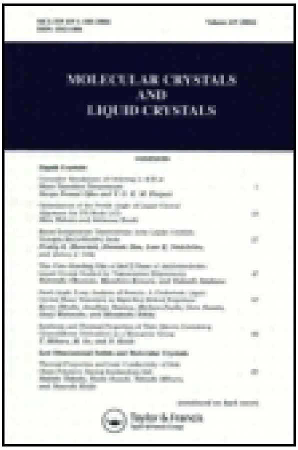

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

The Rheology and Micro-Structure of Flowing Thermotropic Liquid Crystal Polymers

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THE RHEOLOGY AND MICRO-STRUCTURE OF FLOWING THERMOTROPIC LIQUID CRYSTAL POLYMERS

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Abstract We examine and compare the morphology of small molecule liquid crystals, thermotropic main chain, liquid crystal polymers and flexible chain polymer melts. We also compare the rheological behaviour of these fluids and attempt to relate the structural characteristics of the fluid with their observed rheology.

INTRODUCTION

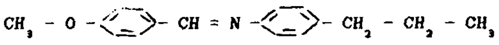
Thermotropic main chain liquid crystal polymers (LCP's) possess properties common to both small molecule liquid crystal (SMLC) and flexible chain polymers. In terms of anisotropy and structure the thermotropics relate more closely to SMLC, however in terms of rheological behaviour the connection is closer to that of conventional flexible polymers. This overlap of behaviour into two already well established fields of science means that in order to obtain a clear understanding of behaviour, all three systems should be examined. Although not considered in this paper the effect of the presence of a solvent in each of these cases should also be explored to incorporate Lyotropic behaviour.

MATERIALS

In order to simplify discussion and limit descriptions to systems that the author is familiar the following restricted examples of fluids will be examined.

Small Molecule Liquid Crystals

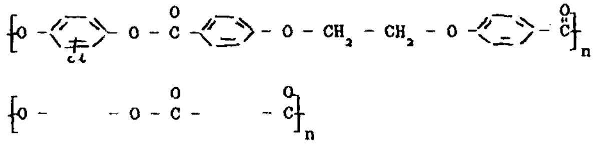
N - (- P - Methoxybenzylidene) - P - butylaniline (MBBA)



A room temperature nematic liquid crystal fluid. Local $P_2(\theta) \sim 0.7 - 0.8$.

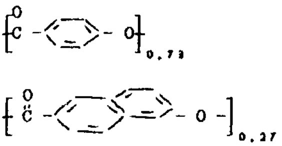
Thermotropic Liquid Crystal Polymer

Polymer A



A "relatively low molecular weight" thermotropic liquid crystal polymer, local $P_2(\theta) \sim 0.9$. Melt processing temperature > ~ 230°C. (Polymer supplied by ICI, PLC).

Polymer B



A higher molecular weight thermotropic LCP than polymer A. Local $P_2(\theta) \sim 0.9$. Melt processing temperature > ~ 290°C. (Polymer supplied by ICI, PLC).

Flexible Chain Polymers

Polyethylene $[CH_2 - CH_2]_n$

$\bar{M}_n = 20,000$, $\bar{M}_w = 130,000$. Local $P_2(\theta) \sim 0$. Melt processing temperature > ~ 140°C. (BP Rigidex Type 006-60).

Small Molecule Liquid Crystal Behaviour

Structural aspects relating to SMLC are covered in a number of texts[1-3], however the rheological literature is more sparse and their are few reviews on the subject[3-4]. Nematic SMLC such as MBBA are found to be optically anisotropic and have a local orientation function $P_2(\theta)$ of order 0.7 - 0.8, surfaces can influence the director orientation and line defects known as disclinations can exist within the material.

A useful insight into the effect of shear on the behaviour of nematic liquid crystals can be gained from the work of Wahl and Fischer[5]. Starting with discs which had been surface treated such that the MBBA between the discs was in the director vertical state, they followed the shear induced flow birefringence and the associated orientation. Figure 1 taken from reference (5) shows the schematic change of director orientation with shear together with the observed birefringence which approaches saturation at high shear levels. A later paper by Wahl[6] showed that the relaxation of birefringence Δ followed the form given by

$$\Delta = \Delta_0 \, e^{-t/\tau} \tag{1}$$

where $\tau = h^2/K$. Δ_0 is the initial birefringence, h the sample thickness and K a material dependant coefficient. Shear causes distortion away from the preferred director vertical state. On cessation of flow the director relaxes back to its minimum energy state relieving the bend elastic distortions that the fluid shear has induced. Both the development of director orientation and its subsequent shear relaxation has been successfully modelled by them using the Leslie Erickson continuum theory of nematics[4,7].

When high shear rates are applied (say > ~ 1 s^{-1}) Wahl and Fischer[5] observed what they thought were disclinations. Graziano and Mackley[8] confirmed this observation. They showed that both "thick" and "thin" disclination loops as shown in figure 2 were nucleated as a consequence of shear and that massive disclination multiplication due to shear was possible. The presence of the disclinations also significantly effected relaxation processes.

Concerning rheology of nematic SMLC; reported data[9-10] suggests that the steady shear viscosity generally decreases with increasing shear rate and approaches a limiting value. There is some evidence to suggest that the fluid rheology is not influenced by the presence of disclinations.

Thermotropic Liquid Crystal Polymers and Conventional Melt

The structure of thermotropic main chain liquid crystal polymers has been studied by a number of workers and representative examples are given in references[11-12]. Rheological reviews are sparse[13-14].

Graziano and Mackley[15] observed that both polymers A and B were optically anisotropic and in both cases it appeared that the bulk of the polymer observed between glass slides did not respond to particular surface boundary conditions; the local director tended to have no preferred orientation axis. In polymer A they observed line defect disclinations as shown in figure 3. The optical texture observed in sample of B (figure 4) was of a smaller scale and subsequently[16] identified as a dense disclination texture. It was shown that simple shear induced a net optical orientation in the direction of shear and also caused major changes in the structural reorganisation of the disclinations. Relaxation after shearing induced a number of textures including the possibility of an observed banding perpendicular to the shear direction.

Up to this point the analogy with SMLC is very close, however if the rheology is examined the similarities and differences between conventional polymer melts become striking.

Firstly if we examine the pressure drop for flow of polymer A into capillary. Figure (5) shows curves, for polymer A flowing into a zero L/D die at different temperatures. The curves show a typical power law behaviour and a set of results for a polyethylene melt are also shown for comparison. Further curves for dies with a finite L/D ratio are shown in figure (6). By assuming that the total pressure drop ΔP is given by,

$$\Delta P = K_E\, Q^{n_E} + K_c\, LQ^{n_c} \qquad (2)$$

where K_E and K_c are power law constants for the entry and capillary section, L the length of capillary and n_E and n_c the power law index for the entry and capillary section. Experiments of the kind shown in figure (5) and (6) revealed power law indices of order 0.4 for both entry and capillary sections. Polymer B was also found to have a power law index of ~ 0.4, as too did the polyethylene in the flow range tested. All these materials would then exhibit an apparent viscosity where

$$\eta_a \approx K\, \dot{\gamma}^{-0.6} \qquad (3)$$

Thus in terms of capillary rheometry alone it is difficult to distinguish LCP's from molten polymers. Where a major rheological difference does appear is in the die swell characteristics and linear viscoelastic behaviour.

Conventional melts usually exhibit strong die swell when they exit from a die[17,18]. The magnitude of the lateral dimension expansion can vary from perhaps 12 in extreme cases to typical values of order 1-3. The swelling is a strong function of polymer molecular weight, capillary shear rate, and L/D ratio of the die. Remarkably LCP's show little or no die swell[19]. This suggests that when the LCP reaches the exit there are no elastic relaxation processes available for swelling unlike the conventional melt case.

In contrast to this apparent lack of elasticity, the small strain oscillatory linear viscoelastic behaviour of thermotropic LCP's shows that the material is highly elastic. Indeed the Storage modulus G' is usually greater than the loss modulus G" for most LCP's as shown by example in figure (7). The complex viscosity η^* is also plotted and this is related to G' and G" by the relation.

$$\eta^* = \frac{[G'^2 + G''^2]^{\frac{1}{2}}}{\omega} \tag{4}$$

where ω is the angular frequency of oscillation.

In order to make a comparison, the G', G" and η^* behaviour of polyethylene is shown in figure (8). Here the usual melt behaviour is seen where G' is less than G" at low angular frequencies ω and G' is greater than G" at high values of ω.

The viscoelastic behaviour of monodisperse polymers now appears to be reasonably well understood and the molecular model of Doi and Edwards[20] predicts amongst other factors both small strain linear viscoelastic and large strain capillary shear thinning behaviour. For molten polymers, the small and large strain behaviour are linked by the Cox Merz emperical rule[21] where

$$\eta_s(\dot{\gamma}) = \eta^*(\omega) \tag{5}$$

where $\dot{\gamma} = \omega$.

The Cox Merz rule states that the apparent shear viscosity changes as a function of shear rate in the same manner as the complex viscosity changes with angular frequency. Doi Edwards theory predicts the Cox Merz rule which suggests that small and large strain mechanisms in melts are from the same physical origin. Doi Edwards theory relies on stress being generated in the melt by the configurational orientation change in deformed chains generating an elasticity which can dissipate by a viscous reptation mechanism, allowing relaxation of the chain to its entropically favoured random configuration. Because of the high local $P_2(\theta)$ in thermotropic LCP's this elastic entropic chain stretching mechanism presumably is not present, although the small strain linear viscoelastic behaviour clearly shows the fluid exhibits a viscoelastic behaviour.

A way around this dilemma and also a possible explanation for the lack of die swell is to examine the strain dependance of G', G" and η^*. Figure 9 shows the strain dependance for polymer B of the oscillatory rheological parameters taken at a fixed angular frequency of ω = 100 radians/s. It can be seen that at low strains the elasticity of the material dominates, however as the strain increases there is a dramatic reduction in particular of G' the elastic component of the material. This observation is consistent with the micro optic shearing observations made on this polymer[22]. At small strain deformations the observed birefringence and defect texture is merely perturbed by the deformation, however at large strains substantial birefringent orientation is induced in the direction of flow together with major changes occurring in the observed fluid structure. These observations suggest that the elasticity in thermotropic LCP's is strain dependant and different in origin to that of a conventional melt. The lack of die swell also suggests that elastic recovery is possible over relatively small strains of say a few percent. The origin of the small strain elasticity may either come from internal energy elastic deformations or be in some way related to the defect structure; entropic chain configurational changes of the form seen in molten polymers seem unlikely and the large strain elastic memory of the polymer is lost. This is reflected for example in the experimental observation that the exit properties of thermotropic LCP's do not depend on upstream flow conditions such as capillary length or capillary entrance geometry[23]. This contrasts strongly with molten polymers where the viscoelastic melt memory significantly effects exit behaviour[18]. In addition from the results reported here, thermotropic LCP's do not obey the Cox Merz rule and the direct connection between small and large strain behaviour is lost.

Stress and strain relaxation experiments for thermotropic LCP's would reveal valuable information on the internal mechanisms associated with these materials. "Normal" viscoelastic behaviour can be expected and has been observed[24] for small strain behaviour. it is only when the deformations become large that the anisotropy and or defect textures will significantly effect results. In conventional molten polymers there is a direct connection between chain configuration, material anisotropy and stress. In thermotropic LCP's the inter relation will be more complex.

The Processing of Thermotropic Liquid Crystal Polymers

Finally the extreme shear sensitivity of thermotropic LCP's should be emphasised. This leads to effects both in extrudates[16,25] and injection mouldings[26] where there appears to be evidence that in a decelerating flow the director alignment becomes unstable and in accelerating flows director alignment occurs along the flow streamline. These observations together with observations of relaxation behaviour during solidification are of vital importance in understanding commercial processing procedures.

In terms of end user properties the potential of the enhanced solid anisotropic properties produced by the material ensures an active future commercial interest for these systems. In terms of processing technology, the lack of die swell means that complex geometrical shapes can be formed without distortion and in particular very fine (sub mm) width scale extrusions can be manufactured. In addition the apparent absence of flow instabilities means that extrusion speeds for thermotropics can in principal be significantly greater than conventional melt processing.

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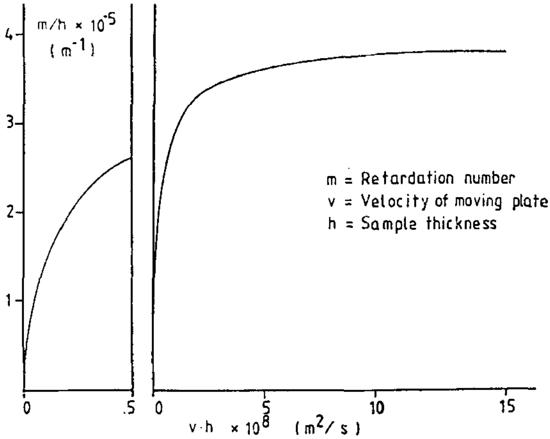
(a) RELATIONSHIP BETWEEN OPTICAL ANISOTROPY AND VELOCITY DURING STEADY SHEAR OF MBBA OBTAINED BY WAHL AND FISCHER (1973)



(b) SCHEMATIC REPRESENTATION OF SHEAR-INDUCED MOLECULAR ORIENTATION IN HOMEOTROPIC SAMPLES OF MBBA PROPOSED BY WAHL AND FISCHER (1973)

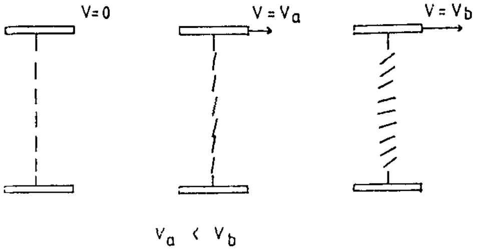


Figure 1

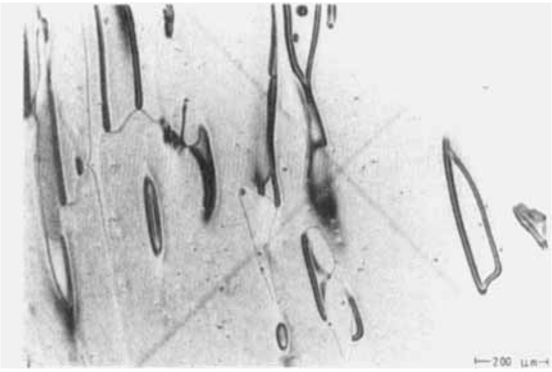


Figure 2. Thick and thin disclinations threads in a sheared sample of MBBA shear rate $\dot{\gamma} = 4\ s^{-1}$. Sample thickness = 150 μm. Sample viewed between cross polars with shear direction vertical. Reproduced from reference (8).

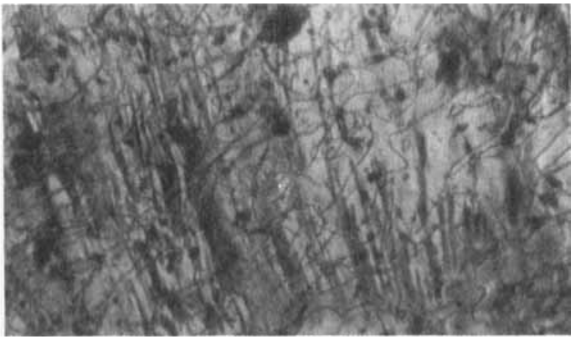


Figure 3. Disclinations observed in Polymer A at T = 240°C. Viewed between crossed polars. Sample thickness ≈ 30 μm. Horizontal field of view = 500 μm s. Reproduced from reference (15).

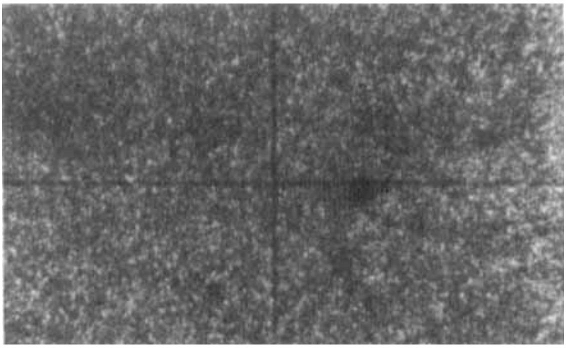


Figure 4. 'Dense disclination' texture observed in Polymer B at T = 280°C. Viewed between crossed polars. Sample thickness ≈ 5 μm. Horizontal field of view 350 μm. Reproduced from reference (16).

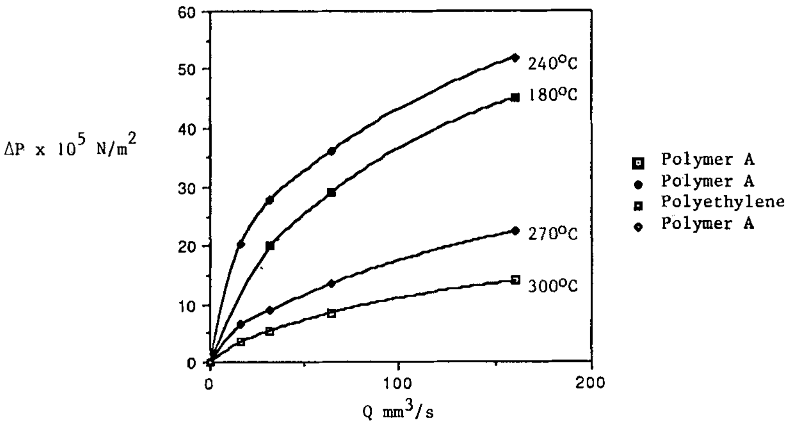


Figure 5. Graph of pressure as a function of flowrate Q, for polymer A, and polyethylene. Capillary diameter = 1.0 mm, L/D = 0. Die entry diameter = 18 mm.

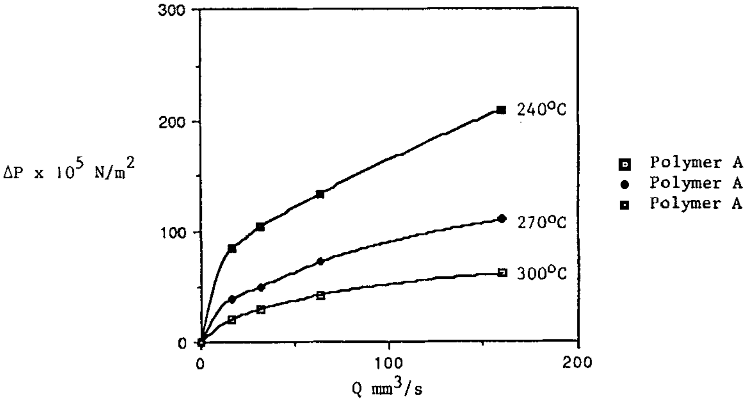


Figure 6. Graph of pressure as a function of flowrate Q for polymer A. Capillary diameter = 1.00 mm, L/D = 16.

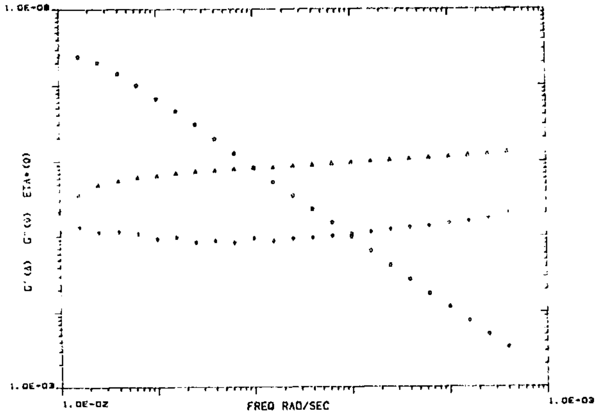


Figure 7. Frequency dependance of G', G" (N/m^2) and η* (N s/m^2) for polymer B. T = 300°C. Strain = 0.1%. Parallel Plate geometry, gap 1.7 mm. (Rheometrics RDS/II).

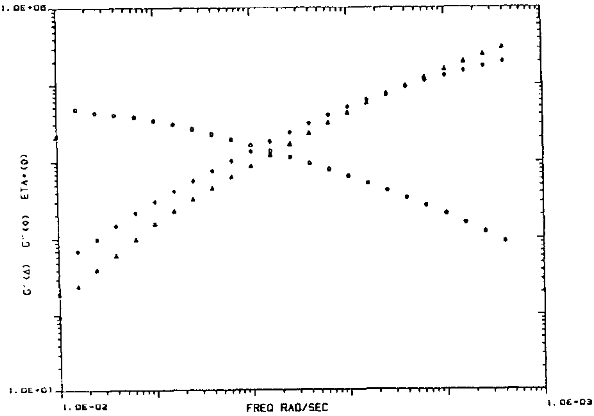


Figure 8. Frequency dependance of G', G" (N/m^2) and η* (N s/m^2) for linear polyethylene (BP 006-60). T = 200°C. Strain = 10%. Parallel Plate geometry.

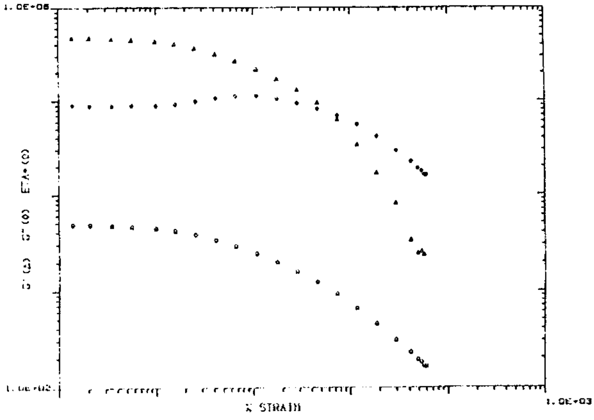


Figure 9. Strain dependance of G', G'' (N s/m^2) and η^* (N s/m^2) for Polymer B. T = 300°C. ω = 100 rad/s.