictures of the start up of shear flow at 0.1 s\(^{-1}\) of a compression-moulded (macroscopically isotropic) Vectra B950 sample at 300 °C as a function of strain. The last picture has been taken after a long relaxation following the shear flow.
Figure 6.13: Reduced light intensity (i.e. intensity during flow divided by intensity at inception of shear flow) around the reversal of the flow direction (at 400 s.u.) for Vectra B950 at 300 °C for three shear rates.

Figure 3.5 already showed the transmitted light intensity as a function of strain (defined as $\gamma \cdot t$). The observed sudden drop of intensity at inception of shear flow is consistent with the above mentioned fast appearance of defects for the three initial orientations. Hence, no critical strain above which a massive multiplication of defects should take place (see Fig. 6.1) [Picken et al. (1991), DeNève et al. (1993)] is found in the present results. No oscillations are observed in the transmitted light intensity as a function of strain, except when air bubbles pass the light beam.

Starting-up of flow of macroscopically isotropic films at 0.1 s$^{-1}$ (region I) shows no clear generation of defects or disclination clouds (see Fig. 6.12). During shearing the defect density increases only a little but the disclination loops remain visible until the end of the experiment. The picture is never homogeneously filled with defects and is comparable with the line texture reported by Graziano and Mackley (1984). This type of flow is very reminiscent of the piled domain flow proposed to occur in region I [Onogi and Asada (1980)].

Reversal of shear flow For some samples the direction of flow was reversed after 400 s.u. of shear. Since the picture is fully dark at this point no details can be observed in
changes of the defect texture. Only a faint and temporary increase in light is observed after roughly 25 s.u. past the reversal point. This is demonstrated more clearly by measurements of the transmitted light intensity shown in figure 6.13. A similar curve was reported by Vermant (1996). For various shear rates the light intensity shows an overshoot after approximately 18-26 s.u. past the reversal point, indicating that reversal of shear flow results in a temporary decrease of the defect density. This intensity overshoot is not related to the overshoot in \( N_1 \) (see chapter 3), which is found at about 56 s.u., but might be related to shear stress that reaches its steady state level again after approximately 25 s.u.

Relaxation after shear flow The dense worm texture gradually relaxes by decreasing its density after cessation of shear flow. See, e.g., Fig. 6.14 for relaxation after shear flow at 0.5 s\(^{-1}\) (onset of region II). After a few minutes the disclination loops become visible again underneath the remaining shear-induced defects. The loops sometimes break-up in smaller loops, which relax further by shrinking and eventually collapse. After a long relaxation period the picture shows a more or less homogeneous clear background in which a few loops remain. No banded texture has been observed for any attainable previous shear rate. The time for the defect texture to relax is very sample dependent. The first 200 s.u. after cessation of flow there may be an overlap in the increase of transmitted light intensity if plotted versus strain for several shear rates in region II but the reproducibility between different samples is rather poor (see Fig. 6.15). After 200 s.u. the intensity-increase shows no relation with either time or previously applied shear rate and the final intensity is not the same for all samples.

6.3.2 Small angle light scattering

In this section preliminary results are shown of small angle light scattering experiments on Vectra B950. Hence, no quantitative information is extracted from the SALS patterns, which would require more data. The H\(_V\)-SALS patterns of a stationary molten compression-moulded sample can be circular or elliptical, depending on the initial orientation of the scattering entities in the laser beam. During start-up of shear flow an elliptical pattern with its main axis perpendicular to the flow direction develops (see Fig. 6.16), comparable to the general SALS observations for LCPs at low shear rates, reported in literature (see Fig. 6.2). It indicates a distorted defect network with its largest correlation distance parallel to the flow direction. During steady shear flow, where the defect texture has fully developed, the scattering pattern almost disappears and the scattered light is found at larger angles. During the relaxation after cessation of shear flow,
Figure 6.14: Optical microscopy pictures of the relaxation after cessation of steady-shear flow at 0.5 s⁻¹ of Vectra B950 at 300 °C as a function of time.
Figure 6.15: Transmitted light intensity $I_\text{c}$ during the relaxation of a Vectra B950 sample after the cessation of steady-shear flow at various shear rates at 300 °C as a function of scaled strain (calculated with the previously applied shear rate).

flow direction

at inception of shear flow

after 33 s.u. of shear flow

after 400 s.u., at cessation of shear flow

after 600 s.u. relaxation

Figure 6.16: SALS patterns during start up of shear flow and after cessation of shear flow.
Figure 6.17: Dichroism vs (scaled) strain for shear flow and relaxation experiments using various shear rates for samples from compression-moulded Vectra B950 films at 300 °C. Inception of shear flow at 0 s.u., reversal of flow at 400 s.u., and cessation of flow at 800 s.u. Initial dichroism values were negative for all four samples, ranging from $-5.8 \times 10^{-4}$ to $-1.3 \times 10^{-3}$.

the scattering pattern becomes more intense and after approximately 3 minutes it becomes elliptical again, with its main direction perpendicular to the flow direction (see Fig. 6.16). It remains elliptical until at least 20 minutes after cessation of shear flow.

6.3.3 Dichroism

Figure 6.17 shows a typical response of the dichroism to a shear flow experiment consisting of a start-up of flow at strain = 0, followed by a reversal of shear flow at 400 s.u., a cessation of flow at 800 s.u. and a subsequent relaxation. Both positive and negative dichroism values are found prior to flow, depending on the initial local orientation of the compression-moulded films. For melt-drawn films oriented perpendicularly to the flow direction, the dichroism is always negative. It is clearly observed that upon inception of shear flow the dichroism, present in the sample before flow, drops immediately to a very low value. During flow (0 to 800 s.u. in Fig. 6.17) no valuable information on the dichroism or the orientation angle is obtained because the transmitted light intensity ($I_{\omega}$) is too small (see also Fig. 3.5); the signal has no meaning
Figure 6.18:  a) Normalized and scaled intensity and b) birefringence vs wavelength for a melt-drawn Vectra B950 film in the flow cell with its preferred direction parallel to the flow direction at room temperature. The peak in the birefringence at approximately 770 nm is due to a local saturation of the diode array.

here and represents only noise. During relaxation after cessation of flow, where \( I_{oc} \) increases to sufficiently high values (see Fig. 6.15), the signal regains its meaning. An interesting and recurrent phenomenon is observed there. The magnitude of the dichroism starts increasing in a positive or negative direction after a period of relaxation of approximately 200 s.u. after which it goes over a maximum to level off eventually. The position and height of this maximum do not seem to have a clear scaling relation with the previously applied shear, since it is found at higher amounts of strain or at shorter times (calculated from the point of cessation of flow) for higher shear rates. Nor does the peak
correspond to a levelling off of the transmitted intensity $I_{dc}$, which still continuous to increase at this point (see Fig. 6.15). The first (apparent) increase of dichroism after cessation of shear flow is probably due to initial the increase of the defect size, as observed by microscopy (see Fig. 6.14), since the dichroism measurement at a single wavelength cannot distinguish between the size and the anisotropy of the scattering entities [Moldenaers et al. (1989), Burghardt and Fuller (1991)]. The maximum in the dichroism may then be the point where the increase in dichroism due to the increasing defect size is compensated by the decrease in the anisotropy.

The final level of the dichroism also shows no relation with the previously applied shear rate. Both the sign of dichroism and the orientation angle do, however, more or less return to their initial values before flow. Except for 10 s$^{-1}$, where the orientation angle during relaxation does not return completely to its initial value, but turns somewhat more into the flow direction. This results in the turn-over from negative dichroism values, prior to flow, to positive values after cessation of flow. The return to the initial orientation angle may be an indication that the influence of the wall is not to be neglected during relaxation.

6.3.4 Spectrographic birefringence

**Figure 6.18 a and b** show the intensity, normalized according to equation (5.5) and the resulting birefringence versus wavelength for a melt-drawn Vectra B950 film at room temperature, initially oriented parallel to the flow direction. Clearly, depolarization and polarization mixing effects have a pronounced influence on the amplitude and period of oscillations (compare chapter 5 for Ultras KR4002). Nevertheless, the birefringence can be determined following the procedure described in chapter 5, but it is even more difficult than for Ultras KR4002. The birefringence at 633 nm in the solid state for this film with a thickness of 44 μm is approximately 0.49. The peak in the birefringence at approximately 770 nm in this and further reported measurements is due to a local saturation of the diode array caused by a strong spectral line of the light source.

As described in section 6.3.1 the drawn films are able upon melting to retain their orientation, which is clearly demonstrated in **figure 6.19 a**. This figure shows relatively large oscillations and more regular periods, indicating less severe depolarization and polarization mixing. In fact, in section 6.3.1 it was observed that the optical appearance of the molten sample is more homogeneous, which results in a higher orientation in the melt than in the solid film, as shown in **figure 6.19 b**. Determination of the exact birefringence is, however, a difficult task because of the uncertainty in the sample thickness at this stage.
Figure 6.19: a) Normalized and scaled intensity and b) birefringence vs wavelength for a melt-drawn Vectra B950 film in the flow cell with its preferred direction parallel to the flow direction after melting at 300 °C.

of the experiment. With the initial sample thickness (44 μm) one obtains a birefringence of 0.42 at 633 nm, which is lower than in the solid state. However, using the final sample thickness, i.e. the thickness after flow (25 μm), results in a birefringence of 0.74. Since the thickness at this point in the experiment may be in between the initial film thickness and the spacer thickness, the exact value of the birefringence is expected to lie somewhere between the two values.

Figure 6.20 shows the evolution of the raw intensity of the transmitted light versus wavelength for the crossed polarizer set-up as a function of time after inception of shear.
Figure 6.20: Evolution of the raw intensity for the crossed polarizer set-up as a function of wavelength with the time after inception of shear flow at 1 s\(^{-1}\) as a parameter for a melt-drawn Vectra B950 film at 300 °C with its orientation initially parallel to the flow direction. The peak in the intensity curves at approximately 770 nm is due to a strong spectral line of the light source.

A flow at 1 s\(^{-1}\) for a drawn film with its orientation initially parallel to the flow direction. Several remarkable features can be observed in this figure. Firstly, the overall intensity decreases instantly at inception of shear flow, which is in accordance with figure 3.5. Secondly, the amplitude of the oscillations decreases rapidly as the flow progresses. The oscillations disappear from the intensity signal after about 8 seconds, indicating that even long before the defect network has fully developed the depolarization and polarization mixing become rather effective. Thirdly, the oscillations do not show a change in the period during the first few strain units, only a slight shift of the full curve. This indicates that the average birefringence and hence the order parameter in the plane of the flow and the vorticity direction of the sample does not change during start up, despite the creation of a polydomain texture.

In the former sections it was already noted that the texture relaxes in a few minutes after cessation of shear flow. The first oscillations become visible again after approximately 4 minutes of relaxation and as time after cessation progresses the oscillations become more
Figure 6.21: a) Normalized and scaled intensity and b) birefringence vs wavelength for a melt-drawn Vectra B950 film at 300 °C in the flow cell, 17 minutes after cessation of steady-shear flow at 1 s⁻¹.

pronounced, without, however, showing a change in period. Figure 6.21 shows curves similar to figure 6.19 for a sample 17 minutes after cessation of shear flow at 1 s⁻¹.

Clearly, the curves before and after flow are almost identical and the birefringence at 633 nm (calculated with a sample thickness of 25 μm) after shear flow is comparable: 0.72.

After a second start-up, relaxation and solidification (not shown here) the curves still show similar features and the sample exhibits a birefringence of the same order of magnitude. Further, it shows a decreased transmission of light ("extinction direction") when the previous flow direction was parallel to one of the crossed polarizers (in the microscope), indicating a preferred orientation.
Figure 6.22: a) Normalized and scaled intensity and b) birefringence vs wavelength for a compression-moulded Vectra B950 film in the flow cell at 300 °C. The peak in the birefringence at approximately 770 nm is due to a local saturation of the diode array.

Similar results are found for a start-up of flow of a film oriented initially perpendicular to the flow direction. Weak oscillations are found in the solid state, that become more pronounced in the melt. At inception of shear flow the intensity and the amplitudes decrease in a rate comparable to that of the film oriented parallel to the flow direction, also without showing a change in period. The birefringence before and after flow of this film is approximately 0.73, and the "extinction direction" after long relaxation is again more or less parallel or perpendicular to the flow direction.
For compression-moulded films no orientation can be measured in the solid state but during melting faint oscillations are observed (see Fig. 6.22). This indicates that the sample exhibits some preferential orientation but also that it exhibits a large amount of depolarization and polarization mixing. The normalized curves are very asymmetric, which is an indication that the average orientation angle is far off the flow direction [Hongladarom et al. (1993)]. Despite these difficulties the birefringence extracted using the procedure described in chapter 5 shows a relatively smooth curve versus the wavelength (Fig. 6.22 b). Again determination of the birefringence is difficult because of the uncertainty in the sample thickness. With the initial sample thickness (40 μm) one obtains a birefringence of 0.58, while using the final sample thickness after flow (26 μm) results in a birefringence of 0.89, which is too high in view of the former results.

Starting-up the shear flow at 0.5 s\(^{-1}\) for such a compression-moulded sample (see Fig. 6.23) instantly lowers the raw intensity and causes a decrease of the amplitude of the oscillations comparable to the oriented films above. However, for these "isotropic" samples a much more pronounced shift of the full oscillating intensity curve in the first few seconds after inception of shear flow is observed to settle down after approximately 6 seconds. The period remains almost unchanged, indicating that the average degree of orientation does not change much. The shift in position may be related to the reorientation of the domains into the flow direction and the accompanying introduction of defects resulting in a changed domain averaging for the polarization mixing (compare to model calculations in the Appendix of chapter 5). After cessation of shear flow the sample relaxes similarly to the oriented films. The orientation after flow is, however, not in the flow direction but returns more or less to the initial orientation before flow, as indicated by the asymmetry of the normalized intensity signal and by direct microscopy observations of the "extinction direction". The birefringence after flow, calculated with a sample thickness of 26 μm, is 0.73, which is in the same order as the oriented films.

The results on macroscopical "isotropic" samples are supported by experiments with oriented films that were placed at an angle with the flow direction. These samples also show asymmetric normalized intensity curves (with larger amplitudes), a shift of the full raw intensity curves in the first few strain units after inception of shear flow, and a return to the initial orientation angle after cessation of flow. This last observation agrees with the dichroism results, where also a return to the initial angle was reported. The quiescent state of the optical measurements (with relatively thin samples) seems, therefore, largely determined by wall effects.
Figure 6.23: Evolution of the raw intensity for the crossed polarizer set-up as a function of wavelength with the time after inception of shear flow at 0.5 s\(^{-1}\) as a parameter for a compression-moulded Vectra B950 film at 300 °C. The peak in the intensity curves at approximately 770 nm is due to a strong spectral line of the light source.

6.4 Discussion

In the present study two steady-state flow-induced textures have been observed for Vectra B950 similar to the observations of Graziano and Mackley (1984). At low shear rates (region I) the material shows a line texture, whereas at higher shear rates (region II) a worm texture is observed. The latter texture was also observed by De'Nève and coworkers (1993). They complemented the textural picture at the high shear rate side with an ordered texture, found in quenched extrudates. The striated texture, found in some lyotropic systems, has not been observed in Vectra B950. The shear rate where this texture is expected to occur is, however, too high to be attained in the optical flow cell.

No real variation in transient textures for start-up experiments in region II, reported for some lyotropic systems, has been encountered. Upon inception of shear flow all samples instantly show a massive multiplication of defects creating a dense worm texture within a approximately 20-30 strain units. However, depending on the initial orientation the optical
appearance of the defects is different, i.e. for samples oriented perpendicular to the flow direction a more homogeneous defect evolution is observed compared to parallel or isotropic samples. In chapter 4 the sharp peak at low strains in the stress growth curves for the samples that were initially oriented perpendicular to the flow direction was associated with the rotation of director from the vorticity into the flow direction. When the orientation is out of the perpendicular direction (i.e. parallel to the flow direction or random) the molecules immediately start a tumbling motion upon inception of shear flow. It can be speculated that both director rotations create the same defects but in a different plane, resulting in a different optical appearance. The rate of formation is, however, comparable, since the decrease in light intensity upon inception of shear flow for all initial orientations is similar.

The fast formation of the worm like defect texture at intermediate shear rates (in region II) is the reason that quantitative measurements, such as dichroism or birefringence measurements, are impossible during steady shear flow or transient experiments during flow (reversal of flow, step-wise increase or decrease of shear rate). Soon after inception of shear flow the transmitted intensity is too low to be able to extract information from the signal. The fully developed defect network is so dense, that even the SALS pattern disappears. Only in start-up experiments the spectrographic birefringence technique reveals that the average orientation does not change in the first few strain units (up to a maximum of approximately 10 s.u.) after inception of flow from all initial orientations. The shift of the full raw intensity curve indicates, however, that for samples initially at angles with the flow direction a change in polydomain averaging takes place. Based on rheological experiments in chapter 4, one would expect that the samples, which are oriented random or perpendicular with respect to the flow direction, show a change in orientation accompanied by the creation of defects in different planes upon inception of shear flow, as discussed above. Perhaps the changes in average orientation only take a measurable effect on the value of the birefringence after the intensity has decreased to levels where no information is obtained any more. Only a limited amount of rheo-optical data is known to compare these results with. Picken et al. (1991) showed a fast and steadily increasing order parameter as a function of strain at inception of shear flow. Calculations with the mesoscopic domain theory using large elasticity parameters support this result, except for a small overshoot at low strains [Kim and Chung (1996)]. Transient responses during flow reversal of PBG solutions show pronounced, initially increasing, oscillatory patterns, comparable to the stress response [Högladaron and Burghardt (1993)]. The slower response of the birefringence for Vectra B950 as compared with the lyotropes is in accordance with the much larger period over which the stresses change in response to a
transient shear flow (see chapter 3).

The optical experiments described in this chapter show more response after cessation of shear flow. It is known, however, that the relaxation of the defect texture evolves in a chaotic way [see, e.g., Mortier (1995)]. Scaling laws applicable to the relaxation of the stress after flow are not always suitable for dichroism and birefringence, as is also shown in the present results. Further, to complicate things even more, not all optical data support each other. The dichroism is usually negative after cessation of shear flow, indicating that the scattering entities are perpendicular to the flow direction. The elliptical SALS pattern is, however, always oriented with its long axis perpendicular to the flow direction after cessation of flow, indicating that the scattering entities are oriented parallel to the flow direction. Apparently, the SALS pattern and the dichroism are not caused by the same scattering entity. Recently, Vermant (1996) explained the region II scattering pattern of PBG solutions (see Fig. 6.2) by assuming two scattering entities. The streak perpendicular to the flow direction is supposed to be caused by defects elongated in the flow direction, whereas the lobes are supposed to be the consequence of orientation fluctuations related to distortions of the director field. Both scattering entities contribute to the dichroism but the major contribution originates from the orientation fluctuations. Although in the present results no SALS pattern with a distinct streak or lobes is observed, the contradicting results of SALS and dichroism during relaxation may suggest that in the case of Vectra B950 also two scattering entities are responsible. The stretched disclination loops visible in the optical picture before flow and after a sufficient long relaxation would then be causing the elliptical SALS pattern. On the other hand, orientation fluctuations returning to their initial orientation before flow would be responsible for the magnitude and sign of the dichroism after flow. This is not reflected separately in the scattering pattern, probably because the scattered intensity falls within the range of the elliptical pattern. This picture is supported by the birefringence, which, like the dichroism, returns to its initial orientation angle after shear flow independent of the previous shear flow.

6.5 Conclusions

The thermotropic LCP Vectra B950 exhibits steady state textures similar to the general picture for LCPs, described in the literature review. The worm texture in region II is very dense, so that transient responses during flow (i.e. flow reversal, stepwise increase or decrease of shear rate) can not be observed. Only a slight temporary increase in the transmitted light intensity is observed upon flow reversal.
The existence of a dense shear-induced defect texture in Vectra B950 very effectively frustrates any quantitative rheo-optical experiment, such as dichroism, birefringence, and even small-angle light scattering. The spectrographic birefringence measurements do show some response at inception of shear flow, revealing that the orientation ofVectra B950 hardly changes in the first few strain units. For macroscopically isotropic samples a change in the polarization mixing is observed upon inception of shear flow. This is probably due to the rotation of the director into the flow direction, a motion accompanied by the introduction of domains and a change in polydomain averaging.

Other techniques, not sensitive to the scattering by the defects, should therefore be used to obtain information on the orientation during flow. However, suitable techniques, like X-ray or neutron scattering, require a relatively long sampling time, making it impossible to measure transients. Hence, the evolution of the orientation at the molecular and the mesoscopic level may remain unknown for this particular material, and probably also for most thermotropes.

Only during relaxation, optical responses can be measured but no clear picture is obtained from the different optical experiments. From both dichroism and birefringence it is clear that the relaxation direction after shear flow for the thin optical samples is largely determined by wall effects. The results from dichroism and SALS seem to disagree when it is assumed that only one scattering entity is responsible. It is, therefore, suggested that two entities are responsible: the disclination loops, which are oriented in the flow direction, and orientation fluctuations that independent of the previous flow return to the initial orientation, imposed by the wall.

6.6 References


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CHAPTER 7

CONCLUDING REMARKS AND FUTURE RESEARCH

The purpose of this brief chapter is to discuss some general conclusions and to propose some directions for future research based on the discussion of the preceding chapters.

From the large number of rheological and the increasing number of rheo-optical reports it appears that there is a substantial diversity in the rheological properties of various LCP systems. The largest differences are found between the lyotropic and thermotropic LCPs, but even within one category the differences can be significant probably related to the variety in molecular architecture. Nevertheless, many common features are observed as well. The thermotropic LCP studied mostly in this thesis, Vectra B950, shows many of the common features and its rheology approaches that of lyotropic systems. On the other hand, it also shows features typical for thermotropes. It takes, therefore, some intermediate position in terms of rheology between the lyotropes and the other thermotropes.

Vectra B950 exhibits the typical three region flow curve, found for many LCPs. In regions I and II the steady-state first normal stress difference is always positive and increases linearly with the shear rate, which is in accordance with the mesoscopic domain theory. However, the negative values of $N_1$ at the transition from region II to region III, predicted by the molecular theories for rigid rods, could not be measured. It is doubtful whether these negative values should be expected for the semi-flexible thermotropic LCPs. It is not clear if the existence of only positive $N_1$ values indicates that tumbling should not occur in thermotropic LCPs. The development of a dense worm texture in Vectra B950 under the act of shear flow in region II resembles that of lyotropic and other thermotropic LCPs and leads us to assume that the material does exhibit tumbling.

The transient rheological and rheo-optical experiments support the assumption that Vectra B950 is a tumbling nematic. The shear and normal stress responses after an inception of shear flow, and the normal stress response after an immediate reversal of the flow direction, or a sudden increase or decrease of the shear rate exhibit oscillations that scale with strain instead of time. A similar behaviour is observed for the decrease of the relative light intensity during start-up of shear flow and the temporary increase of the light intensity after flow reversal. Further, the stress responses after cessation of flow show long decaying tails that also scale with strain. This scaling behaviour is predicted by the mesoscopic domain theory for tumbling systems and has been found for several tumbling
lyotropic LCPs. Direct optical investigations supplying the evidence for director tumbling of Vectra B950 using the techniques of Burghardt and Fuller (1991) or Srinivasarao and Berry (1991) may be an option for future research, since well oriented samples of this material can be made using melt-drawn films.

The damping of the oscillations of the transients during shear (flow reversal, step-up and step-down) is faster than that of lyotropic systems but slower than that of most other thermotropes. One explanation for the difference between the damping of lyotropes and thermotropes is the higher molecular flexibility of the latter. Hence, the intermediate position of Vectra B950 would suggest that this material is a relatively stiff thermotropic material. This seems to be supported by the low contribution of the textural stress to the total stress, as obtained from relaxation experiments, since other thermotropic and flexible lyotropic materials show a high textural contribution. The molecular flexibility of Vectra B950 is, however, unknown and in future research it should be determined to check if the suggestion given above is valid.

The low textural contribution and the slow damping of the transients could also be associated with the type of defect texture. Until present, no detailed attention has been paid to this subject with respect to the rheological behaviour. In general, LCPs exhibit a worm texture during shear flow in region II, Vectra B950 being no exception. In particular for Vectra B950 the defect responsible for the texture has been identified as a loop with a twist character. It is, however, not known whether the defects that constitute the texture are identical for all LCPs and, hence, whether they behave in a similar fashion in response to a shear flow. An indication for the peculiar behaviour of the defect texture of Vectra B950 is found in the intermittent shear flow experiments, in which it appears that the relaxation of the defect texture is more complicated than a simple unwinding of the shear-induced domains. The rebuilding of a partially relaxed defect texture evolves through two processes: the reformation of defects that did not fully relax and the formation of new defects in already defect free parts. The relaxation of the latter part may even continue by increasing the degree of orientation, which may eventually result in the decrease of the dynamic moduli. Insufficient information is, however, available to draw solid conclusions on this subject and future research of the rheological differences among the various LCPs should include a detailed study of the fundamentals and the dynamics of their defect textures. Additional elastic recovery (recoil) experiments may also provide more information on the relaxation behaviour of the defect texture of Vectra B950.

If the defect texture is indeed behaving differently in the various systems, this could be
the explanation why the theoretical models do not describe the features adequately for all LCPs, since in the models only an arbitrary assumption on the elastic contribution to the total stress is included. In this thesis we encountered, e.g., a clockwise loop in the stress paths at start-up of shear flow, that is not accounted for in the most recent calculations using the Larson-Doi mesoscopic model. Therefore, both direct elastic and viscous stresses associated with the defect texture should be included in the future theoretical models.

The degree of orientation of Vectra B950 during shear flow remains undetermined for the time being. Based on the phase difference between the oscillations of $N_1$ after a stepwise increase and a sudden reversal of shear flow it was concluded that the orientation may not be fully in the flow direction during steady-state flow in region II. The description of a dense defect network, consisting of twist loops, was used to show that a mixture of molecular orientations can exist during flow. However, if the density of these disclinations increases, the average orientation should increase, since the orientation inside the loops is in the flow direction. An average orientation in the flow direction is supported by WAXS measurements of quenched rheometer samples. Unfortunately, no direct evidence of a preferred orientation can be obtained from rheo-optical measurements using, e.g., the spectrographic birefringence technique. Future research should, therefore, include, e.g., in-situ synchrotron X-ray measurements to supply direct observations of the molecular orientation during flow. Other techniques that may improve the understanding of the changes in the orientation of thermotropic LCPs during or after (transient) shear flow are parallel or orthogonal superposition, in which a dynamic measurement is superimposed on a steady or transient flow. Further, it would be worth while performing dielectric experiments during flow of thermotropic LCPs.

References


SUMMARY

This thesis concerns the rheology and the underlying structure changes of thermotropic main-chain LCPs. It includes steady-state and transient rheological and rheo-optical experiments, and optical investigations on drawn films. A general introduction is presented in chapter 1 where the concept of liquid crystallinity and the morphology of LCPs are briefly addressed. It also contains an introduction into some rheo-optics and an overview of the literature on general trends in LCP rheology of both melts and solutions. Some of these trends are: 1) a three region flow curve, showing two shear thinning regions at low and high shear rates, separated by a region of constant viscosity; 2) the existence of a shear rate region where the first normal stress difference (N₁) may be negative; 3) pronounced oscillations in the shear stress and N₁ that scale with strain in transient shear flow; 4) long relaxations of both the shear and normal stress after cessation of flow, that also scale with strain.

In chapter 2 some currently available theoretical descriptions of the flow of LCPs are presented. The first is the continuum mechanics approach of Leslie and Ericksen, originally derived for low molecular weight liquid crystals. This model predicts tumbling of the director and has resulted in some useful scaling laws. The second is the molecular model of Doi. A major accomplishment of the latter theory is the prediction of a dynamic transition from tumbling through wagging to flow alignment as the shear rate increases. Most of the unusual rheological phenomena reported in chapter 1 can in principle be predicted using this theory, although it considers monodomains only. An improvement of the last theory is the mesoscopic domain theory by Larson and Doi. However, none of the theories is able to describe all experimental features adequately.

Chapter 3 presents the shear stress and first normal stress difference (N₁) in steady and transient shear flows of the commercial thermotropic LCP Vectra B950 (Hoechst Celanese) at 300 °C. The viscosity curve shows the typical three region flow curve of LCPs. N₁ is everywhere positive and its steady state value increases linearly with the shear rate throughout regions I and II. The growth curves of the shear and the normal stresses for shear rates in region II show slow oscillations that scale with strain. The stress transients during flow reversal and stepwise increase or decrease of the shear rate also scale with strain. The damping of the transients is slower than what is found in other thermotropic LCPs. The oscillations of N₁ after reversal and after stepwise increase of the shear rate do not have a clear phase difference. This indicates that either the orientation is not fully in the flow direction or that the defect texture affects the reorientation of the molecules. The relaxation of the stresses after cessation of flow shows a fast initial part and a long strain-scaling tail. The elastic texture contribution to the total stress is lower than in other semi-flexible systems. Either the viscous / elastic molecular contribution or an additional viscous contribution of the defects seems to be responsible for this low value.

In chapter 4 the changes in the structure during the start-up flow of Vectra B950 are probed by performing transient experiments after various flow histories. The shear and normal stress growth curves of a squeezed sample and of a randomly oriented sample show a pronounced overshoot at low strains, whereas the stress growth curve of a sample
presheared until steady state shows a gradual increase. This first peak is associated with the re-orientation of the director into the shearing plane. All stress transients show a second broad maximum at large strains that results from the generation of a steady defect network. The effect of varying the relaxation period after preshearing is reflected in the appearance of two peaks in the subsequent stress growth curves. One of these peaks shifts linearly with relaxation period and the other is more or less fixed in position. The orientation of the molecules during steady shear flow is on average in the flow direction. Intermediate orientation levels may exist in the transient depending on the amount of strain. The material is able to maintain the flow-induced orientation distribution for a long time after cessation of flow. This is reflected in a similar fashion in the initial magnitudes of the stresses and the dynamic moduli after various preshear strains. Moreover, the dynamic moduli decrease with time after cessation of steady shear flow, indicating that the orientation increases during relaxation.

The aim of Chapter 5 is to demonstrate the feasibility of a spectrographic birefringence technique for measurement of the orientation of highly scattering thermotropic LCPs, and to optimize the technique for quantitative rheo-optical experiments (to be described in Chapter 6). Therefore, the degree of orientation in thermotropic LCP films of Ultras KR4002 (BASF) has been determined as a function of the draw ratio using the spectrographic birefringence technique, diffuse reflectance infrared spectroscopy (DRIFT), and wide-angle X-ray scattering (WAXS). Quantitative measurements of the average birefringence were obtained despite the huge turbidity of the samples. The order parameter calculated from the birefringence was found to depend on the draw ratio according to the Kuhn and Grün equation for pseudo-affine deformation. The infrared dichroism was measured as a function of film thickness by layer removal. The thickness-averaged orientation calculated from the DRIFT measurements also indicated affine deformation of the films. The orientation derived from WAXS appeared to be clearly overaffine. The difference between the results from WAXS and the results from the other two techniques is attributed to preferential orientation of the crystalline fraction due to flow-induced crystallization in the films which is detected only by WAXS. By representing the polydomain sample by a pile of domains, each with varying optical path differences (birefringence multiplied by thickness) and orientation angles, anomalies in the intensity versus wavelength curve, such as reduced amplitudes and irregular periods of oscillations, can be modelled. In particular, modelling of the polarization mixing of several light beams results in irregular curves that resemble the experimental ones.

Chapter 6 starts with a literature review on the rheo-optical investigations of mainly lyotropic LCPs. It describes the use of several techniques to probe the evolution of the LCP structure during flow at both the molecular orientation level and the mesoscopic (domain) level. For steady-state measurements the changes in the structure seem to be correlated with the rheological transitions observed in the three region flow curve. Transient rheo-optical experiments, including birefringence and dichroism, show strain-scaling oscillations with periods almost similar to the ones in the shear and normal stress, indicating that one particular structure unit is responsible. The orientation during relaxation after cessation of shear flow seems to show an inverse relation with the evolution of the dynamic moduli.
Rheo-optical experiments on Vectra B950 show that this material exhibits steady-state textures comparable to some of those reported in literature. The worm texture in region II is very dense, obscuring any quantitative transient rheo-optical observation from (visible light) dichroism, (spectrographic) birefringence, and small angle light scattering (SALS). At start up of shear flow the spectrographic birefringence technique shows no change of orientation in the first few strain units before the light is fully depolarized. Only a slight change in polarization mixing is observed. Contradictory results from dichroism and SALS during relaxation after cessation of shear flow seem to indicate that light scattering in this LCP is caused by two entities. Both the dichroism and the birefringence return to their initial angles after a sufficient long relaxation, indicating that the quiescent state of the optical measurements is largely determined by wall effects for these thin samples.

Chapter 7 contains some concluding remarks and suggestions for future research. The rheological experiments described in this thesis indicate that Vectra B950 takes some intermediate position in terms of rheology between the lyotropes and the thermotropes. Based on indirect evidence it is concluded that Vectra B950 is a tumbling thermotrope. The direct evidence may be provided by rheo-optical investigations. An improved theoretical description of the flow of LCPs should include the molecular flexibility and the nature of the defects. The degree of orientation during flow is undetermined and in-situ X-ray measurements may give more insight.
SAMENVATTING

Dit proefschrift behandelt de reologie en de onderliggende structuurveranderingen van thermotrope hoofdketen vloeibaar kristallijne polymeren (Engelse afkorting: LCPs). Er worden stationaire en overgangs- (transiënte) reologische en reo-optische experimenten aan polymeren, melten en statische optische experimenten aan verstrekte folies beschreven. In hoofdstuk 1 wordt een algemene inleiding gegeven, waarin het concept van vloeibaar kristalliniteit en de morfologie van LCPs kort aan de orde komen. Verder bevat dit hoofdstuk een stukje reo-optica en een kort literatuuroverzicht over de algemene trends in de LCP reologie van zowel smelten als oplossingen. Enkele van deze trends zijn: 1) een drie-gebieden vloeicurve, waarin twee "shear thinning" gebieden bij lage (I) en hoge (III) afschuifsnellenheid werden gescend door een gebied met een constante viscositeit (II); 2) het voorkomen van een afschuifsnelleigingsgebied waar het eerste normaalspanningsverschil ($N_1$) negatief kan zijn; 3) duidelijke oscilaties van de afschui- en normaalspanning, die schalen met de afschuiving tijdens transiënte afschuifstreming; 4) lange relaxaties van zowel de afschui- als normaalspanning die eveneens schalen met de afschuiving.

Hoofdstuk 2 behandelt een aantal beschikbare theorieën voor de beschrijving van de stroming van LCPs. De eerste theorie is de continuüm mechanische benadering van Leslie en Ericsen, die in eerste instantie was afgeleid voor vloeibare kristallen met een laag molecuul gewicht. Dit model voorspelt het roteren ("tumbling") van de director en resulteert in een aantal bruikbare schalingsregels. De tweede theorie is de moleculaire theorie van Doi. Een belangrijk succes van deze theorie is de voorspelling van een dynamisch overgang met toenemende afschuifsnelleiging van een roterende director ("tumbling"), via een tussenvorm (kwispelen of "wagging" genoemd) naar een in de stromingsrichting georiënteerd ("flow aligning") systeem. Hoewel de Doi theorie alleen op monodomeinen van toepassing is, kunnen in principe de meeste ongewone reologische fenomenen die in hoofdstuk 1 aan de orde zijn geweest worden voorspeld. Een verbetering van de Doi theorie is de mesoscopic domein theorie van Larson en Doi. Geen van de bovenstaande theorieën kan echter al het experimenteel gevonden gedrag adequaat beschrijven.

In hoofdstuk 3 komen de metingen van de afschui- en normaalspanning aan de orde tijdens stationaire en transiënte afschuifstremingen van het commerciële thermotrope LCP Vectra B950 (Hoechst Celanese) op 300 °C. De vloeicurve vertoont de karakteristieke drie-gebieden vloeicurve voor LCPs. $N_1$ is overal positief en de stationaire waarde neemt lineair toe met de afschuifsnelleig in gebieden I en II. De opstartcurven van beide spanningen voor afschuijsnelheden in gebied II vertonen langzame oscilaties die schalen met de afschuiving. De spanningstransiënten tijdens het omkeren van de stromingsrichting of het stapsgewijs verhogen of verlagen van de afschuijsnelheid schalen ook met de afschuiving. De demping van de oscilaties is langzamer dan gebruikelijk voor andere thermotrope LCPs. De oscilaties van $N_1$ na het omkeren van de stromingsrichting en na de stapsgewijsse verhoging van de stromingsrichting vertonen geen duidelijk faseverschil. Dit betekent ofwel dat de oriëntatie niet volledig in de stromingsrichting is, ofwel dat de defectstructuur de heroriëntatie van de moleculen beïnvloedt. De relaxatie van de spanningen na stationaire afschuifstreming vertoont eerst een snel verval, gevolgd door een langdurige daling die schaalt met de afschuiving. De elastische bijdrage van de textuur aan
de totale spanning is lager dan wat gevonden is voor andere semi-flexibele systemen. Ofwel de viskeuze / elastische moleculaire bijdrage of een additionele viskeuze bijdrage van de defecten zou verantwoordelijk kunnen zijn voor deze lage waarde.

In hoofdstuk 4 worden de veranderingen van de structuur van Vectra B950 tijdens opstartstromingen bekeken door transiënte experimenten uit te voeren aan preparaten met een verschillende voorgeschiedenis. De opstartcurven van zowel de afschuif- als normaalspanning van een in de reometer geperst preparaat (Eng. squeezed sample) en van een willekeurig georiënteerd preparaat vertonen een uitgesproken pick bij lage deformatie, terwijl de opstartcurven van een preparaat dat van te voren was afgeschoven tot in de stationaire toestand een geleidelijk toename vertonen. Deze eerste pick wordt geassocieerd met de heroriëntatie van de director in het vlak van stroming. Alle spanningstransitieën vertonen een breed tweede maximum bij grotere deformatie die afkomstig is van de ontwikkeling van een stationair defect netwerk. Het effect van een variabele relaxatietijd na de initiële afschuiving is te zien door het ontstaan van twee pieken in de daaropvolgende opstartcurve. Een van deze pieken verschuift lineair met de relaxatietijd, terwijl de ander een vaste positie heeft. De oriëntatie van de moleculen tijdens stationaire afschuifstoming is gemiddeld in de stromingsrichting. Een lagere oriëntatie kan tijdens transiënte stromingen gevonden worden, afhankelijk van de hoeveelheid deformatie. Het materiaal is in staat zijn stromingsgeïncludeerde oriëntatie-distributie voor een lange tijd na stroming te behouden. Dit wordt op dezelfde manier weerspiegeld in de initiële waarden van de spanningen en de dynamische moduli na verschillende hoeveelheden deformatie. Bovendien dalen de dynamische moduli met de tijd na afloop van stationaire afschuifstoming, wat erop duidt dat de oriëntatie tijdens relaxatie toeneemt.

Het doel van hoofdstuk 5 is aan te tonen dat de spectrografische dubbele-brekingstechniek werkt voor metingen van de oriëntatie van sterk verstrooiende thermostrope vloeibare kristallijne polymeren en het optimaliseren van de techniek voor kwantitatieve reo-optische experimenten (te beschrijven in hoofdstuk 6). Daartoe is de oriëntatiegraad van thermostrope LCP folies van Ultrax KR4002 (BASF) bepaald afhankelijk van de verstrekgraad door gebruik te maken van de spectrografische dubbele-brekingstechniek, diffuse reflectie infrarood spectroscopie (DRIFT) en grote-hoek röntgendiffractie (WAXS). Ondanks de sterke turbiditeit van de preparaten werden kwantitatieve resultaten van de gemiddelde dubbele breking verkregen. De ordeparameter die werd berekend uit de dubbele breking blijkt volgens de Kuhn en Grün vergelijking voor pseudo-affine deformatie van de verstrekgraad af te hangen. Het infrarood dichroïsme werd als functie van de foliediktes gemeten door laagjes te verwijderen. De oriëntatie gemiddeld over de dikte, berekend m.b.v. DRIFT resultaten, duidt ook op affine deformatie van de folies. De oriëntatie bepaald m.b.v. WAXS resultaten blijkt duidelijk overaffine te zijn. Het verschil tussen de resultaten van WAXS metingen en de andere twee technieken wordt toegeschreven aan de voorkeursoriëntatie van de kristallijne fractie door stromingsgeïncludeerde kristallisatie in de folies, dat alleen door WAXS wordt gedetecteerd. Door de polydomein preparaten voor te stellen als een stapel domeinen, waarbij elke domein een variabel optisch weglengde verschil (dubbele breking vermengvuldigd met dikte) en een oriëntatiehoek bezit, kunnen afwijkingen in de intensiteit tegen golflengtecurve, zoals een gereduceerde amplituide en onregelmatige
periodes van oscillaties, worden gemodelleerd. Vooral het modelleren van polarisatiemixing van een aantal lichtbundels resulteert in een onregelmatige curve die lijkt op de experimentele curves.

Hoofdstuk 6 begint met een literatuuroverzicht over reo-optische studies van hoofdzakelijk lyotrope LCPs. Het gebruik van verschillende technieken die de ontwikkeling van de LCP structuur tijdens stroming volgen op zowel het moleculaire oriëntatie nivo als het mesoscopische (domein) nivo worden beschreven. Voor metingen van stationaire stromingen lijken de veranderingen in de structuur te correleren met de reologische overgangen zoals gevonden in de drie-gebieden vloeicurve. Resultaten van transiënte reo-optische experimenten, waaronder dubbele breking en dichroïsme, vertonen oscillaties die schalen met de deformatie, waarvan de perioden vergelijkbaar zijn met de oscillaties gevonden in de afschuif- en normaalspanning. Eén bepaalde structuureenheid wordt dan ook verantwoordelijk geacht voor dit vergelijkbare gedrag. De oriëntatie tijdens relaxatie na een stationaire afschuifstroming lijkt een inverse relatie te vertonen met de ontwikkeling van de dynamische moduli.

Uit reo-optische experimenten aan Vectra B950 blijkt dat dit materiaal stationaire texturen bevat die vergelijkbaar zijn met sommige texturen die gevonden zijn in de literatuur. De wormtextuur in gebied II is erg dicht, waardoor kwantitatieve transiënte reo-optische experimenten met behulp van (zichtbaar licht) dichroïsme, (spectrografische) dubbele breking en kleine hoek lichtverstrooiing (SALS) geen resultaat opleveren. De spectrografische dubbele-brekingstechniek levert geen verandering van de oriëntatie in de eerste paar deformatie-eenheden tijdens het opstarten van de afschuifstroming voordat het licht volledig wordt gedeформeerd. Er wordt slechts een kleine verandering in de polarisatie mixing gevonden. De tegenstrijdige resultaten van het dichroïsme en SALS na het stoppen van de stroming lijken erop te duiden dat er twee entiteiten verantwoordelijk zijn voor de verstrooiing van het licht. Na een voldoend lange relaxatie gaat zowel het dichroïsme als de dubbele breking terug naar de beginhoek, wat erop duidt dat de stilstaande toestand van de dunne optische preparaten bepaald wordt door wandeffecten.

Hoofdstuk 7 bevat enkele concluderende opmerkingen en suggesties voor toekomstig onderzoek. De reologische metingen die in dit proefschrift zijn beschreven duiden erop dat Vectra B950, wat betreft het reologische gedrag, een positie inneemt tussen de lyotropen en de thermotropen. Gebaseerd op indirecte bewijzen wordt geconcludeerd dat Vectra B950 een "tumbling" thermotroop LCP is. De directe bewijzen zouden geleverd kunnen worden door reo-optische technieken. Een verbeterde modellering van de reologie van LCPs zou een beschrijving van de moleculaire flexibiliteit en de aard van de defecten moeten bevatten. De oriëntatiegraad tijdens stroming is nog niet bepaald en met behulp van in-situ röntgenmetingen zou het inzicht in dit probleem verbeterd kunnen worden.
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Fred.
CURRICULUM VITAE


Van juli 1991 tot maart 1996 was Fred als onderzoeker in opleiding (OIO) in dienst van de Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO), stichting Scheikundig Onderzoek Nederland (SON). De meeste tijd was hij echter fysiek nog steeds aanwezig in dezelfde vakgroep als tijdens zijn afstudeeronderzoek. Hier heeft hij gewerkt aan het onderzoek dat geleid heeft tot dit proefschrift, waarbij Prof. dr. ir. A. Posthuma de Boer optrad als promotor. Tijdens het eerste jaar van het onderzoek heeft Fred 3 maanden doorgebracht in de groep van prof. G.G. Fuller van de Stanford universiteit in Amerika. Verder heeft hij zich actief bemoeid met situatie van OIO's en postdocs in dienst van NWO door zitting te nemen in de Dienstcommissie Projectmedewerkers (DCP) van NWO. Sinds augustus 1996 is Fred werkzaam als wetenschappelijk onderzoeker bij de afdeling "Applied food physics and sensory science" van het Instituut voor Agrotechnologisch Onderzoek (ATO-DLO) te Wageningen.