Orientation development in injection moulded plaque of liquid crystal copolyesteramide using normal incidence specular reflection

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The orientation development that takes place during injection moulding of liquid crystalline polymer (LCP) is analysed by *FT*i.r. specular reflection. The LCP used is the commercial Hoechst-Celanese product Vectra B900 based on terephthalic acid, *p*-aminophenol and 6-hydroxy 2-naphthoic acid. Dichroic ratios were measured from the 1016 cm^{-1} absorption band which is associated with a vibration of the 1,4-disubstituted benzene rings. The results, which are in good agreement with previous photoacoustic measurements, show that orientation is maximum along the principal axis of the mould with two significant minima of orientation located approximately at 2 and 3.2 cm from the injection gate. Furthermore, as the sample position shifts along the transverse direction towards the mould edge, there is a marked fall-off in orientation and the orientation minima occur at positions closer to the gate.

(Keywords: orientation; *FT*i.r.; specular reflectance; liquid crystalline polymers)

INTRODUCTION

Thermotropic liquid crystalline polymers (LCPs) exhibit LC order in the melt state which can potentially produce a high degree of molecular orientation by melt processing. In particular, injection moulding of LCPs offers one way of obtaining a high Young's modulus in the longitudinal direction in relatively thick profiles and may be utilized to produce complex parts. Most attention has been given to the organic synthesis and identification of phases in these systems, especially with the aromatic copolyesters[1–3]. Relatively little activity has been directed to melt flow, molecular orientation development and processing characteristics[4,5]. However, with the mechanical properties of an LCP object being strongly dependent upon the molecular orientation, it is desirable to know how to control and predict the orientation and its spatial distribution to use these polymers most effectively.

Vibrational spectroscopy[6] is one of the simplest methods for studying the orientation development that takes place during injection moulding of LCPs. The parameter measured in such an experiment is the dichroic ratio R, which is given by:

$$R = A_{\parallel}/A_{\perp} \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances determined for the electric vector parallel and normal to the flow direction, respectively. Under certain circumstances it is possible to assign absorption bands uniquely in i.r. spectra and hence measure an orientation parameter for a particular absorbing unit. If the angle between the vibration transition moment of the absorbing unit and the local chain axis is denoted by α, the second-order moment of the orientation function is given by:

$$\langle P_2(\cos\theta)\rangle = [1/P_2(\cos\alpha)](R-1)/(R+2) \tag{2}$$

where θ is the angle between the chain axis and the injection direction.

In the case of thick samples such as injection moulded plaques of LCPs, R cannot be determined through transmission measurements. However, polarized i.r. spectra can be obtained by *FT*i.r. attenuated total reflection (ATR)[7], photoacoustic detection (PA)[8], specular reflectance (SR)[9] or diffuse reflectance (DR)[10] measurements.

Pirnia and Sung[7] used *FT*i.r. ATR dichroism to obtain the orientation profiles in injection moulded plaques of a copolyester containing 58 mol% hydroxybenzoic acid (HBA) and 42 mol% 2,6-hydroxynaphthoic acid (HNA). They developed a special ATR set-up to improve the quality of the spectra. The important features of this ATR set-up are a double-bevelled symmetrical crystal and a C-clamp sample holder to allow the sample to be rotated without disassembling and reassembling operations, which would change the contact area between the polymer and the ATR crystal. They found a highly oriented skin layer and a less oriented core layer. Broadly speaking, the skin layer was found to have a molecular orientation parallel to the flow direction. However, at a position closest to the gate, transverse orientation was detected due to the radial character of the flow in this

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region. These experimental results are in agreement with the skin/core morphology evidenced by X-ray scattering and optical and electron microscopy[11-13].

More recently, two of the present authors studied a 4 mm thick injection moulded plaque of a copolyesteramide based on HNA, terephthalic acid (TA) and *p*-acetoxyacetanilide (AA) by *FT*i.r. PA spectroscopy, using a commercially available PA cell and X-ray diffraction[14,15]. They found a very marked fall-off in overall orientation between the skin layer and the core. In the vicinity of the mould gate, there is an increased deviation in the chain direction away from the moulding axis as the sample position shifts along the transverse direction from the moulding axis towards the mould edge due to the spreading character of the flow in this region. The deviation decreases with a net increase in orientation in the flow direction as the distance from the mould gate increases. However, a minimum level of orientation is observed at positions 1j, 2h, 4f and 6f (*Figure 1*), which might be due to flow instabilities occurring in the front regions during the filling of the mould. All these results reaffirm the trends shown in the *FT*i.r. ATR dichroism experiments carried out by Pirnia and Sung[7].

Compared to ATR, *FT*i.r. PA spectroscopy appears to be a very attractive technique for studying the orientation development in injection moulded plaques of LCPs. From the experimental point of view, polarized i.r. spectra can be easily obtained using commercially available PA cells. Orientation can be determined in samples that are strongly absorbent and have rough or brittle surfaces[8]. No special sample preparation is needed. In order to enhance the PA signal, the PA cell is often filled with an i.r. transparent gas. Helium is generally used on account of its superior thermal properties. There are, however, a number of limitations. Environmental noise around the equipment often leads to low signal-to-noise ratio so that a great number of scans are required to improve the quality of the spectra. Quantitative analysis using the PA method is difficult. This is due in part to the dependence of the signal amplitude on such sample properties as the thermal diffusion length, absorbance and the various instrumental variables.

Recently, Kaito *et al.*[16] proposed the SR technique as a tool for analysing surface orientation of extruded sheets of a copolyester containing 73 mol% HBA and 27 mol% HNA. They compared the surface orientation functions obtained from polarized electronic spectra with the bulk orientation functions determined from the azimuthal intensity distribution of wide-angle X-ray diffraction. They showed that the chain orientation at the surface is equivalent to that in the bulk at drawdown ratios above ~4.0, but tends to be higher at lower drawdown ratio. It should be noted, however, that access to the direction of the transition moments of monomer units is not at all straightforward.

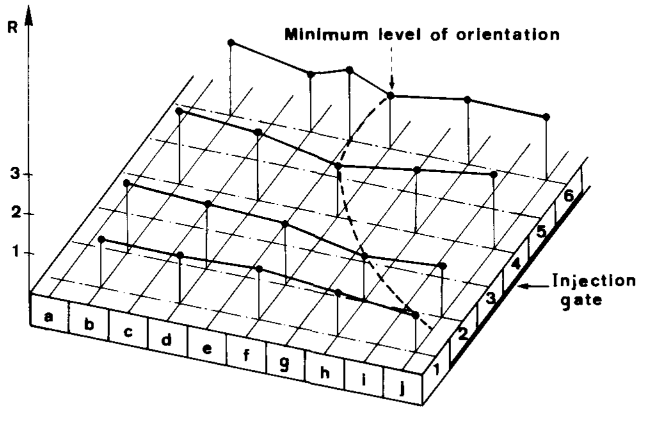

Figure 1 Dichroic ratios of the 1016 cm^{-1} absorption band. Opposite face with respect to the injection gate. *FT*i.r. PA experiments from reference 15

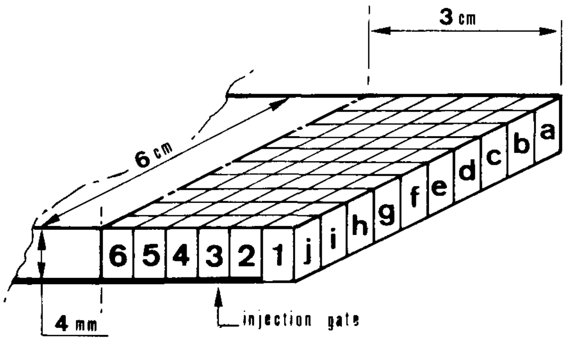

Figure 2 Schematic view of sample sectioning

This paper is primarily concerned with the detailed elucidation of structural gradients along and across the flow directions developed in an injection moulded thermotropic LCP using *FT*i.r. SR measurements. The orientation profiles reported here are compared with the results previously obtained by *FT*i.r. PA spectroscopy on the same LCP which had been moulded under the same conditions[14,15].

EXPERIMENTAL

The polymer used in this study is a wholly aromatic thermotropic copolyesteramide consisting of HNA, TA and AA (Vectra B 900), and was supplied by Celanese Speciality Operations.

The plaque had the dimensions 6 cm × 6 cm × 0.4 cm. The mould was gated at the centre of the width parameter with a gate opening of 5 cm. The mould temperature was kept at 100°C with the melt temperature at 290°C.

Samples (0.5 cm × 0.5 cm) were cut by a low speed diamond saw at different positions from the injection gate (letters ranging from a to j) and mould axis (numbers ranging from 1 to 6) (*Figure 2*).

Polarized *FT*i.r. 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. The samples were placed on the top surface of the accessory and analysed with a 30° angle of incidence. The i.r. radiation was collected at an angle equivalent to the angle of incidence. The samples were rotated 90° in order to obtain the two polarization measurements. The polarizer was set in front of the SR accessory, the polarized beam being parallel to the surface of the sample; 120 co-added interferograms were scanned at 4 cm^{-1} resolution.

RESULTS AND DISCUSSION

Broadly speaking, in the cross-sectional views of the injection moulded plaque, LCP samples are shown to be composed of a brownish white skin layer, a dark transition zone and a core region. In the present paper we will restrict our attention to the molecular orientation development in the skin layer.

Examples of polarized SR spectra compared with transmission absorbance spectra of the skin layer are shown in *Figures 3* and *4*. The nature of the reflection technique clearly leads to complex bands 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. Mathematical differentiation results in second-derivative-like spectra which are suitable for interpretation, when the absorption contribution is not too strong. This is the case for the medium intensity bands of the transmission spectrum. As far as strong absorbing species are concerned, SR and first-derivative spectra cannot be used for quantitative measurements, on account of a too strong absorption contribution to the SR signal. As a matter of fact, in SR measurements, the sampling depth is a function of the absorbance of the considered band and of the order of magnitude of several micrometres, as compared with ATR measurements for which the penetration depth is due primarily to the exponential decay of the evanescent wave and is only secondarily a function of the extinction coefficient[17]. In the PA technique, strongly absorbing groups saturate the PA signal and the penetration depth, which is also a function of the wavenumber of the incident radiation, is of the order of magnitude of 15–20 μm.

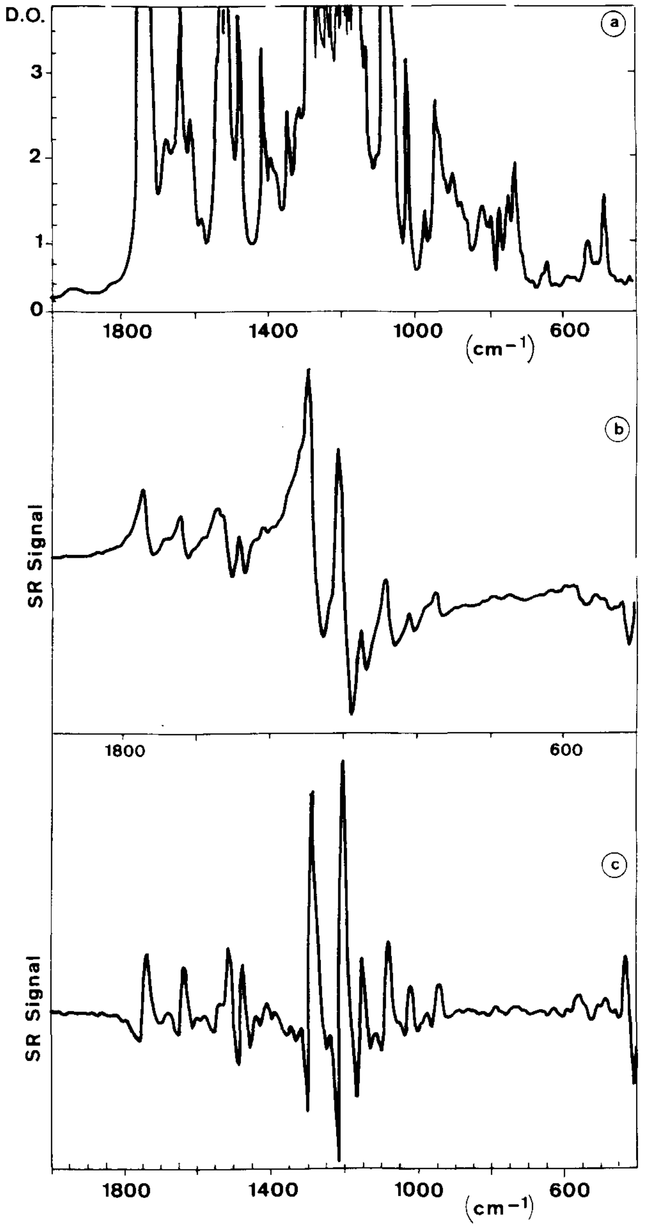

Figure 3 I.r. spectra of samples for parallel polarized light: (a) transmission spectrum of sample 1f; (b) SR spectrum of sample 5b; (c) first-derivative spectrum of (b)

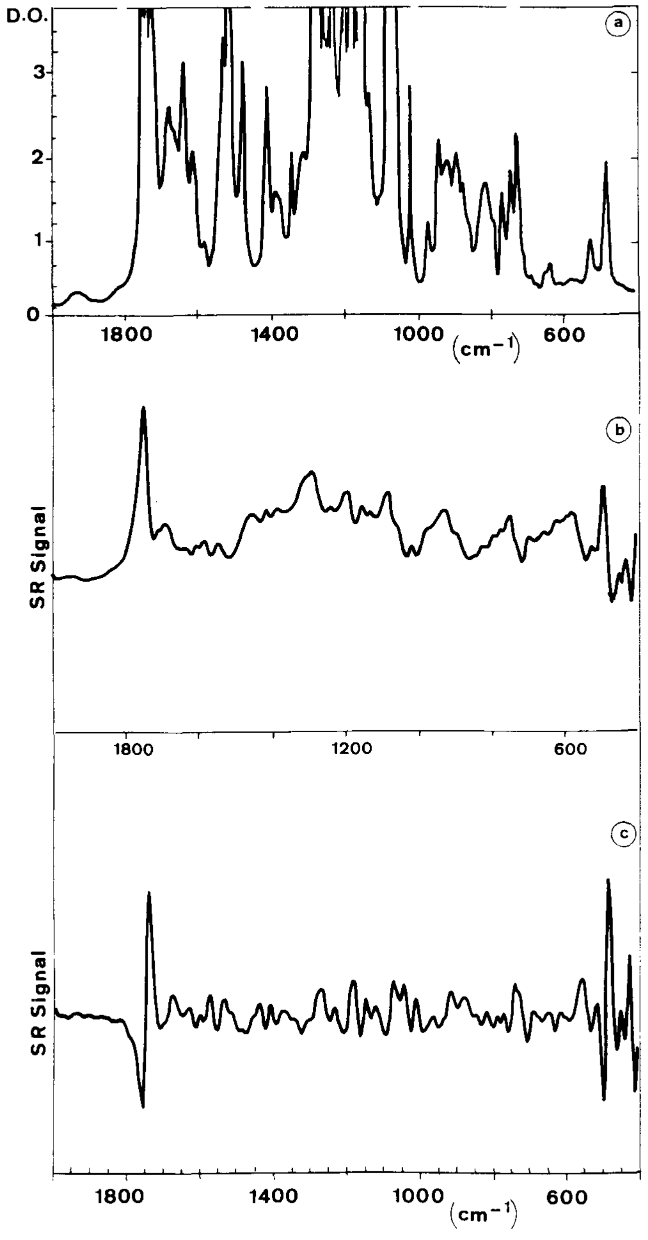

Figure 4 I.r. spectra of samples for perpendicularly polarized light. (a) transmission spectrum of sample 1f; (b) SR spectrum of sample 5b; (c) first-derivative spectrum of (b)

For our analysis, we selected the i.r. band at 1016 cm^{-1} which is well defined and associated with vibrations of the 1,4-disubstituted phenyl ring. According to Varsanyi[18], in the terephthaloyl moiety, the 1016 cm^{-1} absorption band can be assigned to the 18a in-plane mode of the ring with a transition moment lying along the C_1–C_4 axis of the ring. In the case of sample 1f we were able to separate the skin with a thickness of 75 μm

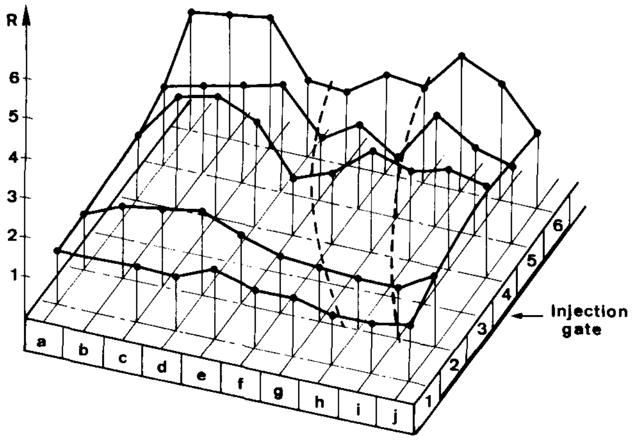

Figure 5 Dichroic ratios of the 1016 cm^{-1} absorption band. Opposite face with respect to the injection gate

and to perform transmission and SR measurements of orientation. A dichroic ratio mean rate $R = 1.05$ is obtained from the transmission spectra while SR values lie in the range $1.05 \leq R \leq 1.06$ for the two faces of the skin. These results confirm the validity of SR orientation measurements using the 1016 cm^{-1} absorption band.

The R values are presented in *Figure 5* for the opposite face with respect to the injection gate. These show the orientation development as a function of distance from the gate. According to the surface sampling character of SR measurements the values obtained are higher than the values deduced from PA spectroscopy.

The significant observations are the following:

1. For the samples 6a–6j cut along the principal axis of the mould the R values are >1 indicating that the average orientation of the C_1–C_4 axis of the benzene rings (which is more or less representative of the chain orientation) is parallel to the direction of the injection. As previously shown and discussed in the literature[5,11,19–21], the 'fountain flow' at the advancing melt front is the basic skin layer orientation forming mechanism. Since it is an elongational type flow, it results in an almost perfect orientation in the injection direction. As the distance from the gate increases, the molecular orientation first increases quite steeply (j, i and h). A significant decrease in orientation takes place at positions g and e. Then, a recovery in orientation is observed (d, c and b). It should be noted, however, that a slight decrease in orientation occurs at the end of the mould.
2. 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. Samples 1a–1j are characterized by poor orientation. The R values are close to 1.
3. The orientation minima occur at positions closer to the gate as the sample position shifts along the transverse direction from the mould axis towards the mould edge. Only one broad minimum is evidenced at positions i and h for the samples cut along lines 2 and 1, respectively. Hence, in a two-dimensional orientation profile (*Figure 5*), the minima lie on two arcs of a circle. It should be noted that these arcs are clearly visible when the injection-moulded plaque is viewed from the top because they are characterized by a pale colour compared to the rest of the plaque.

The orientation minima might correspond to the end of the spreading flow when the radius of the melt front equals the half width of the mould[5]. However, 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 of the mould have very large radii. The spreading radial flow effects on orientation are expected to occur only in the vicinity of the gate. Alternatively, flow instabilities in the front regions or jetting phenomena occurring during the filling stage of the mould might offer an equally plausible explanation of the orientation minima.

Similar results are observed for the skin layer located on the injection gate side except that samples cut along the line j, at the entrance of the mould, exhibit much lower orientation. This points out the importance of the gate design. Generally, the shape of the melt front where the 'fountain flow' dominates the orientation depends on the gate design, the relative dimensions of the mould (width, length, thickness) and the distance from the gate[22].

All these results are in qualitative agreement with the orientation profiles (*Figure 1*) previously obtained by *FT*i.r. PA spectroscopy on the same LC copolyesteramide samples[14,15]. This demonstrates that *FT*i.r. SR spectra can be used to characterize the molecular orientation development that takes place in the skin layer during injection moulding of LCPs. *FT*i.r. SR spectra of good quality can be obtained easily and quickly without special sample preparation. In this respect, this technique is comparable to the PA technique, but it has the disadvantage that only samples with a smooth surface can be studied, the reflectance being partially reduced by surface roughness.

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