# Influence of processing conditions on the anisotropy in injection-moulded thermotropic LCPs

# I. Heynderickx\*

Philips Research Laboratories, PO Box 80.000, 5600 JA Eindhoven, The Netherlands

# and F. Paridaans

Philips Competence Centre Plastics BV, PO Box 218, 5600 MD Eindhoven, The Netherlands (Received 7 December 1992)

The influence of injection-moulding conditions on the anisotropy in macroscopic properties of flat rectangular plates has been evaluated for a thermotropic main-chain liquid crystalline polymer. The anisotropic mechanical and thermal behaviour is correlated to the degree of molecular ordering as determined from X-ray diffraction. The geometry of the injection-moulded plates, such as their thickness and the thickness and shape of the sprue, as well as the injection speed, significantly affect the molecular ordering and the resulting anisotropy in, for example, Young's modulus and heat conduction. The tendencies observed are explained in terms of molecular alignment as a consequence of the combination of shear, elongational fountain flow and the elongational deformation in the sprue.

(Keywords: injection moulding; molecular orientation; mechanical properties)

### INTRODUCTION

Main-chain thermotropic liquid crystalline polymers (LCPs) are a relatively new class of high performance engineering plastics, which have attracted a great deal of interest in the last few decades. Chemists have put a lot of effort into synthesizing rigid rod-like molecules, the majority being aromatic polyesters or copolyesters<sup>1,2</sup>. The resulting materials are melt processable, forming products with outstanding physical properties, such as high thermal and chemical stability and high mechanical stiffness. The orientational effect of the rigid rods in a flowing melt leads to a low viscosity resulting in easy processability<sup>2,3</sup>.

Unfortunately, this new class of polymeric materials also exhibits some disadvantages. Apart from the well known problem of the weakness of weld-lines<sup>3,4</sup>, the main disadvantage in processing a thermotropic LCP into a complex product is the anisotropy of the final properties<sup>3</sup>. Cooling down the product, the melt solidifies and the molecular orientation induced by the processing is, to a large extent, maintained. This gives rise to anisotropy in, for example, shrinkage and mechanical stiffness, two essential properties for an engineering plastic, whose values are hard to predict in the various directions of a complicated-shaped end-product.

A lot of effort has been made in evaluating the anisotropy in mechanical properties induced by the molecular ordering during processing. The flexural modulus has been measured as a function of test angle to the flow direction in injection-moulded thermotropic

LCP plaques<sup>5-7</sup>. In the case of a very thin plate, the stiffness was found to be 10 times larger in the direction of the flow than transverse to it<sup>5</sup>. Thermal expansion or conduction have not been used so far to measure the anisotropy in thermal properties for an LCP.

Much work has also been done on determining directly the degree of molecular orientation in injection-moulded or extruded LCP products. Optical microscopy and scanning electron microscopy (SEM) have been used to elucidate the morphology in skin and core<sup>8-11</sup>. The skin layer formed by freezing the flowing melt near the cold mould walls is highly oriented in the direction of the flow. The core layer, which cools down mainly after cessation of flow, shows little or no ordering and is even said to exhibit a slightly preferred orientation in the direction perpendicular to the flow 12,13. The molecular orientation distribution is determined by wide-angle X-ray scattering (WAXS). As demonstrated for uniaxially aligned low-molar-mass LC materials14, the spread in the equatorial diffraction arcs may be used for the characterization of molecular ordering in terms of a Hermans orientation function S. In the case of an injection-moulded thermotropic LCP sample with a pronounced skin-core and/or polydomain texture, however, it has been pointed out that the determination of a single global order parameter may be misleading 15,16. Nevertheless, the value of S may be interpreted as the spread on the mean molecular orientation averaged over the thickness of the specimen, which in turn is related to the macroscopic anisotropy of the sample. A detailed WAXS analysis of an injection-moulded sample as a function of depth clearly revealed the layered morphology

0032-3861/93/194068-07

© 1993 Butterworth-Heinemann Ltd.

<sup>\*</sup>To whom correspondence should be addressed

by changes both in the mean orientation direction and the spread in orientation  $^{16}$ . In more recent studies, FTi.r. techniques have been applied successfully in determining the mean molecular orientation induced by injection moulding of  $LCP^{17-19}$ . The molecular ordering has been mapped as a function of depth and distance from the gate by measuring the attenuated total reflection dichroism  $^{17}$ . The resulting three-dimensional orientation profile is explained in terms of the ordering effect of elongational and shear flows occurring during mould filling. Refs 18 and 19 report on specular reflectance FTi.r. measurements performed on some of the injection-moulded LCP samples discussed in the present paper.

In most of the literature mentioned above, the macroscopic anisotropy is measured only for a particular set of injection-moulding parameters, and not much has been reported on the influence of this setting on the final properties. Ophir and Ide<sup>6</sup> studied the influence of melt and mould temperature, packing pressure and injection-speed on the mechanical properties of an injection-moulded LCP, but did not evaluate its anisotropy. Suokas<sup>20</sup> looked at the effect of holding pressure, mould temperature and nozzle temperature on the morphology of an injection-moulded LCP. In this paper we will focus on the relation between the anisotropy and the processing conditions by evaluating the influence of injection speed and sample geometry on the macroscopic orientation during mould filling.

#### **EXPERIMENTAL**

# Material

The LCP material used was Vectra A950 (Hoechst-Celanese), a commercially available, injection-grade copolyester of about 70% p-hydroxybenzoic acid (HBA) and 30% 6-hydroxy-2-naphthoic acid (HNA). The melting temperature is reported<sup>21</sup> to be 285°C. D.s.c. measurements reveal a melting trajectory around 285°C, above which the material is in the nematic state. After annealing at elevated temperatures, a second melting peak at about 310°C occurs as a consequence of recrystallization in the melt<sup>21,22</sup>. The clearing temperature of the material lies above its thermal degradation temperature.

In order to study the influence of fillers on the mean molecular orientation induced by injection moulding, some of the experiments were performed on Vectra A530 and A130. Both have the same chemical structure as the copolyester mentioned above, but the A530 contains, in addition, 30% by weight of minerals, while 30% by weight of chopped glass fibres is added to the A130.

# Injection moulding

Flat plates of 80 mm × 35 mm with thicknesses varying between 0.25 and 2 mm were injection moulded on an industrial machine (Arburg 170-CMD). The barrel temperature was 285°C, while the temperature of the mould was controlled at 110°C. Samples were injection moulded with a constant screw velocity, varying in different experiments between 1 and 10 cm s<sup>-1</sup>. With a screw diameter of 18 mm this meant that for an incompressible fluid volume rates between 2.5 and 25.5 cm<sup>3</sup> s<sup>-1</sup> were generated. Depending on the sample thickness, specific pressures between 60 and 150 MPa were needed. The packing pressure for the thickest

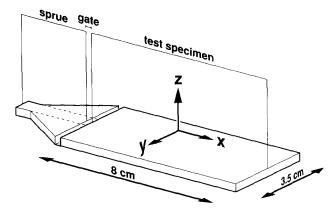


Figure 1 Geometry of the injection-moulded samples used. The thickness of the gate in most of the experiments is 0.5 or 2.0 mm

samples was 45 MPa during 4 s. In order to check the influence of the sprue geometry on the mean molecular orientation in the flat plate, the triangular sprue, with a thickness between 0.5 and 2 mm in most of the experiments, was replaced by a rectangular one, as illustrated by the dashed lines in Figure 1.

# Mechanical testing

The flexural modulus of the injection-moulded LCP samples was determined on rods of 11 mm × 35 mm by a three-points bending measurement. A Zwick 1445 instrument was used in a room temperature environment (22°C and 50% relative humidity). The data presented are the result of averaging the measurements on six rods out of one sample. The spread in these measurements was about 8%. Eliminating the effect of different locations of the rods within the sample, the spread is reduced to within 5%.

# Thermal characterization

Thermal expansion was determined with a thermomechanical analyser (Perkin–Elmer TMS2), measuring the linear displacement during heating and cooling runs between 30 and 150°C with a rate of 5°C min<sup>-1</sup>. The linear expansion coefficients in the directions in the plane of the injection-moulded plate, i.e. along (x-direction) and across (y-direction) the flow, were measured on rods with a length of 5 mm. The length of the rods for the measurement of the linear expansion coefficient perpendicular to the plane of the plate (z-direction), however, was limited by the thickness of the original sample. The coefficients were all determined during the second heating scan.

The anisotropy in heat conduction in the plane of the plate was characterized by a simple technique based on the idea of De Senarmont<sup>23</sup>. As explained elsewhere<sup>24</sup>, elliptical isotherms are visualized on the surface of the injection-moulded flat plate by using a thermochromic material (TM 485, Merck-BDH, Poole). The square of the ratio of the long to short axis of the ellipse is equal to the ratio of the heat conductivity in the directions along and transverse to the flow direction. In thermal equilibrium, the resulting value represents the anisotropy in heat conduction averaged over the thickness of the sample.

# WAXS measurements

The WAXS patterns were recorded by a Statton camera using Ni filtered  $CuK_{\alpha}$  radiation during 60 s. The intensity

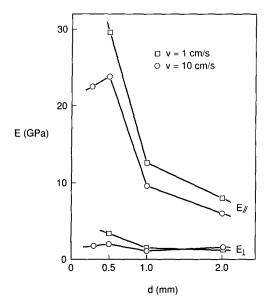


Figure 2 Elastic flexural modulus parallel  $(E_{\parallel})$  and perpendicular  $(E_{\perp})$  to the direction of flow as a function of sample thickness for two different values of the injection speed (screw forward speed)

distribution on the photograph of the radiation scattered by the interchain periodicity was scanned with a microdensitometer. From the angular intensity distribution  $I(\alpha)$  the order parameter S is determined using the Vainstein relation<sup>14</sup>:

$$S = 1 - \frac{3}{2} \left[ \frac{\int_{0}^{\pi/2} I(\alpha) \sin^{3} \alpha \, d\alpha}{\int_{0}^{\pi/2} I(\alpha) \sin \alpha \, d\alpha} \right]$$
(1)

The WAXS samples were cut out over the whole thickness of the LCP plates at a distance of about 2 cm from the gate and about 1.5 cm from one side.

# Contact microradiography

Contact microradiography (CMR) was used to visualize the glass-fibre orientation by the difference in X-ray transmission between the glass fibres and the LCP matrix; Vectra A130 plates with a thickness of 2 mm were milled at the bottom and top surface into slabs with a thickness of 0.2 mm. These slabs, remaining from the core of the original sample, were illuminated during 20 min by an X-ray tube with a driving voltage of 20 kV and a current of 5 mA.

#### **RESULTS**

## Influence of sample thickness

In a first series of experiments the thickness of the sample is varied between 0.25 and 2 mm for two different values of the injection speed, namely 1 and  $10\,\mathrm{cm\,s^{-1}}$ . The thickness of the triangular sprue is 2 mm. The elastic moduli measured in the directions parallel  $(E_{\parallel})$  and perpendicular  $(E_{\perp})$  to the flow are plotted in Figure 2. The changes in  $E_{\parallel}$  as a function of sample thickness d are much more pronounced than those of  $E_{\perp}$ , resulting in an increase in mechanical anisotropy for thinner samples. Since one expects the mechanical stiffness to be greater along than across the mean molecular orientation direction, this plot suggests that the average molecular

orientation in the direction of the flow is largest for the thinnest plates.

The same tendency is observed in the behaviour of the anisotropic heat conduction  $(\lambda_{\parallel}/\lambda_{\perp})$  as a function of sample thickness, as illustrated in *Figure 3* and ref. 24. The ratio  $\lambda_{\parallel}/\lambda_{\perp}$  decreases as the sample thickness increases for screw velocities of both 1 and 10 cm s<sup>-1</sup>. By assuming that heat transport is a lot easier along the molecular axis than perpendicular to it, the result implies that the amount of molecular orientation along the flow direction is reduced in the case of the thicker samples.

Measurements of the linear thermal expansion coefficient in the three dimensions of the flat plates injection moulded with a screw velocity of 10 cm s<sup>-1</sup> are summarized in Table 1. They show that in the direction of the flow (x-direction) there is almost no expansion; in fact for the thinnest sample a contraction is found. In the directions perpendicular to the flow, the thermal expansion is considerably larger, being more than twice as high along the thickness of the sample (z-direction) than along its width (y-direction). As explained earlier<sup>25</sup>, one expects an LC material to shrink after heating in the direction of the mean molecular orientation, and to expand in the two directions perpendicular to it. The amount of thermal contraction in the direction of the director is simply related to the initial order parameter determined with respect to this direction and its change with temperature. Assuming that the change in order parameter with temperature is independent of the initial order parameter (which is reasonable far below the melting temperature), this relation predicts a larger contraction for higher initial order parameters. In other words, the increase in thermal contraction in the direction of the flow in the case of thinner samples suggests a higher order parameter for these samples in this direction and consequently a larger amount of molecular orientation in the flow direction.

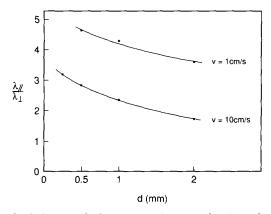


Figure 3 Anisotropy in heat conduction as a function of sample thickness for two different values of the injection speed

**Table 1** Linear thermal expansion coefficients in the three directions (see *Figure 1*) as a function of sample thickness d for samples injection moulded with a speed of  $10 \,\mathrm{cm \, s^{-1}}$ 

d (mm)	$\Delta x/x_0 \ (10^{-6} {}^{\circ}\text{C}^{-1})$	$\frac{\Delta y/y_0}{(10^{-6}  {}^{\circ}\text{C}^{-1})}$	$\frac{\Delta z/z_0}{(10^{-6}  {}^{\circ}\text{C}^{-1})}$
0.5	-11	74	162
1.0	-5	24	53
2.0	3	31	143

**Table 2** Order parameter S with respect to flow direction, determined from X-ray diffraction, as a function of sample thickness d for samples injection moulded with a speed of  $10 \,\mathrm{cm \, s^{-1}}$ 

d (mm)	S
0.25	0.63
0.50	0.39
1.00	0.27
2.00	0.17

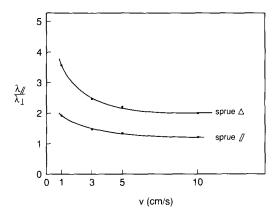


Figure 4 Anisotropy in heat conduction as a function of injection speed, measured on samples with a triangular and rectangular sprue and a thickness of 2 mm

The model of improved molecular ordering along the flow direction for a thinner sample is finally confirmed by X-ray diffraction measurements. The resulting order parameter, as averaged over the whole thickness of the injection-moulded plate, is given in *Table 2*. The value of S, defined here with respect to the flow direction, varies from a relatively high value of 0.6 for the thinnest sample to a much lower value of 0.2 for the thickest sample. It illustrates that the spread in molecular orientation averaged over the thickness of the plate is larger for thicker samples.

#### Influence of injection speed

The strong effect of the injection speed on the mechanical and thermal anisotropy in the LCP flat plates could already be deduced from Figures 2 and 3. Figure 2 shows that the elastic modulus in the direction along the flow is largest in the case of the lowest injection velocity, while the modulus in the direction perpendicular to the flow is not influenced that much by the injection speed. So, a lower injection speed results in a higher anisotropic mechanical ratio. This suggests that an increase in injection speed reduces the amount of molecular orientation in the flow direction.

This suggestion is confirmed by Figure 3, showing an increase of about 2 in the anisotropy in heat conduction for each sample thickness upon decreasing the screw velocity from 10 to 1 cm s<sup>-1</sup>. The gradual change in anisotropy in heat conduction as a function of injection speed is given in more detail in Figure 4 and confirms the idea of a reduction in molecular ordering along the flow for an increasing injection speed.

In order to separate the contributions of molecular ordering in skin and core of a 2 mm LCP plate

injection moulded with different screw velocities, WAXS experiments were performed for these samples on a surface layer about 0.3 mm thick and on a core area about 1 mm thick. The resulting angle  $\theta_{\rm max}$  of the projection of the mean molecular orientation on the plane of the sample with respect to the flow direction and the order parameter S determined with respect to the projected director (averaged over the thickness of the sample) are given in Table 3. In both cases where the molecular ordering is determined in the skin layer, one finds a dominant orientation along the flow direction with an order parameter around 0.5. The molecular orientation in the core gradually changes as the injection speed increases: at a low injection speed there is a dominant orientation in the direction of the flow with an order parameter somewhat lower than that in the skin; at higher injection speeds the order parameter strongly reduces, pointing to a more random distribution of the molecules with respect to the flow direction; at the highest injection speed the molecules are oriented mainly in the direction perpendicular to the flow, with an order parameter somewhat lower than that of the skin layer. This experiment clearly proves that an increase in screw velocity forces molecules in the bulk of the sample to be aligned in the direction perpendicular to the flow. In this respect, we should also refer to the specular reflectance FTi.r. measurements performed on the same samples, which give molecular ordering as a function of depth<sup>18</sup>. Averaging the FTi.r. data over the thicknesses of samples used in the X-ray diffraction experiments gives comparable results.

The gradual change of the mean molecular orientation from a direction along the flow for the lowest injection speed to a direction perpendicular to it for the highest injection speed also affects the mechanical anisotropy of the core. The values of  $E_{\parallel}$  and  $E_{\perp}$  as measured only on the core of the 2 mm thick plates as a function of injection speed, are summarized in *Table 4*. They clearly show that the core is stiffest along the flow direction for the lowest injection speed and perpendicular to it for the highest injection speed.

**Table 3** Local order parameter S with respect to the direction of the projection of mean molecular orientation on the plane of a 2 mm thick plate, characterized by an angle  $\theta_{\rm max}$  to the flow direction, as a function of injection speed, v

$v \pmod{s^{-1}}$	Location	$ heta_{ ext{max}}$ (deg)	S
1	Skin	3	0.50
1	Core	5	0.34
3	Core	11	0.16
5	Core	-	0.00
10	Skin	3	0.45
10	Core	96	0.35

**Table 4** Flexural modulus parallel and perpendicular to the flow direction for the core of a 2 mm thick sample injection moulded with different speeds, v

v (cm s <sup>-1</sup> )	$rac{E_{\parallel}}{ ext{(GPa)}}$	$E_{\perp}$ (GPa)
1	8.3	1.8
3	6.7	2.7
5	5.7	3.1
10	3.6	4.6

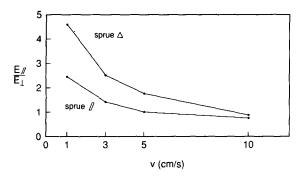


Figure 5 Mechanical anisotropy of the core as a function of injection speed for 2 mm thick plates with a triangular and rectangular sprue

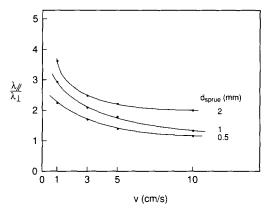


Figure 6 Anisotropy in heat conduction as a function of injection speed for 2 mm thick samples with a different thickness of the triangular sprue

## Influence of sprue geometry

The influence of geometrical effects on the mean molecular orientation in the bulk of the sample has been checked by changing the thickness as well as the shape of the sprue. Changing the shape of the sprue from triangular to rectangular, as illustrated by the dashed lines in Figure 1, implies that the injection-moulded LCP material must undergo a larger elongational deformation velocity in the y-direction when leaving the sprue. Figure 5 illustrates the effect of this change on the mechanical anisotropy of the 1 mm thick core of a 2 mm thick sample. It shows a decrease in the mechanical anisotropy  $E_{\parallel}/E_{\perp}$  as a function of screw velocity for both the triangular and rectangular sprue, albeit more pronounced for the former than for the latter. For a given value of the injection speed the anisotropic ratio of the bulk is smallest for the rectangular sprue. Exactly the same behaviour is observed for the anisotropy in heat conduction, compared for both geometries in Figure 4, i.e. the sharpest decrease in anisotropy as a function of injection speed for the triangular sprue and a reduction in anisotropy by using a rectangular instead of a triangular sprue. Both graphs suggest that the rectangular sprue induces more molecular orientation perpendicular to the flow direction.

By reducing the thickness of the triangular sprue, one applies extra shear to the material during injection. Its effect on the mean molecular ordering in the injection-moulded sample with a thickness of 2 mm is illustrated in *Figure* 6 by the results of anisotropic heat conduction measurements. There is a clear tendency towards decreasing anisotropy for the thinner sprues, to a large extent independent of the injection speed.

Apart from the geometry of the sprue, the thickness of the gate may be varied. A thinner gate would imply a higher shear locally and, at the entrance of the test specimen, a larger elongation in the z-direction. Measurements of the anisotropy in heat conduction, however, demonstrated a negligible effect of the gate geometry on the mean molecular ordering in the flat plate.

## Influence of fillers

It is known that the addition of fillers to an LCP reduces the macroscopic anisotropy of moulded parts<sup>7</sup>. The magnitude of its effect is checked by repeating some of the experiments on the mineral-filled Vectra A530 and the glass-fibre-filled Vectra A130. Table 5 illustrates the influence of the filler on the anisotropy in elastic moduli  $(E_{\parallel}/E_{\perp})$  and heat conduction  $(\lambda_{\parallel}/\lambda_{\perp})$  for a number of processing conditions. The main conclusion is a confirmation of the statement above, namely that addition of a filler reduces the overall anisotropy; this is demonstrated most drastically for processing conditions for the pure material that lead to a high degree of molecular ordering in the flow direction. Measurements on the heat conduction ratio illustrate that the reduction in anisotropy is generally larger when glass fibres are added rather than minerals. The mechanical ratio, however, exhibits the opposite tendency, due to the overall increase in mechanical stiffness through the addition of glass fibres.

Since the addition of glass fibres does not really change the influence of geometry and injection speed on the main molecular orientation profile, their presence is used to visualize the molecular ordering by CMR. The glass-fibre ordering in the core of a 2 mm thick sample injection moulded with screw velocities of 1 and 10 cm s<sup>-1</sup> is shown in *Figure 7*. Figure 7a is taken from the sample with an injection speed of 1 cm s<sup>-1</sup> and clearly shows a dominant orientation of the glass fibres along the length of the sample. Figure 7b, in contrast, is taken from the sample with an injection speed of  $10 \text{ cm s}^{-1}$  and exhibits a dominant fibre orientation in the direction perpendicular to the flow.

# **DISCUSSION**

As reported earlier<sup>8-13</sup>, an injection-moulded sample of LCP clearly exhibits a skin-core texture with a different molecular ordering in each layer. Our experiments also confirmed that the skin layer is always quite well oriented in the direction of the flow, while the bulk is more randomly oriented. The mean molecular orientation is influenced largely by the injection speed and by geometrical effects and in some situations results in a dominant orientation perpendicular to the flow.

If it is supposed that molecular ordering is completely dictated by the different shear flows occurring during

**Table 5** Influence of fillers on the anisotropy in stiffness and heat conduction for two values of the injection speed: A950 is the pure grade, A530 contains 30 wt% minerals and A130 contains 30 wt% glass fibres

v (cm s <sup>-1</sup> )	Anisotropy	A950	A530	A130
1	$E_{\parallel}/E_{\perp}$	7.5	4.5	5.4
	$\lambda_{\parallel}/\lambda_{\perp}$	3.9	3.6	3.0
10	$E_{\parallel}^{\parallel'}/\widehat{E_{\perp}}$	3.8	3.6	3.8
	$\frac{1}{\lambda_{\parallel}/\lambda_{\perp}}$	2.8	2.7	2.6

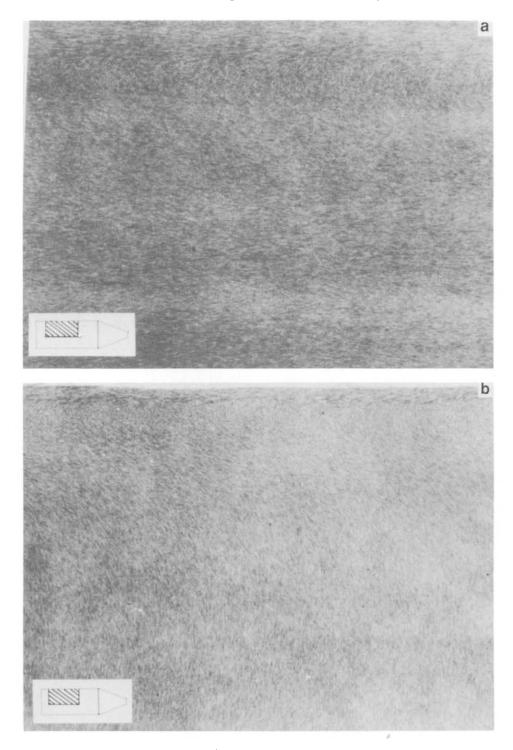


Figure 7 Contact microradiographs visualizing the glass-fibre orientation in injection-moulded LCP samples with a thickness of 2 mm: (a) injection speed 1 cm s<sup>-1</sup>; (b) injection speed 10 cm s<sup>-1</sup>. The insert illustrates the position of the measuring spot with respect to the test specimen

injection moulding of the flat plate, this implies that there is a high shear component near the surface and nearly zero shear in the core of the sample. The high shearing component near the surfaces may be responsible for aligning the molecules along the flow direction in the skin layer, while the lower molecular ordering in the bulk may be interpreted as a consequence of the tumbling behaviour known to occur in slowly sheared LCP materials<sup>25</sup>. Even the presence of bulk molecular orientation in the direction perpendicular to the flow may be explained as being due to the phenomenon known as log rolling<sup>26</sup>, which forces LCP molecules, initially aligned at an angle to the shearing plane, to orient perpendicular to this plane at low shear rates.

Interpreting the evolution of molecular ordering only in terms of shear flows, however, would be insufficient to explain all the observed phenomena. For example, in the case of a thinner sprue, one would expect a higher shear flow and consequently more orientation in the direction of the flow as averaged over the thickness of the sample. But Figure 6 shows that a smaller anisotropic ratio is measured. Moreover, the effect of elongational flows occurring during injection moulding should not be disregarded, since elongation is known to orient LC molecules more easily than shear<sup>12,27,28</sup>.

During injection of the flat plate mould, the material is subjected mainly to two elongations. The first occurs at the flow front, where the material is strongly elongated

along the thickness of the sample. The LCP molecules become aligned in the shearing plane along the front line and are laid down at the surface in the direction of the flow, where they are frozen and immobilized by the relatively low temperature of the mould wall<sup>12</sup>. The second elongation is found in the triangular sprue, where the enlargement in sample width tends to orient molecules perpendicular to the shearing plane. The molecular orientation in the core, where the molecules hardly feel any shear, experiences the influence of this elongation most strongly.

From the model of a skin layer, oriented in the flow direction due to the elongation of the fountain flow in combination with the high shear near the surface, and a core, oriented along or perpendicular to the flow direction as a consequence of the balance between elongation in the sprue and shear, it is easy to understand the decrease in anisotropy as a function of sample thickness<sup>5</sup>. Indeed, for a given value of the injection speed, the shear component near the surface is largest for the thinnest sample, which improves the molecular orientation along the flow direction and consequently enlarges the anisotropy. Moreover, the thickness of the highly oriented upper skin layer, generated by the fountain flow, seems to be nearly independent of sample thickness and, as a consequence, becomes relatively more important for the thinnest samples. Both facts contribute towards a higher anisotropy for a thinner sample.

The decrease in anisotropy with increasing injection speed suggests that it is the elongational deformation rate in the sprue that determines the final amount of molecular orientation perpendicular to the shearing plane in the bulk of the sample. Indeed, the total elongational deformation in the sprue is independent of injection speed, while the elongation rate and the observed anisotropy in the bulk of the sample are directly related to the screw velocity. This is also confirmed by comparison of the anisotropy in injection-moulded plates with a triangular or rectangular sprue. For both geometries, the total elongation at the end of the gate is the same, but in the case of the rectangular sprue the deformation rate is considerably larger than in the case of the triangular sprue. As demonstrated in Figures 4 and 5, the greater rate of elongation results in a smaller anisotropy, interpreted as an increase in bulk molecular orientation perpendicular to the flow direction.

The results plotted in Figure 6 lead to the same conclusion. We have already explained that if the extra shear in the thinner sprue should dominate the molecular ordering, one would observe the opposite behaviour to that shown in Figure 6, namely the highest anisotropy for the thinnest sprue. Considering, however, the rate of elongation in the sprue, it becomes clear that for the same injection speed its value is largest for the thinnest sprue. This would result in a greater amount of molecular orientation transverse to the filling direction, which induces a lower anisotropy, as is observed in Figure 6.

## CONCLUSIONS

The anisotropy in mechanical and thermal properties of injection-moulded LCP flat plates is strongly affected by

processing conditions such as the injection speed and sprue geometry. One finds the lowest macroscopic anisotropy for the thickest sample, injection moulded at the highest speed and experiencing the smallest rate of elongation in its sprue. The observed tendencies are all explained by considering elongation at the fountain flow and in the sprue, as well as shear. In particular, in the core, where the applied shear is small, the degree of molecular orientation perpendicular to the flow direction is directly related to the rate of elongation in the sprue.

# **ACKNOWLEDGEMENTS**

The authors gratefully thank D. Samoy and R. de Zwart for injection moulding the LCP samples and R. Hikmet and J. Meyboom for their help in performing the WAXS experiments. J. Meyboom is also thanked for his contact microradiography measurements.

#### REFERENCES

- Chung, T.-S. Polym. Eng. Sci. 1986, 26, 901
- Noel, C. and Navard, P. Prog. Polym. Sci. 1991, 16, 55
- 'Flüssigkristalline Polymere in der Praxis' (Ed. VDI-Gesellschaft Kunststoftechnik), VDI Verlag, Düsseldorf, 1990
- 4 Engberg, K., Knutsson, A., Werner, P.-E. and Gedde, U. W. Polym. Eng. Sci. 1990, 30, 1620
- Jackson, W. J. and Kuhfuss, F. J. J. Polym. Sci., Polym. Chem. 5 Edn 1976, 14, 2043
- Ophir, Z. and Ide, Y. Polym. Eng. Sci. 1983, 23, 792
- Chivers, R. A. and Moore, D. R. Polymer 1991, 32, 2190
- 8 Thapar, H. and Bevis, M. J. Mater. Sci. 1983, 2, 733
- Weng, T., Hiltner, A. and Baer, E. J. Mater. Sci. 1986, 21, 744
- 10 Sawyer, L. C. and Jaffe, M. J. Mater. Sci. 1986, 21, 1897
- Tomlinson, W. J. and Morton, P. E. J. Mater. Sci. Lett. 1991,
- 12 Ide, Y. and Ophir, Z. Polym. Eng. Sci. 1983, 23, 261
- Joseph, E. G., Wilkes, G. L. and Baird, D. G. Polym. Eng. Sci. 13 1985, **25**, 377
- Vainstein, B. K. 'Diffraction of X-rays by Chain Molecules', Elsevier Publishing Company, Amsterdam, 1966, p. 173
- Mitchell, G. R. and Windle, A. H. Polymer 1983, 24, 1513 15
- 16 Blundell, D. J., Chivers, R. A., Curson, A. D., Love, J. C. and MacDonald, W. A. Polymer 1988, 29, 1459
- Pirnia, A. and Sung, C. S. P. Macromolecules 1988, 21, 2699
- Jansen, J. A. J. PhD Thesis, Philips CCP and University of 18 Utrecht, 1992
- 19 Jansen, J. A. J., Paridaans, F. and Heynderickx, I. Polymer submitted
- Suokas, E. Polymer 1989, 30, 1105
- 21 Ambrosino, S. and Navard, P. Ann. Chim. Fr. 1990, 15, 275 and references therein
- 22 Lin, Y. G. and Winter, H. H. Macromolecules 1991, 24, 2877
- 23 Carlslaw, H. S. and Jaeger, J. C. 'Conduction of Heat in Solids' Oxford University Press, London, 1959, p. 46
- Heynderickx, I., Kadijk, S. E. and van den Brule, B. H. A. A. 24 'Theoretical and Applied Rheology' (Eds P. Moldenaers and R. Keunings) Elsevier, Amsterdam, 1992, p. 534
- 25 Broer, D. J. and Mol, G. N. Polym. Eng. Sci. 1990, 31, 625
- 26 Marrucci, G. and Grizzuti, N. Makromol. Chem., Macromol. Symp. 1991, 48/49, 181
- Larson, R. G. and Öttinger, H. C. Macromolecules 1991, 24, 6270 27
- Viola, G. G., Baird, D. G. and Wilkes, G. L. Polym. Eng. Sci. 28 1985, 25, 888
- 29 Kenig, S. Polym. Eng. Sci. 1987, 27, 887