

## ***Trans-Gauche Rotational Isomers in Partially Oriented Poly(ethylene Terephthalate) Fibers\****

The structural characterization of poly(ethylene terephthalate) (PET) fibers has received considerable attention in order to understand better the relationship between structure and fiber properties and because of interest in how the polymer crystallization process is influenced by parameters such as stress and temperature. In particular, the variation in structure of the as-spun fiber with increasing wind-up speed has been studied extensively.<sup>1-3</sup> At relatively low (<1000 m/min) wind-up speeds the as-spun fiber is amorphous and has little preferential molecular orientation. With increasing wind-up speed the degree of orientation is increased as evidenced by, for example, increasing birefringence<sup>3,4</sup> until at high wind-up speeds (>4000 m/min) extensive crystallization occurs and the properties of the fibers begin to resemble those of a drawn fiber (i.e., higher breaking strength, lower elongation to break).<sup>1,3,5</sup>

We report here structural characterization data concerning a series of partially oriented PET fibers prepared with wind-up speeds of 2000–3500 m/min. These as-spun fibers, supplied by Courtaulds Ltd., Coventry, England, were of round cross section, semimatt (0.4% TiO<sub>2</sub>), 32 filaments per yarn, and of nominally constant diameter (270 dtex/yarn). In particular, we have examined the proportions and degree of orientation of the trans and gauche rotational isomers of the ethylene glycol moiety in the repeat unit as a function of wind-up speed. The importance of these data relates to the fact that only the trans rotational isomer exists in the crystalline state, and so the proportion and degree of orientation of this isomer will greatly influence the subsequent crystallization of the fiber.

The rotational isomers were examined by infrared (IR) spectroscopy using a Nicolet 7199 Fourier transform (FT) IR spectrometer. IR measurements were made within six days of the fibers being spun. A carefully aligned fiber array was placed on a salt disc together with a small amount of paraffin oil, which had the effect of reducing the amount of radiation scattered by the sample and also of improving the alignment of the fibers by enhancing interfiber contact. The absorptions owing to paraffin oil were subsequently digitally subtracted using the FTIR minicomputer.

The absorption band at 973 cm<sup>-1</sup> was used as a measure of trans content, the 898-cm<sup>-1</sup> absorption as a measure of gauche content, and the 632-cm<sup>-1</sup> absorption was used as an internal reference since it is common to both isomers.<sup>6,7</sup> The 988-cm<sup>-1</sup> band from chain folding in the crystals<sup>8,9</sup> was weak in all samples and intensities could not be reliably determined. Band intensities and dichroic ratios were extracted from the spectra using the spectral subtraction capability of the FTIR. For example, when the polarizer 90° spectrum was subtracted from the polarizer 0° spectrum until the band being examined decreased to zero, the scaling factor used in the subtraction then corresponded to the dichroic ratio of that band. Spectral subtraction was also used to resolve overlapping bands so as to allow more reliable baselines to be drawn when calculating band intensities.

To determine the proportion of the isomers, it was necessary to remove the effects of orientation from the spectra, and so the optical relationship, eq. (1), valid for samples with cylindrical symmetry, was used<sup>10</sup>:

$$\text{absorbance} = \frac{1}{3} [\text{absorbance} (\parallel) + 2 \text{absorbance} (\perp)] \quad (1)$$

where absorbance ( $\parallel$ ) and absorbance ( $\perp$ ) refer to the absorbances of the band with the polarizer parallel ( $\parallel$ ) and perpendicular ( $\perp$ ) to the fiber axis. The absorbances of the trans (973 cm<sup>-1</sup>) and gauche (898 cm<sup>-1</sup>) bands could then be ratioed to the common (632 cm<sup>-1</sup>) band to provide indices of trans and gauche content. The limiting dichroic ratio ( $DR_0$ ) of the 973 cm<sup>-1</sup> trans absorption, corresponding to perfect alignment of the polymer chains with the fiber axis, was assumed to equal the value (~2.9) we observed in a highly drawn crystalline fiber sample where x-ray analysis indicated that the crystalline (i.e., trans) orientation was very high. Hermans–Stein orientation functions were then calculated<sup>10</sup> using eq. (2):

$$f = (DR - 1)(DR_0 + 2)/(DR + 2)(DR_0 - 1) \quad (2)$$

Other characterization techniques used included density measurements (water/sodium bromide column), wide-angle x-ray scattering (WAXS, Cu K $\alpha$  radiation), small-angle light scattering (SALS),<sup>11</sup>

\* Issued as NRCC #18317.

stress-strain measurements, and birefringence ( $\Delta n$ ). For totally amorphous fibers, when the form birefringence is neglected, the average orientation (birefringence does not differentiate between trans and gauche isomers) is then given by eq. (3),

$$\Delta n = f_a \Delta n_a \quad (3)$$

where  $\Delta n_a$  is the intrinsic birefringence of amorphous PET. It should be noted that some disagreement exists in the literature<sup>4,10</sup> concerning the absolute value of  $\Delta n_a$ . We have selected the relatively low value<sup>12</sup> of  $\Delta n_a = 0.20$  so that  $f_a$  will represent an upper limit of amorphous orientation, for comparison with the trans orientation from IR measurements.

Several characteristic fiber properties are listed in Table I. These data are included to facilitate comparison with previously published characterization studies on partially oriented PET fibers.<sup>1-5</sup> Wind-up speed alone is an unreliable parameter for comparing fibers from different laboratories, since other spinning parameters may vary. WAXS analysis, as expected,<sup>1</sup> showed no sign of discrete crystalline reflections even for the 3500 m/min sample. SALS examination showed that a poorly defined superstructural ordering did exist, as has been demonstrated in other as-spun PET fibers,<sup>11</sup> but the scattering of light by  $\text{TiO}_2$  particles limited the usefulness of this technique. It may be concluded from these data that the fibers were almost completely amorphous but increased in degree of orientation with increasing wind-up speed.

The structural information obtained from the IR and birefringence measurements is shown in Table II. The trans content is expressed as a trans index and not directly as percent trans because of difficulties in accurately obtaining the necessary conversion factor. By subtracting spectra of samples with different trans content and scaling the gauche bands to zero, it was determined, however, that the pure trans isomer corresponded to a trans index of  $\sim 10$  in these samples, implying the trans content was  $< \sim 20\%$ . This conversion factor is, however, very approximate and applies only to this series of samples, since changes in band shape which occur, for example, on annealing the sample<sup>7</sup> will alter the conversion factor. It should also be noted that the orientation of the gauche form is expressed only as the dichroic ratio of the  $898\text{-cm}^{-1}$  band and not as an orientation function ( $f$ ) because of the lack of an independent measurement of gauche orientation to allow the estimation of  $DR_0$  for eq. (2). An upper limit of the gauche orientation function may, however, be obtained by

TABLE I  
Characteristics of Partially Oriented PET Fibers

Wind-up speed m/min	Density, $\text{g/cm}^3$	Birefringence $\times 10^3$	Tensile strength, <sup>a</sup> $\text{dyn/cm}^2 \times 10^9$	Elongation at break, <sup>a</sup> %
2000	1.341	18.1	1.8	273
2500	1.342 <sub>5</sub>	24.0	2.3	230
3000	1.343 <sub>5</sub>	35.5	2.9	195
3500	1.344 <sub>5</sub>	49.2	3.2	155

<sup>a</sup> Yarn deformed at 100%/min at 25°C and 60% RH.

TABLE II  
Structural Information for Partially Oriented PET Fibers

Wind-up speed, m/min	Trans index <sup>a</sup>	$DR_{\text{trans}}^b$	$DR_{\text{gauche}}^b$	$f_a^c$	$f_{\text{trans}}^d$
2000	1.34	1.40	1.11	0.09	0.30
2500	1.38	1.70	1.17	0.12	0.49
3000	1.56	2.03	1.17	0.18	0.66
3500	1.84	2.28	1.21	0.25	0.77

<sup>a</sup> Absorbance  $973\text{ cm}^{-1}$ /absorbance  $632\text{ cm}^{-1}$ .

<sup>b</sup> Dichroic ratio = absorbance ( $\parallel$ )/absorbance ( $\perp$ ).

<sup>c</sup>  $f_a$  calculated from birefringence; see text.

<sup>d</sup> From eq. (2) using  $973\text{ cm}^{-1}$  dichroism.

substituting for  $DR_0$  in eq. (2) the observed dichroic ratio (2.0) for a highly drawn fiber. For example, it may then be concluded that the gauche orientation function for the 3500 m/min sample was  $<0.26$ . The true value is probably much lower than this.

It is clear from the data in Table II that extensive structural changes are occurring in the range of wind-up speeds 2000–3500 m/min. These changes appear only as a slight increase in amorphous orientation as measured by conventional characterization techniques such as birefringence and WAXS. IR measurements, however, show that the increased orientation is associated with an increase in the proportion of the trans isomer. The level of orientation of this isomer ( $f_{\text{trans}}$ ) is also much higher than the level of orientation ( $f_a$ ) in the fiber as a whole. Because only the trans form exists in the crystalline state and because of the well-known relationship between crystallization rate of PET and degree of orientation,<sup>13</sup> it is reasonable to conclude that the increase in trans component being observed here is the forerunner of the extensive crystallization that occurs<sup>1,3</sup> at higher wind-up speeds. These observations are also consistent with the concept of an intermediate (between amorphous and crystalline) phase in PET.<sup>4,14,15</sup> The trans rotational isomer is concentrated in this phase. The positions of the IR absorptions of the rotational isomers are known to be dependent on whether they are present in the amorphous or crystalline regions.<sup>7</sup> In principle, therefore, even more structural information should be accessible to IR spectroscopy, and this possibility is being explored further.

The authors are grateful to Dr. P. J. Akers of Courtaulds Ltd. for supplying the fiber samples.

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Received November 26, 1979