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The effect of hydrostatic pressure on the position of the 1616 cm^{-1} Raman line of poly(ethylene terephthalate)

S. Webster and D. I. Bower*
Department of Physics, The University of Leeds, Leeds LS2 9JT, UK
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The effect of hydrostatic pressures up to 500 MPa on the position of the 1616 cm^{-1} Raman line of amorphous, randomly oriented poly(ethylene terephthalate) has been studied. The shift varies linearly with pressure, with a sensitivity of 5.6±0.3 cm^{-1} GPa^{-1}. This value is in excellent agreement with the value of 6.4 ± 1.4 cm^{-1} GPa^{-1} recently deduced from measurements of the sensitivity of the position to tensile stress for four combinations of polarization directions of incident and scattered light.

(Keywords: poly(ethylene terephthalate); Raman spectroscopy; hydrostatic pressure)

Introduction

Many papers have appeared reporting the effects of stress on the infra-red and Raman spectra of polymers (see, for example, references 1–17). Most measurements have been restricted to the application of tensile stress parallel to the axis of preferred orientation of highly oriented polymers, and the polarization of the incident laser beam in Raman studies has usually been parallel to that axis. Recently we have made Raman measurements in this laboratory on random and moderately uniaxially oriented samples of poly(ethylene terephthalate) (PET), applying the tensile stress either parallel or perpendicular to the draw direction and using various combinations of polarization directions of incident and Raman-scattered light. Details of these experiments and their results will be published elsewhere[18]. One outcome of the experiments was the prediction[19] of the pressure sensitivity of the position of the 1616 cm^{-1} Raman line for an amorphous, randomly oriented sample, and the measurements reported here were undertaken to test the prediction.

Experimental

Material. The material used was approximately amorphous PET (obtained from ICI Petrochemicals & Plastics Division, Wilton, UK) in the form of sheet 188± 5 μm thick. The sheet was optically isotropic and clear and had a refractive index of 1.5750 at 589.3 nm and a density of 1338.5 kg m^{-3}. Samples measuring ~ 80 μm or less in any direction were cut from the sheet using a scalpel.

Application of hydrostatic pressure. Pressure was applied to the sample using an opposed diamond anvil high-pressure cell (DAC; Diacell Products Mk V). The sample was surrounded by a fluid to provide a hydrostatic high-pressure environment; both silicone oil and purified water were used. At the relatively low pressures used in this study, these fluids are expected to remain hydrostatic. The fluid was contained in a 200 μm diameter hole in a stainless steel gasket pre-indented to a thickness of about 80 μm.

The pressure inside the DAC was determined from the shift of the sharp fluorescence line of small chips of ruby (Al_2O_3:Cr^{3+}) placed in the pressurized sample volume. This is the most widely used method for determining pressure within the DAC, and calibration data are available in the literature[20].

The position of the ruby fluorescence peak was determined using a Lorentzian least-squares-fitting program and the shifts were determined relative to a reference held at ambient temperature and pressure. Where possible, several chips were used inside the sample volume to improve accuracy and as an indication that the environment was indeed hydrostatic.

Raman measurements. Raman measurements were performed using a Leeds/Renishaw Raman Imaging Microscope–Microprobe equipped with a 25 mW HeNe laser operating at 632.8 nm. This gave approximately 8 mW at the sample. The instrument operates in a 180° back-scattering geometry with optical access to the sample through the upper diamond anvil. The exciting light was focused onto the sample with an Olympus ×20 ULWD objective (NA 0.4) which also served to collect the scattered light. The volume of the chip actually sampled was ~ 5 μm^3.

The instrument was operated in spectrograph mode with the spectrum spread across a CCD array detector; the grating was not moved throughout the experiment in order to improve the accuracy with which spectral shifts could be measured. The spectral region covered by the CCD was 1300–1800 cm^{-1} at a resolution of 1 cm^{-1}. An exposure time of 30 s was used to obtain the Raman spectrum of the PET inside the DAC; three measurements were made from different areas of the sample at each pressure and averaged.

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* To whom correspondence should be addressed

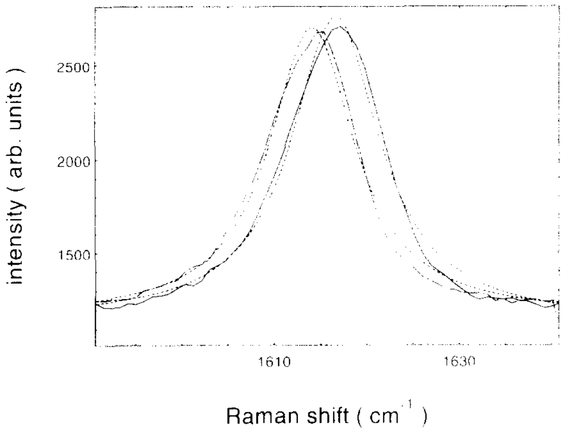

Figure 1 Lorentzian fits to 1616 cm^{-1} Raman line of poly(ethylene terephthalate): - - -, experimental data at 1 atmosphere; . . . . . , experimental data at 560 MPa; - - - - - - - -, Lorentzian fits

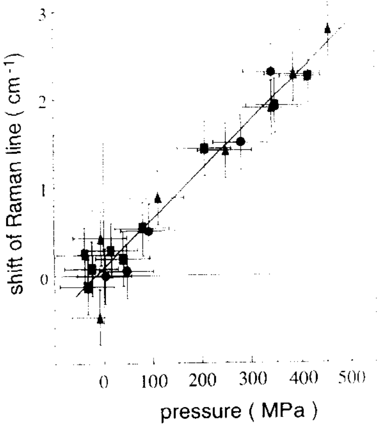

Figure 2 Shift of the 1616 cm^{-1} Raman line of poly(ethylene terephthalate) plotted against applied hydrostatic pressure. Different types of data point indicate different experimental runs. During each run, spectra were obtained from different parts of the same sample and averaged

The position of the PET Raman line at 1616 cm^{-1} was determined using a least-squares routine to fit a Lorentzian peak to the data (see *Figure 1*). The shift of the peak was determined relative to a reference spectrum of PET at ambient pressure.

Results

Preliminary experiments were undertaken using either oil or water to transmit the pressure at pressures up to 3 GPa. The results for oil and water diverged and the shifts became non-linear in the pressure region above 1 GPa. This was attributed to the onset of non-hydrostatic behaviour. Below 500 MPa the shifts were in good agreement for oil and water, and definitive sets of data were obtained covering this low-pressure region in detail, using both liquids as the pressure transmitter. The pressure-induced shifts were observed to be reversible.

A plot of the shift of the 1616 cm^{-1} line against the applied hydrostatic pressure for the definitive sets of data is shown in *Figure 2*. The different data points correspond to the results of three independent experimental runs. The straight line is a least-squares fit to all the data points and the error bars correspond to the errors in the measurements discussed below. A least-squares routine was used to obtain a straight-line fit to all the data points up to 500 MPa. This gave an intercept on the shift axis not significantly different from zero, and a pressure sensitivity of 5.6 ± 0.3 cm^{-1} GPa^{-1}.

Pressure determination. The main contribution to the error in determining the pressure in the DAC is the error in determining the position of the ruby fluorescence peak. At pressures < 500 MPa the error in the pressure due to the uncertainty in the calibration data is less than 3 MPa and is much less than the error introduced through measurement of the peak position. The latter was estimated by combining the standard deviation in the peak position for the reference spectrum with the standard error of the mean in the peak position at the pressure of measurement. This yielded a value of ± 0.42 cm^{-1}, which corresponds to an error in the pressure measurement of ± 56 MPa.

Determination of Raman peak shift. As an estimate of the uncertainty in the shift, the standard deviation of the reference position was combined with the standard error of the mean of the position measurement at a given pressure. This gave a value of $\pm$ 0.14 cm^{-1}.

Discussion

The value of 5.6 ± 0.3 cm^{-1} GPa^{-1} for the pressure sensitivity of the 1616 cm^{-1} line found here for an amorphous, randomly oriented sample is in excellent agreement with the value of 6.4 ± 1.4 cm^{-1} GPa^{-1} predicted on the basis of values recently obtained for the shift sensitivities to tensile stress observed for four combinations of the polarizations of incident and scattered light[19]. In this work the shifts were also determined from Lorentzian fits. Although the peak shape is not quite Lorentzian and changes slightly with tensile stress or with pressure, we believe that the error introduced into shift measurements by the use of Lorentzian fits is very small (see *Figure 1*), and that the comparison of the pressure and tensile data should be even less affected. The value of the shift for hydrostatic pressure should be independent of polarization for an unoriented sample, so that the fact that the present experiment was undertaken using a linearly polarized laser beam and that the collection optics could introduce polarization effects is unimportant.

The prediction of the pressure dependence from the tensile data is based on the assumption that, for small stresses, the stress sensitivity does not change as the stress passes through zero. The present results show that the dependence of position on pressure is linear up to pressures of 500 MPa. The tensile results were obtained using a tensile stress of ~24 MPa; higher stresses caused the sample to craze. The equipment used to determine the correspondingly small shifts, which could be obtained with an accuracy of ~0.01 cm^{-1}, was completely different from that used for the pressure work, and is described elsewhere[19].

It has been tacitly assumed so far that cutting small samples from the isotropic sheet did not produce any molecular orientation. Examination in the polarizing microscope of samples produced in a similar way showed some small birefringence effects. The best estimate that could be made of the birefringence from the colours seen was ~0.02, compared with the maximum birefringence of PET of ~0.23. Results presented in reference 18 show that for such low orientation, most of the Raman shifts measured for different directions of applied uniaxial stress and different combinations of polarization directions of incident and scattered light are likely to differ from those for a random sample by less than the uncertainties in the shifts. It seems unlikely, therefore, that the value obtained for the pressure sensitivity is seriously in error because of orientation induced during sample preparation.

We have examined the width of the carbonyl stretching peak at 1732 cm^{-1} for samples at 1 atmosphere and at 560 MPa and find a slight increase in width at the higher pressure. Melveger[21] has shown that crystallization produces a reduction in the width of the carbonyl peak, so that there is no evidence for pressure-induced crystallization. We could detect no difference in density between relatively large pieces of the original film and small pieces cut off in a similar manner to the samples used in the pressure study, so that there is also no evidence that sample preparation induced significant crystallinity.

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