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Raman spectroscopy of flowing poly(ethylene terephthalate) melts

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Studies have been made of the Raman spectrum of a poly(ethylene terephthalate) melt being extruded through a glass die. The effects observed in the spectrum are interpreted in terms of changes in molecular shape which vary with shear rate and melt temperature.

Keywords Spectroscopy; Raman; poly(ethylene terephthalate); melts; extrusion; shear; temperature

Introduction

The study of flow phenomena in polymers has attracted much interest because the major forming processes for polymers depend on flow under controlled conditions. Many of these rheological studies have aimed at an understanding of macroscopic flow effects such as die swell, melt fracture and frozen-in orientation. Of equal importance is the characterization of mass flow in the injection moulding and extrusion processes. The results of these studies have frequently been discussed in terms of molecular level behaviour, particularly entanglement and orientation. However, such interpretations have normally been essentially empirical since direct observation at the molecular level has proved extremely difficult.

In the absence of specific techniques for study at the molecular level, resort has been made to indirect observation. An example of one such method is the measurement of birefringence in polymer solutions undergoing shearing flow. A good understanding of such systems has been achieved through the work of Frank and Mackley[1,2]. A further approach has been made through morphological studies of solidified material produced under specified flow conditions. A 'shish kebab' morphology has been observed by Keller *et al.*[3,4] in polymers crystallized from solutions being rapidly stirred. Extrusion of highly oriented polyolefin fibres from the solid state has been demonstrated by Southern and Porter[5]. Experiments on flow-induced crystallization are of more direct relevance to the subject at present under discussion. The formation of oriented crystallized material, under quenched cooling conditions, at the die entry region has been observed in poly(ethylene terephthalate) (PET) by Griswold and Cuculo[6] and in polyolefins by Collier *et al.*[7]. None of these experiments involved *in-situ* molecular level investigation.

The molecular property constantly invoked in the interpretation of flow phenomena is orientation. We have therefore addressed ourselves to the direct observation of this property in a flowing poly(ethylene terephthalate) melt. Probably the most versatile, molecular-level structural tool available is Raman spectroscopy.* We report here on the use of this technique for making *in-situ* measurements of flowing poly(ethylene terephthalate) both above the crystalline melting point and at high degrees of supercooling.

The use of laser Raman spectroscopy in the investigation of oriented polymers was first described by Cornell and Koenig[8]. They measured a depolarization ratio (p) in polystyrene where

$$p=\frac{\text{scattered light intensity observed through}\perp\text{analyzer}}{\text{scattered light intensity observed through}\parallel\text{analyzer}}$$

Depolarization of bands in the Raman spectrum may be the consequence of internal molecular symmetry; in order to apply its measurement to the determination of molecular orientation, the bands selected are ideally those which are depolarized in an isotropic sample. Simple measurement of the depolarization ratio as defined above is not of itself capable of giving quantitative information on the orientation in a polymer specimen. Extensive work by Bower *et al.*[9-11] has shown that application of the appropriate mathematical treatment to measurements of intensities of the band at $\Delta\bar{\nu}=1615\ \text{cm}^{-1}$ in PET can provide measurements of P_2 and P_4 orientation functions. Fortunately, it can be experimentally shown as in *Figure 1* that changes in the depolarization ratio indeed

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* Raman spectroscopy is an inelastic light scattering process. If laser radiation of frequency ν_0 illuminates a sample whose molecules vibrate at frequency ν_{vib}, the scattered light will contain weak radiation at $\nu_0 - \nu_{\text{vib}}$. Since $\nu_{\text{vib}} \ll \nu_0$, the illuminating and scattered light is normally in the visible. See Raman spectra of synthetic polymers. Chapter in Developments in Polymer Chatacterization Vol II, Ed. J. V. Dawkins, Applied Science, 1980

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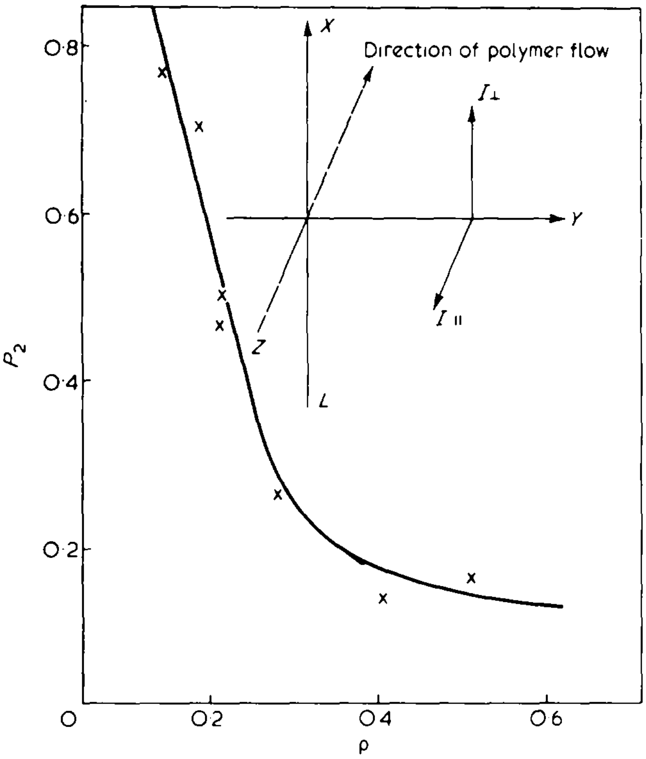

Figure 1 P_2 orientation function in drawn PET *versus* depolarization ratio: laser incident along *X*. Viewing along *Y*. Analyzer direction *X* or *Z*. Melt flow and direction of polarization along *Z*

accompany changes in the orientation function, particularly at high levels of orientation. The use of depolarization ratio changes in the 1615 cm^{-1} band as an indication of variations in molecular orientation in films of poly(ethylene terephthalate) has been demonstrated by Derouault *et al.*[12].

We report here on depolarization ratio measurements on the band near 1615 cm^{-1} in the flowing melt under a range of shear rates. We have quoted values of apparent wall shear rate ($\dot{\gamma}_w$) derived from measurements of output rate (Q) and die radius (R) as is the normal rheological practice where

$$\dot{\gamma}_w = \frac{4Q}{\pi R^3}$$

An additional feature of both static and flowing melts is the existence of order in what, until recently, has been considered to be a totally disordered phase.

A very convenient probe for order in poly(ethylene terephthalate) is afforded by the band near 1725 cm^{-1}. This band is due to carbonyl stretching vibrations; Melveger[13] has proposed that the width of this band at half height reflects the extent of rotational freedom of the carbonyl group about the ring-ester carbon–carbon bond (see III of *Figure 2*) . Melveger further proposed an empirical relationship between the band width and specimen density. Purvis and Bower[10] have preferred to relate the band width to crystallinity rather than directly to density. Crystallinity is merely an extreme manifestation of structural order which reveals itself as density changes and therefore it can be taken that the 1725 cm^{-1} band narrows as the degree of order in the material increases. We have therefore made careful observations of this band and show that a considerable degree of order is generated in the flowing melt under certain conditions.

Experimental

Polymer materials. The polymer was supplied in chip form by ICI Plastics Division at two different molecular weights. Polymer A had an intrinsic viscosity of 0.73 and Polymer B an intrinsic viscosity of 0.59 as supplied. This represents medium and low molecular weights within the range of commercially available polymers. A serious problem in Raman spectroscopy with polymers, particularly severe with PET, is the high fluorescence background. PET is subject to extreme degradation unless dried immediately before extrusion. We have found that drying the polymer, even under vacuum, at temperatures in excess of 100°C as commonly done, can greatly increase fluorescence. Polymer drying temperatures were therefore restricted to only 80°C in a vacuum oven for a maximum of 15–20 h.

Extrusion method. Polymer melt was extruded using a Baughan $1\frac{1}{4}$ inch extruder. A general purpose screw having a length:diameter ratio of 20:1 was used. The spectroscopic cell (or die) was essentially a 70 mm long glass capillary tube of outside diameter 8.5 mm and inside diameter 2.5 mm nominally. This die was almost totally enclosed in a metal holder, which was itself attached to the nose of the extruder by an extension piece. The extension piece contained a melt thermocouple, two melt mixing units, a breaker plate and melt pressure transducer. Band heaters were used to heat both the extension piece and die holder. A diagrammatic arrangement is shown in *Figure 3*. Melt temperature control was effected by two-term temperature controllers; once the extruder was running and its barrel temperature profile stabilized, the melt temperature variation was about ±1°C.

The extruder was fitted with a hydraulic drive and electronic tachometer. Under normal operating conditions, there was little screw speed variation. The output rate was measured in each experiment by weighing a sample extruded in a known time. Shear rates generally in the range 10–1000 s^{-1} were explored since this range is typical of extrusion processes.

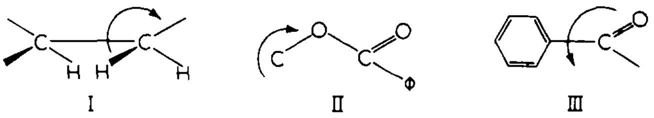

Figure 2 Free and somewhat restricted rotation of molecules

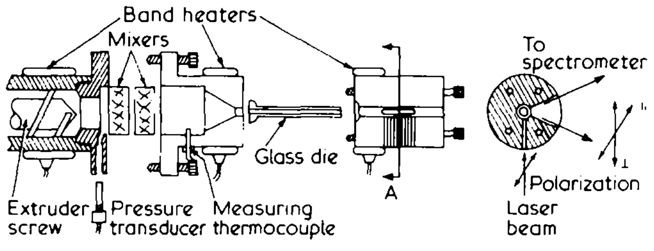

Figure 3 Extruder extension and glass die showing plane of polarization and path of beam

Spectroscopic method. Raman scattering was excited by a Spectra-Physics Model 170 Argon ion laser operating at 488 nm. Plasma lines were removed using an Anaspec Model 300S pre-monochromator. The scattered light was collected by a Coderg T800, triple-monochromator spectrometer. The photomultiplier tube output was handled by an Ortec Brookdeal 5Cl photon counter. Typically 150 mw of power was supplied to the glass die. The spectrometer was operated at 3 cm^{-1} slit width.

The extruder was positioned so that the longitudinal axis of the die was at right angles to the direction of observation of the scattered light. The direction of polarization was parallel to the long axis of the die and hence also parallel to the direction of the melt flow. *Figure 3* shows the arrangement used.

The whole extruder was supported on screw jacks which allowed fine adjustment of the position of the die in the laser beam. Special effort was made to ensure that the incident beam passed through the cell as close as possible to its wall consistent with the best signal/noise ratio in the spectrum. After the melt had been extruded for sufficient time to stabilize the melt temperature, the fluorescent level was generally found to have stabilized sufficiently to give a uniform, flat background.

Depolarization ratios. The measurement of depolarization ratios was carried out by observing the scattered intensity through a pair of Polaroid analyzers. One analyzer was arranged to transmit light with the same direction of polarization as the incident radiation; the other analyzer transmitted light polarized perpendicular to this plane. In order to make a valid comparison of spectral intensities for both analyzer orientations, it is essential that the instrumental conditions do not vary from one intensity measurement to the next. Since, amongst other instrumental changes, the output rate changes from time to time at constant screw speed, it is clear that accurate measurement of the depolarization ratio at a particular shear rate ideally requires $I_{\parallel}$ and $I_{\perp}$ values to be determined concurrently. This was approached by mounting the Polaroid analyzers on a carriage which alternately interposed each analyser between the cell and collecting lens. The carriage was driven by an electromechanical device triggered by a multivibrator electronic circuit. A reciprocating rate of 0.3 0.5 Hz was found to be suitable for our purposes.

Before carrying out the depolarization ratio experiments, it was established that polarization scrambling was not seriously affecting the results. An identical die to that used in the extruder was filled with carbon tetrachloride and depolarization ratios were measured for the bands at 218 cm^{-1} and 459 cm^{-1}. Values of 0175 and 0.003 respectively were obtained as the mean of two determinations on these bands.

Static PET (solid and molten). In order to separate the effects of shearing from those of elevated temperature, we recorded the bands at 1615 cm^{-1} and 1725 cm^{-1} at a series of temperatures from 23°C to 300°C. *Figure 4* shows the apparatus used for this purpose. It is basically an aluminium block heated by a band heater; the temperature is controlled by a three-term temperature controller. A small well containing the specimen in the upper face of the block is covered by a microscope cover slip. The well is swept by a stream of inert gas (nitrogen) through inlet and outlet ports. A thermocouple is inserted into the aluminium block within 2 mm of the sample well. The temperature measured by this thermocouple was within ±2°C of the specimen temperature. The exciting beam enters the specimen through the cover slip and the radiation scattered at 90°C is observed in the normal way.

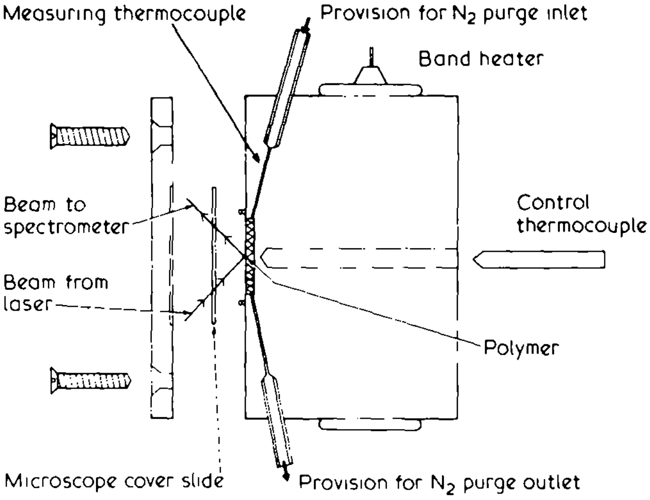

Figure 4 High temperature cell

Precision in spectral measurements. Spectra were difficult to record and therefore signal/noise ratios better than 5:1 were considered acceptable.

The results given in this communication are of particular significance only if the band positions are accurately known. Although our spectra are relatively noisy, repeat experiments and careful attention to scanning procedures enable us to quote bandhead frequencies to an accuracy of ±0.5 cm^{-1}. Errors in band width are approximately ±1 cm^{-1} and in depolarization ratio ±0.05.

Literature values of the melting point of PET appear between 250 and 268°C. Our experience with the polymers used in this programme indicates a value of around 260°C and this value is therefore taken as the melting point (T_m) of semi-crystalline PET. We have carried out experiments mainly on the medium molecular weight polymer in the temperature range 240-290°C. Experiments on the low molecular polymer were carried out at 240 and 278°C. It is possible to extrude PET at temperatures down to (T_m-20). A slight opacity is evident in the extrudate but extrusion pressures do not increase excessively at these temperatures. When the extruder screw is stopped, the material crystallizes in the die almost instantaneously, at these lower temperatures.

Results

Figure 5 shows the effect of temperature on the location of the 1615 cm^{-1} bandhead under static conditions. The bandhead moves to lower frequency with increasing temperature tending to a value of 1608 cm^{-1} at around 300°C. Our studies of the band near 1725 cm^{-1} show clearly that this band is complex in origin, containing 2 or 3 overlapping bands. The exact location of the bandhead depends on the relative prominence of the individual peaks within the system. There is no simple relationship between the 1725 cm^{-1} bandhead and the specimen temperature. However, *Table 1* shows that there is a gradual drift of the bandhead to higher frequency, with increasing temperature, reaching a value of about 1730 cm^{-1} above the melting point.

Table 2 shows the effect of shear rate and temperature on melts of the medium molecular weight polymer at temperatures of 240°–290°C. *Table 3* shows similar results for the low molecular weight polymer at 240°C and 278°C. The term 'relative shift' denotes the shift of the bandhead relative to its position in quiescent material at the same temperature. Our results show no smooth variation of spectral changes with shear rate within the range of discrete shear rates investigated. Since we do not therefore discuss our results with detailed reference to shear rate, we have, for convenience, presented our results in *Tables 2* and *3* in a summarized form.

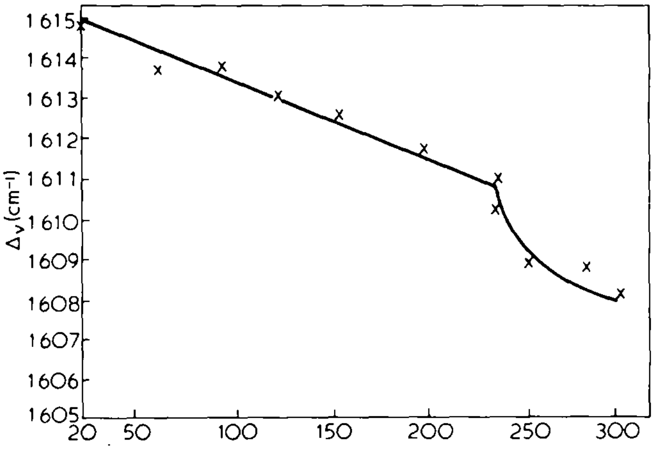

Figure 5 Effect of temperature on 1615 bandhead

Table 1 Location† and band width of the 1725 cm^{-1} band at different specimen temperatures. (For convenience, we quote values of temperature with respect to the melting point T_m = 260°C at appropriate points in this paper.)

Temperature (°C)	Bandhead location (cm^{-1})	Band width (cm^{-1})	Condition of specimen
23	1727	24	amorphous
	1727	11	crystalline
93	1728	25	slightly crystalline
122	1728	17	crystalline
212 (T_m − 48)	1728	22	crystalline
258 (T_m−2)	1730	21	crystalline
280 (T_m + 20)	1730	25	molten
300	1730	26	molten

† The figures above do not agree precisely with some of those quoted in ref. 12. We are satisfied that the current results are superior in precision to those obtained previously

The band near 1615 cm^{-1}. In both crystalline and amorphous PET this band occurs at 1615 cm^{-1} at room temperature, falling to 1610 cm^{-1} just below crystalline melting point (265°C). Above the crystalline melting point the frequency of the band falls further to 1608 cm^{-1} as the temperature is raised to 290°C. Inspection of *Table 2* shows that the application of shear to a supercooled melt† at 240°C causes a frequency reduction of 1–5 cm^{-1}, but above the melting point, the vibrational frequency is raised by similar amounts.

The above comments apply to the medium molecular weight PET. The lower molecular weight material appears to respond to shear in a similar manner but to a lesser extent.

Band system near 1735 cm^{-1}. Several of the spectra recorded on flowing melts demonstrate clearly that this broad feature consists of at least two components (one near 1738 cm^{-1} and the other near 1730 cm^{-1}). Interestingly, there is no evidence of the band resolving into separate components in cast PET under the most careful conditions of observation while evidence of overlapping bands is just evident in crystalline material as shown in *Figure 6*. This is as might be expected as the individual bands become narrower in the crystalline material.

Application of shear changes the band shape, i.e. the relative intensity of the two bands mentioned above in a complex manner. It is clear, however, that the 1738 cm^{-1} band is usually less polarized than that near 1730 cm^{-1} as is particularly evident by comparing spectra through the crossed and parallel analyzers. Taking this tendency to resolve the band with the narrowing of the band by up to 5 cm^{-1}, it is clear that, in some as yet unidentified way, shear can produce significant increase in order in the flowing melt. Once again, the effects observed are more pronounced in the polymer with the higher molecular weight.

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† It is worth emphasizing that the PET is crystalline on being fed to the extruder, is melted and heated to at least 265°C on its way along the extruder barrel. The melt is brought down to the supercooled state before it enters the glass die

Table 2 Summarized effects of melt temperature and shear rate on flowing PET (Intrinsic viscosity = 0.73) melt

Melt temperature (°C)	Shear rate (s^{-1})	1615 cm^{-1} band		1725 cm^{-1} band
		Depolarization ratio	Relative shift	Band width
240	40–220	0.4–0.8	−2 to −5	20–26
248	30–490	0.4–0.8	+1 to +2	21–25
265	20–890	0.3–0.6	+1 to +3	22–26
276	30–690	0.4–0.8	+1 to +5	20–24
290	300–410	0.4–0.6	+2 to +4	21–26

Table 3 Summarized effects of melt temperature and shear rate on flowing PET (Intrinsic viscosity = 0.59) melt

Melt temperature (°C)	Shear rate (s^{-1})	1615 cm^{-1} band		1725 cm^{-1} band
		Depolarization ratio	Relative shift	Band width
240	20–210	0.4–0.5	−1 to −2	24–25
278	70–280	0.4–0.5	+1 to +3	21–24

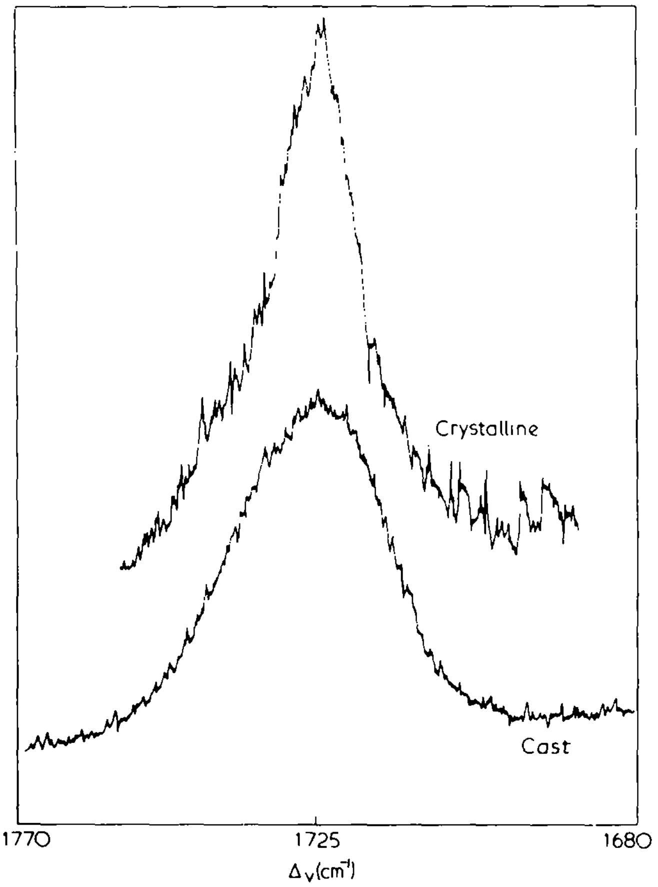

Figure 6 1725 Bands of PET film at 23°C

Discussion

Spectral changes under shear. It is widely held that the subtle variations in the vibrational spectrum which occur in PET as one moves from melt to glass to crystalline material, and alsoas a consequence of temperature changes, result in essence from changes in the rotameric state of the molecules. Several of these can be described including the *gauche:trans* equilibrium in the CH_2–CH_2– units (I) (*Figure 2*). Free, or somewhat restricted, rotation of other groups will also be evident in the spectrum. Two other further examples are as in II and III. It is tempting to speculate on the impact that these three structural features will have on the spectrum. *Gauche/trans* rotation about the C–C axis does give rise to recognized effects in the infra-red spectrum but is very unlikely to alter the frequency of the ring breathing (1615 cm^{-1}) or C=O stretch (1725 cm^{-1}) bands. A similar comment could be made about rotamers of type II above.

The occurrence of an ester ν_{C-O} frequency as low as 1725 cm^{-1} is itself indicative that the benzene ring and C=O are in a specific orientation through π-electron delocalization. Daubeny *et al.*[15] have suggested that the carbonyl group in the PET crystal is 12° out of the plane of the benzene ring.

Rotation of the C=O group as in III will definitely perturb the delocalization and give rise to changes in frequency of both ring breathing and carbonyl stretching modes[16].

Considering the behaviour of the feature near 1615 cm^{-1}, it is clear that in non-crystalline environments, i.e. either in the melt or in the glassy phase, the band moves by about 2 cm^{-1}/100 K. Although we cannot be sure of the shear rate at the sampled point, a relatively large fall (1–5 cm^{-1}) in the frequency of the 1615 cm^{-1} band is observed at ($T_m - 20$); that is, the equivalent temperature of the flowing supercooled melt rises to that of the unstressed melt at 50–250 K higher. Stressing the melt above its melting point has the opposite effect in changing the rotational isomeric composition to that typical of material at temperatures roughly between the melting point (T_m) and $T_m - 250$ K.

The changes in the values of the depolarization ratio of the 1615 cm^{-1} band are inconsistent with well-developed orientation within the range of shear rates measured. This is surprising, but our data are, as yet, too scanty to support interpretation. However, we might venture to suggest that these results support the view that elongational flow effects are mainly associated with the die inlet region. Since our studies concern a region some 20 diameters downstream of the die inlet region, it might be expected that the very short relaxation times in PET (1–10 msec) at the temperatures investigated would cause any die-entry induced orientation to disappear. We do observe development of order under some conditions and it could be that this order, although shear generated, could be directionally randomised. Alternatively, the shear force is supported by only a few molecules within a relatively fluid matrix, as might be expected in a network: these molecules orient while those in the bulk do not. This explanation would suffice for the relatively minor depolarization ratio changes but would not explain the frequency shifts, since species at low concentration affect the Raman spectrum only slightly. We suspect our observations are connected with the incidence of molecularly significant species of a pseudo-crystalline form in the sheared melt involving rotation of the carbonyl group relative to the benzene ring plane. We are currently exploring this possibility.

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