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# Rheo–Raman studies of polyethylene melts

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The effects of shear on molten polyethylene were studied. The experiment shows that increasing shear gives rise to greater amounts of all-*trans* C–C bonds.

**(Keywords: rheology; Raman; polyethylene)**

## *Introduction*

The flow behaviour of polyethylene (PE) melt controls many of its properties in the solid form and during processing, e.g. die swell, bubble stability. To date, little or no information on the molecular conformation of the polymer melt in flow can be obtained directly. This paper presents the results on the rheo–Raman studies of PE melt, allowing a quantitative measurement of the all-*trans* C–C bonds to be made as a function of shear rate. The effects of flow-induced crystallization and molecular orientation are considered.

## *Experimental and theory*

The rheo–Raman rig is shown in *Figure 1*. It has been developed in collaboration with the Department of Chemical Engineering at Cambridge University. It is designed to fit on an upright microscope and has a temperature range of ambient to 450°C. The sample is placed between two circular quartz windows which are in close thermal contact with a silver block heater. The top window is fixed to a removable lid section to allow easy sample loading and clearning. The shearing of the sample is achieved by the rotation of the lower window, which is attached to a metal disc under the control of a stepper motor. The drive system can be operated in three different modes: dynamic, steady and step movement, with a shear strain range of 0.3 to 300% and a shear rate range of 0.003 to 7500 $s^{-1}$. The gap between the windows (i.e. sample thickness) can be varied from 10 to 2500 $\mu$m and is controlled by a set of four micrometers or a second stepper motor. The entire system (i.e. shearing mode and sequence, sample gap setting and temperature control) can be driven from a Windows program running on a PC.

The Raman spectra were taken with a Raman microscope with a 40× objective. The microscope is coupled to a 1 m spectrograph with a single 750 nm blazed holographic grating (300 groove/mm) and a liquid $N_2$ cooled charge-coupled device. Stray light rejection is provided by a holographic edge filter which doubles as the beam-splitter in the microscope. A titanium sapphire laser (at 752 nm) provides the exciting light. The accumulation times were typically 5–10 s.

The Raman spectrum of PE in the solid and molten phases is well characterized[1]. In the C–C backbone region of the solid-state spectrum, the all-*trans* bonds in the lamellae give sharp Raman bands at 1065 (C–C asym.) and 1130 $cm^{-1}$ (C–C sym.). The *gauche* bonds present in the amorphous component of the solid give a broad band at 1080 $cm^{-1}$. Some short *trans* sequences are believed to exist in the amorphous phase. Thus the solid-state spectrum is a mixture of these three bands. On melting, the crystalline arrangement is lost and the resulting structure is thought to be a random mixture of *gauche* and *trans* bonds. Some short all-*trans* sequences must still statistically exist, and as a consequence in the melt the 1080 $cm^{-1}$ band is generally observed with a weak shoulder at 1065 $cm^{-1}$. Orientation of the PE under shear is believed to significantly increase the number of *trans* bonds which, in turn, would increase the likelihood of all-*trans* sequences and the re-emergence of the Raman bands at 1065 and 1130 $cm^{-1}$.

## *Results and discussion*

The solid-state spectrum of a 30 $\mu$m high density PE (HDPE) film at 25°C in the rheo–Raman rig is shown in *Figure 2a*. The crystalline bands at 1065 and 1130 $cm^{-1}$ overlie the amorphous band at 1080 $cm^{-1}$. The PE film was heated to 140°C at which point only the amorphous band at 1080 $cm^{-1}$ can be observed (*Figure 2b*). Varying rates of shear were then applied to the polymer (*Figures 2c–f*). It is immediately apparent that the strength of the Raman bands at 1065 and 1130 $cm^{-1}$ increases in response to increasing shear. Clearly, in order to obtain the 1065 and 1130 $cm^{-1}$ bands at 140°C we have forced the polymer into all-*trans* sequences by shearing. The fraction of molecules in the all-*trans* configuration with respect to shear rate is shown in *Table 1*. The all-*trans*

**Table 1** Fraction of molecules in all-*trans* configuration with respect to shear rate

| Shear rate ($s^{-1}$) | Fraction of all-*trans* bonds |
|---|---|
| 0 | 0.03 |
| 5 | 0.05 |
| 10 | 0.08 |
| 15 | 0.08 |
| 25 | 0.1 |
| 37.5 | 0.13 |
| 50 | 0.13 |

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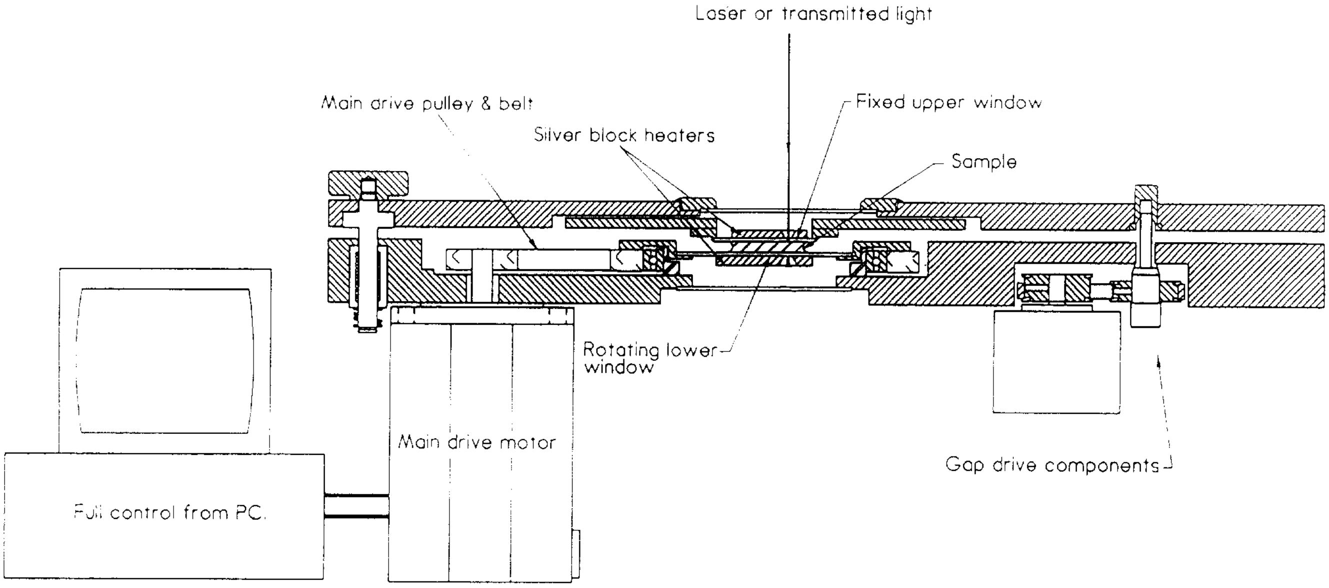

**Figure 1** Diagram of rheo–Raman rig

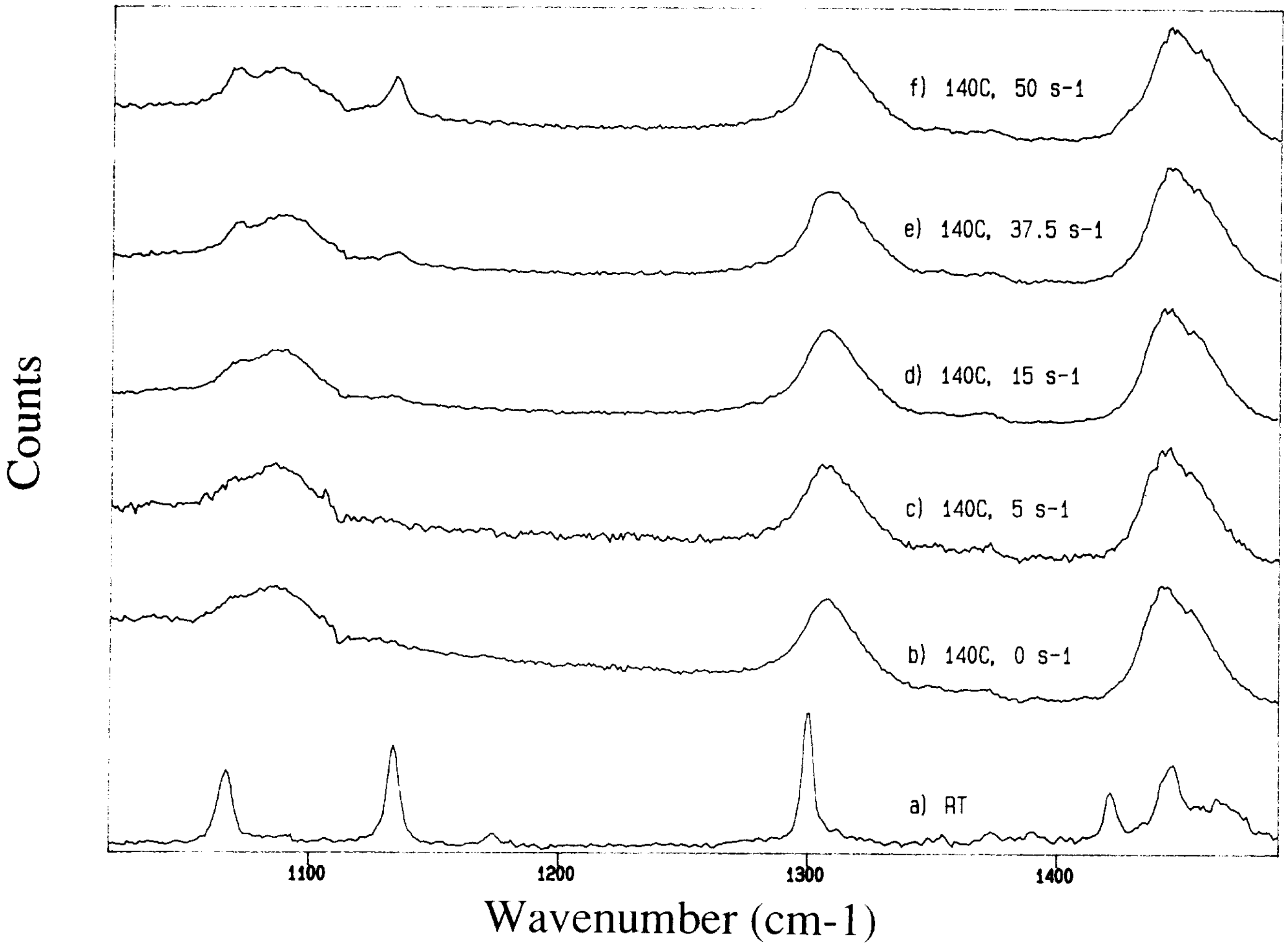

**Figure 2** Effect of shear rate on the Raman spectrum of HDPE at 140°C

content was determined by a crystallinity method developed jointly at BP and DSM[2].

It is possible that the effect observed is, in fact, not flow-induced orientation but flow-induced crystallization. Flow-induced crystallization is supported by the fact that the all-*trans* bands can linger for several hours after cessation of the shear. However, d.s.c. data on films taken from the rig do not show any obvious rise in melt temperature between pristine and sheared polymer. Furthermore, experiments on drawn (i.e. oriented) and isotropic HDPE show a 10°C rise in the melting point of the drawn material over the isotropic, as observed by collecting Raman spectra with a heating rate of 10°C $\min^{-1}$. Similar d.s.c. measurements show no increase in melting temperature between drawn and isotropic samples. This experiment suggests that by orienting the molecules with drawing, the all-*trans* bonds created in the microfibril structure, at the expense of the lamellae, can remain in all-*trans* sequences into the melt. Further work is in progress, aiming to distinguish the two mechanisms and to probe the effects of molecular weight, distribution and long-chain branches on the orientability of the melt.

## *Acknowledgement*

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