

Characterization of the Physical and Molecular Structure of Thermally Elongating Poly(ethylene terephthalate) Fibers

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ABSTRACT: The mechanism of thermally induced elongation in poly(ethylene terephthalate) fiber spun at 3500 m min⁻¹ has been examined. This partially oriented fiber has a crystalline content of about 25% and a high degree of orientation. The effect of time and tension during heat treatment was examined, and it was found that yarns that were allowed to relax during an initial brief heat treatment at 130°C subsequently elongated by up to 5% during a long heat treatment at the same temperature. Yarns that were not allowed to relax during the brief heat treatment did not elongate on subsequent heating. The morphological and mechanical changes associated with these processes have been studied using differential scanning calorimetry, X-ray diffraction (XRD), birefringence measurement, microscopy, and tensile testing. A large increase in crystallinity was observed during the brief heat treatment, but a much smaller increase took place during the long heat treatment. XRD indicated that substantial crystal reorganization occurred during both heat treatments, but *c*-axis growth was most significant in those materials that elongated during long heat treatment. It is proposed that it is this *c*-axis growth, in conjunction with conversion of disordered amorphous material into oriented crystalline material, that is responsible for the observed elongation. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 989–995, 1997

Key words: poly(ethylene terephthalate); fibers; heat treatment

INTRODUCTION

Most yarns made from poly(ethylene terephthalate) (PET) and from other synthetic fiber-forming materials undergo some degree of shrinkage when heat-treated; and the reasons for this, usually associated with relaxation of longitudinal amorphous orientation and crystal growth, are well understood. With PET, crystallization from the melt is hindered by the bulky nature of the repeat unit; and as the glass transition occurs well above room temperature, the slow approach to equilibrium has considerable technological consequences. It is usual to heat set yarns to give a controlled crystal

structure and to stabilize properties, and the work of Gupta^{1–3} (for example) is notable here.

Yarn containing a proportion of fibers that undergo elongation on heat treatment would be attractive for textile applications requiring bulking. Process development within the Asahi Chemical Industry Company had identified a particular set of fiber orientation and yarn heat treatment conditions that gave materials, which showed appreciable elongation during heat treatment, and the work described here was an attempt to elucidate the underlying molecular mechanisms. The investigation concentrated on physical characterization of fibers extruded at approximately 30 m min⁻¹ and wound at a speed of 3500 m min⁻¹, and referred to here as partially oriented yarn. It has been recognized^{4,5} that at around this spinning speed, PET fibers change in character. Fibers

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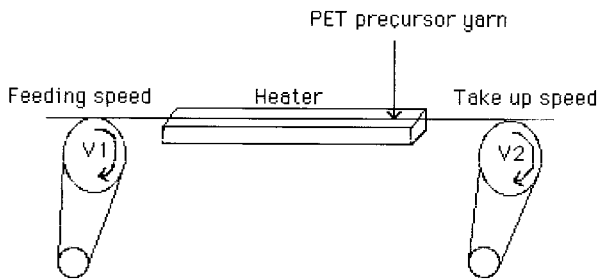


Figure 1 Apparatus used for brief heat treatment.

spun at speeds below about 3500 m min^{-1} show only a slight dependence of crystallinity on spinning speed, whereas those spun at higher speeds show a sharp increase in crystallinity with speed. Clearly, the change in the fiber morphology was important; therefore, the experimental techniques used were primarily those which measure the crystalline and amorphous orientation functions and the total degree of crystallinity, with electron microscopy and tensile testing being used to provide additional information.

EXPERIMENTAL

The PET was synthesized by the Asahi Chemical Industry Company and had a number average molecular weight of 22,000. Heat treatment experiments were carried out on yarn consisting of twenty fibers melt spun at 3500 m min^{-1} . The yarn was subjected to a two-stage process consisting of a brief heat treatment period, during which the time, temperature, and degree of relaxation were variable, and then a long heat treatment under a standard temperature and time condition and with zero tension. Brief heat treatment was carried out by running yarn over a hot plate set at 130°C between controlled speed feed and take up rollers. The simple apparatus used is illustrated in Figure 1. Contact time with the hot plate was 0.75 s, and the degrees of relaxation used, defined as the ratio of the take up speed to the feed speed, were 0.546, 0.60, 0.75, 0.90, and 1.00. Before the long heat treatment, an appropriate length of yarn was extended under a 200 g load, and the precise length was established. Long heat treatment was carried out without tension in an oven at 130°C for 20 min, following which the yarn length was remeasured, and the extension or contraction calculated.

Crystallographic examination was on a Rigaku diffractometer using a copper K_α source. The PET unit cell is triclinic with a repeat distance of

10.75\AA ,⁶ which is slightly less than the length of a fully extended repeat unit. The crystalline orientation function f_c is defined by

$$f_c = \frac{1}{2}(3 \cos^2\varphi - 1)$$

where φ is the angle between a chain axis and the fiber axis. An equatorial scan was used to resolve the main peaks corresponding to the (010), (100), and (110) reflections, and the 2θ position corresponding to the highest intensity peak was noted. The detector was then reset at this angle, and the sample rotated through 180 degrees for a meridional scan. For PET, the (105) plane is about 9–10 degrees off the fiber axis; and as it gives an easily measurable reflection, it can be conveniently used for approximation of the crystallite size along the c -axis. Setting the sample 10 degrees off the horizontal position and scanning the detector between 30 and 60 degrees gives the (105) reflection at approximately 42 degrees. Apparent crystal sizes were determined using the Scherrer equation without correcting for lattice distortion.

Birefringence was measured using a polarizing microscope and a compensator. The intrinsic birefringence of the crystalline and amorphous phases, ΔN_{ao} , and ΔN_{co} , respectively, were taken to be 0.29 and 0.20⁷; and the amorphous orientation function was calculated using the following relationship:

$$\begin{aligned} \Delta N &= X_v \cdot \Delta N_c + (1 - X_v) \Delta N_a \\ \Delta N_c &= f_c \cdot \Delta N_{co} \\ \Delta N_a &= f_a \cdot \Delta N_{ao} \end{aligned} \quad (1)$$

where ΔN is the total birefringence, ΔN_c and ΔN_a are the crystalline and amorphous birefringence values; f_c and f_a are the crystalline and amorphous orientation functions, respectively; and X_v is the crystal fraction.

Melting behavior was examined on a Shimadzu DSC50 at a heating rate of $10^\circ\text{C min}^{-1}$ using a 4.0 mg sample. The heat of fusion used in calculation of percentage crystallinity was 138 J g^{-1} .⁸ Duplicate runs were carried out in all cases.

A Hitachi S520 scanning electron microscope with an operating voltage of 10 kV was used to examine the surface structure of the fibers after etching for 20 min using a Hitachi E3200 ion etching machine with a 1 mA discharge from the nitrogen source. Optical microscope examination of the fiber cross sections was carried out between

Table I Properties of the Precursor Yarn

| | |
|-----------------------------------|---------------------------------|
| Crystallinity by DSC | 25% |
| Crystalline orientation function | 0.7115 |
| Amorphous orientation function | -0.09 |
| Crystal size by X-ray diffraction | (010) 13A, (110) 18A, (100) 15A |

crossed polars at a nominal magnification of 1500 times.

Tensile testing was carried out in the conventional manner under ambient conditions.

RESULTS AND DISCUSSION

The measured properties of the precursor yarn are given in Table I.

The change in length during long heat treatment for yarn produced using different degrees of relaxation is shown in Figure 2, and it is apparent that samples with a high degree of relaxation, that is, v_2/u_1 of 0.546, 0.60, and 0.75, elongate. Yarns with lower degrees of relaxation, that is, above 0.90, contracted during long heat treatment. Figure 3 illustrates the crystalline orientation function before and after long heat treatment for the same materials and shows that the fibers do not lose their crystalline orientation, despite the fact that no tension is applied during the long heat treatment stage. A slight increase in f_c is apparent as the degree of relaxation decreases, and this is attributed to mechanical orientation

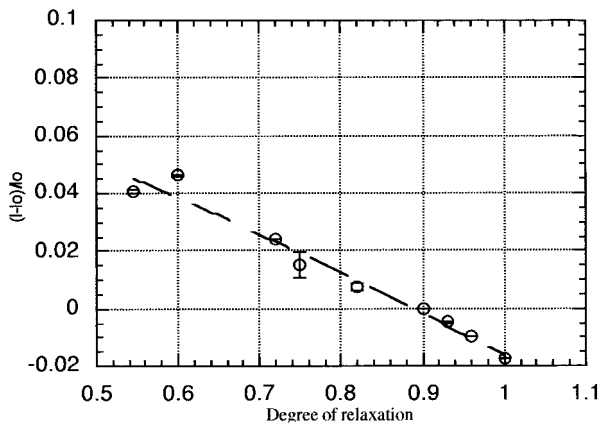


Figure 2 Relationship between the degree of relaxation during brief heat treatment and change in length during long heat treatment. The bars represent the distribution of results from the tested samples.

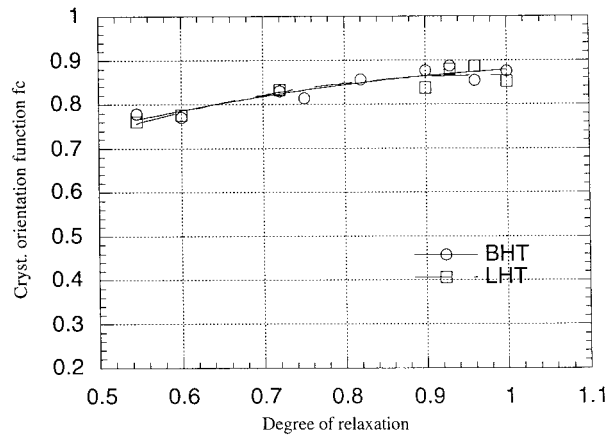


Figure 3 Effect of degree of relaxation during brief heat treatment on crystalline orientation function before (BHT) and after long heat treatment (LHT).

of the crystalline regions due to tension in the brief heat treatment stage.

Figure 4 shows the crystal dimensions for the different degrees of relaxation. Crystal size clearly increases following the long heat treatment with the greatest effect apparent at the higher degrees of relaxation. An increase in the c -axis is most evident in those fibers that elongate during the long heat treatment, and this is considered to be significant. Percentage crystallinity, as assessed by DSC and shown in Figure 5; also reflects the same trend, but the overall increase is less than that indicated by the increase in crystal dimensions measured by XRD. For a relaxation of 0.6, the overall increase in crystallinity is 14.3%, but the average increase in individual crystallite volume is over 120%. It is appreciated that the results from two fundamentally different measuring techniques cannot be strictly compared, but it is reasonable to assume that the total number of crystals present is reducing. The measured size of the c -axis is small. This is partly because the normal to the (105) planes used is inclined at 10 degrees to the c -axis, and the length obtained is therefore a slight underestimate. As previously stated, the observation that the increase in crystallinity is greatest for those fibers subjected to heat treatment conditions that lead to elongation, is thought to be important. Calorimetry also demonstrated that those materials that subsequently elongated during long heat treatment showed a recrystallization peak, which was not observable when the materials were tested after elongation, confirming the importance of crystallization to the elongation phenomenon.

The amorphous orientation function, displayed

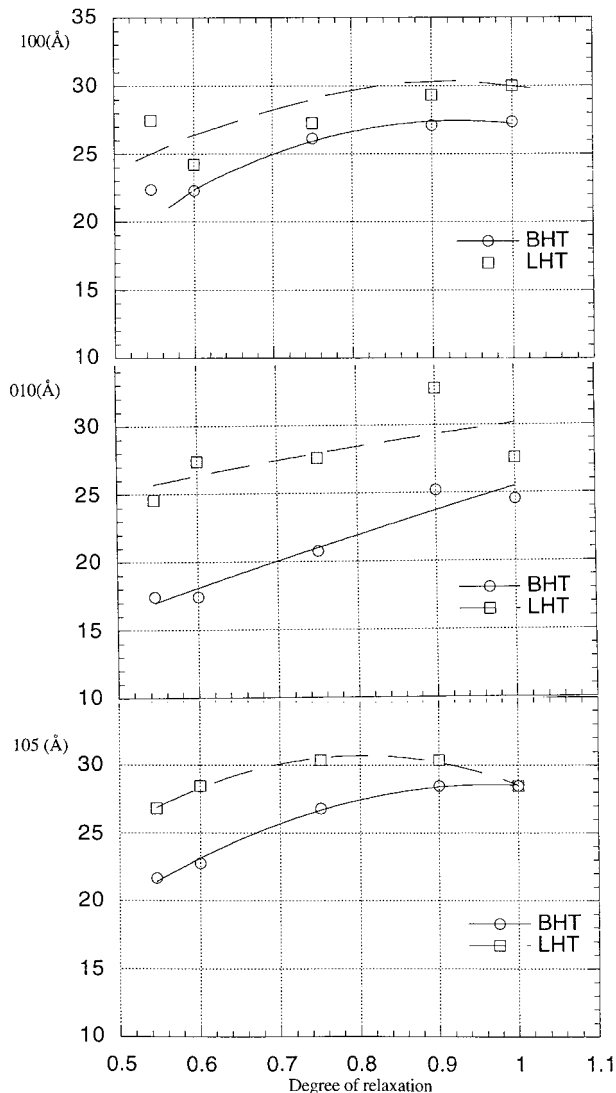


Figure 4 Crystal dimensions after brief heat treatment (BHT) and after long heat treatment (LHT).

in Figure 6, also shows a large increase during the long heat treatment and a clear positive dependence upon the degree of relaxation. This dependence upon relaxation can be explained as due to mechanical tension during the brief heat treatment stage, but the increase during the long heat treatment is more difficult to explain. It is possible that disoriented amorphous regions may be crystallizing, thereby increasing the relative contribution of the oriented amorphous component.

Electron micrographs, shown here as Figure 7(a)–(e), illustrate how the morphology develops during heat treatment for an elongating and non-elongating relaxation condition. The precursor is shown in Figure 7(a), and Figures 7(b) and (c) show material subject to a degree of relaxation

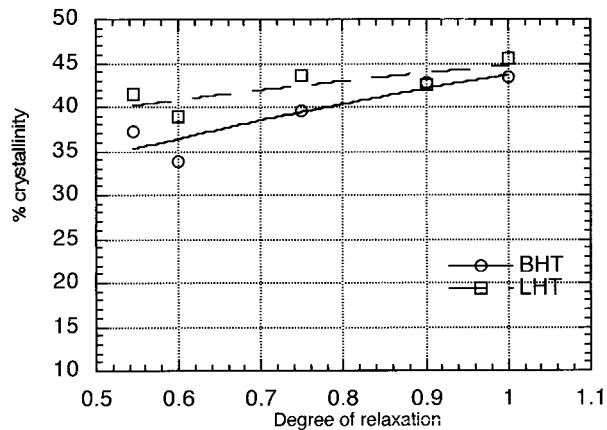


Figure 5 Effect of degree of relaxation during brief heat treatment on the percentage of crystallinity before (BHT) and after long heat treatment (LHT).

of 0.546 after brief heat treatment and long heat treatment, respectively. The structure indicated in Figure 7(b) with the arrow may be the result of lamella rotation as discussed by Peterlin and Sakaoku.⁹ They showed that such a process was possible during the first stage of plastic deformation before necking and that rotation is enhanced by high temperatures and low draw ratios. These conditions are generally consistent with those used to prepare the sample in the micrograph. After long heat treatment, the morphology of the fiber is slightly more defined, but a high degree of orientation is not evident. In the micrographs shown as Figure 7(d), surface morphology is gradually becoming more apparent as the tension on the sample during heat treatment increases, and Figure 7(e) shows a fiber with a highly ordered structure.

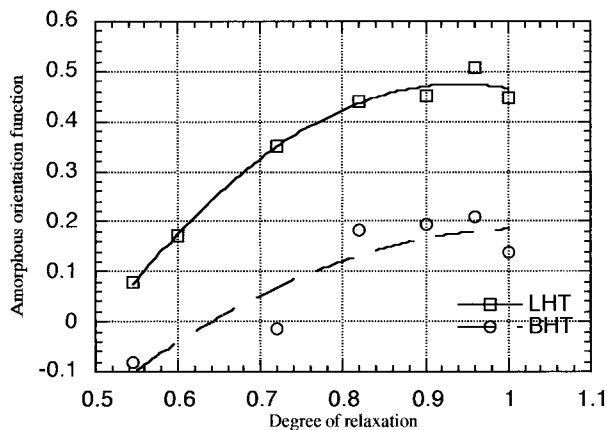


Figure 6 Effect of degree of relaxation during brief heat treatment on amorphous orientation function before (BHT) and after long heat treatment (LHT).

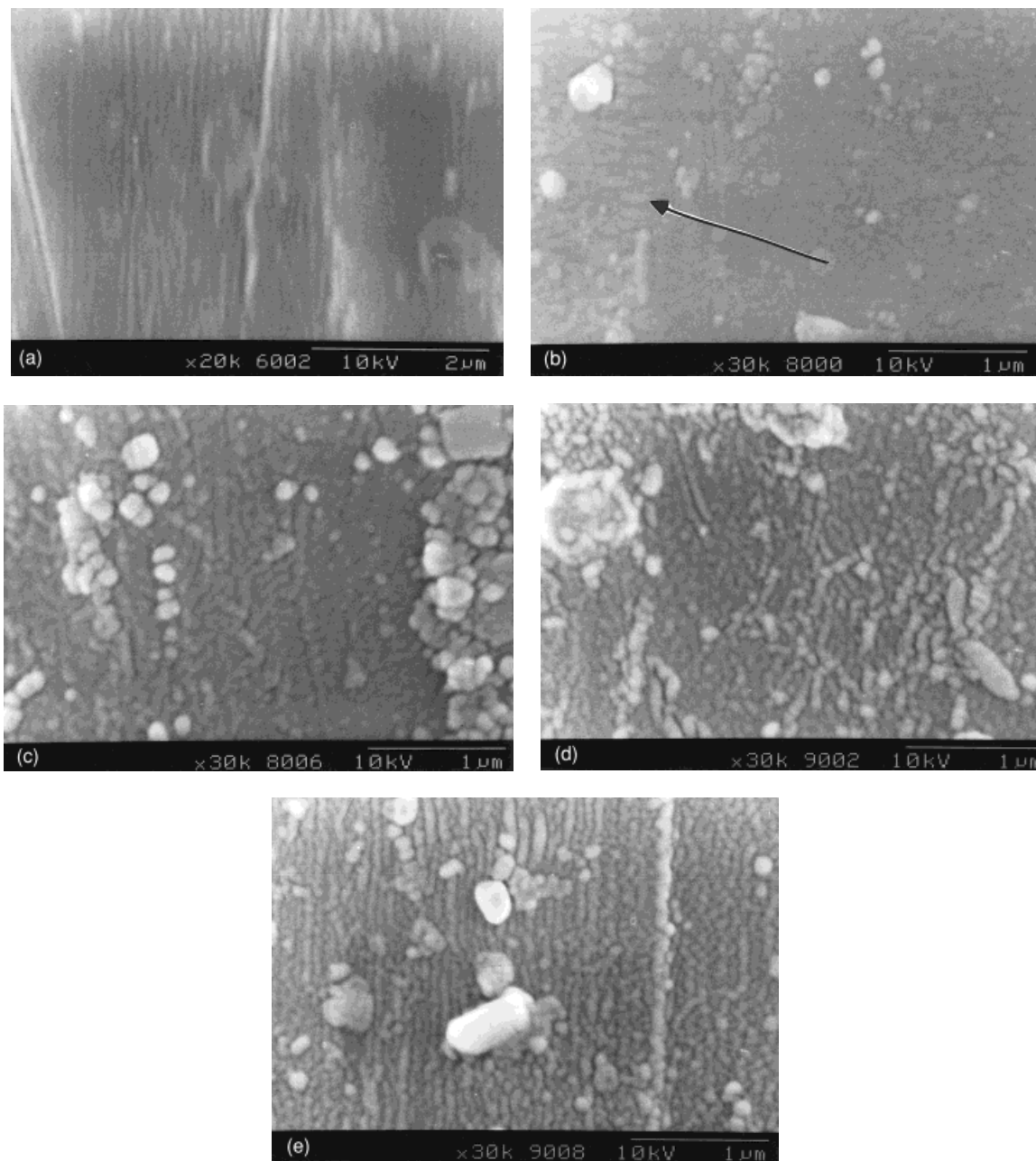


Figure 7 Electron micrographs for various heat treatment and relaxation conditions. In all cases, the fiber axis runs from top to bottom of the micrograph: (a) precursor fiber; (b) after brief heat treatment, in which the degree of relaxation is 0.546; (c) after long heat treatment, in which the degree of relaxation is 0.546; (d) after brief heat treatment, in which the degree of relaxation is 0.90; (e) after long heat treatment, in which the degree of relaxation is 0.90.

Optical microscopy of the fiber cross section indicated that spherulitic structures are present, but visual estimation of their abundance, compared with total crystallinity values from DSC, suggests that they only contribute a part of the total crystalline material. It is assumed that both isolated folded chain crystals and spherulitic as-

semblies are present, but it is thought that it is the isolated folded chain structures that are responsible for the elongation phenomenon.

Figure 8 shows the stress strain curves obtained after brief heat treatment, and these can be interpreted with reference to the work of Bechev and Mishinev,¹⁰ who carried out tensile

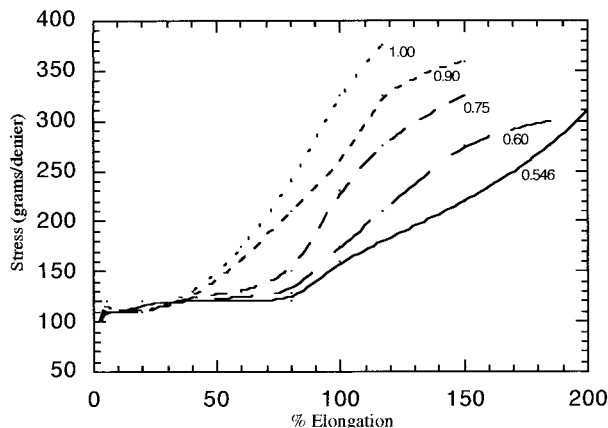


Figure 8 Stress-strain curves obtained for yarn after brief heat treatment for the degrees of relaxation indicated on the figure.

tests on PET yarns of different overfeeds. At a few percent elongation and at a similar stress, all materials investigated here, regardless of the degree of relaxation, show a plateau region in which the fiber deforms without any increase in tensile stress. It is considered that this represents orientational draw, and the length of the plateau depends upon the amount of disordered material present. As the length of the plateau increases with the degree of relaxation, it is presumed that this indicates the presence of a greater proportion of disordered material.

The overall pattern of the results can be explained with reference to the model originally used by Dismore and Statton¹¹ to explain crystallization phenomena in Nylon 66 fibers. They proposed that during heat treatment highly extended and essentially parallel material converted to a folded chain arrangement with a consequent contraction, and it is presumed that the same process occurs here during the brief heat treatment. However, it is thought that full equilibrium is not attained until the long heat treatment, and it is the nature of the locked in condition that determines what happens during the long heat treatment. Figure 9 is a schematic illustration of the proposed process. The "as drawn" yarn has chains that are highly extended and essentially parallel to the fiber length. Crystallinity at 25% is relatively low. Upon heating, the intermolecular bonds will break down, allowing short lengths of chain to move and form a more stable folded chain structure. On further heating, more crystallization takes place; and disoriented amorphous material converts to crystal, concurrent with crystal ripening processes. There is a reduction in the number of crystals present but an increase in total

crystallinity. Most importantly, *c*-axis growth occurs, which essentially pushes material ahead of it, causing the elongation of the fiber. If during the brief heat treatment, the fiber is able to contract fully before the crystallization is complete, then the heat subsequently supplied in the long heat treatment process will cause the disoriented amorphous region to convert to crystal; and this conversion results in the observed elongation.

CONCLUSIONS

PET fiber spun at 3500 m min^{-1} , and then thermally relaxed at a temperature of 130°C for 0.75 s, elongate by up to 5% when subject to a second heat treatment at 130°C for 20 min. Increasing the degree of relaxation during the first or brief heat treatment results in greater elongation during the second or long heat treatment. The change in percentage crystallinity, as measured by calorimetry, is from about 25% in the precursor material to about 35% after the brief heat treatment. This is relatively large; but a much smaller change, bringing the final crystallinity content up to about 40%, occurs during the long heat treatment. Crystallite size increases substantially during both the brief and long heat treatments, indicating that significant crystal reorganization is taking place, and the effects are most apparent with the material allowed the greatest relaxation. It is thought that it is a combination of this crystal reorganization, particularly *c*-axis growth, which is most significant in the highly relaxed materials, and conversion of disordered amorphous material into the oriented crystalline component, that is responsible for the elongation. The observed phenomenon is another manifestation of the slow

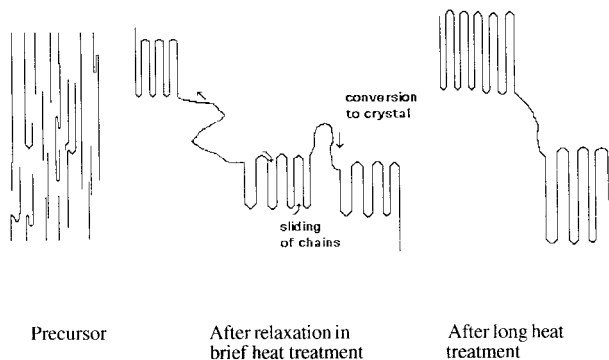


Figure 9 Schematic representation of the elongation process.

morphological equilibration of melt spun PET fibers but may prove technologically useful.

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