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# Structural Information on the Transition Moments in Poly(ethylene-2,6-naphthalene) by Polarization FT-IR Spectroscopy

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**Summary:** Oriented poly(ethylene-2,6-naphthalate) (PEN) has been characterised by polarised FT-IR spectroscopy to determine the structural angles of the transition moments to the molecular chain axis. The bands at 1130 $cm^{-1}$, 1142 $cm^{-1}$ and 1602 $cm^{-1}$, which have been previously assigned as having their transition dipole moments parallel to the chain axis, are confirmed as parallel bands. Bands at 767 $cm^{-1}$ and 831 $cm^{-1}$ are confirmed as perpendicular bands. However the band at 1708 $cm^{-1}$ which has previously been assigned as a perpendicular band, is shown here to have its transition moment at 72° to the molecular axis.

**Keywords:** FT-IR; molecular orientation; poly(ethylene-2,6-naphthalate); refractive index; uniaxial

## Introduction

Poly(ethylene-2,6-naphthalate) (PEN) receives industrial interest as one of a number of high performance polymers. The naphthalene ring in the PEN repeat unit (Figure 1) is thought to give greater rigidity to the macromolecular chain and hence superior mechanical properties relative to other closely related polymers. In comparison with poly(ethylene terephthalate) (PET), PEN has a higher mechanical strength, higher melting point (270 °C, compared with 255 °C for PET) and better hydrolytic resistance. PEN has a relatively high glass transition temperature ($T_g \approx 120$ °C)[1–5] compared with ~72 °C for PET.[1] Such properties of PEN favour its use in applications such as capacitor dielectrics, data storage tapes, packaging, e-paper and flexible OLEDs.

The purpose of the work described here is to determine the angles that the IR dipole transition moments make relative to the macromolecular backbone of the PEN chain. Although several research teams have assigned the various peaks in the IR spectrum of PEN to specific molecular vibrational modes,[6,7] the direction of these moments have not been determined. Knowledge of these angles would significantly reduce the time needed to obtain a quantitative analysis of molecular orientation of PEN films, since it could then be determined from IR spectroscopy alone.

## Theory

A quantitative analysis of the orientation of the molecular chains within a uniaxially drawn polymer can be obtained from polarised IR spectroscopy alone providing the structural details of the transition moments are known, Conversely if the orientation function can be obtained from some other experimental method (e.g. birefringence) then the angles that the transition moments make with the molecular chain can be determined by combining the IR and birefringence data.

A uniaxial distribution is characterised by one single axis, namely the draw

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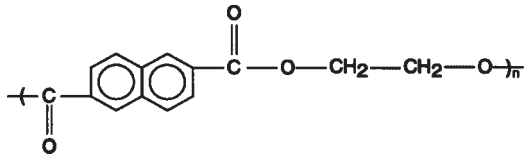

***Figure 1.***
Structural diagram of the repeat unit in PEN.

direction (Figure 2), and the orientation average, $\langle P_2(\cos\theta)\rangle$ of the molecular chain axes to the draw direction can be determined from birefringence measurements. This involves measuring the birefringence ($\Delta n = n_3 - n_1$) of the separate orthogonal refractive indices, and also requires knowledge of the intrinsic birefringence, $\Delta n_0$, of the polymer concerned. $\langle P_2(\cos\theta)\rangle$ is then determined from equation 1.

$$\langle P_2(\cos\theta)\rangle = \frac{\Delta n}{\Delta n_0} = \frac{n_3 - n_1}{\Delta n_0} \qquad (1)$$

For thin films directions 1, 2 and 3 are defined within the drawn sample such that the refractive index $n_3$ is parallel to the draw direction, $n_2$ is normal to the film plane and $n_1$ is within the film plane but normal to the draw direction (Figure 3).

If it is assumed that each IR-active vibrational mode has its transition moment at a well defined angle ($\theta_m$) to the molecular chain axis and that these transition moments are distributed uniaxially about the chain axes then polarised IR spectroscopy can be used to determine these angles via equation 2,3 and 4.

Two IR spectra are obtained for each drawn film (films drawn to a range of draw ratios). For each film one spectrum is obtained with the IR radiation polarised parallel to the draw direction and one with it polarised perpendicular to the draw direction. For each peak in the spectrum (i.e. for each transition moment) the areas $A_{//}$ and $A_{\perp}$ (being the areas in the parallel and perpendicular spectra respectively) are determined and combined via equation 2 to yield the orientation average of the transition moments with respect to the draw direction, $\langle P_2(\cos\theta_\mu)\rangle$where $\theta_\mu$ is the angle between the transition moment (dipole) and the draw direction.

$$\langle P_2(\cos\theta_\mu)\rangle = \frac{A_{//} - A_{\perp}}{A_{//} + 2A_{\perp}} \qquad (2)$$

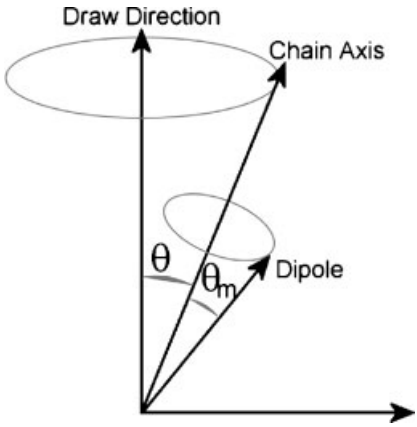


***Figure 2.***
Angles considered in the study of uniaxially drawn films.

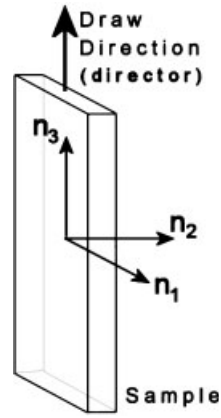


***Figure 3.***
Directions of the three refractive indices in the sample.

 

The angle of each transition moment to the molecular chain, $\theta_m$, is obtained via equation 3 by fitting a straight line to a graph of $\langle P_2(\cos\theta_\mu)\rangle$ against $\langle P_2(\cos\theta)\rangle$ for samples drawn to different draw ratios. The slope of this line $\langle P_2(\cos\theta_m)\rangle$ is then used in equation 4 for the Hermans orientation function, to obtain $\theta_m$

$$\langle P_2(\cos\theta_m)\rangle = \frac{\langle P_2(\cos\theta_\mu)\rangle}{\langle P_2(\cos\theta)\rangle} \quad (3)$$

$$\langle P_2(\cos\theta_m)\rangle = \frac{1}{2}(3\cos^2\theta_m - 1) \quad (4)$$

## Materials

PEN film (nominally 45 μm thick, amorphous and isotropic) was supplied by DuPont Teijin Films Ltd. (Luxemburg). Samples (approximately 75 mm long by 20 mm wide) were cut from this film. Care was taken to avoid any fraying along the cut edges so as not to introduce weaknesses which may cause undesirable drawing or breaking of the samples.

### Uniaxial Drawing

Drawing was carried out using an Instron 4505 tensile testing machine at a temperature of $150 \pm 3\,^\circ C$ and speed of 500 mm/min. This produced a range of samples (with draw ratios between 3.6 and 6.1) which were reasonably transparent and hence suitable for optical experiments.

All samples exhibited necking during the drawing process which means that a neck is initiated in the film and travels down the length of the sample producing drawn material at the 'natural' draw ratio. For PEN this natural draw ratio was found to be approximately 3.6, where draw ratio, λ, is defined as the quotient of final length of a sample and its original length. Producing samples of higher draw ratio can only be achieved once the neck has extended over the whole length of the sample. However producing samples of lower draw ratio can only be achieved if conditions can be found under which the necking phenomenon is not observed. Samples drawn at 85 °C were found to draw reasonably evenly and a sample of draw ratio 2.0 was obtained in this way. However it should be noted that this sample has been drawn below $T_g$ (all others are drawn above $T_g$) and it will not be included in discussions of trends with draw ratio, although it is included in the analysis to determine transition moment angles.

To determine the draw ratio of each sample dots were marked on the undrawn film at 2 mm intervals. After each sample had been drawn, a region over which drawing appeared even was analysed and the length of this region measured from one dot to another, and scaled by the separation of these dots.

### Polarization Spectroscopy

Infrared spectra were taken using a Bomem FT-IR Spectrometer over the range 200–5000 $cm^{-1}$ with resolution 4 $cm^{-1}$. A reference scan was taken at the beginning of each session which was subsequently subtracted from each sample spectrum. Each spectrum (including the reference spectrum) was built up over 100 scans. To prevent absorption of infrared radiation due to water vapour and carbon dioxide, the sample chamber was purged with dry nitrogen. To obtain the two polarised spectra the sample draw direction was mounted parallel, and then perpendicular to the pass direction of the polariser. The polariser itself remained in a fixed orientation to avoid any polarisation sensitivity of the optics within the spectrometer.

Before any peak fitting was carried out a linear baseline correction was applied to the data using the GRAMS32 software. Peak fitting was then undertaken using the GRAMS32 package in the range from 700–3200 $cm^{-1}$, allowing all peaks to be considered as a mixture of Gaussian and Lorentzian lineshapes. This was done with reference to assignments made by Ouchi et al.[6] The difference between the sum of the fitted peaks and the spectrum was minimised using a least squares residual optimisation procedure. Finally, when suitable fitted spectra had been obtained the

 

areas of the fitted peaks were tabulated against wavenumber for each draw ratio and $\langle P_2 \cos\theta_\mu \rangle$ was evaluated according to equation 2 for each band at all draw ratios.

### Compensation Microscopy

A compensating microscope was used to measure the birefringence ($\Delta n = n_3 - n_1$) of all samples.[8] A white light source was used in order that the zeroth order fringe could be identified.

Literature by Orchard and Ward,[9] Voice et al.[8] and Faust and Marrinan[10] suggests that for samples of high birefringence the phenomenon of fringe jumping may be encountered, and this was indeed found to be the case with PEN. Fringe jumping arises due to the differing dispersions of the sample and the compensator. This causes the black fringe to be observed in a position which does not correspond to the zeroth order. To overcome the problem of fringe jumping it is possible to scan across a sample from a region of low birefringence to the region where the measurement of birefringence is needed. The position of the zeroth order fringe can thus be tracked and its true position determined. This allows a graph of apparent fringe number versus true fringe number to be plotted, the slope of which was determined to be 1.159 for these PEN samples. However only 3 points could be obtained for this graph due to a lack of suitable samples.

### Refractometry

To determine the 3 mutually orthogonal refractive indices separately an Abbe Refractometer was used with sodium light source at a wavelength of 589.3 nm. To ensure good optical contact a coupling liquid was employed, which had a higher refractive index than the sample and a lower refractive index than the prism to ensure light entered the prism. This method allowed $n_1$ and $n_2$ (Figure 3) to be determined. However $n_3$ was only able to be determined directly for samples of very low draw ratio, since for samples of higher draw ratio $n_3$ was found to be greater than the refractive index of the prism in the refractometer.

### Differential Scanning Calorimetry

DSC measurements were carried out using a 2920 TA Instruments device in the temperature range from 30 °C to 300 °C using a heating rate of 10 °C /min. Sample weights were around 4 mg. Samples consisting of a flat single layer film were used to reduce heat flow lags. Baseline calibration was undertaken using indium. All samples were sealed in aluminium pans and the measurements were performed under a high purity helium atmosphere. The degree of crystallinity was calculated using the crystallization enthalpy of 190 J/g measured for a 100% crystalline PEN.[11]

## Results and Discussion

### Undrawn Material

For the undrawn sample ($\lambda = 1$) the refractive indices, $n_1$, $n_2$ and $n_3$, were found to be identical within the uncertainties, confirming that the original PEN film supplied by DuPont was isotropic (Table 1). This is also confirmed by the low measured birefringence. The mean refractive index of the undrawn film was found to be 1.647 and Miyata et al.[12] report similar a value; $n = 1.65$.

The DSC heat flow curve of the undrawn PEN (Figure 4) shows a $T_g$ at about 120 °C followed by cold crystallization at $T_c = 188$ °C and melting at $T_m = 268$ °C. The areas of the crystallisation and melting peaks for this film are identical (within experimental uncertainties) and confirm that the crystallinity of the supplied undrawn PEN is essentially zero.

### Development of Crystallinity with Draw Ratio

The uniaxially drawn PEN films display a sharp melting endotherm with a maximum located at a temperature similar to that of the undrawn sample. The cold crystallization peak disappears completely for all draw ratios higher than 2. It is suggested

 

***Table 1.***
Draw ratio, birefringence, refractive indices, $\langle P_2(\cos\theta)\rangle$ from birefringence using $\Delta n_o = 0.41$ and crystallinity of PEN samples.

| λ | Δn | $n_1$ | $N_2$ | $n_3$ | $\langle P_2(\cos\theta)\rangle$ | Crystallinity from DSC |
|---|---|---|---|---|---|---|
| 1.0 | 0.001 | 1.6461 | 1.645 | 1.65 | 0.002 | ~0 |
| 2.0 | 0.041 | 1.6148 | 1.610 | 1.66 | 0.100 | 1.6 |
| 3.6 | 0.234 | 1.608 | 1.578 | | 0.571 | 31.2 |
| 3.7 | 0.217 | 1.5895 | 1.579 | | 0.529 | 31.9 |
| 3.9 | 0.234 | 1.5968 | 1.57 | | 0.571 | 34.2 |
| 4.5 | 0.30 | 1.589 | 1.56 | | 0.732 | 35.4 |
| 5.0 | 0.30 | 1.5796 | 1.55 | | 0.732 | 36.2 |
| 5.7 | 0.29 | 1.5735 | 1.549 | | 0.707 | 37.2 |
| 6.1 | 0.31 | 1.573 | 1.547 | | 0.756 | 38.1 |

that the orientation induced by stretching triggers the increase of crystallization. As can be seen from Figure 5 the relationship between crystallinity and draw ratio indicates a rapid rise in crystallinity at low draw ratios and a levelling out at $\lambda > 4$.

## Development of Molecular Orientation with Draw Ratio

Huijits and Peters report in their work[13] that evidence is provided for the linear relationship between birefringence and molecular orientation and thus equation 1 is assumed a valid method for determining the overall orientation of the films.

To determine the average molecular orientation of the drawn films from equation 1 requires knowledge of the intrinsic birefringence of PEN. Several values are available in the literature. Huijits and Peters[13] have measured the birefringence of PEN samples and extrapolated to estimate the value for perfectly aligned molecules and quote a value of $\Delta n_0 = 0.487 \pm 0.017$, although they remark that this value is likely to be too high. Carr, Zhang and Ward[14] have calculated the intrinsic birefringence by summing the bond polarisabilities and quote a value of $\Delta n_0 = 0.332$. However they point out that this value is expected to be an underestimate due to the use of bond polarisability data for a benzene ring in the absence of suitable data for a naphthalene ring. Miyata et al.[12] report a value of $\Delta n_0 = 0.336$. In the light of this information an average value of $\Delta n_0 = 0.410$ was used in this research.

The refractive indices, $n_1$ and $n_2$, measured using the Abbe refractometer, are expected to be equal to each other for uniaxially drawn films, however, $n_2$ appears to be slightly lower than $n_1$ in all cases, nonetheless $(n_1 - n_2) \ll \Delta n$. This result hints at a preferential orientation relative to the sample surfaces. Such an effect is

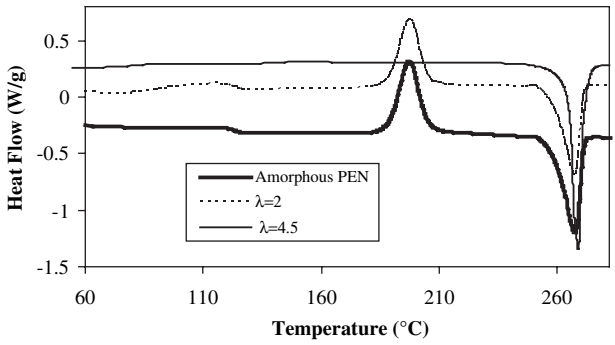


***Figure 4.***
DSC curves for undrawn and drawn (λ = 2 and 4.5) films, shifted vertically for clarity.

 

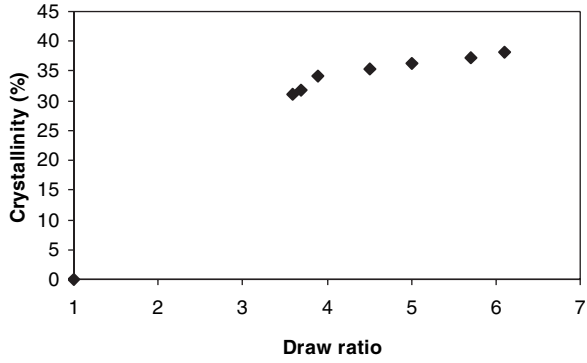


***Figure 5.***
Crystallinity from DSC versus draw ratio.

noted by Hayashi et al.,[15] Cakmak and Kim[16] and Murakami et al.[17] who all report that the naphthalene plane orients parallel to the broad surface of the film on both uniaxial and biaxial drawing. Thus it is concluded that the drawing process is not strictly uniaxial, but a close enough approximation to it.

A graph of $\langle P_2(\cos\theta)\rangle$ versus draw ratio can be seen in Figure 6. This shows a rapid rise at low draw ratio and a levelling out at draw ratios above 4.5. This suggests that the polymer is drawing according to the psuedo-affine regime[18] characteristic of semi-crystalline polymers. A comparison of Figures 5 and 6 shows a strong correlation between crystallinity and $\langle P_2(\cos\theta)\rangle$, although when plotted against each other the data is too clumped to conclude whether the relationship is strictly linear, but it certainly supports this idea.

### Development of Orientation of Specific Bands with Draw Ratio

The parallel and perpendicular spectra obtained for the most highly drawn PEN film are shown in Figure 7. The development of $\langle P_2(\cos\theta_\mu)\rangle$, obtained via polarised FT-IR spectroscopy, with increase in draw ratio is shown for selected bands in Table 2.

### Determining Transition Moment Angles

For each band considered $\langle P_2(\cos\theta_m)\rangle$ was evaluated using equation 3. A quadratic fit to a graph of $\langle P_2(\cos\theta_\mu)\rangle$ against $\langle P_2(\cos\theta)\rangle$ was used (since not all bands showed linear

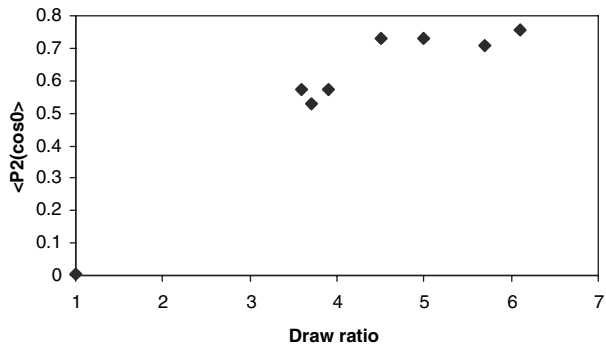


***Figure 6.***
Graph of $\langle P_2(\cos\theta)\rangle$ against draw ratio.

 

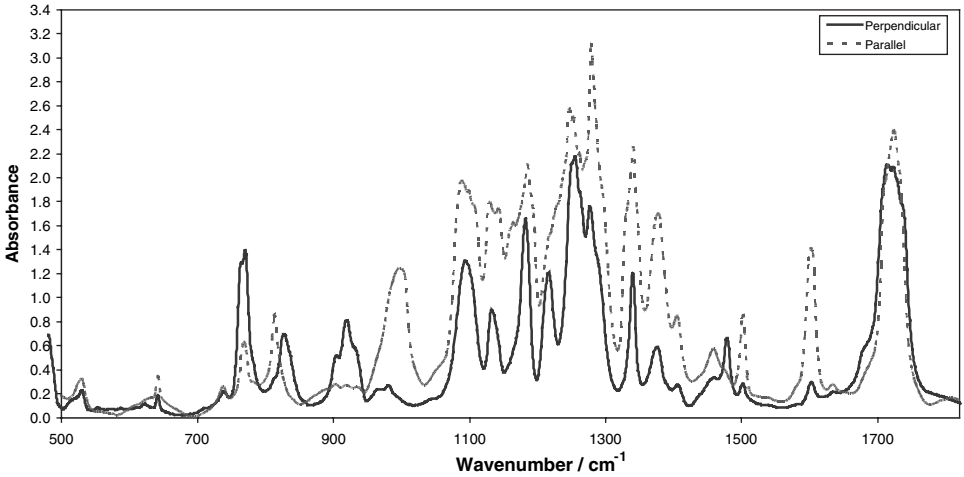


***Figure 7.***
Parallel and perpendicular spectra for drawn PEN film with draw ratio $\lambda = 6.1$.

behaviour). Four such plots are shown in Figure 8. Equation 4 was then used to evaluate $\theta_m$ from the local slope at low orientation ($\langle P_2(\cos\theta)\rangle = 0.01$) and high orientation ($\langle P_2(\cos\theta)\rangle = 0.8$) (Table 3). The choice of $\Delta n_0$ has a slight effect on the values of $\theta_m$ determined. But using the widest range of published values for $\Delta n_0$ affects $\theta_m$ by $< \pm 5^\circ$.

## Conclusions

The first obvious conclusion from Table 3 is that some bands (1047, 1376, 1502 and 1708 $cm^{-1}$) show a linear relationship between $\langle P_2(\cos\theta_\mu)\rangle$ and $\langle P_2(\cos\theta)\rangle$, and hence have no change of $\theta_m$ with overall molecular orientation. The band at 1602 $cm^{-1}$ can probably also be included in this group since at low angles there exists extreme sensitivity of $\theta_m$ to changes in $\langle P_2(\cos\theta_m)\rangle$.

Bands at 767 and 831 $cm^{-1}$ are seen to have transition moment angles approaching 90° as the molecular orientation increases. These two bands were assigned as ⊥ by Ouchi[6] and the work here supports this assignment for well oriented films. Further confirmation is provided when the nature of the vibrational assignments are considered; 767 $cm^{-1}$ is attributed to the out of plane bending of the aromatic ring CH groups (positions 3, 4, 5, 6, 7 and 8 in Figure 9) and 831 $cm^{-1}$ is attributed to the rocking of the trans $CH_2$ units in the aliphatic section of

***Table 2.***
$\langle P_2(\cos\theta_\mu)\rangle$ from FT-IR.

| λ | 767 $cm^{-1}$ | 831 $cm^{-1}$ | 1047 $cm^{-1}$ | 1084 $cm^{-1}$ | 1096 $cm^{-1}$ | 1130 $cm^{-1}$ | 1142 $cm^{-1}$ | 1333 $cm^{-1}$ | 1376 $cm^{-1}$ | 1502 $cm^{-1}$ | 1602 $cm^{-1}$ | 1708 $cm^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.0 | 0.001 | −0.021 | — 0.007 | — 0.013 | — 0.002 | 0.004 | 0.030 | — 0.010 | 0.014 | — 0.003 | — 0.004 | −0.018 |
| 2.0 | −0.053 | −0.094 | 0.046 | 0.059 | 0.027 | 0.050 | 0.024 | 0.024 | 0.053 | 0.070 | 0.030 | −0.035 |
| 3.6 | −0.145 | −0.130 | 0.177 | 0.073 | 0.085 | 0.085 | 0.130 | 0.388 | 0.331 | 0.070 | 0.539 | −0.223 |
| 3.7 | −0.185 | −0.232 | 0.185 | 0.102 | 0.130 | 0.173 | 0.178 | 0.403 | 0.378 | 0.240 | 0.545 | −0.180 |
| 3.9 | −0.187 | −0.158 | 0.186 | 0.087 | 0.128 | 0.207 | 0.200 | 0.330 | 0.308 | 0.246 | 0.479 | −0.222 |
| 4.5 | −0.209 | −0.277 | 0.211 | 0.180 | 0.208 | 0.288 | 0.294 | 0.397 | 0.452 | 0.243 | 0.657 | −0.286 |
| 5.0 | −0.282 | −0.309 | 0.222 | 0.160 | 0.135 | 0.356 | 0.351 | 0.364 | 0.441 | 0.439 | 0.643 | |
| 5.7 | −0.274 | −0.277 | 0.221 | 0.209 | 0.216 | 0.298 | 0.527 | 0.401 | 0.359 | 0.086 | 0.910 | |
| 6.1 | −0.322 | −0.322 | 0.301 | 0.148 | 0.214 | 0.346 | 0.392 | 0.469 | 0.490 | 0.201 | 0.687 | −0.264 |

 

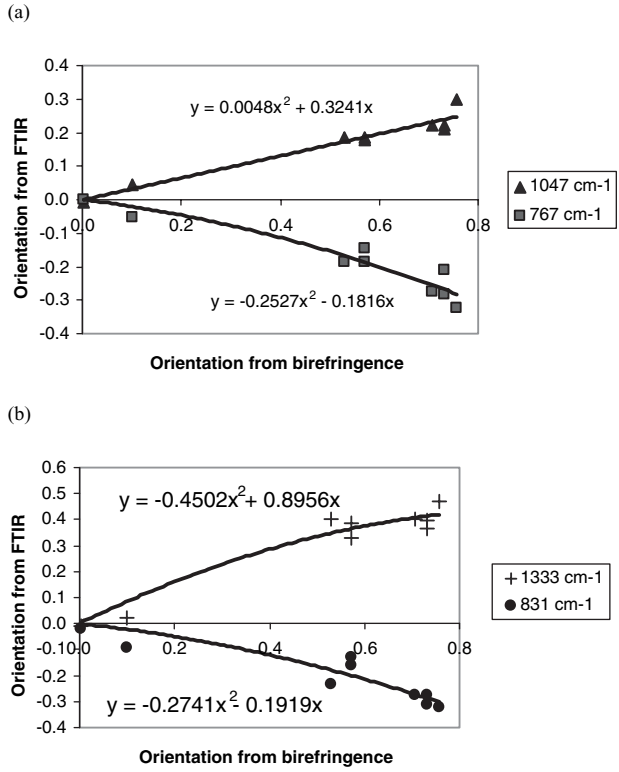


***Figure 8.***
Variation of molecular orientation determined from FT-IR, $\langle P_2(\cos\theta_\mu)\rangle$, for four transition moments, plotted against $\langle P_2(\cos\theta)\rangle$ determined from birefringence.

the chain (positions 11 and 12 in Figure 9). Both of these vibrations would intuitively be assigned as perpendicular to the chain axis.

Bands at 1130 and 1142 $cm^{-1}$ exhibit a large change of angle with increasing molecular orientation, although the transition moments become increasingly aligned to

***Table 3.***
Band positions, assignments (as reported by Ouchi et al.[6]) and the calculated angles of the transition moments with respect to the chain axis, $\theta_m$.

| Wavenumber ($cm^{-1}$) | Assignments[6] | $\theta_m$ (°) at low orientation | $\theta_m$ (°) at high orientation |
|---|---|---|---|
| 767 | Bending aromatic ring CH out of plane | 63 | 90[a)] |
| 831 | Crystal state only and assigned to the rocking of $CH_2$ Trans | 63 | 90[a)] |
| 1047 | Antisymmetric C–O stretching vibration | 42 | 42 |
| 1084 | Symmetric C–O stretching vibration | 52 | 38 |
| 1096 | Symmetric C–O stretching vibration | 51 | 37 |
| 1130 | Napthalene ring vibration | 58 | 0[b)] |
| 1142 | Napthalene ring vibration | 63 | 0[b)] |
| 1333 | Wagging in $CH_2$ Trans (crystal state formed by heating) | 16 | 48 |
| 1376 | Wagging in $CH_2$ Gauche (crystal state) | 31 | 31 |
| 1502 | Aromatic ring vibration | 40 | 44 |
| 1602 | Aromatic ring vibration | 17 | 0[b)] |
| 1708 | C=O stretching | 73 | 72 |

[a)] $\theta_m$ assumed to be 90° despite local gradient slightly >1 due to experimental uncertainty.
[a)] $\theta_m$ assumed to be 0° despite local gradient slightly <−0.5 due to experimental uncertainty.

 

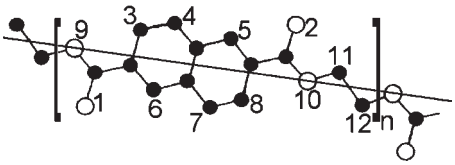


***Figure 9.***
Schematic representation of the PEN repeat unit (hydrogen atoms not shown). The long straight line represents the molecular chain axis.

the chain axis as the molecular orientation increases. This confirms Ouchi's assignment of the combined band at 1135 $cm^{-1}$ as being 'parallel', even if only for highly oriented films.

The band at 1602 $cm^{-1}$ also confirms Ouchi's assignment of this as a $\parallel$ band. However the band at 1708 $cm^{-1}$ due to the C=O stretching vibration (positions 1 and 2 in Figure 9), which is assigned by Ouchi as a $\perp$ band, is shown in this work to have an angle of 73° to the chain axis, independent of the degree of orientation of the molecules.

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