Preparation of high-modulus and high-strength nylon-6 fibre by the zone-annealing method

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(Received 19 March 1981)

In order to produce ultra-high strength fibre, a new method which was developed in our laboratory, called the zone-annealing method', has been applied to nylon-6. In spite of very simple apparatus and easy procedure, the dynamic modulus of the zone-annealed fibre was 10.8×10^{10} dyne cm^{-2}, which corresponds to 2.2–4.0 times that of the high-tenacity fibre available commercially. To elucidate the effectiveness of the zone-annealing process, the relationship between mechanical properties and superstructure of the fibre obtained has been investigated. It was found that the structure of the amorphous regions, especially the orientation of amorphous chains, played an important role in improving the mechanical properties. The principle and the characteristics of this method are also described in this paper.

INTRODUCTION

Recently, the preparation of high-modulus and high-strength polymer materials has been actively studied by many researchers, and a variety of interesting techniques have been proposed, such as hydrostatic extrusion by Ward et al.[1], solid-state extrusion by Porter et al.[2], fibrous growth from polymer solution by Pennings et al.[3], spinning from liquid crystal by Kwolek[4], and solution-spinning by Smith[5].

We have also succeeded in preparing ultra-high strength fibres or films from commercially available inexpensive semicrystalline polymers such as polyester[6-12], nylon[9,11,13], polypropylene[14] and polyethylene[11,15,16], by a new annealing method called the 'zone-annealing method' in our laboratory. In previous papers[6,7], we reported the application of this method to the preparation of ultra-high strength fibre of poly(ethylene terephthalate). This method is not only of interest as a new technique for approaching the theoretical strength of a polymer, but also opens up the possibility for the industrial production of ultra-high strength fibres.

The purpose of the present paper is to show that this method is also effective with nylon-6 fibre for preparing ultra-high strength fibre.

EXPERIMENTAL

Material

The original material used in the present study is as-spun nylon-6 fibre of 0.49 mm diameter, supplied by Toray Research Center, Inc. The as-spun fibre was produced by the usual melt-spinning and did not undergo any special conditioning during storage. The fibre has a birefringence of 5×10^{-4} and a crystallinity of 27.7%.

Zone-drawing and zone-annealing

The apparatus employed for the zone-annealing process is the usual tensile tester partially reconstructed. A band heater 2 mm wide was attached to the crosshead. The temperature of the heater can be held constant throughout the experimental period by a control system. The upper end of the fibre was fixed and the desired tension was applied to the lower end by weighting. The band heater was moved up or down along the fibre axis and its moving speed was selected from 2, 4, 8, 10, 20 and 40 mm min^{-1}.

The zone-annealing process consists of two steps: zone-drawing and zone-annealing. The zone-drawing was done on the original fibre by moving the band heater from the lower part of the fibre to the upper part under tension. The fibre was drawn easily and quickly, producing necking. The temperature, the moving speed of the band heater, and the tension were determined so that the drawn fibre has as high an orientation and as low a crystallinity as possible. The zone-drawn fibre was subsequently zone-annealed using the same apparatus as that used in the zone-drawing, except that three band heaters were superimposed vertically with separation. Both the temperature of the band heater and the tension applied to the fibre during zone-annealing were much higher than those in the case of zone-drawing. The zone-annealing was repeated six times. Although the heater must be moved upward when the fibre lengthens by zone-annealing, there is no effect of the moving direction of the heater if the length of the fibre does not change.

Measurements

The tensile properties of the fibres were determined at 23°–25°C, RH 65%, with the usual tensile tester. The length of the monofilament used for the measurement was

20 mm. Young's modulus, the tensile strength, and the elongation at break were estimated from the stress–strain curves. The dynamic viscoelastic properties, E', E'' and $\tan \delta$, were measured at 110 Hz on 20 mm long fibres with a dynamic viscoelastometer. The measurement was carried out in two temperature ranges; one from room temperature to $-140°C$ and the other from room temperature to $180°C$. In the former range the experiments were performed at a cooling rate of $2°C$ min^{-1} in a stream of dry air cooled with liquid nitrogen, and in the latter range at a heating rate of $1.5°C$ min^{-1} in a stream of dry nitrogen gas.

The birefringence was measured with a polarizing microscope equipped with a Berek compensator. When the fibres with high retardation were measured, $X–Z$ planes of various thicknesses which were cut from a single crystal of quartz were simultaneously used as an additional compensator.

The density of the fibres (d) was measured at $25°C$ by a flotation method using toluene–carbon tetrachloride mixtures. The degree of crystallinity (X_c) was calculated from the density by the usual method using a crystal density of 1.230[17] and an amorphous region density of 1.084 g cm^{-3} [18].

The orientation factor of the crystallites (f_c) was determined by an X-ray diffraction method proposed by us in the previous paper[19]. Further, the orientation factor of the amorphous chains (f_a) was calculated from the following equation by substituting the values of X_c, birefringence (Δ_t) and f_c measured separately.

$$f_a = \frac{\Delta_t - X_c f_c \Delta_c^\circ}{(1 - X_c)\Delta_a^\circ}$$

where Δ_c° and Δ_a° are the intrinsic birefringences of the crystal[20] and the amorphous phase[20], 0.0780 and 0.0689, respectively.

RESULTS AND DISCUSSION

Principle and characteristics of zone-annealing method

Generally, the strength of conventional polymer fibres is very low compared with theoretical strength value. The largest cause of lower strength is the folding of molecular chains, which builds up lamellae which are not useful for improving the strength. According to Peterlin's model[21], the fundamental unit of a highly oriented fibre structure is a long and narrow microfibril formed by deformation and breaking of spherulites. The microfibrils consist of stacking of fully oriented lamellae and amorphous layers. In the amorphous layers, although there are many loop chains and end chains, the tie chains carrying the force are very few. Further, the tie chains which connect between the lamellae or microfibrils have varying lengths and stresses. When force is applied to the fibre, therefore, a large stress concentration takes place on the relatively stressed tie chains and the tie chains break successively. Thus, deformation and fracture of the fibre proceed rapidly through the amorphous layers under high stress.

For these reasons, substantial improvement of the mechanical properties of the fibre cannot be expected when the lamella or folding is the main basic element of the structure. It is necessary to reconstruct the fibre structure. Although the ideal structure of an ultra-high strength fibre is the extended-chain single crystal, it is

desired, at least for practical fibres, to extend and align all the molecular chains under the same tension to induce cooperation in competition with the force. The crystalline regions are constituted only of extended-chain crystals, while the amorphous regions contain a number of tie chains which pass through many crystals and have a similar extent of stresses and lengths.

The zone-annealing method has been investigated with a view to producing fibres with such a structure. As it is difficult to convert directly an unoriented original fibre into the extended-chain texture, the zone-annealing procedure is divided into two stages: zone-drawing and zone-annealing. *Figure 1* shows the principle of this method. In the first stage, an amorphous (or as low in crystallinity as possible) as-spun fibre is converted into a fibre with high orientation and low crystallinity (if possible, amorphous state) by zone-drawing at a temperature below the crystallization temperature and above the glass transition temperature of the polymer. In the second stage, the zone-drawn fibre is further converted into a highly oriented and highly crystalline fibre by zone-annealing at a suitable temperature for crystallization under high tension. In other words, the zone-drawing is carried out with the intention of arranging the molecular chains in a bundle, preventing the fibre from crystallization; whereas, the zone-annealing is carried out to form perfectly extended-chain crystals in the fibre, inhibiting back-folding and relaxation of the molecular chains by means of high tension.

This method possesses the following advantages:

(1) The quantity of heat required for drawing or annealing can be decreased, because the fibre is heated only in the narrow heating zone.

(2) The applied high tension acts concentrically and effectively on the narrow area softened by heating.

(3) The generation of numerous nuclei can be prevented, because the fibre is not heated over a wide range at the same time.

(4) Thermal degradation of the fibre can be prevented, because of the short heating time.

(5) The zone-annealed fibre possesses a high dimensional stability at elevated temperatures. In particular, creep does not occur at all below the zone-annealing temperature.

(6) If optimum conditions are selected, this method is applicable to a variety of polymers.

(7) This method can be applied not only to fibres but also to films by the use of a slit-shaped heater.

Embodiment of zone-annealing for nylon-6 fibre

Since nylon-6 crystallizes easily on cooling from the molten state, even as-spun fibre already has a fairly high crystallinity and contains a large number of spherulites. The fibre used in this study has a crystallinity of 27.7%. Therefore, the zone-annealing process for nylon-6 fibre
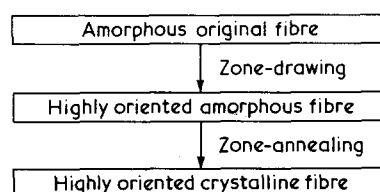

Figure 1 Principle of the zone-annealing method

Table 1 Most suitable conditions for zone-drawing and zone-annealing

Conditions	Zone-drawing	Zone-annealing
Temperature of the heating zone ($^\circ$C)	80	180
Moving speed of the band heater (mm min^{-1})	40	10
Tension applied to the fibre (kg mm^{-2})	1.6	15.8
Repetition (times)	1	6

Table 2 Mechanical properties of original fibre, zone-drawn fibre, and zone-annealed fibre

Sample	Young's modulus ($\times 10^{-10}$ dyne cm^{-2})	Strength at break (kg mm^{-2})	Elongation at break (%)
Original fibre	0.98	—	—
Zone-drawn fibre	2.28	24.3	86.8
Zone-annealed fibre	9.91	100.3	13.6

Table 3 Birefringence, orientation factors of crystalline and amorphous regions (f_c and f_a), and crystallinity

Sample	Birefringence ($\times 10^3$)	f_c	f_a	Crystallinity (%)
Original fibre	0.5	—	—	27.7
Zone-drawn fibre	43.8	0.806	0.511	30.9
Zone-annealed fibre	60.3	0.849	0.792	48.9

does not follow accurately the principle shown in *Figure 1*. A most important factor in this process is strongly to promote the unfolding of lamellae. At this point, the zone-drawing and the zone-annealing in which a narrow portion of the fibre is heated under high tension can be said to constitute a very suitable and favourable method.

Although many experimental conditions can be considered in this process, we checked the temperature and moving speed of the band heater, the tension applied on the fibre, and the number of repetitions of zone-annealing as important variables. Although the purpose of zone-drawing is to obtain a fibre with as high an orientation as possible, when the zone-drawing temperature is too high, crystallization takes place and when the tension is too large, the fibre often whitens because of local microfractures of the fibre. Further, the conditions for zone-annealing were examined. In particular, the influence of applied tension and the band heater temperature, during zone-annealing, on modulus, tensile strength, and birefringence of the obtained fibres was examined in detail. The most suitable conditions for zone-drawing and zone-annealing which were selected after many preliminary experiments are shown in *Table 1*. Those selected were employed for subsequent experiments in this study.

Changes in tensile properties, orientation and crystallinity with zone-drawing and zone-annealing

The tensile properties of the original fibre, the zone-drawn fibre, and the zone-annealed fibre are listed in *Table 2*. Although Young's modulus and the strength at break

are still small in the zone-drawing stage, these values increase rapidly on zone-annealing. The value of Young's modulus reaches 9.91×10^{10} dyne cm^{-2}, which is surprisingly high and is 2.0–3.6 times as large as that of commercial high-tenacity nylon-6 fibre, 2.7–5.0×10^{10} dyne cm^{-2}.

Table 3 shows the changes in orientation and crystallinity with zone-drawing and zone-annealing. Both the superstructural factors increase in the order of the processes. If examined in further detail, it is seen that the zone-drawing is particularly useful for increasing birefringence and the zone-annealing increases the crystallinity. This tendency can also be seen in X-ray Laue photographs shown in *Figure 2*. Compared with the data for poly(ethylene terephthalate) fibre[6], however, the
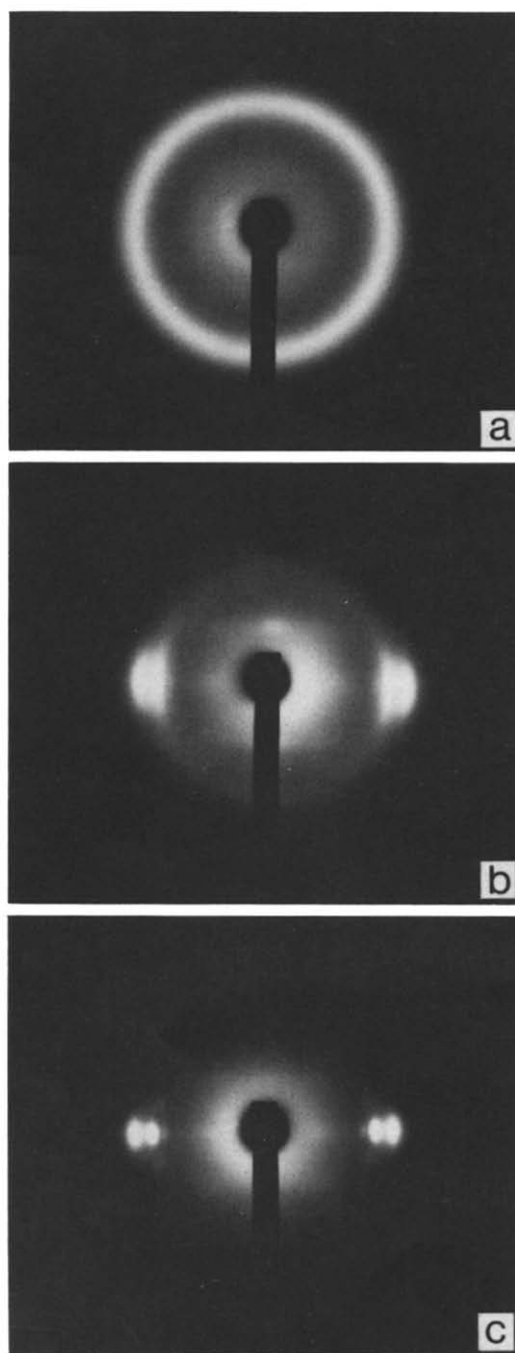
Figure 2 X-ray Laue photographs of (a) the original fibre, (b) the zone-drawn fibre, and (c) the zone-annealed fibre
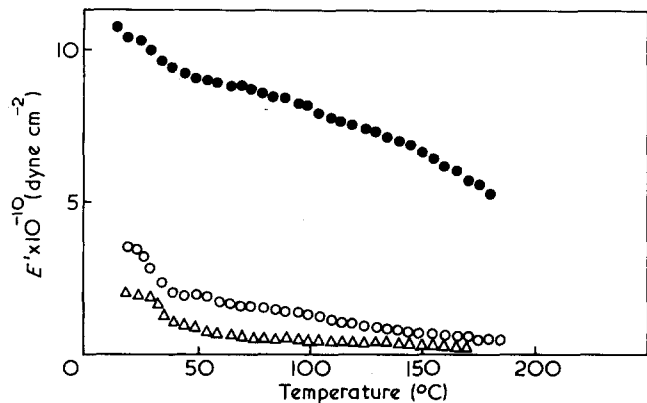
Figure 3 Temperature dependence of dynamic storage modulus *E'* in the higher temperature range for the original fibre (△), the zone-drawn fibre (○), and the zone-annealed fibre (●)
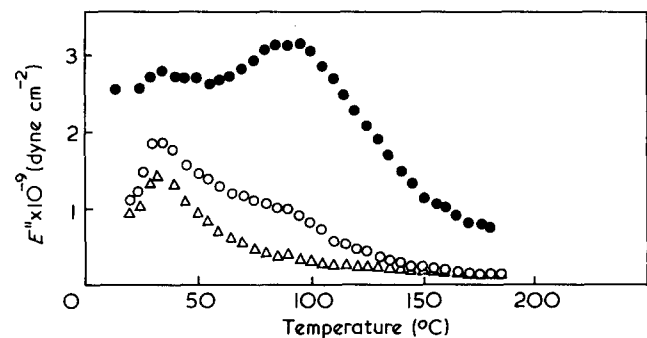

Figure 4 Temperature dependence of loss modulus *E''* in the higher temperature range for the original fibre (△), the zone-drawn fibre (○), and the zone-annealed fibre (●)
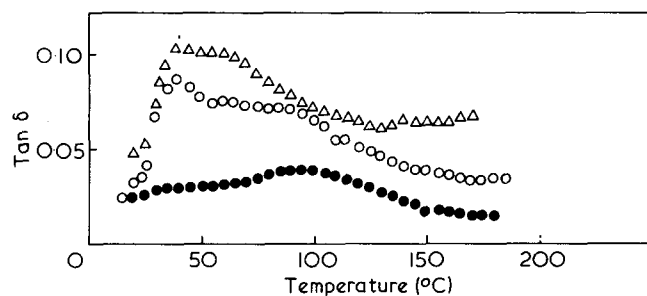

Figure 5 Temperature dependence of tan δ in the higher temperature range for the original fibre (△), the zone-drawn fibre (○), and the zone-annealed fibre (●)

increment of increase in crystallinity by zone-annealing is significantly small. Although the orientation factor of the crystallites (f_c) easily reaches a very high value by zone-annealing, the orientation factor of the amorphous chains (f_a) increases steadily and roughly in the same manner as Young's modulus and the tensile strength. This fact suggests that the orientation of the amorphous chains contributes to the improvement of the mechanical properties of the fibre.

Dynamic viscoelastic properties

Figures 3, 4 and 5 show the temperature dependences of dynamic storage modulus, *E'*, loss modulus, *E''*, and tan δ in the higher temperature range. It is obvious that the dynamic storage modulus increases only slightly by zone-

drawing but increases rapidly by zone-annealing. The *E'* value of the zone-annealed fibre at room temperature is 10.8×10^{10} dyne cm^{-2}, which is still higher than that of Young's modulus and is 2.2–4.0 times that of the high-tenacity fibres.

As seen in *Figures 4* and *5*, two dispersion peaks appeared at about 30° and 90°C. The dispersion peak at ~30°C corresponds[22] to the glass transition of nylon-6; whereas, the peak at ~90°C is ascribed [23-25] to micro-Brownian motion of large amorphous molecular segments due to breakdown of hydrogen-bonds in the amorphous regions. In the order of the original fibre, the zone-drawn fibre, and the zone-annealed fibre, the peak at ~30°C becomes obscure, while the peak at ~90°C becomes gradually clear as it changes from an indistinguishably weak shoulder to an isolated peak. Also the *E''* peak increases in height in the same order. Because the intensity of the *E''* dispersion peak indicates the energy dissipated as frictional heat per cycle in a sinusoidal deformation, the increases in the *E''* peak intensity imply increases in intermolecular friction[26]. Further, the peak at ~90°C shifts to a higher temperature in the same order. Compared with the peak for fibres prepared by other annealing methods[25], the peak for the zone-annealed fibre is very broad and occurs at a higher temperature. The fact indicates that the motions of the amorphous chains are very difficult in the vicinity of this temperature.

Figures 6 and *7* show the temperature dependences of *E'* and *E''* in the lower temperature range, respectively. The
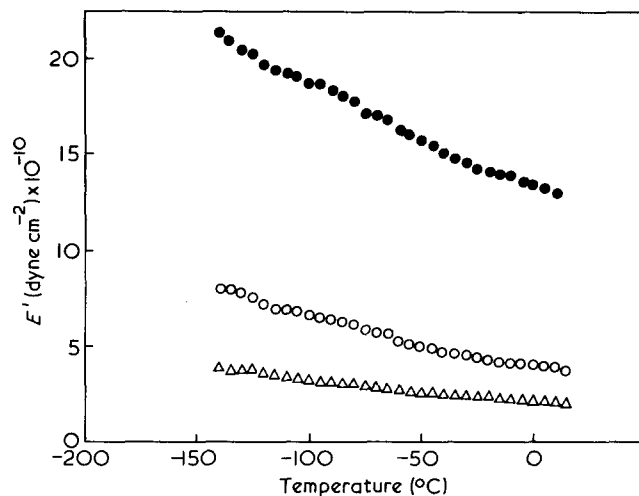

Figure 6 Temperature dependence of dynamic storage modulus *E'*, in the lower temperature range for the original fibre (△), the zone-drawn fibre (○), and the zone-annealed fibre (●)
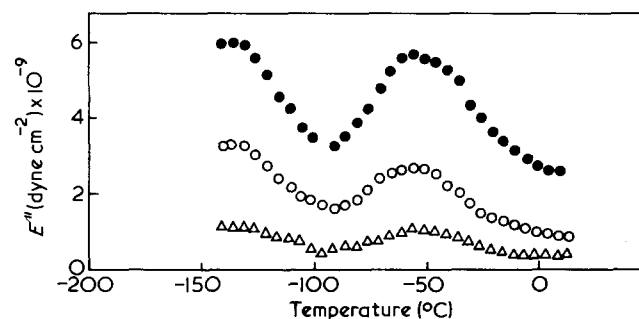

Figure 7 Temperature dependence of loss modulus *E''*, in the lower temperature range for the original fibre (△), the zone-drawn fibre (○), and the zone-annealed fibre (●)
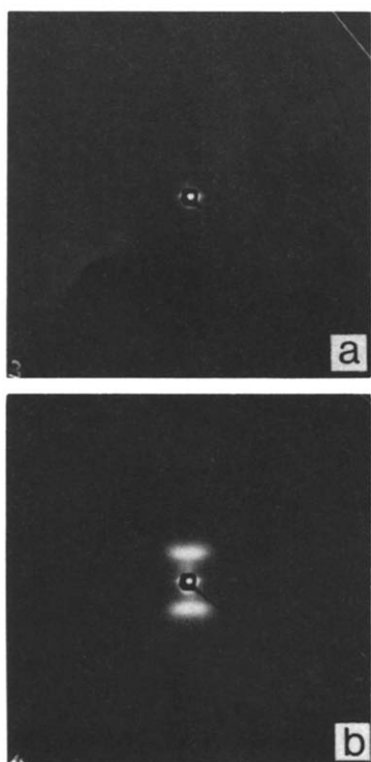
Figure 8 Small-angle X-ray scattering photographs of (a) the zone-annealed fibre and (b) the fibre which was annealed under release at 175°C after cold-drawing at room temperature up to 3-fold

I000   900   800
Wave number (cm⁻¹)

Figure 9 Changes in i.r. absorption band at 930 cm⁻¹ assigned to extended-chain conformation in α-crystals with zone-drawing and zone-annealing

E' value at $\sim -140°C$ is 21.5×10^{10} dyne cm⁻² and is the maximum E' value among the experimental data in the literature. In *Figure 7*, two dispersion peaks are observed at $-55°C$ and $-137°C$. These peaks are assigned[27,28] to the β and γ dispersions, respectively. Both the peaks also increase clearly in height by zone-drawing and zone-annealing, although the temperature positions remain unaltered. We discussed in the previous paper[26] that the intensities of these dispersion peaks depend strongly on the orientation of amorphous chains. On the basis of these experimental results, it was assumed that the amorphous chains in the zone-annealed fibre are highly oriented and their movements are strongly prevented over the wide temperature range owing to the increased interaction between the adjacent molecular chains.

Superstructure of the zone-annealed fibre

Figure 8 shows small angle X-ray scattering photographs for the zone-annealed fibre and the fibre which was annealed under release at 175°C after cold-drawing at room temperature up to 3-fold. The latter fibre is considered[29] to consist of a stacking of highly oriented lamellae and amorphous layers. Both the photographs show layer line scattering patterns. Although the long periods calculated from *Figure 8* showed the same value for both the fibres, 96.4 Å, the intensity of the layer line diffraction in the zone-annealed fibre is much weaker than in the fibre annealed under release. This indicates that the lamellae in the zone-annealed fibre are far smaller in quantity. Further, the horizontal breadth of the long period diffraction of the zone-annealed fibre is larger than that of the fibre annealed under release. Since the length of streak is inversely related[30] to the transverse dimension of the ultimate scattering units, i.e. lamellae, it is thought
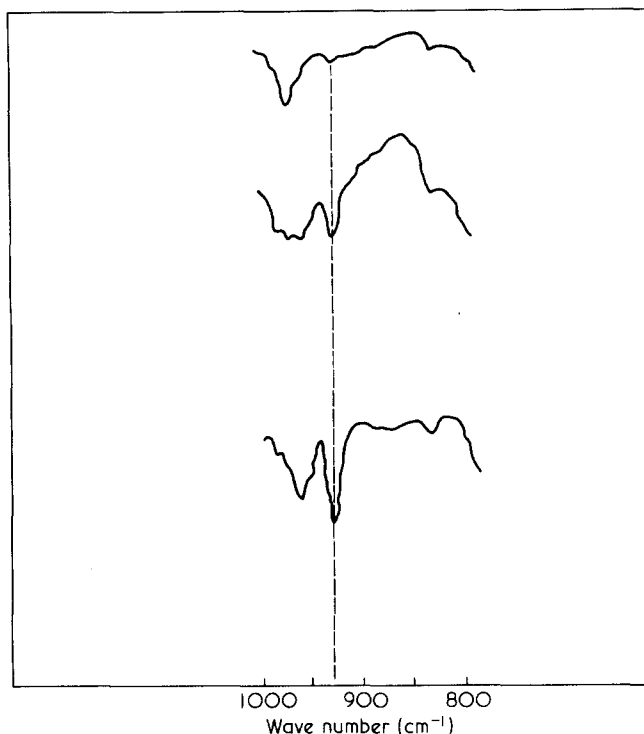
that the lamellae existing in the original fibre split into minute lamellae by zone-drawing and zone-annealing under high tension; then some of the lamellae are changed to amorphous materials by unfolding. However, the degree of crystallinity increases by zone-drawing and zone-annealing, as seen in *Table 3*. It seems reasonable to assume that the incremental increase in crystallinity is attributed to formation of extended-chain crystals. This assumption is also strongly supported by the experimental result that the i.r. absorption band centred at 930 cm⁻¹ assigned[31] to extended-chain conformation in α-crystals increases rapidly with zone-drawing and zone-annealing, as shown in *Figure 9*.

It can be concluded that the fibre structure must consist mainly of highly oriented extended-chain crystals and fully extended amorphous chains, although a fair amount of lamellae is also contained in the fibre. Further, such a firm structure leads to the excellent mechanical properties of the fibre.

ACKNOWLEDGEMENTS

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