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# Rheo-optical Raman study of chain deformation in uniaxially stretched bulk polyethylene

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A rheo-optical study has been developed to examine the nature of the structural changes, other than the well known chain orientation, that can appear during uniaxial drawing of polyethylene samples. Stretching was performed at room temperature in samples of melt-crystallized high- and low-density polyethylene. Raman spectra were simultaneously collected along with stress and strain data in order to gain insight into the molecular basis of the properties resulting from the mechanical process. The need for real-time studies was to detect possible transient occurrences that cannot be observed with non-rheo-optical studies. These facts originate from the rapid relaxation phenomena of this polymer. By these means, a band shift and asymmetric band broadening were observed on the C–C asymmetric stretching Raman mode ($1064\,\mathrm{cm}^{-1}$), which has been attributed to some degree of backbone chain deformation. The band shift and, accordingly, the rate of bond deformation did not show a linear stress dependence. There is no substantial band shift during the first moments of the stretching. That initial zone was followed by a stage, during formation of the transition fronts, where the band shift begins to be appreciable. Finally, a third stage was observed when the observation zone falls into the neck. In that stage, a linear dependence was found between the band shift and the applied load. Qualitatively, the observed trend can be thought of as the consequence of the initial isotropic nature of the stretched sample. For that kind of sample, the transference of the load on the polymer backbone is not effective until the sample shows a high degree of orientation in the stretching direction. The band shifts were reversible as the load was removed.

**(Keywords: polyethylene; uniaxial drawing; chain deformation)**

## INTRODUCTION

In the past few years, as a natural extension of studies on polymer deformation, there has been increasing interest in the effect of uniaxial stress on the infra-red or Raman spectra of these materials. In this way, new systems have been developed that allow the simultaneous on-line collection of optical properties such as Raman or *FT*i.r. spectra with mechanical behaviour data (see for example ref. 1). Rheo-optics is the term coined for such techniques.

For the scope of this work, stretching is considered as a large deformation process from which, starting from an isotropic sample, a highly oriented material with a high increase of its length is obtained. For polymers, such deformation is the sum of different elastic and plastic deformations. The mechanical process of sample deformation begins with the elastic deformation of the sample (the Hookean zone). After that stage, and according to Peterlin[2–4], the structural changes that can take place during cold-drawing of a bulk crystalline polymer occur in a three-stage process: plastic deformation of the original spherulitic structure, inhomogeneous transformation of the spherulites into fibre by micronecking, and plastic deformation of the fibre structure. Plastic deformation begins in the vicinity of the yield point and is absent during the first stage of sample deformation, i.e. the elastic zone. The yield point marks the birth of the transition fronts that will delimit the macroscopic neck.

As far as spectroscopic experiments are concerned, when stress is applied to a polymer sample, frequency shifts, intensity and band shape changes, dichroism, etc., are to be expected on some specific vibrational bands. Those effects are especially evident on bands with a high contribution of skeletal vibrations. In this way, spectroscopy becomes a powerful tool to understand the underlying mechanisms of deformation in polymers when the correlation between structural and spectroscopic changes is possible.

A purpose of this paper is the qualitative study of the sensitivity of molecular vibrations to mechanical stress through the analysis of variations in the spectra such as frequency shifts. In the literature, the frequency shift has been interpreted in terms of different mechanisms such as reduction of force constants due to bond weakening and distortion of valence angles and bond lengths[5–8]. These transient structural changes, which appear during stretching of the sample, must be explored by rheo-optical methods. In any other way, and due to the strong

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viscoelastic nature of the polymeric materials involved in the present report, these changes immediately vanish after removal of the load, strongly impeding any study based on non-rheo-optical tests.

To date, the main body of rheo-optical studies based on i.r. (mainly *FT*i.r.) spectroscopy comprises the analysis of the process of chain orientation. Those works, and due to the nature of the i.r. technique, were carried out on film samples of a variety of polymers[1,9,10]. In them, the dependence of the orientation function with the relative strain, and, accordingly, with the state of mechanical deformation, was investigated. One find was the coincidence of the beginning of chain orientation with the yield point. Thus, this orientation process was practically absent before that point and reached its maximum extent during the stage of formation of the transition fronts (frontiers between the isotropic and oriented zone), remaining nearly constant during the propagation of the neck. The plot of the degree of orientation is a sigmoidal-like curve centred in the stage of neck development.

On the other hand, a different trend in rheo-optical i.r. spectroscopy-based methods is the analysis of chain deformation through the study of the band shift caused by external stresses. However, this has been studied for chemically simple polymers such as polyethylene (PE) or polypropylene, and almost exclusively on either ultradrawn films[6,8] or high-modulus ultradrawn fibres[11,12]. Both types of samples are of ultrahigh molecular weight and, what is more important, show a high degree of initial orientation. These restrictions were imposed to achieve a system as similar as possible to an isolated extended polymer chain loaded in both extremes, the system on which theoretical predictions about the response of a polymer chain to stress have been made. In addition, the molecular chains in these systems have maximum sensitivity to deformation. However, the use of preoriented samples impedes the study of the transformation from the isotropic to the fibrillar state. Furthermore, in these cases, study of either the band shift caused by residual stresses in prestressed samples when different loads were applied[11,12] or the peak frequency changes during the stress relaxation that follows the application of, commonly, a high and sudden load[8,9] have been the approaches to analyse those phenomena that can be found in the literature. However, those strategies cannot be regarded as strictly rheo-optical because, in both cases, spectra were recorded when the deformation of the sample has been carried out. Therefore, there is a lack of knowledge about the real-time spectroscopic behaviour of a bulk sample, with no initial orientation, withstanding a deformation process such as uniaxial stretching.

For that purpose, and based on a rheo-optical instrument designed to study thin films in i.r. spectroscopy[1,10,12], we have developed a rheo-optical system to study the deformation of bulk samples that proved to be possible by Raman spectroscopy. We will explore the degree of chain deformation that could appear in the different stages existing in the stress–strain curve of this kind of polymer, i.e. elastic zone, formation of the transition fronts, and propagation of the neck.

Two different polyethylenes were used in this study, low-density polyethylene (LDPE) and high-density polyethylene (HDPE). Both compounds have well known macroscopic behaviour and structural characteristics. Also, theoretical predictions are available for an isolated single PE chain, since its simple chemical structure has made possible calculations based on molecular models.

**Table 1** Physical characteristics of the PE samples used in this work

|  | Flow index (g/10 min) | Density (g cm$^{-3}$) | $\overline{M_w}$ |
|---|---|---|---|
| HDPE | 4.0 | 0.955 | 70 000 |
| LDPE | 0.25 | 0.920 | 115 000 |

## EXPERIMENTAL

### *Materials*

Two commercial polyethylenes, one low-density sample (PBD 150) and one high-density sample (PAD 25055)—supplied by Dow Chemical Iberica (Tarragona, Spain)—were used in this work. Both were free of any additive. Physical characteristics are summarized in *Table 1*.

### *Apparatus and samples*

The electromechanical apparatus is based on a previous one described in detail elsewhere[1,10,13].

The main parts of the stretching device are a driver motor, a computer-regulation system, stress and strain transducers and signal adapters. The clamps move symmetrically from the central point of the sample so that this point remained at its initial position during the whole stretching experiment. The rate of drawing was 1 mm min$^{-1}$ in all cases.

Raman spectra were collected by a Dilor *XY* spectrometer with multichannel detection (512 intensified diodes) in backscattering configuration. The 514.5 nm line of an Ar$^+$ laser was used as the source of illumination. The power of the laser was 250 mW and the acquisition time for spectra was 10 s maximum.

Plates of the materials were prepared by compression moulding of the as-received pellets at a temperature of 160°C. The sheets so formed were rapidly quenched to room temperature. The samples were cut with the dimensions outlined in *Figure 1* from 1 mm thick plates. This special shape was used to ensure two objectives. The main target was to get samples that showed a continuous increase of the specific load in the stretching process, since an objective of this work was the study of the dependence of the band shift with stress and its correlation with theoretical models. That was fulfilled with the used shape since, when plastic deformation takes place, the transverse area of the transition front increases continuously as it propagates along the sample and, accordingly, the load has to increase to maintain a constant rate of stretching. This implies a continuous increase of the specific load in the central zone of the sample, the zone of laser incidence, as is shown in the stress–strain curves of both materials (*Figure 2*). The second target was to ensure the appearance of the neck at a fixed point of the sample, to aim our laser exactly at the position of neck emergence. With this geometry of the specimen, the neck always appears in the central point where the section is the smallest.

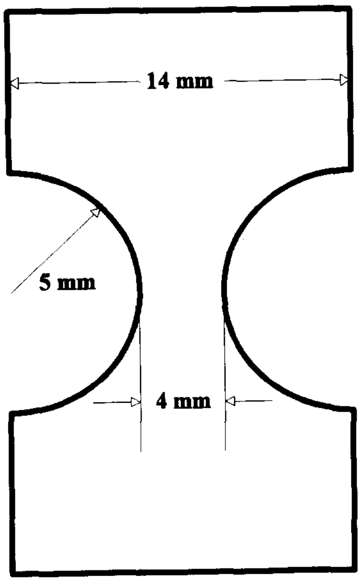

**Figure 1** Samples of the polymer were cut by a die from 1 mm thick plates. The die had the dimensions outlined in the figure

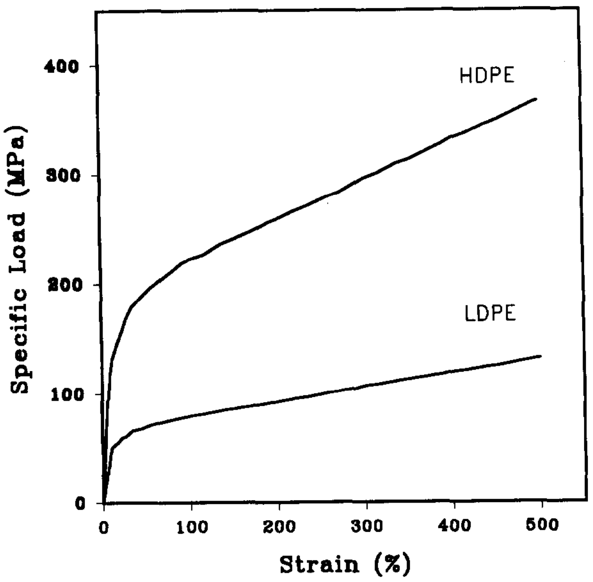

**Figure 2** Typical specific load–strain curve for the samples used in this work. The specific load is expressed in MPa and strain in percentage of the initial length

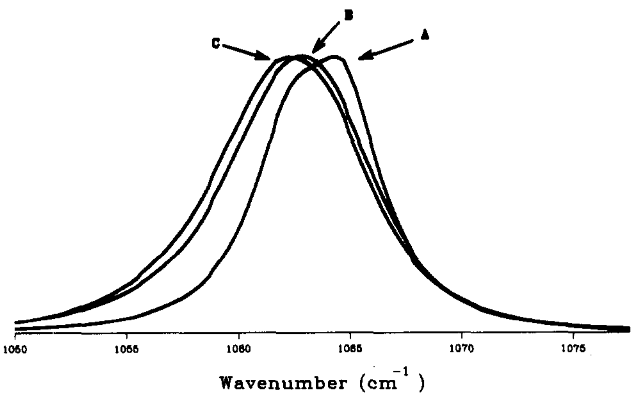

**Figure 3** Example of the changes in shape and position of the 1064 cm$^{-1}$ HDPE Raman band: (A) unloaded, (B) at 200 MPa, (C) at 300 MPa

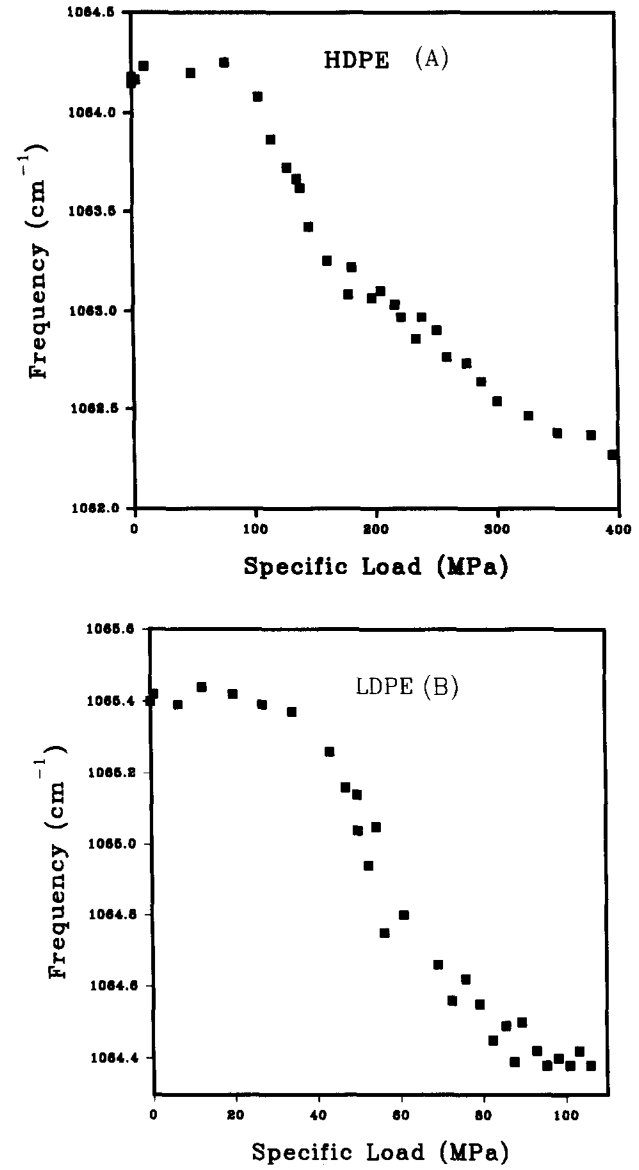

**Figure 4** Frequency shift of the asymmetric C–C stretching mode and its dependence on the specific load: (A) HDPE, (B) LDPE. The wavenumber at maximum intensity has been considered as the peak position plotted on the graph

## RESULTS AND DISCUSSION

The mechanical response of the materials studied here can be seen in *Figure 2*. In that figure, the specific load ($\sigma$) was calculated by estimating the cross-section on the point where Raman measurement was obtained by measuring the initial and final cross-section of the specimen and the shape of the transition front. The continuous increasing of $\sigma$ in the observation region after the yield point was due to the shape of the sample as explained in the 'Experimental' section.

From bibliographic data[6] and our preliminary work[14], it was concluded that the Raman-active $B_{1g}$ asymmetric C–C stretching mode (1064 cm$^{-1}$) has the strongest sensitivity to uniaxial stress of the whole Raman spectrum of polyethylene (PE). Consequently, this band is the most appropriate to study the effect of load on the polymer chain through Raman spectroscopy.

In both polyethylenes, asymmetric band broadening and band shift to lower wavenumbers were found when the samples were exposed to stress (these phenomena can be observed for HDPE in *Figure 3*). In our experimental arrangement, the maximum band shift found for HDPE was about 2 $\mathrm{cm}^{-1}$ at the final load (*Figure 4A*) and 1 $\mathrm{cm}^{-1}$ for LDPE (*Figure 4B*). The changes in bandwidth and the shift of the peak were progressive and dependent on the applied external specific load for both PEs. LDPE showed a lower response, as could be expected from the lower values of the specific load. Resolution has been estimated at about 0.6 $\mathrm{cm}^{-1}$ considering the spectral resolution of the array of diodes and slit widths.

The observed frequency shift in LDPE was too low for quantitative considerations. However, the similar trend of the band shift observed in *Figures 4A* and *4B* would make it possible to extend the results obtained in HDPE to the former material. Therefore, further studies in this work will be restricted to the latter polymer.

The behaviour of the band shift of HDPE can be seen plotted against $\sigma$ in *Figure 4A*. The band shift was followed by determining the peak maximum. Three zones can be distinguished in this figure. The first corresponds to loads up to approximately 100 MPa. As observed in *Figure 2*, this zone coincides with the elastic zone of HDPE stretching and only a slight or no shift was observed. The second zone corresponds to the short interval corresponding to the development of the transition fronts. This takes place for $\sigma$ between about 100 and 200 MPa; there is a clear shift in that zone. After that, a linear region was found corresponding to the zone where the transition front propagates. The point of laser incidence is in the neck region where there exists oriented material bearing a continuous increase of the specific load.

Wool *et al.*[6], based on molecular deformation of the chain (changes in angles and bond lengths), have studied those phenomena theoretically. That study is a normal coordinate analysis of an isolated PE single chain loaded in both extremes. For that purpose, the authors made use of conformational energy minimization methods in which anharmonic (Morse) potential energy functions were selected for the C–C stretching modes in the valence force field. That study predicted a shift of the maximum of the band to lower wavenumbers and asymmetric broadening; those modifications being caused by the loaded state of the chain in terms of the anharmonic function used for the C–C stretching vibration. Furthermore, a linear relationship between the band shift and the applied load was found. The slope of the plot of peak frequency vs. the specific load is called the frequency shifting coefficient ($\alpha$), which is defined as[6]:

$$\alpha = \left(\frac{\partial \nu}{\partial \sigma}\right)_T$$

The coefficient $\alpha$ calculated for the C–C asymmetric stretch was $-5.8\,\mathrm{cm}^{-1}\,\mathrm{GPa}^{-1}$. Although our results showed good agreement with those theoretical predictions, there is a major disagreement; no linear stress dependence has been found for the band shift in our samples. However, three linear regions were considered in order to obtain values of the shift factor to compare with those of the literature. These linear zones were the ones previously described, which are defined in $\sigma$ ranges of 0–100 MPa, 100–200 MPa and 200–400 MPa. The experimental values of the coefficients corresponding to these linear regions were $-0.2\,\mathrm{cm}^{-1}\,\mathrm{GPa}^{-1}$ (coefficient of linear regression $CLR = 0.912$) for the elastic zones $-11.7\,\mathrm{cm}^{-1}\,\mathrm{GPa}^{-1}$ ($CLR = 0.981$) during formation of the transition fronts, and $-4.4\,\mathrm{cm}^{-1}\,\mathrm{GPa}^{-1}$ ($CLR = 0.991$) for the zone after establishment of the neck for HDPE ($-0.4\,\mathrm{cm}^{-1}\,\mathrm{GPa}^{-1}$, $-12.3\,\mathrm{cm}^{-1}\,\mathrm{GPa}^{-1}$ and $-3.5\,\mathrm{cm}^{-1}\,\mathrm{GPa}^{-1}$, respectively, for LDPE). Our shifting coefficients are of the order of the theoretical frequency shifting coefficient and the experimental values found by the same authors for samples of PE films[6], $-11.2\,\mathrm{cm}^{-1}\,\mathrm{GPa}^{-1}$.

Nonetheless, we have not considered the non-linear behaviour observed in our samples as a fault in the theoretical description of the phenomena given by Wool *et al.* In that sense, we looked for interpretations based on the particular nature of the polymer or its structure. However, in a similar work on melt-crystallized bulk isotactic polypropylene (iPP)[15], the majority of the observed bands showed analogous sigmoidal behaviour as the band studied here. Then, owing to the different nature of the polymers in which this common relationship was found between frequency shift and load, those explanations of the phenomena based on particular characteristics of the polymer (such as, for example, modifications on the correlation splitting phenomena, changes in the crystalline state, etc.) can be discarded. In that sense, the observed trend seems to be caused by the isotropic and spherulitic structure of the sample used in this work and that of IPP, which would mask the inherent linear response of the band shift.

The effect of the structure is, then, easy to understand. During the first stage of the stretching process, we have an unoriented material. In that stage, and when plastic deformation starts to take place, the load is mainly applied on that material, which promotes relative chain displacements and orientation with low transference of the load in the chain direction due to the disorientation of this initial material. Obviously, only the component of the load in the chain axis direction is to be expected to cause bond deformation and, accordingly, frequency shifts. Then, the observed band shift would be minimum or almost absent during this stage, where the degree of orientation shows its lowest values during the stretching. The applied load would be effectively transferred to the polymer backbone only when the chains show preferred alignment in the stress direction, so the highest sensitivity of the Raman band must arise at the stages of maximum orientation. When the observation zone falls in the extension of the transition front, the observed band shift is lower than expected for the values of the load. In that zone, some chains are already incorporated in the micronecks whereas the rest of them remain in the residue of the original spherulitic structure. The oriented chains would suffer direct transmission of the load on their backbone, showing band shifts. As the number of chains in the oriented state increases, the magnitude of the band shift is higher until, already in the neck, all the chains have passed from the spherulitic to the fibrillar state and the band shift would show the inherent linear trend predicted by theory and experimentally found in PE samples with uniaxial anisotropy. In this zone, the neck, the polymer has a high degree of orientation and, although it is not as high as that of the ultra-oriented samples, the behaviour that we observed must be similar to the one observed on samples such as ultra-oriented films or fibres.

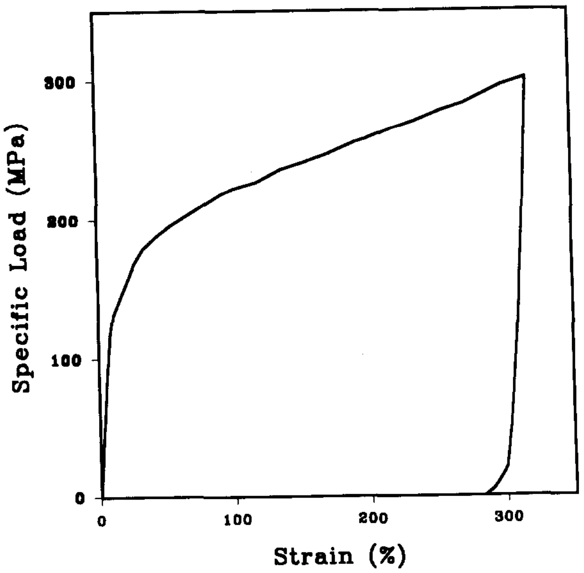

**Figure 5** Stress–strain curve for the stretching–recovery process suffered by samples of HDPE. Samples were stretched at a constant rate of 1 mm min$^{-1}$ until they reached 300 MPa. At this point, the direction of movement was immediately reversed, proceeding at 1 mm min$^{-1}$ until the sample got unloaded

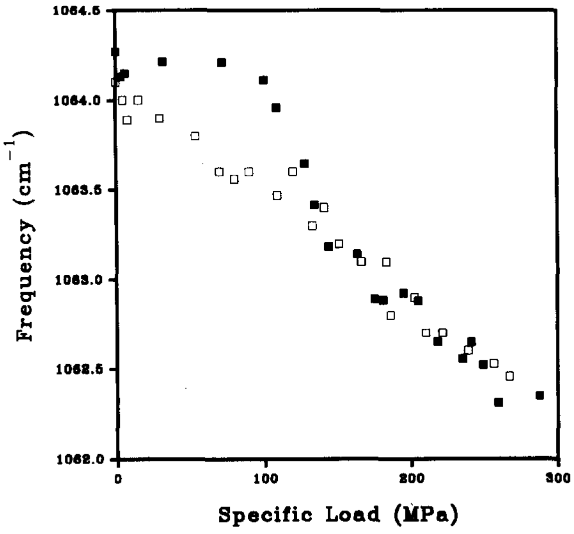

**Figure 6** Frequency shift of the 1064 cm$^{-1}$ HDPE Raman band and its dependence on the specific load during the cyclic deformation process described in the text: (■) stretching direction, (□) reverse direction

Further support for this interpretation is given in the next group of results. Samples of HDPE were subjected to a two-stage mechanical process. That process started with a stretching similar to those used before, which deformed the samples until the observation zone undoubtedly fell in the oriented zone of the neck. Immediately after that stage, the motor reversed its motion, performing a second stage of controlled recovery. That recovery ended at zero load; that process can be seen in *Figure 5*. Owing to the irreversibility of the orientation of the chains, we have an oriented material during that second stage that will reveal the inherent behaviour of the band shift when the orientation process does not interfere. The rheo-optical analysis of that deformation–recovery cycle can be seen in *Figure 6*. Two facts deserve further comment. First, as we expected, the band showed a linear shift during the whole recovery. The shifting coefficient calculated by linear least-squares fitting of the data was $\alpha = -4.4\,\text{cm}^{-1}\,\text{GPa}^{-1}$ (*CLR* = 0.988), which coincides with the value obtained in the third region of the stretching stage where the orientation of the polymer chains is similar. Secondly, the band position returned to the initial value when the discharge of the sample was complete. The phenomenon of the band shift was reversible, in good agreement with a band shift caused by distortion of the bond geometry. Then, it must be considered as a molecular explanation of at least part of the elastic behaviour that the polymer samples show, especially in the deformed state.

Finally, as the C–C stretching mode is sensitive to the polarization of the light source, a different set of spectra were collected in which the polarization direction of the exciting laser was changed to analyse possible artifacts coming from this source. The intensity of this band suffered relative changes compared to other bands of the spectra. However, the properties of the band observed in our rheo-optical analysis did not show any considerable difference ($<5\%$, result not shown).

As a future continuation of the qualitative findings presented here, modifications of the equipment are being designed to quantify the contribution of the degree of orientation on the frequency shift phenomena during uniaxial drawing of an isotropic bulk PE sample.

## CONCLUDING REMARKS

The Raman band associated with the C–C asymmetric stretching mode (1064 cm$^{-1}$) is highly sensitive to the applied load. No linear dependence of the frequency shift vs. the applied stress was found when an isotropic bulk sample was deformed. That behaviour was thought to be caused mainly by the different degrees of orientation that the sample suffers along the stretching process. The changes in shape and position of the Raman band were completely reversible after removal of the load. This recovery followed the decrease of the load with no apparent lag time. The observed linear trend of the band shift during the recovery stage ratifies the role played by the degree of orientation during the stretching state.

## ACKNOWLEDGEMENT

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