Origin of nonlinearities in the Bagley plots of thermotropic copolyesters
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Origin of nonlinearities in the Bagley plots of thermotropic copolyesters

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Synopsis

The origin of the nonlinearity observed in Bagley plots of thermotropic copolyesters has been investigated experimentally. With the aid of a two-piston slit rheometer the dependence of the viscosity on the hydrostatic pressure has been determined directly. This dependence only accounts for part of the nonlinearity of the Bagley plots. Using slit dies with either a convergent or a divergent entrance, concave as well as convex pressure profiles are obtained. This can only be explained by a change in the molecular orientation induced by the flow in the entrance zone. The presence of wall effects has been evaluated by measuring the pressure profiles in slits of different heights; it does not explain the nonlinearity of the Bagley plots. The origin of the nonlinearity of Bagley plots must be due to both pressure and molecular reorientation effects. The nature and importance of these reorientation effects are shown to depend on the entrance geometry. © 1996 Society of Rheology.

I. INTRODUCTION

The complexity of the rheological behaviour of liquid crystalline polymers (LCPs) has been extensively discussed in the recent literature. Rheological measurements using rotational instruments have revealed a number of peculiarities in the steady-state and transient behaviour at low shear rates in both lyotropic [as reviewed by Moldenaers (1995)] and thermotropic systems [Cocchini et al. (1991); Kalika et al. (1990); Driscoll et al. (1991); Guskey and Winter (1991); Han and Kim (1994); Giles and Denn (1994)]. Capillary rheometers, on the other hand, have been used to determine the viscosity of LCPs at shear rates encountered during industrial processing [e.g. Wissbrun et al. (1987); Frayer and Huspeni (1990); Kalika et al. (1990)].

When using capillary data, one has to take into account the Rabinowitsch correction as well as the extra pressure drops occurring at the entrance and exit of the die. The latter are determined by plotting the pressure drop over the capillary as a function of its length-to-diameter ratio (L/D) for given shear rates, which results in a so-called Bagley plot [Bagley (1957)] Extrapolation to zero L/D of these usually linear plots yields the

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entrance pressure drop. Nonlinear Bagley plots have been reported in the case of liquid crystalline polymers [La Mantia and Valenza (1989); Rietveld and Tanguyen (1990); Turek et al. (1992); Wissbrun (1993); Lefeuvre et al. (1994); Langelaan et al. (1994)]. In the case of amorphous polymers such deviations from linearity in the Bagley plots are commonly attributed to the pressure dependence of the viscosity [Penwell et al. (1971); Kamal and Nyun (1973); Laun (1983)]. In the case of LCPs additional sources of nonlinearity in the Bagley plot exist, as discussed by Langelaan et al. (1994). In addition to the pressure effect, the dependence of the viscosity on the local molecular orientation could affect the shape of the Bagley plot [Baird et al. (1979); La Mantia and Valenza (1989); Rietveld and Tanguyen (1990); Turek et al. (1992); Wissbrun (1993); Langelaan et al. (1994)]. Effects due to a non-uniform temperature distribution over the channel or wall effects, such as wall slip, can also cause deviations from linearity. Wall slip reduces the shear rate and, since the slip velocity changes with pressure, the shear rate will depend on the axial position in the channel. This will also result in a nonlinear Bagley plot [Hatzikiriakos and Dealy (1992)].

It is in general impossible to determine the cause of the nonlinearity in the Bagley plot for LCPs by simply measuring the pressure drop over different dies. Several sources of nonlinearity might affect the data obtained. Even if the temperature effect and the occurrence of wall slip were to be neglected, it would still be impossible to distinguish between the other possible phenomena. Consequently the observed nonlinearities are often completely attributed to either a pressure dependent-viscosity [Izu et al. (1993); Lefeuvre et al. (1994)] or orientation effects [La Mantia and Valenza (1989); Turek et al. (1992); Wissbrun (1993)]. The former assumption has sometimes led to extremely high values for the pressure-dependence coefficient of the viscosity [Lefeuvre et al. (1994)]. Langelaan et al. (1994) measured the pressure profile in a long slit and concluded that nonlinearities could be totally explained simply by the pressure dependence of the viscosity. Gotis and Langelaan (1994) showed by model calculations that the pressure dependency observed in the slit measurements alone could not explain the nonlinearity of the Bagley plot, and concluded that reorientation effects are important.

In this work the two contributions will be determined separately in order to assess the importance of reorientation effects in both capillary and slit flow. The pressure dependence of the viscosity will be measured directly using a specially designed apparatus [Kadijk and van den Brule (1994)]. This method does not require any assumptions about the development of the flow. By comparing the pressure drops in capillaries and the pressure profiles in slits with different entrance geometries, the contributions of pressure and molecular orientation to the nonlinearity of the Bagley plots can be estimated. The possible contribution of wall effects will be evaluated separately.

II. EXPERIMENTAL

A. Materials

Two thermotropic copolyesters, Vectra A950 (Hoechst-Celanese) and Rhodester (Rhône-Poulenc), were used in this study. The Vectra A series has a characteristic composition of 73% para-hydroxybenzoic acid (HBA) and 27% 6-hydroxy-2-naphthoic acid (HNA). Rhodester is an aromatic copolyester consisting of terephthalic acid (TA), HBA, methylhydroquinone (MHQ) and dicarboxydiphenylether (DDE). Its crystal structure and melting behaviour have been studied by Löffler and Navard (1992).

The Vectra A950 shows a broad melting peak around 280 °C, whereas the nominal melting point of the Rhodester sample is approximately 290 °C, as determined by differential scanning calorimetry (DSC) measurements. However, Lin and Winter (1988, 1991)
demonstrated for a Vectra A900, which is identical in chemical nature to Vectra A950, that recrystallization may take place in the nematic state above the nominal melting point. Huang et al. (1992) argued that this phenomenon is common to at least those thermotropic copolyesters that contain HBA as a major component. DSC measurements showed that a recrystallization process also takes place above the nominal melting point in the case of the Rhodester sample. As it was our objective to measure the rheological properties of the purely nematic material, without interference of recrystallization in the melt, a suitable thermal history had to be applied to the sample during preparation. Preheating a Vectra A900 sample to temperatures above 320 °C seems to result in a nematic melt that remains relatively stable up to temperatures of 290 °C [Lin and Winter (1988)]. It was confirmed by our experiments that the same thermal history is suitable for the Vectra A950 material. The Rhodester sample behaved similarly, but had to be preheated to 325–330 °C to prevent self-nucleation. The melt then remained stable to 300 °C. Therefore, after the samples were introduced into the rheometer they were heated to either 320 °C (Vectra) or 327 °C (Rhodester), held at these temperatures for 5 minutes, then cooled to the measurement temperatures. The validity of this procedure has been verified by carrying out DSC measurements and is confirmed by the fact that it results in a time-independent value for the viscosity.

Since the ester bonds in polyesters are susceptible to hydrolytic chain scission [Zimmerman (1984)], the Vectra A950 and the Rhodester were vacuum dried at 120 °C prior to use for 8 and 10 hours, respectively. The samples were then immediately introduced into the rheometer. Giles and Denn (1994) pointed out the importance of offgassing in the case of Vectra A. They assumed that the formation of a gaseous phase is associated with a phase separation of the low molecular weight fractions at their respective melt temperatures rather than with degradation. Since we used a capillary rheometer, the effect of offgassing was minimised as the local pressures were high enough to keep the gas dissolved. To check whether offgassing and/or degradation was important in the case of the Rhodester sample, combined DSC/TGA measurements have been performed using a Secatram TGDSC111 apparatus. No significant loss has been measured, even after 60 minutes, when the material was exposed to a thermal procedure similar to that used in the rheometer. However, above 330 °C degradation was observed.

### B. Measurement methods

A Göttfert 2002 capillary rheometer has been used for the viscosity measurements. It is equipped with slits as well as capillaries, the latter covering \(L/D\) ratios from 5 to 100. The dimensions of the different geometries used are summarized in Table I. In each case the entrance angle is 180 °. With the slits the pressure was not only measured in the reservoir, i.e., 15 mm upstream from the entrance of the die, but also at three positions along the slit. The pressure transducers are of the Dynisco class I type with nominal ranges of 7, 20, 50, 100, 140 and 200 MPa and an accuracy that is better than 0.5% of the

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<td>Round-hole dies</td>
<td>(D = 0.5) mm (L = 5,15,30,50) mm</td>
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<td>Round-hole dies</td>
<td>(D = 1) mm (L = 5,10,20,30,50) mm</td>
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<td>Slit die</td>
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<td>Slit die</td>
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full scale output, as could be concluded from the full calibration data provided by Dynisco. The standard temperature control of the instrument has been used. The temperature was measured at the entrance of the capillaries and at three positions along the slit dies. Since the samples have to be subjected to specific pretreatments and, owing to the limited thermal stability of these materials, only a short period of time was available for thermal equilibration, the temperature was accurate to within \( \pm 1^\circ C \). In all experiments the Nahme-Griffith number is smaller than or equal to 1, consequently viscous heating effects can be ignored.

A slit rheometer, specially designed at Philips (referred to as the Philips rheometer below) was used to measure the pressure dependence of the viscosity. This instrument has been described in more detail by Kadijk and van den Brule (1994). Its symmetric design comprises two cylindrical reservoirs separated by a slit with a length of 100 mm, a width of 20 mm and a variable height of 0.5, 1 or 2 mm. Each cylinder has an independently controlled piston capable of generating hydrostatic pressures of up to 180 MPa via a servo-hydraulic mechanism. The pressure in the slit was measured by three Staiger-Mohilo pressure transducers (0–200 MPa); one is situated at the centre of the slit and is used to determine the hydrostatic pressure, the other two are positioned at a distance of 35 mm on each side of the central transducer and are used to measure the pressure drop needed to calculate the viscosity. The pressure readings are accurate to within \( \pm 0.1 \) MPa, resulting in relative errors for the pressure difference and the viscosity of less than 10% at the low shear rates and less than 5% at the high shear rates. Two platinum resistor temperature sensors are mounted close to the slit and special measures have been taken to thermally isolate the slit from its environment. The entrance region of this instrument is completely different from that of the Göttfert capillary rheometer: the cross-sectional shape of the channel in the Philips rheometer changes gradually and does not cause a sudden contraction flow. The width of the cross-section actually strongly diverges, whereas the height converges toward that of the slit. Kadijk and van den Brule (1994) showed that this instrument allows for accurate measurements of the pressure dependence of the viscosity of isotropic polymers.

Special care has been taken in cleaning the measurement geometries. When material, especially Rhodester, is left in contact with air between two measurements, there is a risk of oxidation, which results in the formation of a very hard, carbonized substance. As this may lead to changes in the die dimensions, the slit dies of the Göttfert were opened and cleaned between each run. The capillaries were flushed with an isotropic material immediately after every measurement. From time to time they were mechanically cleaned. In the Philips rheometer pistons on either side of the die prevented contact between the sample and air and the whole apparatus was kept under a nitrogen atmosphere.

The extrudates of both Vectra A and Rhodester displayed periodic distortions. The resulting patterns are very similar to those described by Bedford and Burghardt (1994). These authors reported such a flow instability for slit flow of lyotropic LCPs. This kind of instability may therefore be a general feature of LCPs. It creates large scale orientation fluctuations, and could possibly play a role in reorientation processes.

### III. RESULTS AND DISCUSSION

#### A. Nonlinear Bagley plots

The rheological behaviour of both the Vectra A 950 and the Rhodester LCP samples were studied using the Göttfert 2002 capillary rheometer, and the appropriate thermal pretreatment discussed in the previous section. The Bagley plots were obtained by varying the length \( L \), while the diameters of the capillary \( (D) \) and reservoir \( (D_r) \) were kept
constant. As pointed out by Sylvester (1969), it is important that this $D/D_r$ ratio is kept constant. Figure 1 shows the Bagley plot obtained for a Vectra A950 sample at 295 °C using capillaries with a diameter of 1 mm in an apparent shear rate range from 50 to 5000 s$^{-1}$.

The curves in Figure 1 are concave. The nonlinearity is more pronounced at small $L/D$ ratios. Similar results are obtained for a Rhodester at 320 °C, as shown in Figure 2(a) for capillaries with a diameter of 1 mm and in Figure 2(b) for capillaries with a diameter of 0.5 mm. Although it is less clearly seen, the graph for the thinner capillaries [Figure 2(b)] also yields concave curves with the nonlinearity being most pronounced at small $L/D$ ratios. However, an additional nonlinearity is observed at the very high pressures which occur at the highest shear rates. The pressure readings during flow in the Philips rheometer became erratic at these high pressures, possibly due to the presence of crystallites, suggesting pressure- or flow-induced crystallization.

Contrary to the results reported by Turek et al. (1992), no clear S-shaped Bagley plots could be observed, even though we used a very wide range of $L/D$ ratios. Langelaan et al. (1994) argued that recrystallization may have taken place in the experiments of Turek et al. since these authors worked at relatively low temperatures, i.e., close to the nominal melting point, without suitable thermal pretreatment. The same phenomenon may have caused the additional nonlinearity observed in Figure 2(b) at high pressures. The thermal pretreatment discussed above may “delay” the onset of crystallization not only in terms of time, but also in terms of pressure. In the measurements on Rhodester (discussed below) such high pressures were avoided.

The hypotheses for explaining nonlinear Bagley plots have already been briefly mentioned in the introduction; they will be discussed here in detail as far as they are relevant to the understanding of our results. This discussion will form the basis of our experimental verification.

1. The pressure dependence of the viscosity was suggested by Izu et al. (1993) and Lefeuvre et al. (1994) as an explanation for the observed non-linearities. By calculating the pressure dependence directly from the Bagley plots, Lefeuvre et al. (1994) obtained an extremely high value for the pressure coefficient $\beta$, defined as:
However, since a Bagley plot is in itself insufficient for distinguishing between reorientation effects and pressure effects, we measured the pressure dependence of the viscosity directly, over a wide range of pressures, using the Philips rheometer (see section III B). Langelaan et al. (1994), on the other hand, used the pressure profile in a slit to determine $\beta$ following a method proposed by Laun (1983). Their value for $\beta$ is of the same order of magnitude as those for flexible polymers. It was assumed that the slit was sufficiently long to prevent an entrance effect. It will be shown below that this is not valid in general (see section III D). In a second paper, Gotsis and Langelaan (1994) showed by model calculations that the pressure dependence of the viscosity, as determined from the slit measurements, could not explain the nonlinearity of the Bagley plots.

2. Pressure-dependent wall slip can lead to concave pressure profiles as shown by Hatzikiriakos and Dealy (1992). These authors found evidence for such a phenomenon when measuring high-density polyethylene in a capillary rheometer. As the viscosity of

$$
\beta = \frac{1}{\eta} \left( \frac{d\eta}{dp} \right)_{T}
$$

FIG. 2. Bagley plot for a Rhodester at 320 °C using (a) capillaries with diameters of 1 mm, (b) capillaries with diameters of 0.5 mm.
this material is known to barely depend on pressure within the range covered in their experiments, the curved shape of the Bagley plots could be attributed to wall slip. For an isotropic melt it is generally difficult to deduce from the curvature of the Bagley plot the contribution of either the pressure effect on the viscosity or wall slip. The problem is even more complicated in the case of an anisotropic LCP (see section III C). The possibility of a wall effect will be verified by measuring the pressure profiles in slits with different heights.

3. It has already been suggested [Langelaan et al. (1994)] that some of the peculiarities observed in the Bagley plots of LCPs may be attributed to temperature effects. Applying a suitable thermal pretreatment rules out recrystallization as a cause of nonlinearities at low $L/D$ ratios. Nicholson et al. (1992), on the other hand, showed that shear-induced crystallization may take place in random copolymers. From their in situ x-ray measurements it was concluded that this shear-induced crystallization disappears upon cessation of flow, demonstrating why it could not be observed by studying the extrudates. We will return to this effect in section III D.

4. The elongational flow at the entrance can induce an orientation that is subsequently lost during the shear flow in the capillary [La Mantia and Valenza (1989)]. Such a change in orientation could cause a nonlinearity in the Bagley plot. Turek et al. (1992) found that the orientation indeed changes with the $L/D$ ratio. This idea was used by Wissbrun (1993) to model the nonlinearity of the Bagley plots. The importance of the entrance effect on the viscosity will be demonstrated below by comparing the pressure profiles in slits with different entrance geometries (see section III D).

B. Pressure dependence of the viscosity

In contrast to earlier studies [Izu et al. (1993); Lefevre et al. (1994); Langelaan et al. (1994)] the pressure dependence of the viscosity was measured here directly in a slit viscometer described by Kadijk and van den Brul (1994). The viscosity was measured at a given piston velocity as a function of the hydrostatic pressure at the centre of the slit. A pressure range of up to 100 MPa covers values encountered in both processing and capillary rheometry. Typical data are presented in Figure 3 for Vectra A950 at 295 °C.

**FIG. 3.** Apparent viscosity as a function of the applied pressure at the centre of the slit for Vectra A950 at 295 °C at piston speeds of 0.1 and 2 mm/s, corresponding to apparent shear rates of 9.4 and 188.5 s$^{-1}$ (Philips rheometer).
The pressure coefficient $b$ can be calculated from the slope of these curves on a semi-logarithmic graph. It seems reasonable to assume that $b$ is independent of pressure in the pressure range under investigation. The value of $b$ as a function of shear rate is given in Figure 4 for Vectra A950 at 295 °C. In this figure it can be seen that $b$ is approximately $7 \times 10^{-9}$ Pa$^{-1}$, it is only a weak function of shear rate. This value agrees well with that obtained by Langelaan et al. (1994) for Vectra A900 at 300 °C, i.e., $b \approx 6.1 \times 10^{-9}$ Pa$^{-1}$. The results obtained for Rhodester are similar with $b$ being estimated as $8 \times 10^{-9}$ Pa$^{-1}$. The values of $b$ obtained for Rhodester and Vectra are of the same order of magnitude as those of isotropic polymers (for a review of these values see Kadijk and van den Brule (1994) and Langelaan et al. (1994)).

Analogous to the pressure coefficient $b$ the temperature coefficient of the viscosity can be defined as

$$\alpha = -\frac{1}{\eta} \left( \frac{d\eta}{dT} \right)_p.$$

The ratio of $\beta$ over $\alpha$ is more or less the same for all isotropic polymers (approximately $4 \times 10^{-7}$ °C/Pa) [Kadijk and van den Brule (1994), van Krevelen (1990)]. The temperature dependence of Vectra A950 was investigated between 285 and 320 °C with the Philips rheometer. These data yielded an average value of $\alpha = 1.7 \times 10^{-2}$ °C at 40 MPa. It is nearly independent of shear rate in the range between 1 and 200 s$^{-1}$. This yields a $\beta/\alpha$ ratio of $4.1 \times 10^{-7}$ °C/Pa. The temperature dependence of the viscosity for Rhodester was investigated on a Göttfert 2002 in the shear rate range between 100 and 5000 s$^{-1}$ and at temperatures between 300 and 320 °C. An average value of $\alpha = 3.8 \times 10^{-3}$ °C was obtained for the temperature coefficient yielding a $\beta/\alpha$ ratio of $2.1 \times 10^{-6}$ °C/Pa. The ratio for Vectra is close to the above mentioned value for isotropic polymers, while the ratio of Rhodester is roughly an order of magnitude larger. The difference is mainly due to the relatively small temperature dependence of the viscosity. Low values for the temperature dependence have also been observed in a thermotropic system of HBA/PET 60/40 by Gotsis and Baird (1985). They attributed the small temperature dependence to a competition between the change of the nematic order toward
isotropy, resulting in an increase of the viscosity, and a decrease of the viscosity with increasing temperature due to increased mobility. Since degradation sets in at 330 °C, i.e., below the clearing temperature, this argument could not be verified.

Lefeuvre et al. (1994) calculated the pressure coefficient for the viscosity directly from the Bagley plots. The resulting values of \( \beta (10^{-6} \text{ to } 10^{-8} \text{ Pa}^{-1}) \) depended strongly on the shear rate and are orders of magnitude larger than the values measured here. The possibility of an interference of orientation and wall effects has already been mentioned. In determining \( \beta \) from Bagley plots there exists, apart from the potential for errors related to experimental artifacts, also the potential for errors inherent to the calculation procedure. First, as reported by Steuten et al. (1994), the pressure coefficients for isotropic polymers calculated from nonlinear Bagley plots are more than an order of magnitude higher than those obtained in slit die measurements. Steuten et al. applied the approximations proposed by Laun (1983), in which a quadratic fit to the Bagley curve, i.e.,

\[
p_{\text{tot}} = a + b(L/D) + c(L/D)^2,
\]

(3)

is used to determine \( \beta \) from

\[
\beta = \frac{2c}{b^2}.
\]

(4)

This quadratic form is based on the assumption that the exponential dependence of the viscosity on the pressure can be written as a series expansion up to the second-order term. When the nonlinearity becomes significant, as in the case of Bagley plots of LCPs, the higher-order terms are no longer negligible. The use of the quadratic approximation will then result in an overestimation of \( \beta \). Second, the calculation of the pressure coefficient from Bagley plots is affected by the entrance pressure drop \( (\Delta p_{\text{ent}}) \). The latter is caused by a combination of shear and extensional flow phenomena which also depend on pressure. It occurs at the position in the capillary where the pressure reaches a maximum. Assuming that the entrance pressure drop has the same pressure dependence as the shear viscosity and that the exit pressure is negligible in comparison with the entrance pressure drop, one finds by integration of the pressure field:

\[
p_{\text{tot}} = \Delta p_{\text{ent}} e^{\beta p} - \frac{1}{p} \ln \left( \frac{L}{D} \right),
\]

(5)

where \( \Delta p_{\text{ent}} \) is the entrance pressure drop and \( \sigma_0 \) the shear stress at atmospheric pressure.

If \( \beta \) for a thermotrope is determined from the Bagley plots rather than measured directly, unreasonably high values for \( \beta \) are found. For the Vectra A 950 sample, for example, values ranging from \( 5 \times 10^{-7} \) to \( 3 \times 10^{-8} \text{ Pa}^{-1} \) are obtained when applying equation 5 to figure 1 in comparison with a value of \( 7 \times 10^{-9} \text{ Pa}^{-1} \) as determined with the Philips rheometer. As seen in the results of Lefeuvre et al. (1994), the values of \( \beta \) obtained directly from the Bagley plots also depend strongly on the shear rate, which was not the case with the values of \( \beta \) derived from the slit measurements (see figure 3). The values obtained from the Bagley plots are higher at low shear rates, indicating that the nonlinearity of the Bagley plots is most pronounced at the lowest shear rates. Lefeuvre et al. attributed this dependence of the pressure coefficient on the shear rate to the type of texture. Since the slit flow and the capillary flow are very similar and will yield similar textures, this does not seem to be an appropriate conclusion. The decrease in \( \beta \) and thus in nonlinearity with increasing shear rate may be associated with molecular reorientation processes, as will be discussed below.
Figure 5 compares the Bagley plot that results from the inclusion of the true pressure dependence of the viscosity, as measured using the Philips rheometer and equation (5) ($\beta = 7 \times 10^{-9}$ Pa$^{-1}$), with the Bagley plot obtained for Vectra A950 at 500 s$^{-1}$. This clearly demonstrates that pressure dependence alone cannot fully account for the nonlinearity of the Bagley plot. Gotsis and Langelaan (1994) came to the same conclusion, using a numerical method to calculate the Bagley plot, assuming a pressure dependent shear viscosity. By using equation (5), the pressure dependence of the entrance pressure drop is also taken into account, which was ignored by Gotsis and Langelaan.

C. Wall effects and the occurrence of slip

As discussed above, the Bagley plots of a material exhibiting a pressure-dependent wall-slip velocity are concave. In the case of a LCP the matter is even more complicated since wall slip is not the only wall effect that may cause concavity. The occurrence of wall-induced orientation is well established for LC materials with low molecular mass. Well-oriented wall layers have also been observed in LCP fibers and injection-molded parts [Sawyer and Jaffe (1986)]. Recent in situ measurements by Bedford and Burghardt (1994) have shown that well-oriented wall layers are also formed during the slit flow of lyotropic LCPs. In our experiments the extrudates from the slit dies showed similar features. This wall-induced orientation with a change in viscosity along the channel diameter may have a similar effect on the shape of the Bagley plot as the pressure-dependent wall slip.

To investigate the influence of wall effects we measured the pressure profiles for Vectra A950 in slits of different heights using the Philips rheometer. The apparent flow curves as measured in slits with heights of 0.5 and 1 mm are given in Figure 6 for two sets of conditions, i.e., $T = 310$ °C and $P = 80$ MPa [Fig. 6(a)] and $T = 295$ °C and $P = 40$ MPa [Fig. 6(b)]. The pressure drops obtained for a slit of 2 mm height were too small to be reliable. At the highest pressure and temperature no gap size effect was observable within the experimental accuracy and hence wall effects are absent. At the lowest pressure and temperature the narrower slit tended to yield higher viscosities, which is the opposite of what would be expected in the case of a pressure-dependent wall slip or a wall-induced orientation. The reason for the higher viscosities is not yet under-
stood, but both tendencies clearly demonstrate that wall effects are not responsible for the concave curvature of the Bagley plot.

D. Molecular reorientation

To obtain a better understanding of the nature of the remaining nonlinearity in the Bagley plots, pressure profiles along slit dies were measured using both the Göttfert and the Philips rheometer. In the case of the Göttfert device a 180° entrance contraction was used, similar to that used for the capillaries. Although the flow was axisymmetric in the case of a capillary geometry and planar symmetric in the case of the slit, in both cases the main feature in the flow field just before the entrance was a stretching along the flow direction.

Figure 7(a) shows the pressure profiles for the Rhodester sample in such a slit die with a length of 100 mm and a height of 1 mm. The reservoir pressure was measured together with the pressure at three positions in the die. The error bars in this and following figures indicate possible nonlinearities due to the calibration procedure of the transducers. They

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FIG. 6. Apparent flow curves for Vectra A950 as obtained in slits with heights of 0.5 and 1 mm; (a) T = 310 °C and P = 80 MPa, (b) T = 295 °C and P = 40 MPa.
are not shown when they are smaller than the symbol. Contrary to the upward curvature expected for pressure or wall effects, the curves all show a downward curvature. This implies an increase in the viscosity along the die. To check that this was not an artifact of the instrument, an isotropic poly-(ethyleneterephthalate) (PET) with a viscosity similar to that of the least viscous LCP, i.e., Rhodester, was measured. Since this is also a polyester, it was subjected to a similar pretreatment as the LCPs. The same pressure transducers were used at temperatures that were similar to those used for the LCPs, i.e., from 270 to 300 °C. The pressure profiles obtained for the PET were linear within experimental error.

Further evidence for a downwards curved pressure profile in the entrance zone can be seen in the pressure profiles of the Rhodester sample in a die with the same length, but with a height of 0.5 mm, as presented in Figure 7(b). Higher L/D ratios were obtained, for which the pressure profiles were linear. If, however, these linear profiles are extrapolated to the entrance of the die, a pressure at position zero is obtained that can be even higher than the actual pressure measured in the reservoir (i.e., 15 mm before the entrance of the die). The difference between the pressure measured in the barrel and the pressure

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**FIG. 7.** Pressures profiles for Rhodester at 320 °C as measured in a slit die with (a) h = 1 mm and (b) h = 0.5 mm, using the Göttfert rheometer with a converging entrance flow.
determined through extrapolation from a linear profile is shown in Figure 8. The pressure drops calculated in this way even become negative at low shear rates, which is of course impossible. It is therefore evident that a region with a downward curvature should exist after the entrance. A similar result was obtained in the case of Vectra A950. The observed pressure profiles are given in Figure 9. It should be pointed out that the entrance pressure drops obtained from the Bagley plot using capillaries with diameters of 0.5 mm (filled symbols), both using the Göttert 2002 rheometer with a converging entrance flow.

FIG. 8. Difference between the measured and the extrapolated value of the pressure at the entrance of a slit die (“Apparent” \( \Delta p_{\text{ent}} \)) with \( h = 0.5 \) mm for Rhodester at 320 °C (—dotted circles) and entrance pressure drop obtained from the Bagley plot using capillaries with diameters of 0.5 mm (filled symbols), both using the Göttert 2002 rheometer with a converging entrance flow.

FIG. 9. Pressure profiles for Vectra A950 at 295 °C in a slit die with \( h = 1 \) mm, using the Göttert capillary rheometer, with a converging entrance flow.
Huspeni (1990) reported negative values for the entrance pressure drop obtained from a Bagley plot for a Xydar LCP. These authors performed a linear extrapolation of what was most probably a nonlinear Bagley plot. Their results are similar to those in case of the slit die as presented in Figure 8.

The geometry of the entrance region of the Philips rheometer is completely different from that in the other rheometer, as discussed in section II. Due to the strongly diverging width of the Philips rheometer, the director is oriented perpendicular to the main flow direction when passing the sprue, causing an increase in viscosity [Mie\kowicz (1983)]. Subsequently, the shear flow in the slit will reorient the director toward the flow direction. The results of birefringence measurements on lyotropic LCPs along a slit by Bedford and Burghardt (1994) support this picture. The reorientation implies a decrease of the viscosity along the slit, the opposite of what takes place in the G"ottfert capillary rheometer. The pressure profiles measured at various hydrostatic pressures in the centre of the slit of the Philips rheometer are shown in Figure 10 for Vectra at 295 °C, using the pressure in the centre as a reference value. They show an upward curvature. Once again, the pressure dependence of the viscosity alone cannot explain the nonlinearity of these pressure profiles. The pressure-dependent viscosity and entrance pressure drop described by the measured $\beta$-value of $7 \times 10^{-9}$ Pa$^{-1}$ roughly account for half of the nonlinearity in the pressure profile in the Philips rheometer. Hence, the other half of the nonlinearity should mainly be due to a molecular reorientation during the flow through the slit.

The fact that upwardly or downwardly curved pressure profiles can be obtained, depending on whether the entrance geometry is diverging or converging, is proof of the effect of reorientation of the director on the viscosity. Indeed, upwardly curved pressure profiles rule out the hypothesis that (shear-induced) crystallization contributes significantly to the nonlinearity of the Bagley plots. If that were the case, the viscosity would always increase along the slit, whereas in the case of reorientation it may either increase or decrease.

The observations described above can be used to evaluate the data and model calculations from Langelaan et al. (1994) and Gotsis and Langelaan (1994). When considering their data, it should be pointed out that the geometry of the entrance region of their slit consisted of a tapered channel that gradually converges toward the entrance of the slit.
This channel was 40 mm long, converging at an angle of 30° in the width direction and 5° along the height. For such entrance angles it is known [Gibson (1988)] that the flow field is dominated by shear rather than by extensional flow. As a result the material probably underwent a very large shear deformation before entering the die. Moreover, the elongational flow will be much smaller in their slit rheometer than in the case of the capillary measurements, implying a smaller effect of the reorientation. For these reasons, the flow was fully developed at the first pressure transducer and thus they only observed a pressure effect. However, for LCPs in contraction flows, a $L/H$ ratio of 30, as used by Langelaan et al. (1994), is not always sufficient for a fully developed flow, i.e., for the slit profiles for Rhodester [Figures 7(a) and 7(b)] a $L/H$ of about 50 is required. Based on their model calculations, Gotsis and Langelaan (1994) suggested that the deorientation model is not applicable to their material. The essential point in their argumentation is that they assume that the flow could be fully developed at the first pressure transducer. As a result these authors observed mainly a pressure effect. This does not invalidate the de-orientation model as such [Gotsis and Langelaan (1994)]. As has been demonstrated experimentally above, the detailed entrance configuration should be taken into account when evaluating entrance effects.

The nature of the deorientation process is not yet clear. Wissbrun (1993) suggested that, in the case of capillaries, director tumbling at low shear rates decreases the overall orientation. Detailed viscosity measurements by Giles and Denn (1994) suggested that the transition from tumbling to flow aligning occurs at a shear stress of 8000 Pa (which corresponds to a shear rate of about 100 s$^{-1}$) in the case of Vectra A. The range of shear rates at the wall used in this study was 50 to 5000 s$^{-1}$. In capillary flow there is always a distribution of shear rates, so part of the material in the capillary will be in the tumbling regime whereas the material closer to the wall will be in the flow-aligning regime. This could explain the observed decrease in the nonlinearity of the Bagley plot with increasing shear rate. When the flow rate increases, more material will be in the flow-aligning regime. Material in the flow-aligning regime will not loose the orientation imposed by the elongational flow at the entrance, therefore an increase in the shear rate will lead to less deorientation and a smaller change in viscosity along the die.

IV. CONCLUSIONS

By measuring the Bagley plots in capillaries and the pressure profiles in slits with contracting and diverging entrance geometries, experimental evidence has been provided for the contribution of both pressure and molecular orientation effects to results of the viscosity measurements of thermotropic copolyesters. The pressure dependence of the viscosity, as determined in a two-piston slit rheometer, is described by a pressure coefficient $\beta$ of $7 \times 10^{-9}$ Pa$^{-1}$ for Vectra A950 and $8 \times 10^{-9}$ Pa$^{-1}$ for Rhodester. These values are of the same order of magnitude as those for isotropic polymers. By varying the geometry of the entrance zone the pressure profiles in the slit can be made to curve either upwards or downwards. These shapes cannot be explained by the pressure dependence of the viscosity alone. Thermal history effects (recrystallisation) have been excluded by applying an appropriate thermal pretreatment, while the contribution of wall effects has been proven to be small. Hence orientational effects seem to be the only possible source of the remaining entrance effect. Therefore any theoretical development for flows of this type should incorporate the effect of entry flow on molecular reorientation.
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