

# Longitudinal Growth of Polymer Crystals from Flowing Solutions. X. Conditions for Continuous Growth on the Rotor Surface

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## Synopsis

Ultrahigh strength polyethylene fibers can be generated by stress-induced crystallization from a supercooled solution subjected to Couette flow, usually referred to as the "surface-growth" process. Under appropriate conditions, continuous fiber production can be realized for a period as long as 19 days, whereas under other circumstances a rapid interruption of the growth process is met. The present investigation deals with the origin of fiber fracture during "surface growth." The limiting values of process variables required to maintain continuous growth have been established. Interruption of the continuous growth can occur in three different ways: (1) formation of a closed fiberloop around the rotor; (2) limited crystal growth rate; (3) rapid crystallization, leading to depletion of the gel on the rotor surface. The gel layer is being formed by adsorption of long molecules on to the rotor surface and subsequent "reptation," resulting in a dense entanglement network of these molecules. These factors determine the boundaries of the triangularly shaped domain for continuous growth in a graph of the two main variables, namely the takeup speed and the rotor speed. Furthermore, it was noticed that the introduction of a wedge-shaped groove in the surface of the Couette rotor leads to a substantial reduction of failure. Continuous growth could be established in the temperature range from 103–125°C when *p*-xylene was used as a solvent. For *p*-xylene solutions at a crystallization temperature of 110°C and using a teflon rotor of 115 mm diameter, a maximum takeup speed and rotor speed were 16 and 180 mm/s, respectively. Basically the restrictions of the process appeared to be due to the limited rate of crystallization and rate of adsorption of polyethylene molecules on the surface of the rotor.

## INTRODUCTION

Previous papers of this series reported on the production of ultrahigh strength and modulus fibers of high molecular weight polyethylene using the "surface-growth" technique.<sup>1-7</sup> It has recently been shown that this method also has considerable potential for the formation of highly oriented polymer films and blended fibers.<sup>8-11</sup> Basically, the surface-growth method consists of sliding a fibrous seed crystal through a supercooled entanglement network that is adsorbed on the surface of the rotating cylinder of a Couette apparatus.<sup>12</sup> This gel layer of entangled molecules is formed by the shear flow of a dilute solution.<sup>13,14</sup> Once the seed crystal has been brought into contact with this gel layer and longitudinal crystal growth<sup>15</sup> has been initiated by stretching the network in the flow field, the growing macrofiber can be wound up on a bobbin and the process may even be continued for 19 days collecting 10<sup>4</sup> m of fiber.<sup>16</sup>

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Under optimum conditions of takeup speed, rotor speed, and crystallization temperature, high molecular weight polyethylene fibers are produced that have tensile strengths up to 4 GPa and Young's moduli up to 105 GPa. The crystallization variables cannot be altered at random, however, and a discontinuity of the longitudinal growth process was encountered several times as a result of fiber fracture, especially under those conditions leading to optimal mechanical properties.

The purpose of the present investigation was to explore the limiting values of the crystallization variables and to find the major causes of fiber fracture. The early sections of this paper report on the observations concerning the takeup force, which throw some light on the causes of fracture and the influence of process variables upon these. Subsequently, the resulting conditions for continuous growth are dealt with. Finally, the limitations to the process are discussed in relation to the underlying mechanism of fiber formation.

## EXPERIMENTAL

Details of the surface-growth process using a rotor with a vertical<sup>1</sup> as well as a horizontal axis<sup>6</sup> have been described elsewhere.

### Materials

Two linear polyethylenes were used. One, Hostalen Gur, had an intrinsic viscosity of 15 dL/g in decalin at 135°C, an  $M_n$  of  $10^5$  g/mol as determined by osmometry, and an  $M_w$  of  $1.5 \times 10^6$  g/mol as determined by light scattering in  $\alpha$ -chloronaphthalene at 135°C. The other, Hifax 1900, had, according to the supplier (Hercules), an intrinsic viscosity of 24 dL/g and  $M_w$  of  $4 \times 10^6$  g/mol. The polymer was dissolved at a concentration of 4.29 g/L of solvent (approximately 0.5 wt %), by stirring with a paddle stirrer for a period of 24 h at 30 rpm and 130°C in the case of *p*-xylene and at 150°C in other cases. We used the solvents *p*-xylene, *n*-dodecane, decalin, paraffin oil (viscosity at 20°C: 68 cP), and a mixture of paraffins supplied by Shell under the tradename Shellsol K. *p*-Xylene was employed, except where another solvent is indicated.

Solvents were characterized by differential scanning calorimetry using a Perkin-Elmer DSC-2 apparatus. Calibration of the DSC was carried out using the known melting endotherm of indium. All solutions were stabilized by 0.5 wt % of the antioxidant ditertiary-butylparacresol and were kept under purified nitrogen in order to prevent oxidative degradation.

The cross-sectional area of the fibers was determined from the mass per unit length using a density of 1000 kg/m<sup>3</sup>.

Tensile tests were carried out using a Zwick Z1.3B tensile tester at a crosshead speed of  $2 \times 10^{-4}$  m/s and an original sample length of 25 mm.

Scanning electron micrographs were obtained with a Jeol JSM U3 electron microscope.

### The Apparatus for Fiber Growth

The Couette apparatus used in this work consisted of one with a rotor having a diameter of 115 mm placed in a vessel with an internal diameter of 130 mm,

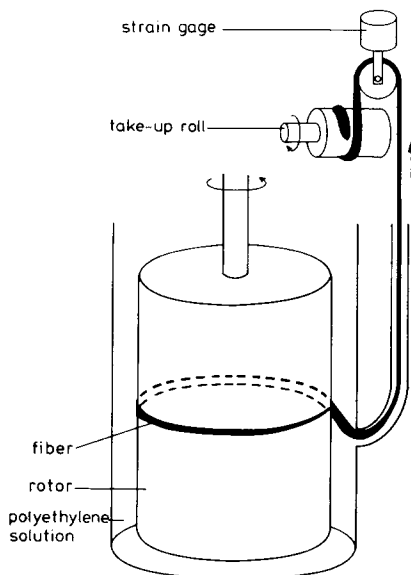


Fig. 1. Sketch of the apparatus used for surface growth, showing also the growing, which is ribbon-shaped and has a tapered end.

and another one with dimensions of 179 and 191 mm, respectively. The conical rotors were 130 mm high, and had diameters of 105 and 75 mm at the top and 115 mm at the bottom. All rotors were made of teflon.

The apparatuses were immersed in a silicone-oil bath the temperature of which was controlled to within  $\pm 0.05^\circ\text{C}$ . The takeup force was measured by means of a Statham-strain gauge (model UC-3), which has been described elsewhere.<sup>17</sup>

## RESULTS

Longitudinal growth of polyethylene fibrous crystals by the surface-growth technique could be extended for many days, but the proper conditions had to be found by trial and error. The alteration of variables such as rotor speed, takeup speed, or temperature frequently led to interruption of the process by fracture of the growing fiber. In order to gain insight into the problem of fracture, the takeup force in the fiber was measured under a variety of conditions. For this purpose a crystallization apparatus that allows the measuring of the takeup force was employed. As shown schematically in Figure 1, it consists of a coaxial cylinder apparatus to which a side tube is attached. In most cases, the annular gap of this Couette instrument is filled with a 0.5 wt % solution of high molecular weight polyethylene in *p*-xylene. In the present work use was made of an inner teflon cylinder, usually referred to as rotor.

Fiber growth was initiated by bringing a fibrous seed crystal through the side tube into contact with the rotating inner cylinder. The takeup force in the fiber arising from the friction with the moving rotor was recorded in all stages of the growth experiment by leading the fiber over a strain gauge. The course of the process was followed not only by recording takeup force, but also by measuring the cross-sectional area of the fiber.

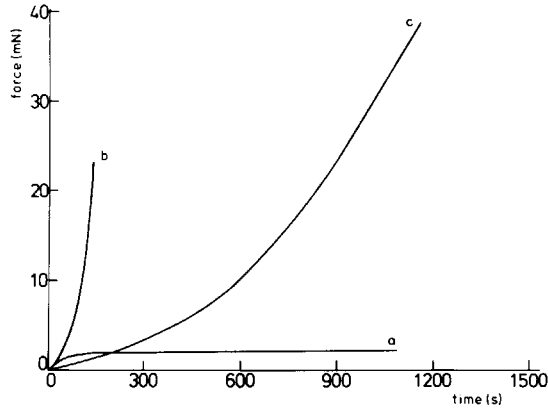


Fig. 2. The tension (or the force) developed with time in a fibrous seed as a result of the friction with the rotor. Rotor speed was 52 mm/s and rotor circumference 360 mm. Seed length and temperature were: (a) 60 mm, 110.5°C; (b) 180 mm, 110.5°C; (c) 180 mm, 113.5°C. Takeup speed was zero.

In the following a number of pertinent observations will be described that give an insight into the process of fracture and the influence of the main variables, which are rotor speed, takeup speed, and temperature, on this process.

### Takeup Force during Initiation

The tension developed in the polyethylene seed fiber is shown in Figure 2. When a 60 mm long seed is brought into contact with the rotor, and is not wound up, virtually no tension develops: the force reached a value of only 3 mN. This short seed crystal did not grow longitudinally even after a lengthy period of time of 30 min. Apparently, this seed crystal did not make proper contact with the adsorbed layer on the rotor surface, in line with previous observations that surface growth requires intensive contact with the rotor surface.

Use of a seed of 180 mm corresponding to half the rotor circumference led to a rapid increase in tension: values in the order of 20–40 mN were obtained in a period of 200 s, at a crystallization temperature of 110.5°C. At a higher temperature of 113.5°C, the same force level was reached in a much longer period

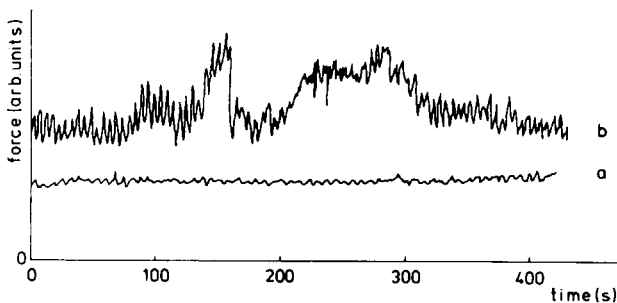


Fig. 3. Typical takeup force patterns recorded during surface growth of polyethylene fibers from a 0.5 wt % *p*-xylene solution. If force was stable (a) long-time growth was possible, whereas the unstable pattern (b) generally preceded fracture.

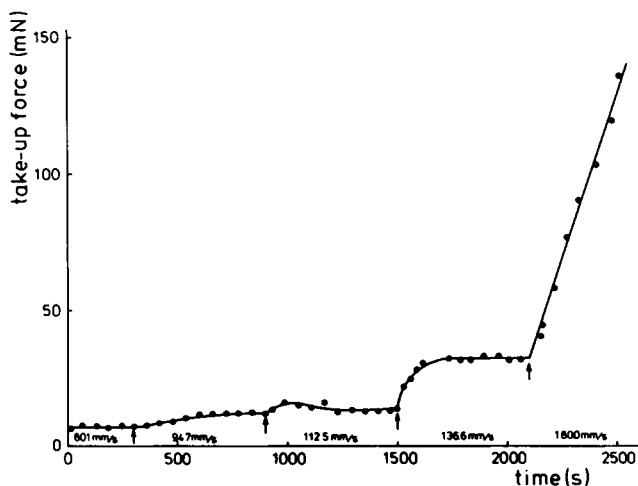


Fig. 4. Plot showing how force approaches a steady level, after an increase of rotor speed (indicated by the arrows). The figures refer to the rotor speeds in each period. At a speed of 180 mm/s the force kept increasing with time until the fiber broke. Rotor diameter was 115 mm, takeup speed 0.53 mm/s, and temperature 113°C.

of about 1000 s, in line with the expectations that the longitudinal crystallization rate decreases with increasing temperature.

### Takeup Force during Steady Fibrous Crystallization

When force levels in the order of 50 mN were attained in the fibrous seed, the takeup roll was started, and the takeup force was recorded as a function of time. A steady state could be expected for a takeup speed equal to the longitudinal growth rate. During the growth process two essentially different strain gauge signals were noticed, and, in general, it could be judged from these force signals whether failure would occur or not. The two types of takeup signal are displayed in Figure 3. The first signal [Fig. 3(a)] shows small variations having a frequency corresponding to the rotation of the inner cylinder. These small variations must be due to some deviation of the rotor shape from cylindrical symmetry. The amplitude of this disturbance was found to be linearly proportional to the magnitude of the takeup signal. Fibers produced when the force was this regular also displayed a regular cross section, which indicated that a steady state situation had been achieved. The second signal displayed rather drastic irregularities, as is illustrated in Fig. 3(b), and fiber cross section varied with time in this case. When the takeup force was this irregular, failure always followed in a short while.

Whether the takeup force was constant or irregular depended on process variables such as rotor speed and takeup speed. The influence of these variables on the takeup force will be dealt with in the following sections.

### Rotor Speed

A first aspect of the influence of rotor speed on the take-up force is illustrated in Figure 4, which shows how force changes when the rotor speed is suddenly

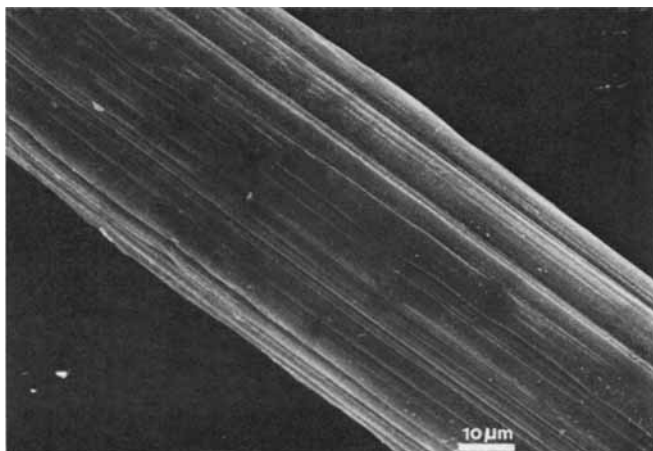


Fig. 5. Scanning electron micrograph of a high molecular weight fiber grown from a 0.5 wt % *p*-xylene solution. This fiber is produced by surface growth at 109°C, using a rotor speed of 95 mm/s, a takeup speed of 6.3 mm/s, and a rotor of 179 mm diameter.

increased. If the rotor speed was enhanced, the takeup force increased to a higher plateau value in 200 s. This indicates that a new steady state had been attained and that the longitudinal growth process was capable of adjusting to the new rotor speed. The rotor speed was increased stepwise from 38 to 136 mm/s, and in each case the takeup force reached a constant level. When the peripheral rotor velocity again was raised to 180 mm/s, the takeup force continued to increase until a value of 150 mN was reached after 400 s and the fiber fractured. In this final situation it was observed that several windings of the fiber had wrapped around the rotor. The two or three windings got connected to each other, such that a closed loop was formed. It could also be observed that the winding which was taken up was disrupted from those which were still on the rotor. This disruption corresponded to a sudden increase of the takeup force, indicating that this phenomenon of loop formation causes a rise of the fiber tension and may induce fracture. Loop formation and the ensuing increase of takeup force could be shifted to higher rotor speeds by increasing the takeup speed.

Just prior to fracture, it was often observed that the fiber was covered with knotlike structures every 0.3–1.0 m. Such a knot is shown on the scanning electron micrographs of Figures 5–7 together with a smooth section of the fiber. The knots have the appearance of a contracted fiber, which may well have pro-

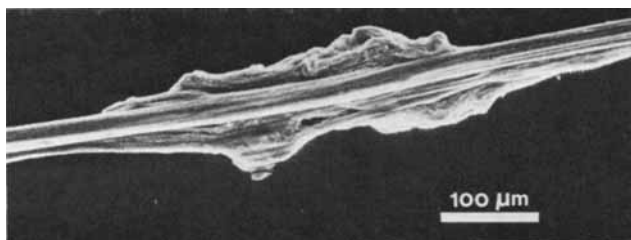


Fig. 6. Same as Figure 5, but section of fiber with a knotlike structure.

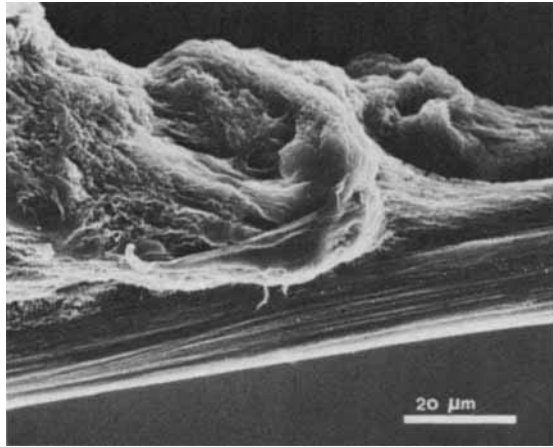


Fig. 7. Magnification of knotlike structure of Figure 6.

vided for connection of two windings. This fiber must have contracted when it broke, in agreement with earlier observations.<sup>12</sup> Knots are therefore indicative of the tendency of the fiber to grow longitudinally at a higher rate than being taken up, so that loop formation follows.

It was found that fracture occurs not only at high rotor speeds, but also a substantial reduction of the rotor speed caused breakage of the growing filament. The influence of rotor speed on take-up force was therefore monitored in a broad range. Figure 8 shows, as a function of rotor speed, the average force as well as

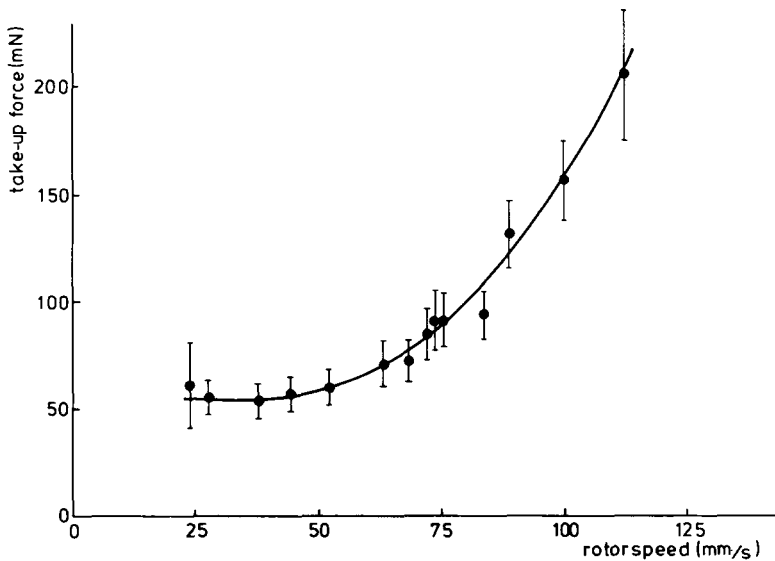


Fig. 8. Takeup force vs. rotor speed. The bars indicate the variations of the force, expressed as the difference between the highest and the lowest force measured within a period of 2 min, and are a measure of the process instability. Polyethylene fibers were surface grown at 113.5°C, takeup speed of 4.2 mm/s, using a rotor with 115 mm diameter. Data have been obtained by scanning up and down the rotor speed range. Each measurement was taken after 15 min of equilibration at the set rotor speed.

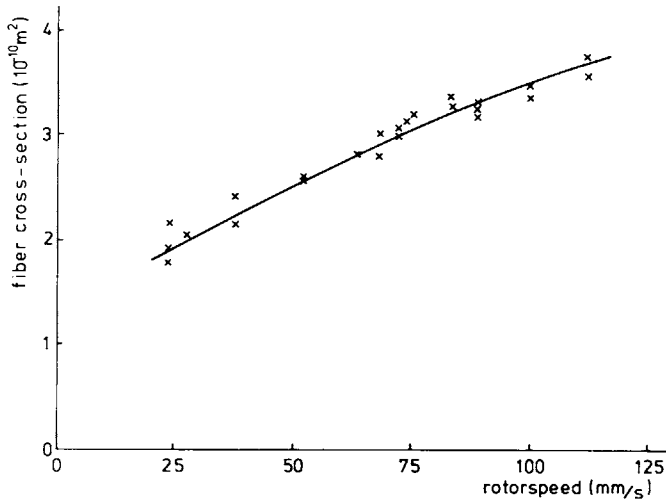


Fig. 9. Cross section of fibers grown at various rotor speeds. Same process conditions as Figure 8.

the variation of force. The latter is expressed as the difference between the highest and lowest signals recorded within a period of 2 min. In accordance with Figure 4, both the force and its variation are great at high speeds, where fracture becomes more likely. At low speeds force is low, but very irregular. This indicates that the growth process is unstable. Figure 8 does not reveal why failure actually occurs at low rotor speeds. It is conceivable that instead of takeup force the takeup stress (force per unit fiber cross-sectional area) should be considered. This is readily apparent from the fact that takeup stress must always be lower than the stress at break, whereas such a restriction does not exist for the force. Measurements of fiber cross section corresponding to the same data are shown in Figure 9, displaying a decrease of cross section with decreasing rotor speed. In view of the constant force, an increase of stress at low speeds must result as is indeed shown in Figure 10. The figure reveals for fibrous growth at  $113.5^\circ\text{C}$

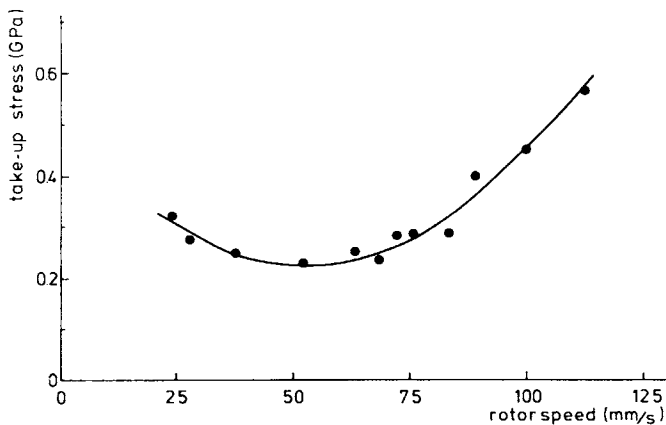


Fig. 10. Takeup stress of fibers as a function of rotor speed. Same process conditions as Figure 8.



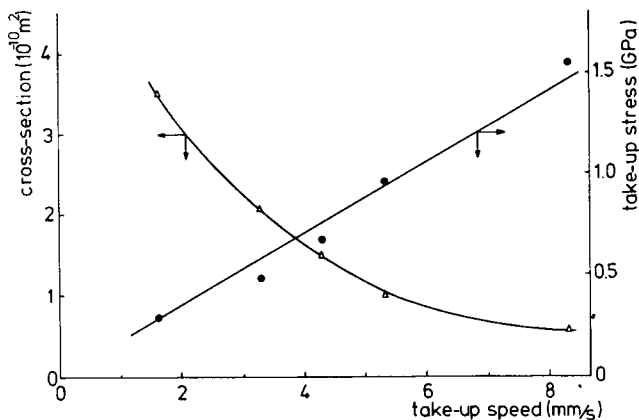


Fig. 11. Influence of takeup speed on cross section ( $\Delta$ ) and takeup stress ( $\circ$ ) of fibers grown at  $113^\circ\text{C}$  and rotor speeds of  $50.5 \text{ mm/s}$ , using a rotor having  $115 \text{ mm}$  diameter.

that stress plotted vs. rotor speed displays a minimum. A similar pattern was observed in measurements taken at  $110^\circ\text{C}$ . This minimum is in accordance with fracture occurring both at low and at high rotor speeds. The high stress at low speeds can be ascribed to the small cross section, while enhanced takeup stress at high rotor speeds is related to loop formation.

### Takeup Speed

The takeup speed is closely related to the residence time of the fiber on the rotor. This explains that the cross section of the fiber is small at high takeup speeds, where residence time is reduced. Actually, cross section was found to be inversely proportional to takeup speed.<sup>12</sup> As a result of the growth process taking place at the edges of the fiber, which has the shape of a ribbon, the takeup force is nearly independent of cross section.<sup>12</sup> The decrease of cross section and ensuing increase of stress with increasing takeup speed are illustrated in Figure 11 for crystallization at  $113^\circ\text{C}$ . At a stress of  $1.5 \text{ GPa}$  fracture occurred. Fracture stress is below the room-temperature strength of  $3\text{--}4 \text{ GPa}$ . This is due to the decrease of breakage strength by a factor of about 3 as a result of the increase of temperature from  $20^\circ\text{C}$  to  $113^\circ\text{C}$ .<sup>2,11</sup>

It was generally observed that a sufficiently large reduction of the takeup speed also led to fracture, as a result of loop formation. The limiting takeup speed depended on process conditions such as rotor speed and temperature. The observation of fracture at low speeds suggests that stress is high in this region, and consequently a plot of stress vs. takeup speed measured over a sufficiently wide range would display a minimum.

It is remarkable that an increase of the takeup speed has exactly the opposite effect to that of increasing the rotor speed. At low takeup speeds and at high rotor speeds, loops are formed, whereas the fiber is thin at high takeup speeds and low rotor speeds. This suggests combining high takeup speeds with high rotor speeds, so as to compensate for the decrease of cross section as a result of the former variable by an increase of the latter. For crystallization at  $110^\circ\text{C}$  the matter is straightforward: cross section is directly proportional to rotor speed,<sup>15</sup>

and inversely proportional to takeup speed,<sup>12</sup> which amounts to a direct proportionality of cross section  $\phi_c$  to the ratio of rotor speed  $V_r$  to takeup speed,  $V_t$ :

$$\phi_c \sim \frac{V_r}{V_t} \quad (1)$$

Equation (1) is in full agreement with experimental results.<sup>5</sup> This relationship indicates that if rotor speed and takeup speed are simultaneously increased, such that their ratio remains constant, cross section will also be constant. Crystallization conditions at which this ratio is kept constant have the advantage of combining high mass growth rate<sup>15</sup> (i.e., the amount of fibrous material produced per unit of time), with high takeup speed, while fracture is also avoided. This approach proved to be successful. Although, at 110°C and a rotor speed of 50 mm/s, the maximum takeup speed was 8 mm/s, a takeup speed of 16 mm/s could be attained at a rotor speed of 150 mm/s.

Further simultaneous increase of rotor and takeup speed revealed a limitation to surface growth of a completely different nature, as is illustrated by the following observation. Fibers could be grown at a temperature of 113.5°C, rotor speed of 110 mm/s, and takeup speed of 4 mm/s (data of Figs. 9–11). The rotor speed was relatively high for the given takeup speed and there were indications of loop formation, such as an irregular force. One would expect that an increase of takeup speed to 11 mm/s would reestablish the steady process, and, indeed, force became more stable. Nevertheless, after 1 hr fracture occurred, although the takeup stress was about 0.4 GPa and thus considerably below the expected fracture stress of about 1 GPa. The fibers grown in this period had a gel-like appearance and withdrew a large amount of solvent. This appearance is in strong contrast to the normal fibers, which are nearly dry when emerging from the takeup tube. The gel-like material could readily be removed from the wet structure by gently rubbing with a paper tissue. A fiber, after cleaning in this way, had a room temperature strength of 0.86 GPa, which is less than  $\frac{1}{3}$  of the strength of 2.93 GPa of the fiber produced at the lower takeup speed of 4 mm/s. It is evident that the strength of the fiber would have been much lower still, if we would not have removed the loose gel-like material. In our opinion, this low tensile strength indicates that the process of fiber formation cannot keep pace with the high takeup speed and rotor speed.

Fracture under conditions of simultaneous high rotor and high takeup speed is not merely due to a decrease of fiber tensile strength. It was found that takeup force increased, which seems to be due to reduced stress-relaxation as a result of diminished rate of extended-chain crystallization, which is reflected in the lower tensile strength. Part of the increased takeup force may also be due to the enhanced formation of embryonic crystallites in the adsorbed layer on the rotor, because the shear rate in this layer increases with rotor speed. These crystallites hamper the chain mobility in the adsorbed layer, through which the fiber slides.

### Continuous Growth Domain at 110°C

All observations described above suggest that at a given crystallization temperature there exists a certain range of rotor and takeup speeds within which

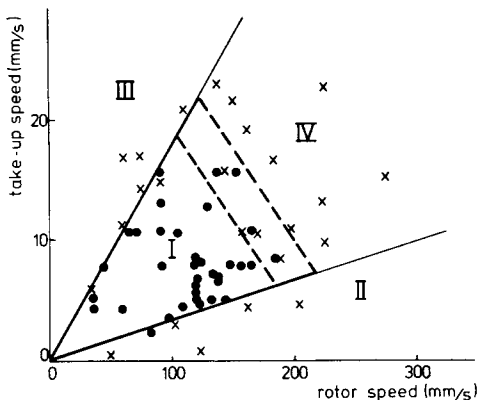


Fig. 12. Rotor speed-takeup speed domain, leading to continuous surface growth at 110°C. Within the triangular area I growth continued for 1 h or more (●). Outside this region fracture occurred within this time (×). The rotors employed had diameters of 115 and 179 mm.

bounds continuous growth should be possible and beyond which limits fracture is likely to take place. These limits have been explored for 110°C. If growth could be extended for over 1 h, it was referred to as continuous growth, and indicated by filled data points in Figure 12, where the takeup speed is plotted vs. rotor speed. If fiber growth did not last for 1 h, the experimental observation is indicated by a cross. Figure 12 reveals that there exists a triangular area, indicated by I, within which bounds continuous growth was possible, and areas II, III, and IV refer to the takeup speed/rotor speed values that led to fracture. For a given takeup speed, breakage occurs as well at high as at low rotor speeds, but at intermediate values growth is continuous. This is in agreement with the minimum of takeup stress as a function of rotor speed displayed in Figure 10.

Area II covers the range of low takeup speeds and high rotor speeds and is inaccessible because the longitudinal growth rate is higher than the takeup speed, which leads to loop formation.

Area III designates the experimental conditions for which fibers are thin, as a result of which takeup stress reaches the tensile strength of the fibers.

In region IV breakage occurs because the strength of the fibers is low, which is indicative of an imperfect fiber formation process. Moreover, in this area the high rotor speed causes great shear forces resulting in a high takeup force, which also contributes to failure.

It has been mentioned that loop formation may be reduced by the use of a rotor surface, in which a wedge-shaped groove has been turned.<sup>6</sup> The growing process is in this case initiated by placing a fibrous seed into this groove. The groove apparently keeps the growing fiber in its track and thus limits longitudinal growth by the presence of the fiber that is about to leave the rotor surface. The beneficial effect of the groove is illustrated by the increased upper limit for the rotor speed; using a grooved surface, a maximum rotor speed of 150 mm/s was reached at 110°C and takeup speed of 2.1 mm/s, whereas at the same temperature and takeup speed the maximum rotor speed for a smooth teflon surface was only 80 mm/s, as was concluded from 10 attempts to establish growth at higher speeds, which constantly led to fracture.

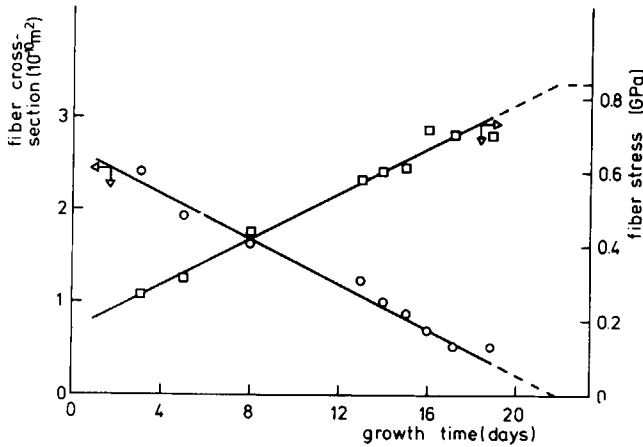


Fig. 13. Influence of the growth time on the cross section and the take-up stress during the growth of polyethylene fibers. The fiber was crystallized using a rotor in which a 0.5 mm deep wedge-shaped groove had been turned. The rotor diameter was 179 mm, the rotor speed 95 mm/s, and the take-up speed 6.3 mm/s.

In order to devise an experiment with maximum growth time, one should, on one hand, select rotor speed/take-up speed conditions in the center of area I of Figure 12 and, on the other hand, use a grooved rotor. Proceeding in this manner, it appeared possible to continue growth during 19 days, which resulted in a  $10^4$  m long fiber.

It is interesting to study the cause of fracture after such a long period of uninterrupted growth. Figure 13 shows the fiber cross section and take-up stress in the course of the 19 days. The take-up force was approximately constant, which, in combination with the decreasing cross section, caused the stress to rise, and finally to reach fracture strength. The decrease of fiber cross section with time must be due to a decrease of polymer concentration, to fractionation, to polymer degradation as a result of the flow and the presence of traces of oxygen, and to the grinding of the rotor surface by the friction of the fiber. The role of

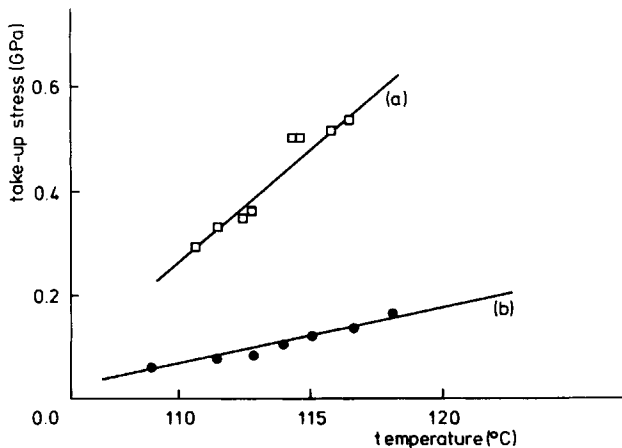


Fig. 14. Influence of temperature on the take-up stress measured during the surface growth of a polyethylene fiber, using a 179 mm diameter rotor: (a) smooth rotor, rotor speed 109 mm/s, take-up speed 7.85 mm/s; (b) rotor with groove, rotor speed 150 mm/s, take-up speed 1.05 mm/s.

TABLE I  
Estimate of Maximum Takeup Speed ( $V_t^{max}$ ) for Surface Growth, as a Function of Temperature ( $T$ )<sup>a</sup>

$T$ (°C)	$V_t^{max}$ (mm/s)	$V_r$ (mm/s)
110	16	130
113.5	8	100
116	5	120
118	2	100

<sup>a</sup> The rotor speeds  $V_r$  at which these  $V_t^{max}$  were obtained are quoted. The polyethylene fibers were crystallized from a 0.5 wt % *p*-xylene solution, using a rotor with a diameter of 115 mm.

grinding is in agreement with earlier observations of the effect of surface roughness.<sup>12</sup> The influence of grinding was demonstrated by shifting a fiber to a fresh part of a smooth rotor after growth during 24 h. This displacement resulted in an increase of cross section by a factor of 1.3, an effect which remained for at least 1 h.

### Temperature

Most of the results presented above were obtained by performing crystallization experiments at 110°C. In view of the strong influence of temperature on the crystallization process<sup>15</sup> and concomitantly on the morphology<sup>4</sup> and mechanical properties,<sup>2</sup> we have explored a rather wide temperature range from 103°C to 125°C.

It was generally observed that the takeup stress increased with rising temperature. The increase in takeup stress in the range 110–120°C for a smooth teflon rotor and for one modified with a groove is illustrated in Figure 14. The stress level is lower in the case of the grooved rotor, which seems to be due to the low takeup speed, in accordance with Figure 11, which shows the increase of stress with takeup speed. The takeup speed/rotor speed values employed for the experiments with a grooved rotor, which result in low stress (Fig. 14), would lead to loop formation and breakage if a smooth rotor were used. This illustrates once more that the conditions for fibrous crystallization are changed by the introduction of a groove.

The stress increase with temperature is evidently related to the decrease of crystallization rate, which causes the fibers to become thinner.<sup>5</sup> Moreover, stress may be high at elevated temperatures, because due to the lower longitudinal growth rate of extended chain crystals the stress-relaxation due to crystallization is diminished.

The ensuing effect on the conditions for continuous growth has not been studied as elaborately as for the case of 110°C. At 110°C the triangular domain where continuous growth takes place can be characterized by a maximum takeup speed of 16 mm/s and a maximum rotor speed of 180 mm/s. These parameters will be used to concisely illustrate the effect of temperature.

Table I shows that the maximum takeup speed decreases with temperature. At 110°C and 118°C the highest speeds were 16 and 2 mm/s, respectively. This effect is not unexpected because the stress increase with temperature must be compensated by the use of a lower takeup speed.

Table II compiles a number of data on the maximum rotor speed at which the

TABLE II  
Estimate of Maximum Rotor Speed ( $V_r^{\max}$ ) for Surface Growth, as a Function of Temperature ( $T$ )<sup>a</sup>

$T$ (°C)	$V_r^{\max}$ (mm/s)	$V_t$ (mm/s)
103	12	3
107	45	3
110	180	8
118	250	2

<sup>a</sup> The takeup speeds ( $V_t$ ) at which  $V_r^{\max}$  are obtained are quoted. The polyethylene fibers were crystallized from a 0.5 wt % *p*-xylene solution, using a rotor with a diameter of 115 mm.

fiber could still be grown continuously at various temperatures. At 103°C and 118°C the maximum rotor speeds were 12 and 250 mm/s, respectively. At high temperatures loop formation apparently takes place at much higher speeds. This is in line with the observation that crystallization rate decreases with temperature and increases with rotor speed.<sup>15</sup>

### Influence of Solvent Quality

In all experiments described above use was made of the solvent *p*-xylene. Surface-growth was not restricted to this solvent, but it was found that the temperature required for continuous growth depended on the solvent employed. It was investigated whether there exists a relationship between the range of temperatures where growth may be continuous and the solvent quality. As a measure of solvent quality, we employed the equilibrium dissolution temperature of polyethylene in the solvent. Equilibrium dissolution temperatures were obtained from the literature<sup>18</sup> if available, and otherwise estimated by differential scanning calorimetry of a 5% solution of high pressure annealed high-molecular-weight polyethylene. For this purpose the peak temperature of the dissolution endotherm was measured at a heating rate of 0.31°C/min. For both solvents *p*-xylene and decalin, this peak value was 2°C below the equilibrium dissolution temperature. This constant difference was added to the peak tem-

TABLE III  
Influence of Equilibrium Dissolution Temperature of Polyethylene,  $T_d^0$ , in Solvent Used for Surface Growth on Temperature Resulting in Least Fracture,  $T_c$ <sup>a</sup>

Solvent	$T_d^0$ (°C)	$T_c$ (°C)
Decalin	116.5 <sup>b</sup>	102
<i>p</i> -Xylene	118.6 <sup>b</sup>	114
Mixture of paraffins	127.5 <sup>d</sup>	124
<i>n</i> -Dodecane	129.4 <sup>d</sup>	124
Paraffin oil <sup>e</sup>	134.0 <sup>d</sup>	128

<sup>a</sup> Growth was performed using a 0.5 wt % solution of high molecular weight polyethylene, at rotor speed of 50 mm/s and takeup speed of 1.1 mm/s.

<sup>b</sup> Equilibrium dissolution temperature obtained from Ref. 18.

<sup>c</sup> Tradename Shellsol K, purchased from Shell, containing 97% aliphatics and 3% aromatics; initial boiling point 250°C.

<sup>d</sup> Equilibrium dissolution temperature estimated by DSC.

peratures obtained using the other solvents, which resulted in our estimates of the equilibrium dissolution temperatures.

Attempts were made to grow fibers at a rotor speed of 50 mm/s and a takeup speed of 1.05 mm/s. For each solvent Table III gives an estimate of the temperature where fracture was least prominent. This temperature appeared to be 4°C below equilibrium dissolution temperature for nearly all solvents. This stresses the role of crystallization, which is also governed by equilibrium dissolution temperature.

The solvent decalin behaved exceptionally. Optimal temperature was 13°C below equilibrium dissolution temperature, and even at this value fracture occurred in many experiments. This was related to a small fiber cross section and is a result of poor adsorption of polyethylene on the teflon rotor surface in the presence of decalin.<sup>12</sup> The cross section may be increased by a decrease of temperature, which seems to cause the low optimal temperature in the case decalin was used as a solvent.

### **Influence of Polymer Concentration**

Earlier investigations have shown that surface-growth can be established in a concentration range from 0.01<sup>1</sup> to 0.7 wt %<sup>11</sup> of polymer in *p*-xylene and that fiber cross section decreases with decreasing concentration. Presently, we were able to establish fibrous crystallization in a 2 wt % solution too, e.g., at 110°C, rotor speed of 65 mm/s, and takeup speed of 3.1 mm/s. The influence of process variables on the possibility to establish continuous growth was not studied at concentrations other than 0.5 wt %. In a 3 wt % solution the force acting on a fibrous polyethylene seed was of the order of 5*N*, which was so large that all attempts to initiate fibrous crystallization in the range of 112°C to 118°C led to breakage of the seed. This suggests that the mobility of the macromolecules in solution is severely limited at this relatively high concentration, due to a large density of chain entanglements.

### **Influence of Polymer Molecular Weight**

Typical for the surface-growing process is the extremely high molecular weight of the polymer used. Experiments were made to find out whether such long chains are really essential. Normally, high polyethylenes having weight average molecular weight ( $M_w$ ) of  $4 \times 10^6$  or of  $1.5 \times 10^6$  g/mol were used, and no significant difference was observed in experiments comparing these high polymers. The attempt was made to induce crystal growth in a 0.5 wt % solution in *p*-xylene of a polyethylene having much lower  $M_w$  of  $9 \times 10^4$  g/mol. A seed fiber did not grow under normal conditions. Longitudinal growth could be induced at very low temperatures of 103–107°C in combination with high rotor speeds of 100–500 mm/s and low takeup speeds of the order of 0.5 mm/s. The fibers produced had tensile strengths of only 0.3 GPa, whereas fibers grown from the high molecular weight solutions normally exhibit strengths of 3 GPa. These observations suggest that strong fibers can only be grown from a solution of very long chains, probably as a result of their ability to form entanglements with long relaxation times.

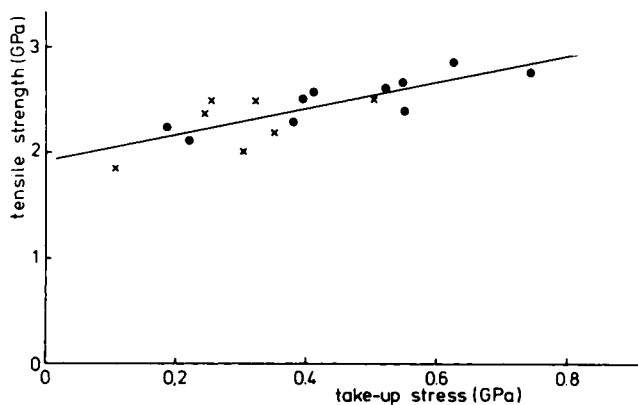


Fig. 15. Influence of takeup stress on the tensile strength at room temperature of high molecular weight polyethylene fibers. Fibers were surface grown at 110°C from a 0.5 wt % *p*-xylene solution. (x) Rotor speeds varying from 93 to 223 mm/s, and takeup speeds from 8 to 17 mm/s, rotor diameter 179 mm; (O) rotor speeds in between 34 and 155 mm/s, takeup speeds of 4 to 16 mm/s, rotor diameter 163 mm.

## DISCUSSION

The evidence presented above indicates that high takeup stresses lead to failure of the growth process. A minimal stress, however, is required to prevent dissolution.<sup>19</sup> Accordingly, one may suggest producing fibers at moderate stresses. However, the mechanical properties and, in particular, the tensile strength of the fibers depend on the takeup stress, as is shown in Figure 15 for a series of fibers grown at 110°C. Fibers crystallized at stresses of 0.1 and 0.7 GPa had tensile strengths near 2 and 3 GPa, respectively. The increase of tensile strength with the takeup stress indicates that creep takes place during the surface-growth process, in line with other observations of stress-relaxation<sup>19</sup> and creep<sup>20</sup> taking place in surface-grown materials at temperatures of 90–120°C. The amount of creep required to attain the optimal mechanical properties, however, may also be supplied in a separate hot-drawing stage. It has been shown that this leads to excellent mechanical properties.<sup>7,20</sup>

In general, the limitations of the surface growth process should originate in the mechanism of fiber formation. It has been concluded that fiber formation involves<sup>12,15</sup> (1) adsorption<sup>21</sup> of entangled clusters of polyethylene molecules on the rotor surface, (2) formation of entanglements with long relaxation times between cilia of the fiber and adsorbed molecules, (3) extension of the molecules by shear flow, and, (4) crystallization. For surface growth, entanglements must be present indeed. This can be seen from the fact that a high molecular weight polymer is required, and from the rapid decrease of fiber cross section as a result of a reduction of the polymer concentration.<sup>1</sup> The importance of coil deformation, which involves relaxation times increasing with polymer concentration in the semidilute region of coil overlap,<sup>22,23</sup> is illustrated by the high forces measured in a relatively concentrated solution. The large force measured in such a solution containing 3 wt % of polyethylene led to fracture. Ample illustration of the role of crystallization has been presented earlier<sup>15</sup>; it appeared that secondary crystal nucleation may account for the temperature and rotor speed dependence of mass growth rate in a quantitative way. Furthermore, it has been



shown that surface-growth is limited by a maximum temperature at which the driving force for longitudinal crystallization vanishes.<sup>15</sup> This can be seen from the rise of takeup stress upon increasing temperature.

Fibers produced at the highest rotor and takeup speeds exhibit low tensile strengths and are covered with a layer of gel-like material. This suggests that clusters of entangled molecules which give rise to the gel are present at the growth site, but that the gel is not transformed into fibrous material. It seems therefore that transport of polymer molecules is sufficiently fast, but that adsorption takes place at too slowly a rate, so that the counteracting force needed for coil extension by the flow is insufficient. This hypothesis that adsorption is a limiting factor is demonstrated by a number of observations made by various workers.<sup>11,12,24</sup> Experiments varying the rotor surface material and roughness revealed that an increase of polymer adsorption induces a rise of lateral growth rate.<sup>12</sup> The fact that lateral growth rate is higher using a teflon rotor as compared to experiments with a metal one illustrates this.<sup>12,11</sup> Concomitantly with the decreased lateral growth rate, a brass rotor led to a relatively low ultimate takeup speed.<sup>11</sup> This is in line with the present observations of the breakage of thin fibers, and is predicted by the influence of lateral growth rate on the takeup stress.<sup>24</sup> It is conceivable that surfaces having more adsorption sites or larger attraction energy will lead to an enhanced rate of adsorption. Other experiments have revealed that, using surfaces with increased roughness and ensuing increased lateral growth rate, the polymer coils not only adsorb faster, but can be deformed further too.<sup>15</sup> The just-mentioned experiments are examples of increased adsorption efficiency, but lateral growth rate depends also on the macroscopic rotor surface area covered by the growing fiber.

A large enhancement of longitudinal growth rate by a factor of 10 or more was achieved in film formation on a slightly conical rotor,<sup>9</sup> at which the growth front shifts along the rotor axis so that it constantly meets a fresh adsorbed layer. Fiber formation was not possible at these high rates. We employed a more strongly tapered conical rotor on which a fiber forming two or three windings could be grown. This resulted in an increase of maximum takeup speed to 25 mm/s, as compared with 16 mm/s attained with a cylindrical rotor at the same temperature of 110°C. The high number of turns in experiments with this rotor caused a high takeup force which in many cases gave rise to breakage of the fiber. Another means of increasing the useful surface area for adsorption was by sweeping the fiber up and down the rotor, so as to ensure that it constantly meets freshly adsorbed molecules.<sup>11</sup> This resulted in an increase of lateral growth rate, and, at 110°C, in a rise of maximum takeup speed from 25 to 50 mm/s.

The evidence just presented indicates that the rate of attachment of clusters to the rotor surface is a limiting factor, and suggests that attachment takes place by adsorption of polymer segments. One may reject this conclusion and propose that it is not adsorption of clusters of entangled molecules that is rate determining, but the formation of entanglements between these clusters and the loops of molecules that remain permanently adsorbed on the rotor.

It has been noted, however, that the takeup force is unaffected by changing with width of the ribbon-shaped fiber. This indicates that entanglements with adsorbed molecules are not created between the broad surface of the ribbon sliding over the rotor, but only at the edges of the fiber.<sup>12</sup> We may therefore conclude that adsorbed molecules are rapidly withdrawn by the fiber and that

permanently adsorbed molecules play no role in surface growth. This conclusion is supported by the observation that broad films can be produced<sup>9</sup> without causing large forces.

## CONCLUSIONS

Although not all problems have been solved in depth, we can draw the following conclusions.

Fracture may occur in three ways: (1) by loop formation, (2) by the growth of too thin fibers, and (3) by the crystallization of too weak fibers.

1. Loop formation takes place at low temperatures and high ratios of rotor speed to takeup speed, and is essentially due to too rapid longitudinal crystal growth.

2. Fibers are too thin at high temperatures and at low ratios of rotor speed to takeup speed, which is basically due to a combination of too slow lateral fiber growth rate and too short residence time of the fiber on the rotor.

3. Fibers become too weak at high values of both rotor and takeup speed. Under these conditions the rate of adsorption of polymer on the rotor surface is insufficiently fast, as compared to the high crystallization rates.

One may, furthermore, conclude that a high molecular weight polymer is required to provide for sufficiently long relaxation times of the chain entanglements.

When taking these effects into account, and, when using a rotor surface modified with a groove, there is still a considerable range of conditions, where the growth process is sufficiently stabilized so as to continue for weeks. Although fibers grown in this stable range do not have the highest strength and modulus, these may readily be improved in a hot-drawing stage.

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