# The relation between molecular orientation and birefringence in PET and PEN fibres

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Polarized Raman spectroscopy and birefringence measurements on a wide range of as-spun poly(ethylene terephthalate (PET) and poly(ethylene 2,6-naphthalenedicarboxylate) (PEN) fibres have been correlated. Evidence is provided for the linear relationship between birefringence and molecular orientation. An intrinsic birefringence value of 0.244 is obtained for PET and a value of 0.487 for PEN.

**(Keywords: orientation; Raman spectroscopy; birefringence)**

## *Introduction*

Our understanding of the mechanical properties of polymers in general, and of polymer fibres in particular, is to a large extent founded on the concept of molecular orientation[1]. Measurement of optical anisotropy or birefringence is probably the most common method used to characterize the orientational order in polymers. Measurement of birefringence is a relatively simple experimental technique. However, this optical method affords only relative measurements of molecular orientation. By correlating polarized Raman spectroscopy and optical measurements on a wide range of poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalenedicarboxylate) (PEN) fibres we are able to deduce an accurate value for the intrinsic birefringence of PET and PEN. As far as is known, this is the first time that this approach has been applied to PET and PEN fibres.

The classical relation between optical anisotropy or birefringence and molecular orientation is:

$$\Delta n = \Delta n_{\max} \langle P_2 \rangle \qquad (1)$$

where $\Delta n$ is the observed optical anisotropy, $\Delta n_{\max}$ the intrinsic birefringence, and $\langle P_2 \rangle$ the mean second-order Legendre polynomial of the orientation distribution function or Hermans function[2] ($\langle P_2 \rangle = 0$ means no average molecular orientation, whereas $\langle P_2 \rangle = 1$ means full alignment of the molecular units). It should be recognized that only the orientational component of birefringence is taken into account in equation (1). This equation can be derived by assuming birefringence to be proportional to the total polarizability anisotropy and by averaging the contributions of the anisotropic units to this anisotropy. Some knowledge of the intrinsic birefringence ($\Delta n_{\max}$) is required in order to quantitatively extract the order parameter from the optical anisotropy according to equation (1). The intrinsic birefringence is the maximum possible orientation birefringence, corresponding to the (usually hypothetical) situation where all polymer chains (units) are perfectly aligned ($\langle P_2 \rangle = 1$). Very often a distinction is made between the intrinsic birefringence of the amorphous and the crystalline regions[1]. The range of published values for the intrinsic birefringence of PET is very wide (0.2–0.3)[3,4] and few data have been determined on fibres. The intrinsic birefringence of PEN has not previously been determined, as far as we know.

Polarized Raman spectroscopy is a more elaborate experimental technique than birefringence measurement, but this spectroscopic method provides absolute values of the $\langle P_2 \rangle$ order parameter (and of $\langle P_4 \rangle$, the next orientational order parameter)[5,6]. We present the first experimental results from orientational order studies by polarized Raman spectroscopy on a wide range of PET and PEN fibres.

Polarized Raman spectra are obtained from polyester filaments having a diameter of tens of micrometres. The nature of such thin samples requires a micro-Raman set-up. The source of laser radiation is an argon-ion laser tuned to a wavelength of 514.5 nm. To ensure linear polarization, the laser beam is directed through a prism polarizer. A modified microscope is used to focus the laser light to a spot with a diameter of approximately 5 μm. The laser power on the filament is limited to a maximum of 2 mW in order to avoid laser damage. The Raman scattered light is collected in the backscatter geometry and passes a polarization analyser. The scattered light is then directed to a triple monochromator with an intensified silicon photodiode array detector. Due to the array detector no scanning of the monochromator is required.

The order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are calculated from Raman spectra by measuring the depolarization of a Raman active vibration for various sample orientations[6]. Spectra are collected with the propagation direction of the incident and scattered light perpendicular to the fibre axis. The incident light beam is polarized either along or perpendicular to the fibre. The orientation of the sample fibres (about five for each type of yarn) is achieved by a rotation stage. The intensity of the Raman line is determined via curve fitting of the spectral shape using Lorentzian peak shapes and assuming a linear background. The intensity ratio of two polarizer–analyser configurations (analyser parallel and perpendicular to

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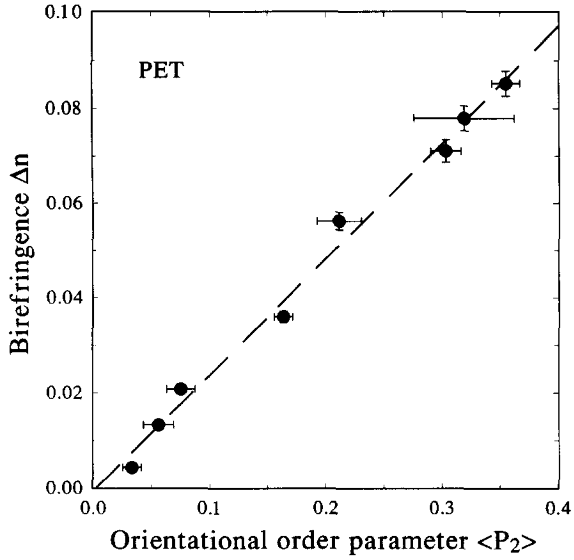

**Figure 1** The variation of birefringence with molecular orientation in poly(ethylene terephthalate) (PET) fibres. The order parameter $\langle P_2 \rangle$ is obtained by polarized Raman spectroscopy (1615 cm$^{-1}$ vibrational line). The dashed line is a linear regression fit of the data. Estimated experimental errors are given by the bars

polarizer) yields the depolarization ratio. This observed ratio is corrected for the difference in the reflection and refraction of the two polarization components of the scattered light in order to obtain the depolarization ratio of the vibrational line[6]. Furthermore, the basic scattering properties (described by the Raman tensor) of the studied vibration must be known. The ratio of the Raman tensor components can be determined from depolarization measurements on isotropic samples ($\langle P_2 \rangle = \langle P_4 \rangle = 0$).

The molecular orientation $\langle P_2 \rangle$ in PET fibres is obtained by studying the benzene ring vibration at 1615 cm$^{-1}$. The Raman tensor of this vibration is assumed to be cylindrically symmetric, the principal axis making an angle of 19°12′ with the molecular chain axis[5]. In the case of PEN fibres, the naphthalene vibrations[7] at 1474 and 1631 cm$^{-1}$ are analysed. Again, cylinder symmetry is assumed for the differential polarizability tensor. A more detailed description of the applied experimental procedure will be published elsewhere[8].

The birefringence of the fibres is determined at a wavelength of 589 nm on a polarizing microscope equipped with a de Sénarmont compensator. The filaments are cut and immersed in dibutylphthalate. The diameter of the filament and the phase difference are measured, which together produce the birefringence.

Low- and medium-oriented PET and PEN fibres were made by spinning from the melt. The winding speed was varied between 100 and 4500 m min$^{-1}$ for PET and between 500 and 5500 m min$^{-1}$ for PEN[9], thus changing the amount of molecular orientation in the fibres.

The spectra obtained with our polarized micro-Raman scattering set-up are of good quality, indicating the usefulness of this technique for studying the structure of polyester fibres. Other vibrational lines are sensitive to molecular orientation, in addition to those studied in this investigation. We presently consider only the major and most reliable Raman lines of PET and PEN.

It is quite difficult to obtain an entirely isotropic sample for determining the basic scattering properties of the vibrations studied. Therefore, we used an approach for finding the isotropic depolarization, which differs from the method of Purvis and Bower[5]. Our depolarization measurements show an increase in molecular orientation with increasing spinning speed. The isotropic depolarization is obtained by an extrapolation towards zero winding speed. This yields slightly different values for the Raman tensor components of PET ($\alpha_1/\alpha_3 = -0.122 \pm 0.004$)[8] as compared with values published by Purvis and Bower ($\alpha_1/\alpha_3 = -0.18 \pm 0.02$)[5] and Lewis and Bower ($\alpha_1/\alpha_3 = -0.154 \pm 0.004$)[10]. The discrepancies have a negligible effect on the second-order parameter $\langle P_2 \rangle$, but do influence the values of the fourth-order parameter $\langle P_4 \rangle$.

The order parameters determined by Raman spectroscopy correspond to the orientation of the principal axis of the vibration studied. To obtain the molecular orientation, a correction should be made for the angle between this axis of the Raman tensor and the molecular chain axis. In the case of PET fibres, the accepted value of about 19° was used. We did not apply this kind of correction to the PEN results, because the angle between the principal axis of the assumed cylindrically symmetric Raman tensor and the chain axis is not accurately known. Considering the suggested type of vibrations[7] in regard to the molecular structure of PEN (2,6 substitution) it may be expected that the angle is less for PEN than for PET. In this case the difference between the average orientation of the principal axis of the naphthalene vibration and the orientation of the polymer chains is negligible (within the experimental errors). We analysed both the 1474 and 1631 cm$^{-1}$ lines in order to obtain experimental support.

The relation between the measured birefringence and the order parameter $\langle P_2 \rangle$ obtained from Raman spectroscopy is illustrated in *Figure 1* for PET and in *Figure 2* for PEN. A linear relation is observed for both PET and PEN fibres. The orientation range covered by the PEN fibres is about twice as large as that covered by the PET fibres. No significant difference is observed between the variation of the order parameter belonging

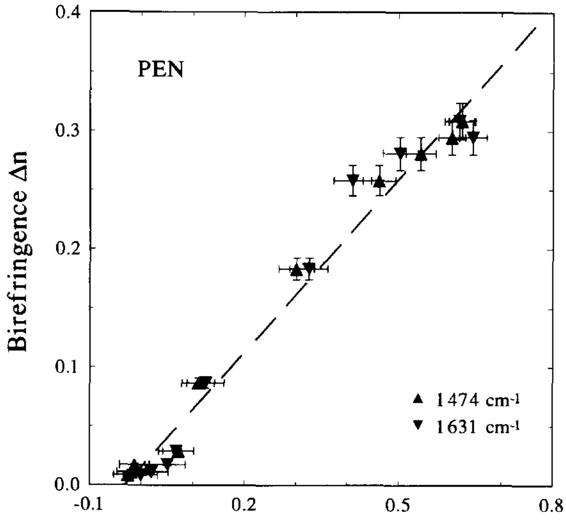

**Figure 2** The variation of birefringence with molecular orientation in poly(ethylene 2,6-naphthalenedicarboxylate) (PEN) fibres. The order parameter $\langle P_2 \rangle$ is obtained by polarized Raman spectroscopy (1474 and 1631 cm$^{-1}$ vibrational lines). The dashed line is a linear regression fit of the data. Estimated experimental errors are given by the bars

to the 1474 cm$^{-1}$ vibration and that obtained from the 1631 cm$^{-1}$ line. Consequently, the principal axes point towards the same direction for both vibrations. The linear relations shown in *Figures 1* and *2* are a direct proof of birefringence being an excellent relative measure of average orientation, as given by equation (1). These results can be perfectly understood if the total polarizability anisotropy is determined by the terephthalate units for PET and by the 2,6-naphthalenedicarboxylate units for PEN. This assumption is very plausible, since the conjugated $\pi$-electrons give the major contribution to the polarizability.

The intrinsic birefringence is obtained from the slope of the straight lines in *Figures 1* and *2*. A value of $0.244 \pm 0.010$ is calculated for PET and $0.487 \pm 0.017$ for PEN. The value of 0.244 for PET agrees perfectly with results from previous Raman studies on tapes[11] ($\Delta n_{\max} = 0.24$), n.m.r. investigations on films[12] ($\Delta n_{\max} = 0.23$), and sonic compliance measurements on fibres[13] ($\Delta n_{\max} = 0.236$). The intrinsic birefringence of PEN has not been determined before, as far as we know. A value slightly lower than 0.487 may be obtained if correction is made for the angle between the principal axis of the Raman tensor and the chain axis.

In interpreting our data, no distinction is made between amorphous and crystalline contributions. Some authors[3] arrive at different values for the amorphous and the crystalline intrinsic birefringence of PET, whereas others claim almost equal values for both phases. The crystallinity of our PET fibres is rather low (density measurements yield values less than 20% at the highest orientation). Crystallinity data are not available for the PEN fibres. We found no indication of any deviating crystalline contributions to the orientation for both PET and PEN. Correlating birefringence and Raman spectroscopy on drawn PET fibres of higher orientation and crystallinity will give more insight. These investigations are currently in progress[8].

We conclude that polarized micro-Raman spectroscopy gives quantitative information about molecular orientation in PET and PEN fibres. Birefringence is linearly related to the average orientation, the scaling factor (intrinsic birefringence) being 0.244 for PET and 0.487 for PEN. More detailed studies on drawn PET fibres have to be undertaken in order to observe any semicrystalline effect.

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