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Molecular orientation behaviour of thermally treated biaxially stretched poly(ethylene naphthalene 2,6 dicarboxylate) films studied by polarised infrared spectroscopy

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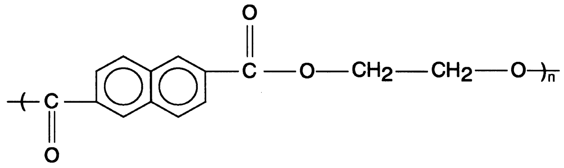
Abstract

PEN films of different morphologies have been studied by polarised infrared spectroscopy. These different structures have been obtained by thermally treating biaxially stretched PEN films. Calculations of orientation factors from the 767 and 1138 cm^{-1} bands which are characteristic of naphthalene ring vibrations predominantly in the amorphous phase show that the amorphous phase is significantly disoriented when annealed at a temperature of 260 °C despite the increasing crystallinity. © 2002 Published by Elsevier Science Ltd.

Keywords: Polarised FTIR spectroscopy; Poly(ethylene naphthalene 2,6 dicarboxylate); Orientation

1. Introduction

The naphthalene group in the repeat unit of poly(ethylene naphthalene 2,6 dicarboxylate) (PEN) as can be seen below gives a stronger rigidity to the macromolecular chain and hence superior mechanical properties than the phenylene groups in PET.



Such improved characteristics of PEN will favour its applications as films in capacitors, video tapes as well as in packaging. The investigation of the initial morphology (amorphous, semi-crystalline or oriented sample) and its evolution in terms of molecular mobility and structural analysis which in turn leads to a better knowledge of the physical properties of PEN films are essential to predict its aptitude to a given industrial application. Dynamic mechanical (DMA) and dielectric relaxation spectroscopy (DRS) have already been carried out on non-treated amorphous and thermally treated amorphous PEN and compared to non-treated semi-crystalline biaxially oriented PEN samples [1]. Infrared spectroscopy provides information on polymer chain conformations of solid polymers [2]. Many studies have been reported on IR analysis of polyethylene terephthalate (PET) [3–5] but only a few studies have been reported on the structural analysis of PEN with different morphologies [6–10] and never by polarised FTIR spectroscopy. Infrared spectroscopy can provide information on molecular orientation, and it has already been used together with Raman spectroscopy to study biaxial orientation in PET [11] but no literature has been found on a similar study of PEN.

2. Experimental

PEN samples were obtained from Du Pont de Nemours as biaxially stretched (draw ratio between 3 and 4 in each direction) films with a thickness of 2 μm. Studies were done on the virgin semi-crystalline PEN and on samples obtained by annealing the virgin one at annealing temperatures of 240, 250 and 260 °C. The thermal treatments were performed in the oven of a dynamic mechanical instrument (2980 TA instruments) described in Ref. [1] to achieve the same controlled conditions for each sample. The films were heated from room temperature to the annealing temperature

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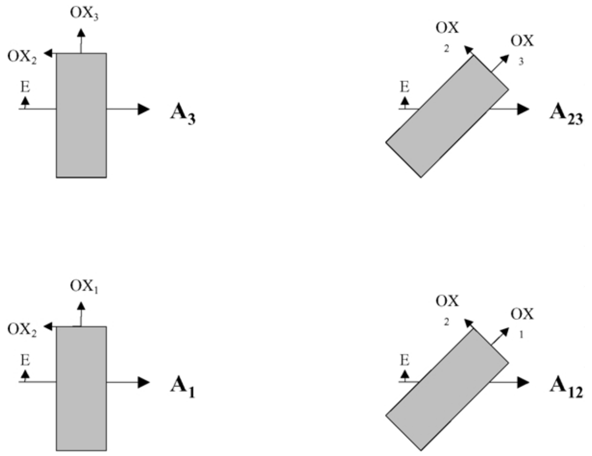

Fig. 1. Positioning of sample with respect to IR beam to obtain different absorbances.

at a rate of 20 °C/min. The annealing time was 1 h and after that period the sample was slowly cooled down to room temperature at a rate of −5 °C/min.

Unpolarised FTIR spectra were recorded in Lyon (France) using a 1760X FTIR spectrometer from Perkin–Elmer in the transmission mode using 2 cm^{-1} resolution and 30 scans. In order to avoid saturation in absorbance it was compulsory to use the 2 μm biaxially stretched PEN samples. The peak at 767 cm^{-1}, insensitive to crystallinity and due to deformation of aromatic CH out-of-plane has been taken as a reference to compare the peak areas of two peaks: 1332 cm^{-1} ($\gamma_w(CH_2)$ *trans*) and 1094 cm^{-1}, (ν_s(O–C) *gauche*) to see their evolution with crystallinity.

Polarised IR spectra were obtained using a Perkin–Elmer 580B double-beam dispersive spectrometer in Leeds, UK. Polarisers were mounted in both the sample and reference beam paths to polarise the incident infrared radiation. The PEN film was then placed in the sample beam in four different orientations as shown in Fig. 1. To mount the sample plane at 45° to the incident beam the film was pressed between two right-angled KBr prisms (see Fig. 2), using nujol (liquid paraffin) as a liquid of similar refractive index to PEN, to minimise multiple reflections within the thin film. Spectra obtained in this way are known as tilted film spectra. All spectra were collected in transmission mode with a resolution of approximately 2 cm^{-1}. Corrections were made to the raw absorbance data to account for imperfections in the polarisers, reflection losses within the sample and internal field effects, according to the methods described by Abell [12]. In order to do all the corrections, the refractive indices in the three dimensions were measured with an Abbe refractometer (prism with refractive index $n \sim 1.7$) ZEISS MT449 with a sodium light source. Bowing found at 30° with respect to the machine direction (and 60° with respect to the transverse direction) means that the PEN film sags in the centre when it is stretched.

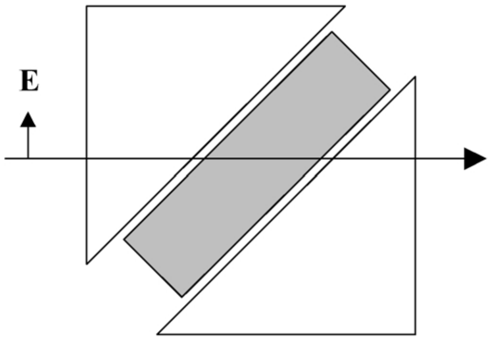

Fig. 2. PEN film sandwiched between KBr prisms for tilted film measurements.

3. Theory of orientation analysis from polarised IR measurements

To describe the orientation of the PEN chain with respect to the film, axes $OX_1X_2X_3$ are defined in the film where OX_3 is the machine direction, OX_1 is the transverse direction in the plane of the film, and OX_2 is perpendicular to the film plane. It is then necessary to define a set of axes in the naphthalene ring, $Ox_1x_2x_3$, where Ox_3 is along the local chain direction in the naphthalene ring, Ox_1 is in the plane of the ring but perpendicular to Ox_3, and Ox_2 is perpendicular to the ring plane. Euler angles θ, ϕ and ψ as defined in the paper by Jarvis et al. [11] are then used in the orientation functions, where θ and ϕ are the polar and azimuthal angles, respectively, of Ox_3 to the $OX_1X_2X_3$ system, and the angle ψ represents a rotation of the Ox_3 axis which takes Ox_1 out of the x_3X_3 plane.

Since infrared spectroscopy is sensitive to dipole moment changes (transition moments) within the sample yet another set of angles must be defined. These are θ^{rc} and ϕ^{rc}, where θ^{rc} is the angle between the transition moment and the local chain axis, Ox_3, and ϕ^{rc} is the azimuthal angle of the transition moment (i.e. the angle between Ox_1 and the projection of the transition moment in the Ox_1x_2 plane). The superscripts ‘rc’ represent angles between the ‘ring vibration’ and the ‘chain’.

In order to characterise the biaxial orientation of the PEN molecules with respect to the film axes ($OX_1X_2X_3$) it is necessary to determine all four second order moments of the orientation distribution function, $\mathbf{P}_{200}$, $\mathbf{P}_{220}$, $\mathbf{P}_{202}$ and $\mathbf{P}_{222}$ (as defined by Jarvis et al. [11]). However, infrared spectra only allow the determination of the orientation of the *transition moments* with respect to the sample axes. By utilising the structural information given by the band assignments (namely, the values of θ^{rc} and ϕ^{rc}) and the Legendre addition theorem, it is possible to obtain the required orientation functions from Eqs. (1) and (2) [12,13].

$$\mathbf{P}^{\mathrm{r}}_{200} = \mathbf{P}^{\mathrm{rc}}_{200}\mathbf{P}_{200} + 12\mathbf{P}^{\mathrm{rc}}_{220}\mathbf{P}_{202} \tag{1}$$

$$\mathbf{P}^{\mathrm{r}}_{220} = \mathbf{P}^{\mathrm{rc}}_{200}\mathbf{P}_{220} + 2\mathbf{P}^{\mathrm{rc}}_{220}\mathbf{P}_{222} \tag{2}$$

where $\mathbf{P}^{\mathrm{r}}_{lmn}$ are orientation functions of the transition moment with respect to the film axes $OX_1X_2X_3$, $\mathbf{P}^{\mathrm{rc}}_{lmn}$ are

Table 1
Angles and values of $\mathbf{P}^{\mathrm{rc}}_{200}$ and $\mathbf{P}^{\mathrm{rc}}_{220}$ for the bands at 767 and 1138 cm^{-1}

Band (cm^{-1})	θ^{rc} (°)	ϕ^{rc} (°)	$\mathbf{P}^{\mathrm{rc}}_{200}$	$\mathbf{P}^{\mathrm{rc}}_{220}$
767	90	90	− 0.5	− 0.25
1138	0	0	1	0

Only approximate values are quoted for the band at 1138 cm^{-1} due to the lack of published information on the exact direction of the transition moment.

orientation functions of the transition moment with respect to the chain axes $Ox_1x_2x_3$, $\mathbf{P}_{lmn}$ are orientation functions of the chain with respect to the film axes $OX_1X_2X_3$.

A least squares computer fitting procedure was used to fit a mixture of Lorentzian and Gaussian lineshapes to each peak in the four tilted film spectra yielding the four absorbances (peak areas) A_1, A_3, A_{12} and A_{23} for each band analysed; where the subscripts refer to axes in the sample. Only one of A_{12} and A_{23} is needed in combination with A_1 and A_3 to determine the absorption along all three sample axes. Corrections for non-perfect polarisation of the incident radiation, multiple reflections within the thin film and internal field effects [11,12] yield corrected absorbances ϕ_1, ϕ_2 and ϕ_3. These absorbances are related to the orientation functions by

$$\frac{\phi_1 - \phi_2}{\phi_1 + \phi_2 + \phi_3} = 4\mathbf{P}^{\mathrm{r}}_{220} \tag{3}$$

$$\frac{2\phi_3 - \phi_1 - \phi_2}{\phi_1 + \phi_2 + \phi_3} = 2\mathbf{P}^{\mathrm{r}}_{200} \tag{4}$$

From the band assignments (values of θ^{rc} and ϕ^{rc}) it is possible to determine the $\mathbf{P}^{\mathrm{rc}}_{lmn}$ from

$$\mathbf{P}^{\mathrm{rc}}_{200} = \frac{1}{2}(3\cos^2\theta^{\mathrm{rc}} - 1) \tag{5}$$

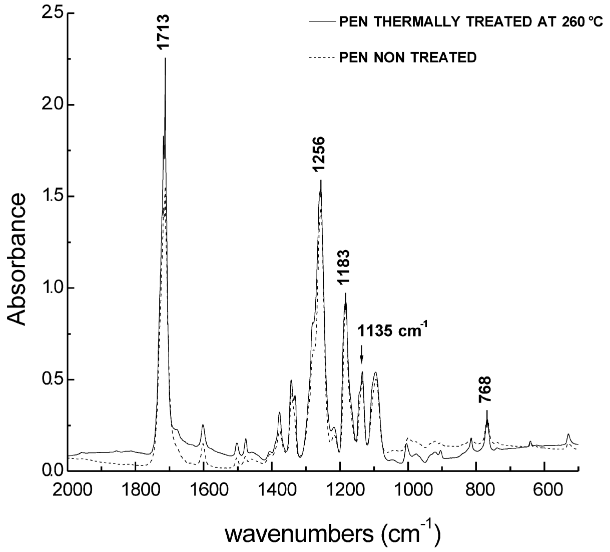

Fig. 3. Unpolarised FTIR spectra in the range 2000–500 cm^{-1} of non-treated (dashed line) and annealed at 260 °C (solid line) semi-crystalline biaxially stretched PEN films.

$$\mathbf{P}^{\mathrm{rc}}_{220} = \frac{1}{4}((1 - \cos^2\theta^{\mathrm{rc}})\cos 2\phi^{\mathrm{rc}}) \tag{6}$$

Thus by choosing a suitable pair of bands it is possible to use Eqs. (3)–(6) for each band to solve Eqs. (1) and (2) for $\mathbf{P}_{200}$, $\mathbf{P}_{220}$, $\mathbf{P}_{202}$ and $\mathbf{P}_{222}$.

The two infrared vibrations studied in this paper were the bands at 767 and 1138 cm^{-1}, both of which are assigned to vibrations of the naphthalene ring. The band at 767 cm^{-1} is attributed to a CH out of plane bending mode for which θ^{rc} is 90° and ϕ^{rc} is 90°. The band at 1138 cm^{-1} is assigned (by Ouchi et al. [6]) as a parallel vibration due to a naphthalene ring vibration and for quantitative analysis it has been assumed here that θ^{rc} and ϕ^{rc} are both zero. These angular values generate values of $\mathbf{P}^{\mathrm{rc}}_{200}$ and $\mathbf{P}^{\mathrm{rc}}_{220}$ as shown in Table 1. A lack of published information of the exact direction of these vibrational transition moments precludes a more accurate analysis here.

4. Results

4.1. FTIR unpolarised spectra

Fig. 3 shows the whole range FTIR spectra without polarisation of the non-treated semi-crystalline biaxially oriented PEN film and the biaxially stretched PEN film annealed at 260 °C. When the biaxially stretched PEN sample is heated the crystallinity increases. It was already known that the crystallinity increases with annealing temperature from a previous study using DSC [14]. Since *trans* conformation is characteristic of the crystalline state whereas *gauche* conformation is characteristic of amorphous state it would be expected that the quantity of *trans* conformers increase and the quantity of *gauche* conformers decrease on heat treating. Peaks which are characteristic of the crystalline state, according to Ouchi et al. [6] appear on the treated sample (1332, 1005, 905, 835, 810 cm^{-1}) but are less intense on the untreated biaxially stretched sample (see Fig. 4 in the case of the band at 1332 cm^{-1}).

However, the peaks characteristic of amorphous conformation (*gauche* at 1094, 1043, 1371, 1453 cm^{-1}) do not decrease with the increase of annealing temperature (see Fig. 5 in the case of the band at 1094 cm^{-1}). This is shown in Table 2 for the two peaks chosen: the band at 1332 cm^{-1} being sensitive to *trans* conformation and the band at 1094 cm^{-1} being sensitive to *gauche* conformation. Ouchi et al. [6] have stated that the 1135 and 1180 cm^{-1} band intensities (naphthalene ring vibrations) should decrease when crystallinity increases and this is not what is observed in our case (see Fig. 3). The intensities of these two peaks increase with thermal treatment and thus with increase of crystallinity. The initial drawing process produces a highly stretched molecular network with predominantly oriented *trans* conformations [15]. The increase in *gauche* conformations observed on annealing could, therefore, be

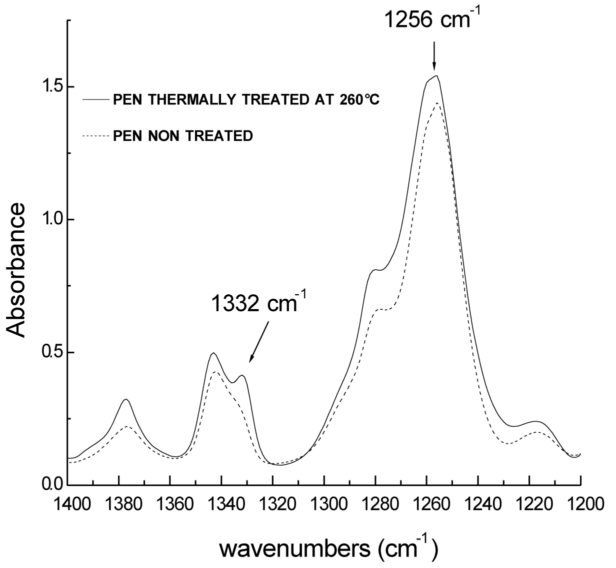

Fig. 4. Unpolarised FTIR spectra in the range 1400–1200 cm^{-1} showing the increase in the crystalline peak intensity at 1332 cm^{-1} with heat treatment.

attributed to disorientation of the amorphous phase. It appears that this effect is greater than any decrease of *gauche* conformations due to increasing crystallinity.

FTIR is a reliable method to follow changes in morphology but in this case two factors are changing simultaneously and in opposite directions (crystallinity and orientation) so it was difficult to make conclusions about the evolution of the *gauche* conformation with crystallinity. Orientation and morphology have been studied in PEN with X-rays and Pole figures [16]. To complete this orientation study, the FTIR polarisation method was planned in order to try to quantify the orientation of the amorphous phase and prove that this phase was disorienting at the same time as annealing occurred.

4.2. Polarisation study

Spectra corresponding to film mounting positions to yield A_1, A_3 and A_{23} (see Fig. 1) were obtained for the untreated biaxial sample and the biaxial samples annealed at 240, 250 and 260 °C. Peak areas were determined for the bands at 767 and 1138 cm^{-1} by using a least squares computer fitting procedure to fit a mixture of Lorentzian and Gaussian lineshapes to each peak, and corrections made for non-perfect polarisation of the incident radiation, multiple reflections within the film and internal field effects, the latter making use of the refractive indices of the films as measured using an Abbe refractometer.

Table 2
Band area evolution with thermal treatment for the bands at 1332 and 1094 cm^{-1}

PEN (2 μm)	Non-treated	Treated at 260 °C	Assignment [5]
A_{1332}/A_{767}	3.5	4.5	$\gamma_w(CH_2)$ *trans*//crys.
A_{1094}/A_{767}	5.9	6.95	ν_s(O–C) *gauche*//

Table 3
Orientation functions for the four PEN samples studied: untreated, and heat treated at 260 °C

	$\mathbf{P}_{200}$	$\mathbf{P}_{220}$	$\mathbf{P}_{222}$	$\mathbf{P}_{202}$
Untreated	0.30	0.15	−0.28	−0.07
260 °C	0.11	0.07	−0.20	−0.03

Using Eqs. (3) and (4) $\mathbf{P}^r_{200}$ and $\mathbf{P}^r_{220}$ were determined for each band, and along with Eqs. (5) and (6) were used to solve Eqs. (1) and (2) for the orientation functions (shown in Table 3) for the local chain axes in the naphthalene rings with respect to the sample stretching axes. However, the nature of the biaxial orientation is more easily pictured if the square of the direction cosines, $\langle \cos^2(x_iX_i) \rangle$, are evaluated rather than the four orientation functions $\mathbf{P}_{200}$, $\mathbf{P}_{220}$, $\mathbf{P}_{202}$ and $\mathbf{P}_{222}$. Equations relating the direction cosines to the orientation functions are given by Jarvis et al. [11]. Table 4 shows the related angles for all pairs of axes, x_iX_i, for untreated and annealed films.

5. Discussion

As can be seen from Table 4 the untreated biaxially oriented PEN film has the local chain axis in the naphthalene ring oriented preferentially in the plane of the film (since the angle between x_3 and X_2 is close to 90°), but with no preferred orientation with respect to X_1 or X_3 (since the angles of x_3 to X_1 and X_3 are approximately equal to each other, and both close to 54.7°, the angle corresponding to random orientation).

The untreated biaxial film also shows a very slight preferential orientation of the naphthalene ring normals to

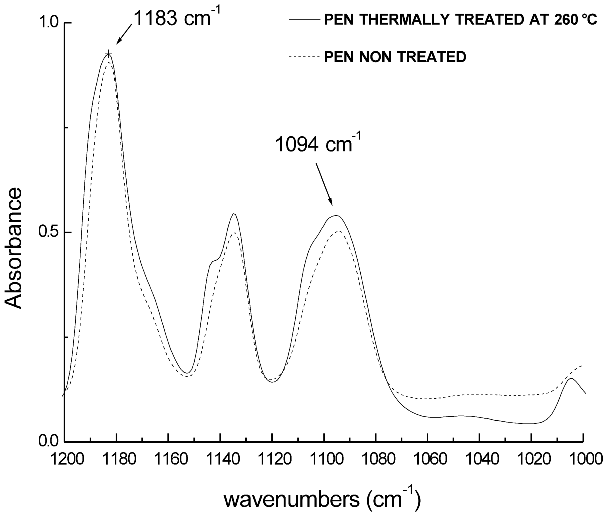

Fig. 5. Unpolarised FTIR spectra in the range 1200–1000 cm^{-1} showing the increase in the *gauche* band intensity at 1094 cm^{-1} with thermal treatment.

Table 4
Angles corresponding to the direction cosines for the four PEN samples studied; untreated, and heat treated at 260 °C

Samples	Angles (in degrees) between axes in naphthalene ring and sample								
	x_1X_1	x_1X_2	x_1X_3	x_2X_1	x_2X_2	x_2X_3	x_3X_1	x_3X_2	x_3X_3
Untreated	78	19	75	49	65	52	42	82	43
260 °C	70	36	62	48	65	52	49	66	50

be in the plane of the film (since the angle between x_2 and X_2 is 65°). Again no real preference for orientation towards X_1 or X_3 is shown (since the angles x_2 makes with X_1 and X_3 are approximately equal and close to 54.7°).

Comparison between the film annealed at 260 °C and the untreated film shows a reduction in orientation with annealing for x_1 and x_3 with respect to all sample axes (X_1, X_2 and X_3) (since all angles reduce (or increase) towards 54.7°). In particular the angle for x_3 with respect to X_2 shows a large reduction suggesting that as the biaxial film is heat treated the orientation of the local chain axis in the naphthalene rings to the plane of the film is significantly reduced. It is interesting to note that the angles of x_2 with respect to the sample axes (X_1, X_2 and X_3) do not significantly change with heat treatment. However, these angles are quite close to 54.7° even before heat treatment and hence it appears that the orientation of the naphthalene ring planes is essentially random (with perhaps very slight preference for out of plane orientation as mentioned above) regardless of heat treatment.

Since the band at 1138 cm^{-1} has been attributed to the amorphous regions of PEN by Ouchi [6] and the band at 767 cm^{-1} reported to be insensitive to crystallinity [5], the above analysis is a strong evidence for the reduction in amorphous orientation with annealing at 260 °C. Thus the increase in *gauche* conformers on annealing (along with increased crystallinity) can be explained by a reduction in the orientation of the amorphous phase.

6. Conclusion

The polarised IR spectroscopic analysis of heat treated biaxially oriented PEN films undertaken here was to explain the apparent discrepancy between increasing crystallinity upon annealing with a corresponding increase in the *gauche* conformer content. Bands at 1138 cm^{-1} (characteristic of the amorphous phase) and 767 cm^{-1} (insensitive to crystallinity) have been analysed to reveal a reduction in the amorphous orientation with annealing at 260 °C.

Acknowledgments

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