Variable temperature and stretching cell for Raman spectroscopy studies of polymers

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A variable temperature cell for use in laser spectroscopy studies of polymers and for the drawing of compounds is described. 'In situ' polarized Raman spectra of polyethylene at different draw ratios and different temperatures are recorded. The depolarization factors allow assignment of the vibrational types to the Raman active modes and the chain orientation study.

(Keywords: Raman spectroscopy; variable temperature and stretching apparatus; depolarization ratios; vibrational assignment; polyethylene)

INTRODUCTION

The measurement of molecular orientation in polymers by spectroscopic methods is of value for two main reasons. The mechanical properties of polymers are strongly influenced not only by the structure of the material but also by the magnitude of the molecular orientations. Thus, there is a great deal of interest in the mechanism governing the molecular orientation introduced into samples of polymers by drawing or other fabrication processes. Furthermore, polarized Raman analysis of stretching oriented polymers provides a method for the assignment of vibrational modes and consequently for the characterization of crystalline and amorphous phases[1].

In both cases, orientations in films or sheets are obtained by applying a large deformation in either one or two perpendicular directions at a suitable temperature.

Although methods for spectroscopic measurements carried out under static conditions are mentioned in the literature[2-7], it was necessary to devise an apparatus in which we could heat or cool the entire sample *in situ* to a precise temperature, maintain this temperature while the spectrum was recorded, produce a large unidirectional deformation at a suitable temperature and employ other processes such as annealing or heat-setting that are necessary to improve the thermal stability of drawn films.

The present work describes a very simple holder for use in laser Raman spectroscopic studies of polymers submitted to all the diverse thermal and drawing operations.

As an example of the application of the sample holder we show the results obtained by Raman spectroscopy with high density polyethylene (PEHD) in the 1000–1500 cm^{-1} range. In this study we were particularly interested in the effect of draw ratio on the chain orientation and vibrational mode assignments using all the possibilities of this variable temperature cell.

SAMPLE STRETCHING AND VARIABLE TEMPERATURE DEVICE

The Raman cell for these studies is shown in *Figure 1*. It consists essentially of a stretching device (L), designed to displace samples equally from both ends, enclosed in a double Pyrex tube (A) connected to a conventional vacuum system in order to thermally isolate the system. The sample (C) is maintained at a controlled temperature by circulating nitrogen gas through a tubular system comprising a two-coil assembly, one coil of which is immersed in a Dewar flask containing liquid nitrogen, and the other coil surrounding a cylindrical regulable heater element. Inlet tubes F and G permit the introduction and evacuation of inert gas.

Temperatures are measured using a standard chromel–alumel thermocouple (I) inserted into the cell, close to the sample. The system enables temperatures from 100 K to above 500 K to be maintained with an absolute accuracy better than ±0.5 K.

The laminar sample, cut into shapes having the dimensions shown in *Figure 2*, is clamped to a two-nut displacement system; an axial screw-thread moving in two different senses allows symmetrical displacement. By means of this system the laser beam is maintained on the same part of the sample at all extensions, thus eliminating errors arising from non-uniformity of samples (due to physical or morphological factors).

With this arrangement, changes of sample, variation of equilibrium temperature, thermal treatment in an inert atmosphere and uniaxial deformation can all be carried out quickly and easily.

OPERATING TECHNIQUES

Polarized Raman spectra are obtained with a microprocessor controlled Jobin-Yvon HG.2S laser Raman

spectrometer. All the data are collected and processed with a Commodore microcomputer data system; a Microlink (BIODATA) interface enables the computer to drive the Double Spectrometer and data acquisition from the photomultiplier. The 514.5 nm line of an argon-ion laser is used to illuminate the samples with 300 mW laser power; scattered radiation is collected at 90° by a f/1 lens system.

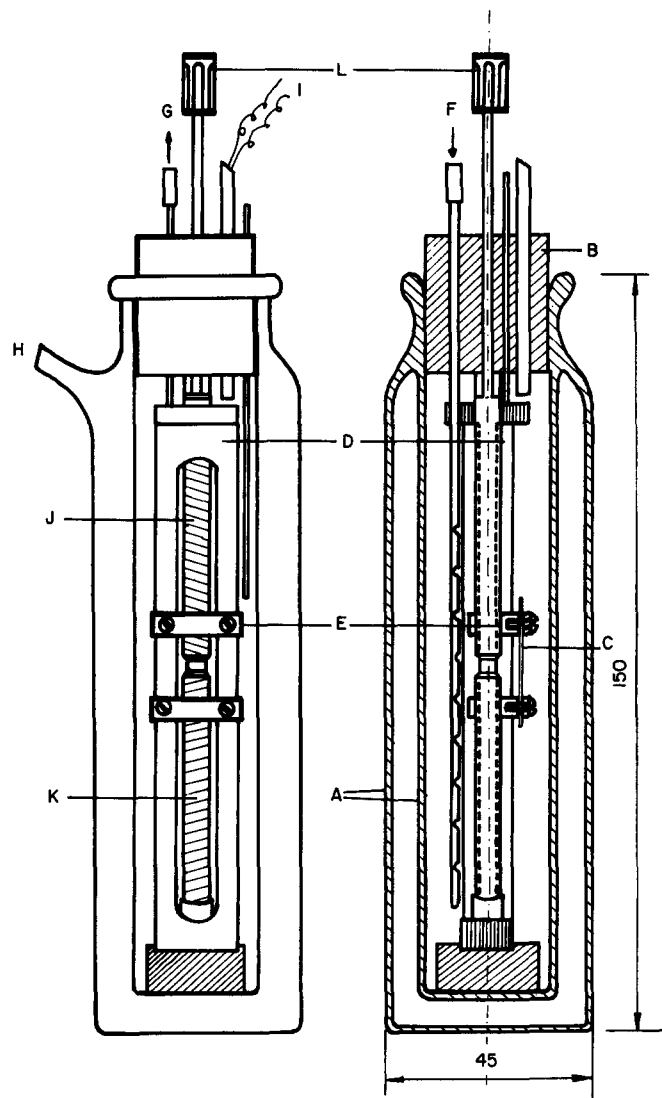The rotation of the plane of polarization of the incident

light is obtained with a half-wave plate; the analysis of the scattering light is carried out using polaroid film and a 1/4 wave plate is used to reduce grating polarization effects. The slit setting on the spectrometer of 250 μm gives a resolution of about 2 cm^{-1} at 19 430 cm^{-1}.

The commercial polyethylene used in this study was of a high density type with weight-average molecular weight of 100 000 and number-average molecular weight of 6400 (supplied by Rio Ródano, Miranda de Ebro, Spain). Samples were melt pressed at 160°C into an isotropic laminar form with the dimensions shown in *Figure 2*. After melting the samples were allowed to cool slowly to room temperature over a period of 2 h.

The position of the cell and the thermal control system of the sample cell is shown in *Figure 1*; the specimen is mounted vertically, so that the drawn direction is normal to the direction scattering plane.

A flow of nitrogen gas at about 0.6 bar was passed through the previously heated and/or cooled cell in order to maintain the sample at a constant temperature. The experimental procedure was to heat the polymer at 360 K for 30 min and to orient the chains by drawing; the spectra was then recorded at 150 K and 250 K.

The draw ratio was determined from the displacement of ink marks spaced initially 2 mm apart on the surface of the sample. In each case the draw ratio was determined for the central part of the sample, which was the part most deformed.

LASER RAMAN STUDY OF POLYETHYLENE

In the first place the cell was used for studying several properties of polyethylene. This important polymer is a well known and extremely suitable compound for detailed comparative studies of molecular orientation. A great deal of Raman data are available in the literature[2-5,8-11] for polyethylene in a variety of different physical states, ranging from an isotropic amorphous glass to a highly crystalline fibre or sheet.

Crystalline polyethylene has an orthorombic unit cell with space group PnmaD_{2h}^{16} in which the two chains pass parallel to the c-axis[12] and isomorphous to the chain factor group. The scattering geometry is shown in *Figure 3*. The laser beam enters the sample along the x-axis and can be polarized along the y or z direction. The scattered radiation is observed in the y-axis polarized along the z or x direction. The z-axis corresponds to the draw direction and chain orientations of the completely oriented sample.

Figure 1 Schematic illustration of the cell (dimensions in mm) A, Pyrex glass; B, Teflon; C, polymer sheet; D, Copper; E, sample holder; F, thermalized gas N$_2$ inlet; G, gas N$_2$ outlet; H, vacuum(10^{-3}mm Hg); I, chromel/alumel thermocouple; J, right hand thread; K, left hand thread; L, stretching mechanism
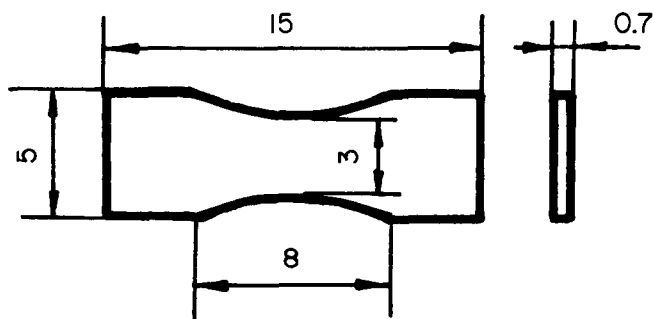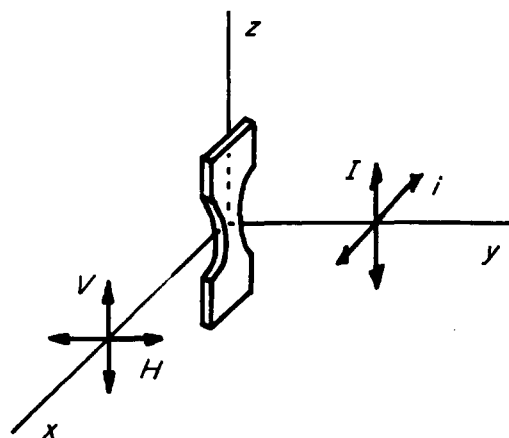

Figure 2 Dimensions of original sample (in mm)

Figure 3 Scattering geometry used in the Raman experiment

The symmetry of the Raman active vibrations within the unit cell and the polarizability tensor elements for this geometry, according the selection rules[13] for the D_{2h} group on the uniaxially oriented polyethylene, are the following:

Chain factor group	Space group	Polarizability tensor elements
a_g	A_g	α_{zz}^2
	B_{1g}	α_{xy}^2
b_{1g}	A_g	α_{zz}^2
	B_{1g}	α_{xy}^2
b_{2g}	B_{2g}	α_{xz}^2
	B_{3g}	α_{yz}^2
b_{3g}	B_{2g}	α_{xz}^2
	B_{3g}	α_{yz}^2

The cylindrical symmetry of the sample leads to obtain the following vibrational symmetry types, $i_V:B_{2g}+B_{3g}$; $I_V A_g$; $i_H:B_{1g}$; $I_H:B_{2g}+B_{3g}$. Calculating the vertical and horizontal depolarization ratio ($\rho_V=i_V/I_V$; $\rho_H=i_H/I_H$) only the A_g+B_{1g} types and the $B_{2g}+B_{3g}$ types of vibration can be separate with this geometry of the sample. The representation of ρ_H+1/ρ_V allows us to distinguish these vibrational types.

Our experimental apparatus has been checked to give the known depolarization ratio of the 459 cm^{-1} line in CCl_4[14] (we estimate it with an error less than 1%).

With the microprocessor we obtained a Raman spectrum and the depolarization ratio, for every polarization state, from 1000 cm^{-1} to 1500 cm^{-1} by the co-addition of 1000 scans. The results of the peaks which appear in the spectra at 150 K for the different draw ratios are represented in *Figures 4* and *5*.

From these results we can conclude that the maximum orientation of the chains for these samples corresponds to a draw ratio of 4. It is interesting to note that the orientation increases abruptly as the draw ratio went from 3 to 4. The assignments based on the anisotropic scattered data (i.e. $\rho_H + 1/\rho_V$ versus λ) shown in *Figure 5* are given in
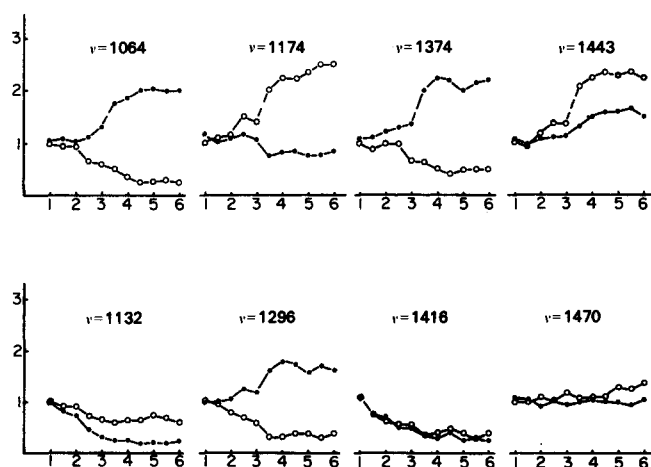

Figure 4 Plot of depolarization ratio derived from Raman spectra against draw ratio (λ=number of original length) (O---O)ρ_H; (●---●)ρ_V
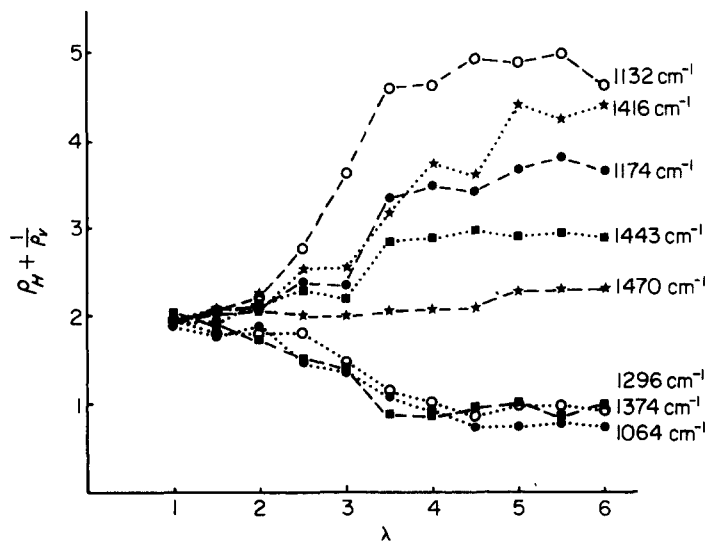

Figure 5 Plot of $\rho_H+\dfrac{1}{\rho_V}$ against draw ratio

Table 1 Assignment of the vibrational modes of semicrystalline polyethylene

γ(cm^{-1})	Vibration type	Assignment
1064	$B_{2g}+B_{3g}$	γ_a (C–C)
1132	A_g+B_{1g}	γ_s (C–C)
1174	A_g+B_{1g}	CH$_2$ rocking
1296	$B_{2g}+B_{3g}$	CH$_2$ twisting
1374	$B_{2g}+B_{3g}$	CH$_2$ bending
1416	A_g+B_{1g}	CH$_2$ bending
1443	A_g+B_{1g}	CH$_2$ bending
1470	A_g+B_{1g}	CH$_2$ bending

Table 1; the results are similar to those proposed by previous authors[15,16].

The contribution of the amorphous region to the C–C stretching and the CH$_2$ twisting modes are very weak. The only values corresponding to the amorphous phase were the CH$_2$ bending motions situated at 1443 cm^{-1} and 1470 cm^{-1}. The strong peak situated at 1416 cm^{-1} is assigned to the CH$_2$ bending motion corresponding to the crystalline phase, characterized by a decreasing of ρ_V and ρ_H versus λ. The 1443 cm^{-1} peak has an opposite behaviour of the depolarization ratios, but their variation is less than the former and corresponds to this vibration in a 'semiordered amorphous phase'[17-20]. According to the variation of the depolarization ratios it can be concluded that the crystalline phase is aligned in the draw direction while the 'semiordered amorphous phase' is oriented perpendicularly.

Finally, the 1470 cm^{-1} band is not polarized and assigned to a 'disordered amorphous phase'[17-20].

The results obtained with this equipment thus far indicate its potential use in following the chain orientation in polymers with continuous stretching of the sample, to control the evolution of the crystallinity with thermal treatments to the polymer, through the study of some characteristic Raman bands, and the analysis of crystal and amorphous transitions by stretching or temperature variation.

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