Measurement of Molecular Orientation within Bulk Polymeric Samples using Anisotropic Raman Scattering

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Summary A method of measuring molecular orientation with excellent spatial resolution in polymeric samples is described; it is possible to study clear moulded polymer specimens, films and fibres using anisotropic Raman scattering.

IT is established that the tensile strength, sensitivity to solvent attack, hardness and other properties of polymeric materials are profoundly influenced by the degree of orientation of the molecules within the specimen.[1,2] Laboratory methods of monitoring orientation include the microscopic examination of the specimen under polarised light or with electrons,[1,2] or the recording of the i.r. spectrum with polarised i.r. radiation[1] but neither method is completely satisfactory because it operates in two orthogonal coordinates and gives little or no information about variations in orientation within the bulk of the specimen. The only available methods for this more detailed type of analysis require the preparation of sections and the mere cutting operation almost inevitably severely distorts the molecular orientation. We report a novel non-destructive method of monitoring orientation at freely selected points within a polymer specimen with good spatial resolution and precision.

The Raman scattered radiation has directional properties governed by the symmetry of the molecular vibration giving rise to it and the orientation of the molecule relative to the incoming laser beam direction, that of its electric vector, and the viewing direction of the spectrometric system.[3] As a consequence, once the spectra of standard specimens of known orientation have been analysed for their directional pecularities the Raman spectrum of an unknown can in principle be interpreted in terms of the orientation of molecular species with respect to laboratory axes.

In our experimental arrangement the laser beam (mixed Ar/Kr ion device operating at 4880 Å with a power of 100—200 mW) is of known plane polarisation and is brought to a focus within the specimen by a short focal length lens. The form of the focus is a cylinder (length *ca.* 200 μ, diameter 70 μ).

The scattered radiation is collected by a large diameter lens and polarizer and passed to either a Cary 82 or a Cary 83 Raman spectrometer. The focussing lens and the sample are both mounted independently on micrometric stages so that their positions could be adjusted along three orthogonal axes with precision of around $\pm 15\,\mu$. The Raman spectrum of polyethylene terephthalate contains a number of prominent bands whose intensity is highly anisotropic. After recording a complete set of directional spectra the bands at $\Delta\nu$ 1616 cm^{-1} was selected for our purpose. A number of specimens including uniaxially drawn sheet, high pressure mouldings and sheet cut with a blade have been studied and variations in the ρ value as defined in the figure investigated. In the case of the latter sample the ρ value falls rapidly away from the cut edge and then rises asymptotically to a value of *ca.* 0·35 as the sampling position is moved deeper into the specimen. The minimum of the curve occurs only 0·003 inch from the cut face. We feel this behaviour is indicative of the changes in molecular orientation which occurs in the specimen due to the intrusion

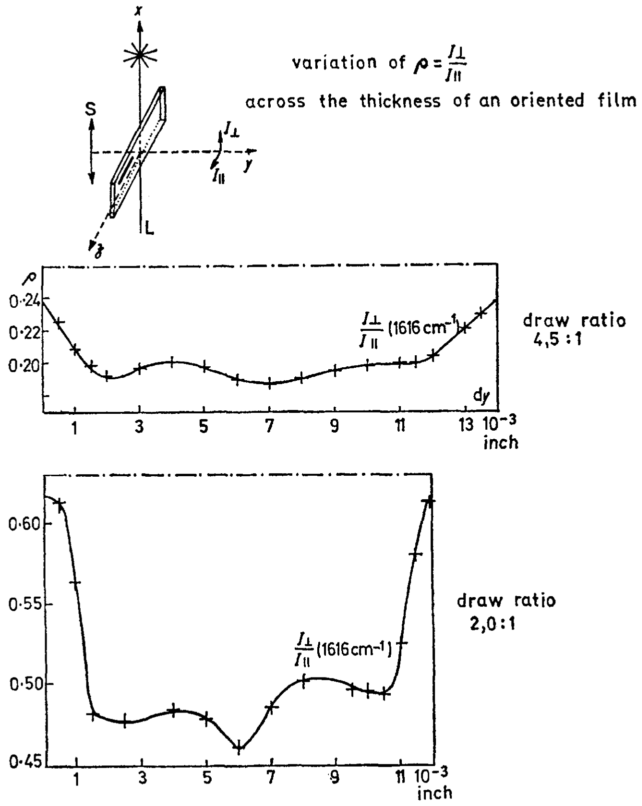

FIGURE. *Variation of orientation within a drawn polymer sheet. Reproducibility: ca.* 0·003 *in* ρ *and hence better than* 0·001 *inch on distance scale.*

of the cutting edge. The minimum in the curve may be indicative of orientation of the molecules parallel to the cutting direction close to the edge. At deeper penetration the orientation would then seem undisturbed.

The figure shows the value of $\rho = I_\perp/I_\parallel$ plotted as a function of the distance from the edge d_y of a P.E.T. sheet. It will be observed that the orientation is by no means homogenous across the film thickness. The discrepancy of the average of ρ when the draw ratio increases is indicative of better state of orientation, and the smaller variation of ρ between the surfaces and the core for higher draw ratio suggests that the homogeneity of the sample is improved. The detailed analysis of the data given in the figure is by no means straightforward. A plane polarised beam of radiation suffers dichroic distortion when passed through a transparent oriented polymeric specimen when the electric vector of the incident radiation is not parallel or perpendicular to the orientation sense. As a consequence, in inhomogeneous samples it requires measurements to be made at a series of ever deeper penetrations to quantify the exact nature of the laser radiation giving rise to Raman scatter.

Anisotropic Raman scatter from a molecule set at an angle other than 0 or $\pi/2$ to the electric vector direction of the source is itself complex in nature. A preliminary verbal account of the analysis of this type of data has been presented very recently by Ward and Bower[4] but a detailed description is too lengthy to be given here. It is evident, however, that our experiments indicate changes in orientation if not the exact direction of these changes. Thus to conclude: we demonstrate a new method of measuring molecular orientation inside transparent polymeric specimens with excellent spatial resolution. The detailed analysis of the data will, however, be given shortly in a more lengthy dissertation in which a description of experiments on film, fibre and injection moulded specimens will be included.

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