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Orientation measurements from the surfaces of injection moulded plaques of thermotropic liquid crystalline polymer using normal incidence specular reflection

This article is dedicated to the memory of Dr B. Jasse who succumbed to the disease in the course of this work

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Abstract

This article reviews the application of FTIR methods (attenuated total reflection, specular reflectance and photoacoustic detection) to orientation measurements of polymers, and to thermotropic liquid crystalline polymers (LCPs) in particular. FTIR specular reflectance dichroism studies are then applied to determine molecular orientation from the surface of injection mouldings (square plaques with dimensions 60 × 60 × 2 mm, unfilled polymer; 60 × 60 × 4 mm, filled polymer) of a LC copolyester based on hydroxybenzoic acid, terephthalic acid, 4,4′-oxydibenzoic acid and chlorohydroquinone. The effects of the melt temperature (265–315°C) and of the addition of fillers (mica, silica or glass beads) on the development of orientation are investigated. Scans are presented showing the quality of orientation with respect to orthogonal axes. The orientation profiles are related to the flow behaviour of LCPs during processing (spreading radial flow at the entrance to the mould, converging flow in the first half of the mould and fountain flow). At some positions, orientation minima occur which assume parabolic profiles and are associated with an arc-like band-pattern consisting of dark and brownish white bands at the surface of the mould. The light-coloured arcs correspond to regions in which the chains are not planar and tend to lie with their long axis in the thickness direction.

Keywords: FTIR; Specular reflectance; Molecular orientation

1. Introduction

In the nematic melt, the rigid molecular units of structural thermotropic liquid crystalline polymers (TLCPs) form domains characterized by a high-degree of molecular alignment. In the quiescent state, the domains directors are randomly spatially distributed throughout the system. However, under the conditions of shear and extension during processing, the structure of the domains changes and they may disappear completely. The situation has been portrayed as an initial polydomain structure which breaks up into smaller domains, the material reorientating itself during the flow [1–3]. The degree of orientation that exists in the solidified material is a product of the flow type, intensity and duration, as well as relaxation effects [4].

Injection moulding of TLCPs offers the potential of better properties. A number of studies of the structures which can arise in TLCP mouldings showed that a skin-core model can often give a simplification view of the structure which, when studied on a small scale, reveals a complex hierarchical structure [5–10]. This is a result of a combination of “fountain flow” at the advancing front and shear flow near the walls of the mould [11,12]. During the “fountain flow”, the fluid elements from the core of the moulding are elongated while flowing along the streamlines towards the front. They reach their maximum state of elongation at the surface of the advancing front and then roll on the cold walls of the mould cavity. If they do not solidify rapidly, they are further sheared in the high shear stress region near the walls of the mould. The core region, on the other hand, is a low shear stress region of a continuous flow of melt. As a result, there is no trend of deformation and orientation of the dispersed phase domains in the core region. The implication of the skin/core morphology is an anisotropy of properties that is thickness dependent [4,13–15].

Infra-red (IR) spectroscopy [16] is one of the simplest method for studying the orientation development that

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takes place during injection moulding of TLCPs. Orientation of a molecular group is characterized by the dichroic ratio, *R*, which is given by

$$R = A \parallel /A \perp \qquad (1)$$

where $A \parallel$ and $A \perp$ are the intensities of the absorption band characteristic of the group for parallel and perpendicular polarization of radiation with respect to the orientation direction, i.e. the principal flow direction in the mould.

In the case of optically opaque thick samples such as injection moulded plaques of TLCPs, *R* cannot be determined through transmission measurements. The more traditional IR techniques for thick samples studies are photoacoustic detection (PA) [17–19] and the various reflectance techniques [18,19] with attenuated total reflection (ATR), diffuse reflectance (DR) and specular reflectance (SR) being the most common.

During the last decade there have been a number of studies of the orientation development in TLCP injection mouldings using IR dichroic ratio measurements [20–28]. Pirnia and Sung [20] utilized ATR to determine 3D molecular orientation profiles in injection mouldings of a copolyester based on hydroxybenzoic acid (HBA) and 2,6-hydroxynaphthoic acid (HNA). According to their findings, transverse orientation develops in the vicinity of the injection gate due to the radial character of the flow in this region during the mould filling stage. The rest of the positions exhibit flow direction orientation. The chains are mostly planar with respect to the mould walls, especially in the skin layers. The strong orientation of molecules in the skin layers generally decreases as the core is approached, but is also a function of the location in the mould. In the core, little orientation is noticed for the first half of the mould suggesting that the polydomain structure persists. It should be noted that ATR is very dependent upon good and reproducible contact between the sample and the reflection element. An extremely flat sample area of the order of 400 mm^2 was needed. Also a special sample holder was required to allow the sample to be rotated without disassembling and reassembling operations which would have changed the contact area between the polymer and the ATR reflection element.

Later, two of the present authors applied infrared PA spectroscopy to the characterization of injection moulded plaques of a LC copolyesteramide based on HNA, terephthalic acid (TA) and *p*-acetoxyacetanilide (AA) [21–23]. Their results reaffirmed the trends shown in the FTIR ATR dichroism measurements carried out by Pirnia and Sung [20]. Compared to ATR, FTIR PA spectroscopy appears to be a very attractive technique. From the experimental point of view, polarized IR spectra can be easily obtained using commercially available PA cells. Sample morphology needs not be altered in contrast to ATR. However, the sampling depth of FTIR PA spectroscopy (ca. 10–20 μm) is greater than that for ATR (2–5 μm). Further, in order to obtain quantitative information from PA spectrum, a number of factors must be taken into consideration [17–19].

Recently, SR spectroscopy was used to analyse the surface orientation of extrusion- [24,25] and injection- [23] mouldings of TLCPs. These studies demonstrated the potential of SR in the application to TLCP systems. Polarized SR spectra of good quality can be obtained easily and quickly using commercially available accessories. However, compared to PA spectroscopy, SR has the disadvantage that only samples with smooth surfaces can be studied. Also, from the point of view of interpretation of the spectra, this technique is not as straightforward as the ATR and PA techniques because it leads to complex bands [19] presenting an absorbance–reflectance character with first-derivative like appearance depending on the orientation of the sample, i.e. the absorbing group with respect to the polarized incident beam [23]. The first application was to extrusion-moulded sheets of a copolyester consisting of HBA and HNA units, although Kaito et al. [24] used the SR technique in the UV region (π^*–π transitions of the constituent monomer units). In this study, polarized electronic spectra were obtained from the SR spectra using the Kramers–Kronig relation and the Fresnel equation. The orientation functions at the surface were evaluated from the dichroic ratio of the absorption index dispersion and compared with the bulk orientation functions determined from the azimuthal intensity distribution of wide-angle X-ray diffraction. One of the problems encountered in attempting to analyse the data in terms of orientation functions was the determination of the transition moments of the constituent monomer units. In a subsequent study [24], in order to avoid this difficulty, Kaito et al. used SR spectroscopy to obtain polarized IR spectra. The depth of penetration of the IR radiation for the absorption bands observed in the region 600–1900 cm^{-1} was estimated at 10 μm. It should be noted that the Kramers–Kronig transformation is time-consuming and not available in all FTIR soft-ware systems. In addition, Kramers and Kronig have used some assumptions which are not valid for all types of samples [19]. In a recent investigation of the orientation behaviour in TLCP injection mouldings by SR spectroscopy [23], we preferred mathematical differentiation of the spectra which resulted in second-derivative like spectra suitable for interpretation. The orientation profiles obtained for the skin layers were in qualitative agreement with previous PA measurements on the same TLCP injection mouldings [21,22]. However, according to the surface sampling character of SR measurements, the values of the dichroic ratios were higher than those deduced from PA experiments.

In the present work, FTIR SR spectroscopy was chosen to analyse the surface orientation of injection mouldings of a LC copolyester consisting of HBA, TA, 4,4′-oxydibenzoic acid (ODBA) and chlorohydroquinone (ClH) and how it depends on the injection moulding temperature. The effects of a set of fillers upon orientation development are also discussed.

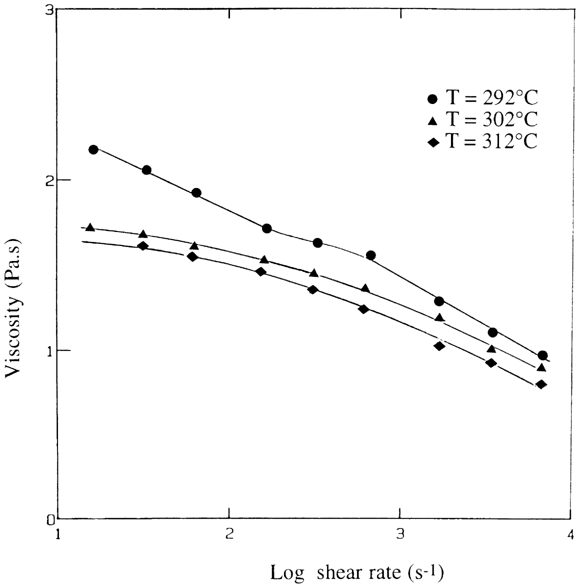

Fig. 1. Plots of apparent viscosity vs. shear rate at different measurement temperatures.

2. Experimental

2.1. Materials

The TLCP used in this work is a copolyester composed of HBA (14.4 mol%), TA (21.4 mol%), ODBA (21.4 mol%) and ClH (42.8 mol%) (Rhône Poulenc Company) [29]. DSC curves reveal a glass transition at approximately 105°C and a broad melting endotherm in the temperature range 240–295°C above which the material is in the nematic state. The apparent viscosity as a function of shear rate was measured with a capillary rheometer at 292, 302 and 312°C. The melt viscosity was found to be very sensitive to temperature and shear rate (Fig. 1). Some experiments were performed on samples containing mica, silica or glass beads (Table 1).

2.2. Injection moulding

Prior to injection moulding the TLCP was dried at 100°C for 24 h. It was then injection moulded in the form of square plaques with dimensions 60 × 60 × 2 mm (unfilled polymer) and 60 × 60 × 4 mm (filled polymer) (Fig. 2). The mould was gated at the centre of the width parameter with a gate opening of 50 mm. Typical melt temperatures during injection moulding were 265–315°C with the mould temperature set at 80°C. Injection and solidification times were about 0.7 and 20 s, respectively. This rapid cooling of the material in the mould allowed the flow-induced morphology to be effectively frozen in.

Table 1
Materials

Filler	Length or diameter (μm)	Specific surface area ($m^2 g^{-1}$)	Filler content (%)
Mica	9.5	—	30
Glass beads	30	0.7	30
Silica	10	160	10

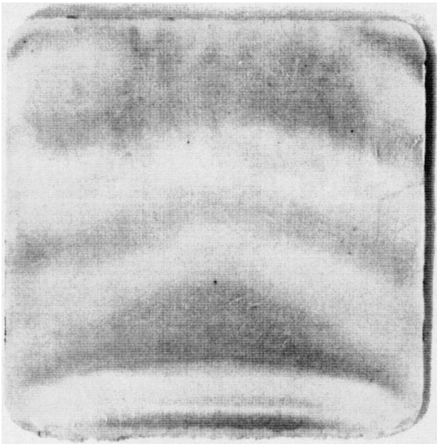

Fig. 2. Square plaque of copolyester HBA/TA/ODBA/ClH injection-moulded at 290°C melt temperature.

2.3. Polarized FTIR spectra

Polarized FTIR SR spectra were obtained on a Nicolet 205 FT-IR spectrometer equipped with a FT 30 Spectra-tech baseline SR accessory and a SPECAC gold wire grid polarizer as described in a previous paper [23]. Positioning of the plaque was done with a manually controlled *x*–*y* stage and a spot size of the IR radiation was adjusted by using a mask with a 4 mm diameter opening. Spectra were recorded at different positions from the injection gate (letters ranging from a to i) and mould axis (numbers ranging from 1 to 9).

3. Results and discussion

As mentioned earlier, the SR technique leads to complex bands [19] which present an absorption–reflectance character with first-derivative like appearance. Mathematical differentiation results in second-derivative like spectra which are suitable for interpretation when the absorption contribution is not too strong [19,23]. In a previous study [23], we showed that the IR band at 1016 cm^{-1} could be used to quantify the orientation of the injection mouldings of TLCPs by SR measurements. This absorption band is of suitable intensity and does not overlap with neighbouring bands. It originates from the 1,4-disubstituted phenyl ring and can be assigned to the 18a in-plane mode of the phenyl ring with a transition moment lying along the C_1–C_4 axis [30].

3.1. Unfilled samples

Fig. 3 shows typical differentiated IR SR spectra recorded at the surface of a plaque of copolyester HBA/TA/ODBA/ClH that was injection moulded at 290°C. The good signal-to-noise ratio allowed us to measure dichroic

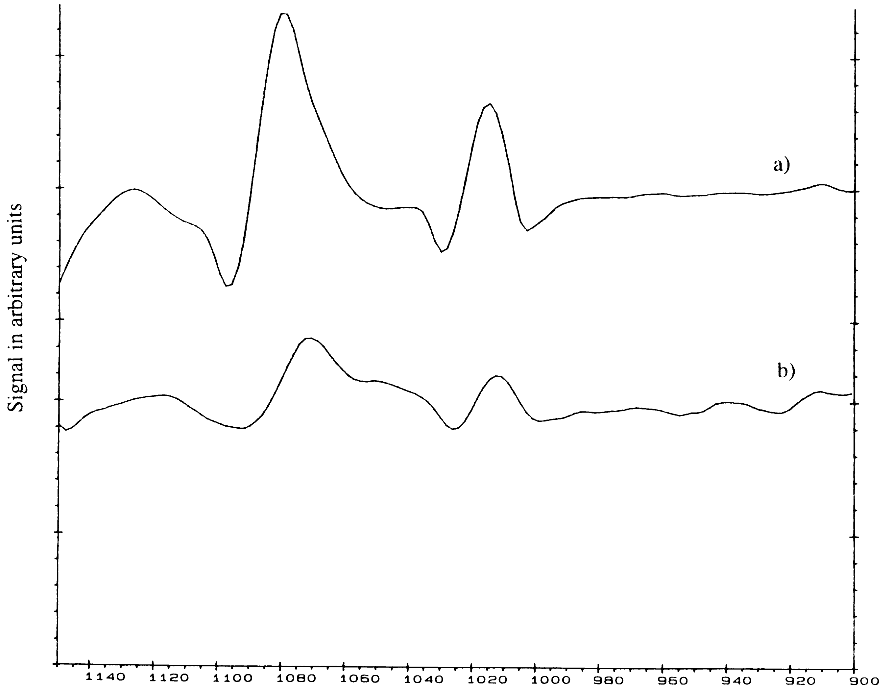

Fig. 3. Differentiated IR SR spectra in the range from 900 to 1150 cm^{-1} for (a) parallel and (b) perpendicular polarized light (sample was taken at the surface of a plaque that was injection-moulded at 290°C melt temperature).

ratios from which the orientation profile of the skin layer could be established (Fig. 4). As mentioned earlier, the molecules in the skin are expected to be well aligned along the flow direction due to the elongation of the fountain flow in combination with the high shear near the surface [11,12] and to the rapid cooling by the relatively low temperature of the mould wall. Our experiments confirm this basic skin layer orientation forming mechanism. The dichroic ratio values are higher than 1, thus indicating that the average orientation of the C_1–C_4 axis of the aromatic rings, which is more or less representative of the chain orientation is parallel to the injection direction. The significant features of the orientation profile of the skin layer are the following:

1. At the entrance to the mould there is a marked fall-off in orientation as the sample position shifts along the transverse direction from the mould axis towards the mould edge. The dichroic ratio values are close to 1 at positions 1a and 1i. This might be due to the radial character of the flow in these regions [4]. In the present work, the width of the injection gate and that of the mould are nearly the same so that the front lines at the entrance to the mould assume a nearly flat, straight line profile, the spreading radial flow effects occurring mainly at the mould edges.
2. Broadly speaking, there is an increase in orientation in the flow direction as the distance from the gate increases. At some positions, however, the dichroic ratios seem to exhibit erratic behaviour. A closer inspection of the orientation profile reveals three orientation minima assuming parabolic profile.

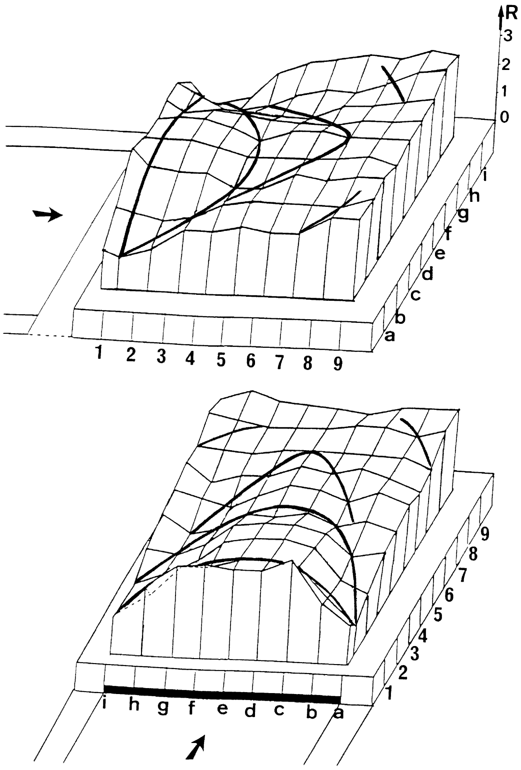

Fig. 4. Dichroic ratios of the 1016 cm^{-1} absorption band. Skin layer of a plaque that was injection-moulded at 290°C melt temperature (opposite face with respect to the injection gate).

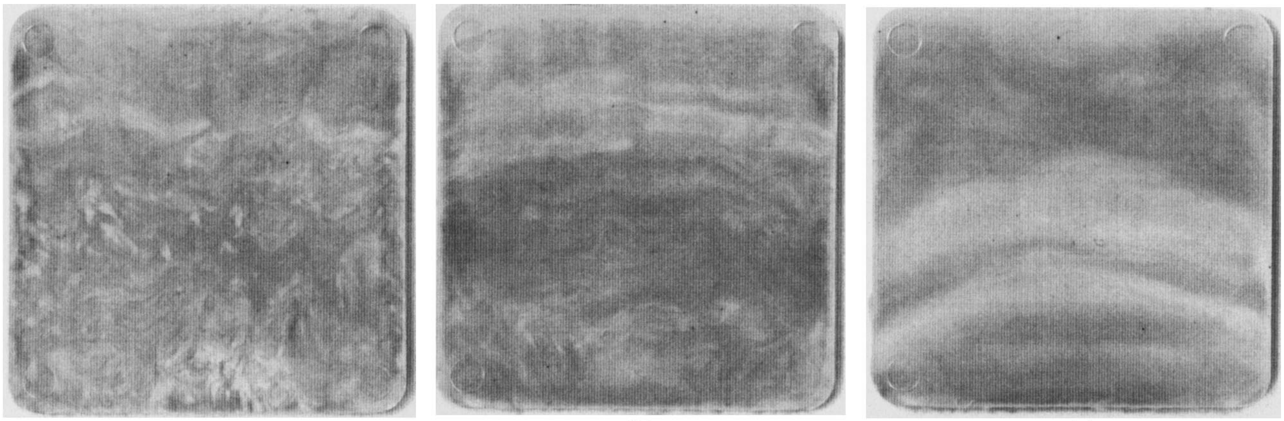

Fig. 5. Square plaques of copolyester HBA/TA/ODBA/ClH injection-moulded at 265, 275 and 285°C (opposite face with respect to the injection gate).

All these results are in qualitative agreement with the orientation profiles previously obtained by PA and SR spectroscopy for a LC copolyesteramide injection-moulded plaque [21–23]. Until now, no explanation has been found for the orientation minima or for their relation with molecular ordering. It should be noted that these orientation minima are associated with gradual changes in colour at the surface of the plaque (Fig. 2). Visually, the surface of the plaque shows an arc-like band pattern consisting of dark and brownish white bands. This band pattern was analysed by FTIR microscopy directly in the reflection mode [Jasse, B., unpublished data]. The dichroic ratio values obtained confirmed that the molecular orientation is disturbed at the locations of the bands. The light-coloured arcs correspond to regions in which the chains are not perfectly planar and tend to lie with their long axis in the thickness direction.

In order to study the influence of the melt temperature on the mean molecular orientation, one set of plaques was prepared at a constant mould temperature of 80°C with melt temperature in the range from 265 to 315°C. Indications were that the melt did not flow suitably to give high preferred orientation in the mouldings below melt temperature of about 285°C. As shown in Fig. 5, irregular domains are observed visually for the plaques that were injection-moulded at 265 and 275°C. The orientation was improved when the melt temperatures were greater than 285°C. It is evident from the IR orientation profiles given in Fig. 6 that the level of orientation increases sharply when the melt temperature is raised from 290 to 295°C and then levels off. Also, it should be noted that the orientation minima become more and more pronounced with increasing processing temperature. These observations are consistent with the DSC curve and the viscosity data (Fig. 1) obtained for the 'as received' granulated copolyester. The DSC trace of a typical sample reveals a broad melting endotherm in the temperature range 240–295°C. If the processing temperature is below 290°C, then the residual non-melted crystallites act as crosslinking agents hindering chain orientation

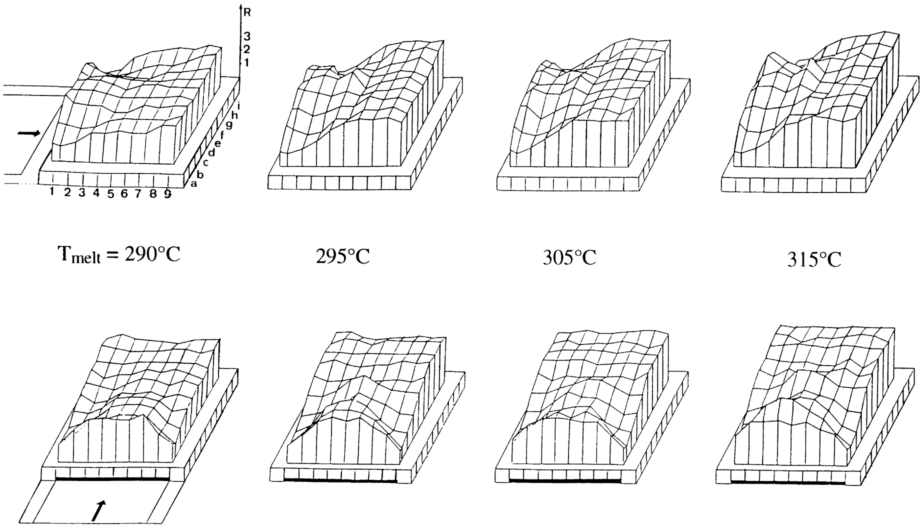

Fig. 6. Dichroic ratios of the 1016 cm^{-1} absorption band. Skin layer of plaques that were injection-moulded at 290, 295, 305 and 315°C (opposite face with respect to the injection gate).

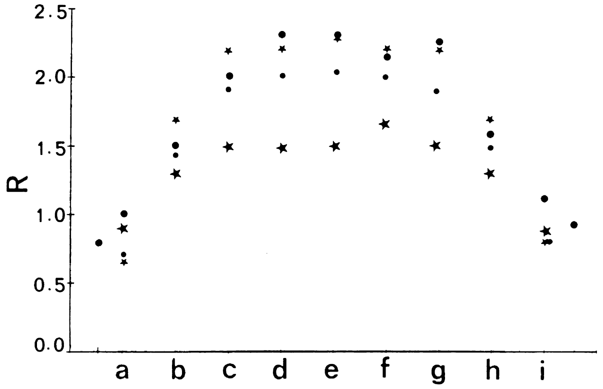

Fig. 7. Dichroic ratios of the 1016 cm^{-1} absorption band at positions 1a–1i for unfilled samples (●) and samples filled with mica (*), silica (•) and glass beads (★) (injection gate side).

and resulting in an imperfectly developed microstructure. At 290°C, the majority of crystallites are molten and processability is greatly improved. However, evidence of a persistent texture stabilized by incomplete melting is still provided by the increase in viscosity observed at low shear rate. For the present purpose, it is important to note that shear flow in this region of shear rate does not cause orientation of the LCP. When the temperature is raised from 290 to 300°C, complete melting is observed. There is a large drop in viscosity at low shear rate yielding a region where the viscosity is a weak function of rate. Melt fluidity, and consequently molecular orientation are greatly improved. Thereafter, this sharp increase in orientation is not observed in mouldings prepared at temperatures from 305 to 315°C. This may be explained by relaxation effects. Increased temperature favours increased orientation relaxation through (i) an increase in mobility afforded by reduction in viscosity and (ii) a longer time prior to solidification. These results agree with conclusions drawn by Thapar and Bevis [13] who studied the influence of processing conditions on the mechanical properties of a copolyester consisting of *p*-acetoxybenzoic acid and *p*-acetoxynaphthoic acid. Clearly, the melt temperature is a critical parameter to adjust in injection mouldings of TLCPs.

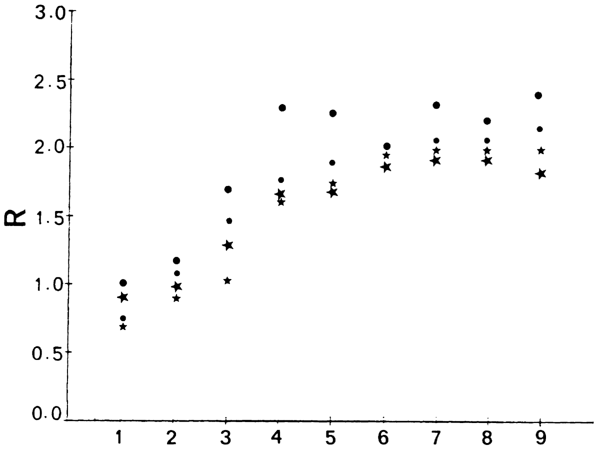

Fig. 8. Dichroic ratios of the 1016 cm^{-1} absorption band at positions a1–a9 for unfilled samples (●) and samples filled with mica (*), silica (•) and glass beads (★) (injection gate side).

3.2. Filled samples

The differentiated IR SR spectra of filled samples recorded in the range from 900 to 1150 cm^{-1} without the use of a polarizer were quite similar to those obtained for unfilled samples. The signal-to-noise ratio remained quite good, thus allowing us to measure dichroic ratios of the 1016 cm^{-1} absorption band. The results reaffirm the trends shown in the SR dichroism experiments reported above for the unfilled copolyester:

1. In general, at the surface of the plaques the dichroic ratio values are higher than 1, thus indicating that the chains are more or less aligned along the flow direction.
2. In the vicinity of the mould gate, there is an increased deviation in the chain direction away from the mould axis, represented by a decrease of the dichroic ratio as the sample position shifts along the transverse direction from the mould axis towards the mould edge (Fig. 7). At positions 1a and 1i, the dichroic ratio values are smaller than 1 (ca. 0.7–0.9) thus indicating that the molecular chains orient in a direction transverse to the flow direction, a spreading flow occurring in these positions during the filling stage of the mould [4].
3. In the first half of the mould, there is a net increase in orientation in the flow direction as the distance from the gate increases (Fig. 8). The maximum effects are observed at the mould edges. In these positions, after having experienced spreading flow at the entrance to the mould, the melt front flattens and is subjected to converging flow [4]. As a result, development of orientation in the flow direction is established.

It is known that the addition of fillers to an LCP reduces the macroscopic anisotropy of moulded parts [31,32]. As reported earlier [28], the addition of fillers does not really change the direction of the molecular orientation, but only its amplitude. Clearly, the addition of mica, silica and, to a greater extent, glass beads tends to reduce molecular ordering. It also results in a flattening of the orientation profiles, the orientation minima observed with unfilled samples being less apparent.

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