

Studies on the Orientation Phenomena by Fiber Formation from Polymer Melts. Part I. Preliminary Investigations on Polycapronamide

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The formation of fibers from polymer melts is accompanied by macromolecule orientation along the fiber axis, the degree of which is highly dependent on spinning conditions. This phenomenon, interesting in theoretical as well as in technological aspects, was observed by several authors.¹⁻³ Some of them^{2,3} assumed the spinning orientation to be analogous to orientation occurring by cold-drawing. The evident differences between those processes, however, inclined us to suppose that their mechanisms are not identical.

The present paper begins the studies whose purpose is to explain the mechanism of macromolecule orientation occurring when synthetic fibers are spun from polymer melts. The first part gives the qualitative analysis of the phenomenon based on the investigations carried out on polycapronamide. The next parts will contain the quantitative interpretation and experimental results obtained from other polymers.

SCHEME OF THE FIBER FORMATION (SPINNING) PROCESS

Through the round orifice of the spinneret (Sp) of diameter φ_0 (see Fig. 1) the polymer melt of temperature T_0 is pressed at the mean linear velocity V_0 . The polymer stream F takes the path l through the cooling medium (air) and is wound on the winding drum (D) which revolves with constant circumference-velocity V_E . Along the path l , the solidification and cooling of polymer proceeds as well as the drawing to obtain the final fiber diameter φ_E which is related to the velocity by the continuity equation:

$$V_0 \varphi_0^2 \gamma_0 = V_E \varphi_E^2 \gamma_E = \text{const.}$$

where γ_0 and γ_E are corresponding polymer densities.

THEORETICAL

In the above-described process, the orientation of macromolecules along the fiber axis might be achieved as the result of the action of two different mechanisms which may be described with the aid of the following simplified models:

- (1) The deformation (extension) of the polymer chain network in the solid polymer region.
- (2) The action of the velocity field on the liquid melt stream.

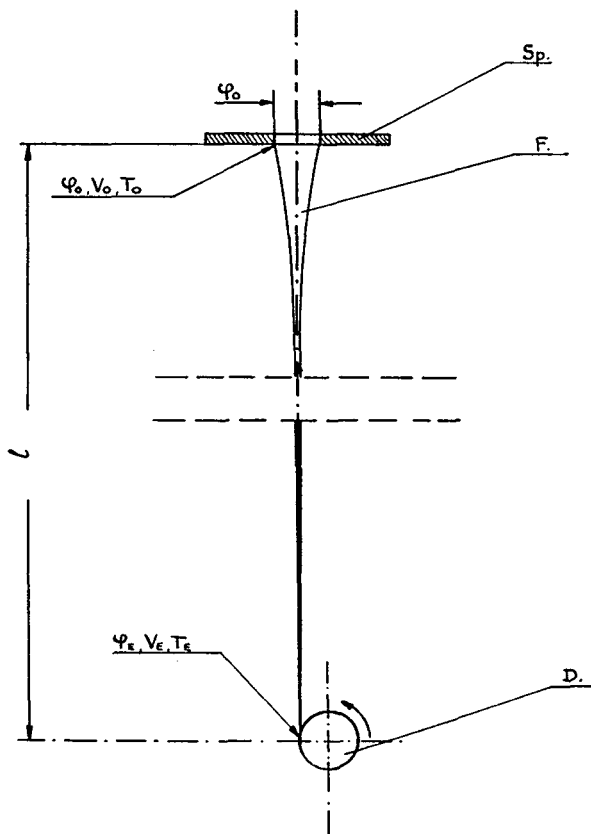


Fig. 1. The scheme of a fiber formation (spinning) process.

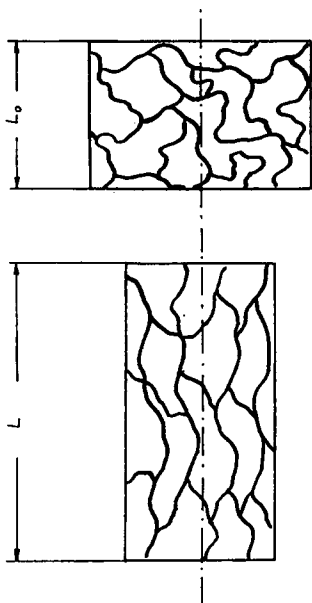


Fig. 2. The model for the first mechanism of orientation (extension of the chain network).

The above two mechanisms are different in principle. The first of them (Fig. 2) is characteristic for the deformation of gels and amorphous polymers (Müller⁴). Similar to it is the familiar "cold-drawing" process. The main factor determining the degree of orientation here is the deformation ratio $\lambda = l/l_0$ (draw ratio), i.e., the ratio of final to original length of the sample. The occurrence of some "tie points" in the network as well as the high viscosity cause the relaxation factors (temperature, internal friction) to have only secondary significance. The stress necessary for such deformation is as a rule high and, like the degree of orientation, is highly dependent on deformation ratio and practically independent of deformation speed. According to the theory of Kuhn and Gr \ddot{u} n,⁵ the statistical reactionary force (statistische R \ddot{u} ckstellkraft) resulting from the change of entropy upon extension of statistically skinned polymer chains amounts, for low extensions to:

$$R = \frac{kT}{A} L^{-1} (h/NA)$$

where

- k = Boltzmann constant
- T = absolute temperature
- A = length of the statistical chain-unit
- N = number of statistical units in macromolecule
- L^{-1} = inverse Langevin function
- h = macromolecule end-to-end distance.

The ratio h/NA in the above formula may be treated as proportional to the deformation ratio λ .

At very high extensions at which the breaking of "tie points" occurs the stress necessary for deformation rises still more steeply with the deformation ratio.

When the polymer occurs in both high-temperature and low-temperature structural forms, the orientation of fibers containing the quenched high-temperature form is often accompanied by structural transformation. Crystalline polymers frozen in the amorphous state in the orientation process can undergo crystallization. These transformations consist of the partial breaking of original structures in consequence of the action of high stresses needed for deformation, and the forming of new, thermodynamically more stable structures.

The second mechanism of orientation, which extends on liquid stream of polymer melt, is analogous to the streaming orientation observed in capillaries or in a Couette apparatus. This mechanism differs, however, from normal streaming orientation in that the velocity field has a parallel velocity gradient, as compared to the transverse field in capillaries or in a Couette apparatus (Fig. 3).

For this model, the factors determining the degree of orientation are the parallel velocity gradient dV/dl and the relaxation time τ , which latter factor determines the rate of simultaneously-occurring thermal disorientation (diffusion). In comparison

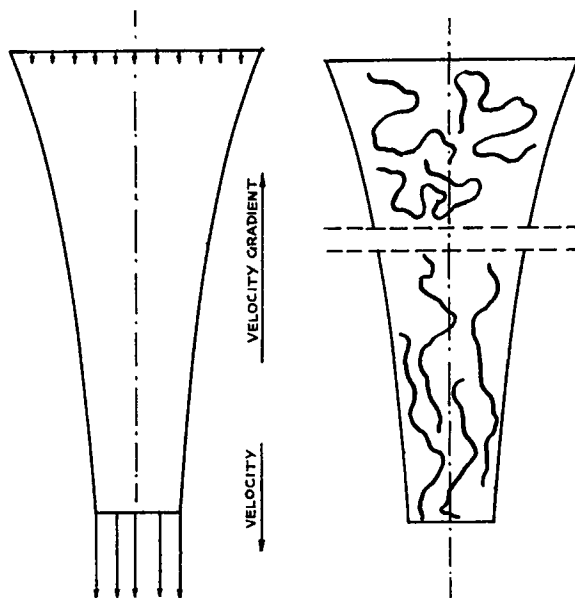


Fig. 3. The model for the second mechanism of orientation (action of the velocity field of the parallel velocity gradient).

to the previous mechanism, the deformation ratio (defined as a ratio of final to original linear velocity) does not play any important role in the orientation process, because of the relative freedom of macrobrownian movements and lack of "tie points" between macromolecules.

The stress which is, generally speaking, considerably lower than that regained by mechanism (1) depends, as does the degree of orientation, on the velocity gradient dV/dl and the relaxation factor. This relation becomes clear when the Trouton's equation for traction:⁶

$$\sigma = 3\eta dV/dl$$

is compared with Debye's formula for relaxation time:

$$\tau = (\text{const.}/kT)\eta$$

where, σ = traction stress and η = viscosity.

The remarkable freedom of the macrobrownian movements and low stresses lead one to expect no structural transformations from orientations through the second mechanism. The amorphous and slow-crystallizing polymers will orient in amorphous state; the polymers which have different high-temperature and low-temperature forms and which can be supercooled will orient in this form without transforming to the low-temperature form.

To establish the mechanism responsible for the orientation of polycapronamide fibers, the influences of spinning conditions in fiber birefringence and spinning stress have been investigated and the x-ray patterns for fibers oriented by melt-spinning, on the one hand, and by cold-drawing, on the other, have been compared.

EXPERIMENTAL

Material: Polycapronamide, commercial product of Gorzowskie Zakłady Włókien Sztucznych, intrinsic viscosity in 95.6% H_2SO_4 at 25°C.: 170 $\text{cm}^3/\text{g}.$, containing in melt about 6% low-molecular-weight products soluble in water.

The Apparatus for spinning consisted of the spinning head, where the melting of polymer proceeded, the gear pumps system which regulated the melt feeding-rate in the range 2.0–16.0 $\text{cm}^3/\text{min}.$, the spinnerets of 1–80 orifices with diameters 0.15–2.0 mm. and receiving-machine with take-off velocities regulated in the range of 200–4000 meters/min.

Birefringence was measured by the compensation method, using a Leitz SY polarizing microscope equipped with a micrometer eyepiece for measuring

of fiber diameter, a Berek compensator, and a MONLA lamp. The measurements were carried out in white light (a daylight filter was used).

Spinning stress was measured by a spring tensiometer KOVO at a distance $l = 4$ meters from the spinneret (above the winding-drum D in Figure 1) and calculated on the final cross-section of the fiber $(\pi/4)\varphi_E^2$.

X-ray patterns were obtained on the Hilger HRX apparatus using $\text{CuK}\alpha$ Ni-filtered radiation and plane film camera with a distance from object to film of 50 mm. The patterns were photometered by means of an MF2 nonrecording microphotometer with turning table.

RESULTS AND DISCUSSION

The Parameters of the Fiber Formation Process

The main parameters of the spinning (fiber formation) process which can affect the orientation of macromolecules are:

- (a) The deformation ratio under dynamic conditions: $S = V_E/V_0$ (corresponding to the draw ratio $\lambda = l/l_0$ under static conditions)
- (b) The mean parallel velocity gradient on the path between 0 and l_E :

$$G = \overline{dV/dl} = (1/l_E)(V_E - V_0) = (V_E/l_E)[1 - (1/S)]$$
- (c) The mean relaxation time τ_m along the path 0, l_E .

While the parameters S and G may be estimated simply from the spinning conditions, the lack of numerical values of τ and its changes between 0 and l makes the estimation of τ_m impossible.

In the estimation of mean velocity gradient G according to above-shown formula, the constant spinning-distance $l_E = 4$ meters has been used. Such a treatment is only formally right and may be used for comparative purposes only. The distance over which there is a velocity gradient is in reality much shorter than 4 meters, and hence the velocity gradient is higher than those estimated. Because we did not know the velocity distribution over the path l , all the velocity gradients have been referred to the whole distance $l_E = 4$ meters.

The mean relaxation time had to be replaced by another parameter characterizing the intensity of relaxation processes.

When the polymer contents and its molecular weight are practically constant, the mean relaxation time τ_m depends only on the temperature distribution along l . When, in addition, the original

TABLE I
 The Grouping of Experiments^a

Parameter analyzed	Series no.	Spinning conditions (technical)				Fiber formation parameters		
		φ_0 , microns	φ_E , microns	V_0 , meters/min.	V_E , meters/min.	S	G , sec. ⁻¹	Z , meters ⁻¹
Deformation ratio S	1	↗	const.	↘	const.	↗	~ const.	const.
Velocity gradient G	2	const.	↘	const.	↗	↗	↗	↗
	3	const.	const.	↗	↗	const.	↗	↘
Cooling rate Z	4	const.	↘	↘	const.	↗	~ const.	↗
	5	↘	↘	const.	const.	const.	const.	↗

^a ↗ = parameter increases. ↘ = parameter decreases. const. = parameter remains constant. ~ const. = parameter remains nearly constant.

melt temperature T_0 and the cooling-medium temperature T_u are constant too, the cooling rate may be substituted for the comparative relaxation rate. From considerations of heat transfer phenomena by melt-spinning,⁷ the following relationship was obtained for the cooling-rate criterion:

$$Z = -\frac{d \ln \theta}{dl} \quad \text{where } \theta = T - T_u$$

The cooling rate parameter Z , in contrast to the mean relaxation time τ_m , may be simply estimated from spinning conditions by means of the approximation

$$Z = (1/l_E)Bi^*Fo^*$$

where Bi^* and Fo^* are the resulting Biot and Fourier numbers on the path 0, l_E . The numerical values of parameter Z have been calculated according to the above-mentioned rule.⁷

Though absolute values of Z estimated according to the above formula may be not accurate, both because of the formula's approximate character and because of the free choice of some constants contained in the numbrs Bi^* and Fo^* , the parameter Z may undoubtedly be used as a *comparative* measure of the relaxation processes. Thus, the calculated parameter Z behaves similarly to the cooling rate and mean relaxation time τ_m .

The spinning conditions are closely bound up one with another, hence the parameters S , G , and Z are not independent. Simultaneously changing one of them and leaving the other two strictly constant is not possible, in general. For the analysis of the influence of individual parameters on the fiber birefringence and spinning stress, it was necessary to group the experiments in the series listed in Table I.

Birefringence of Fibers

The results of birefringence measurements for fibers obtained in the 1st series of spinning experi-

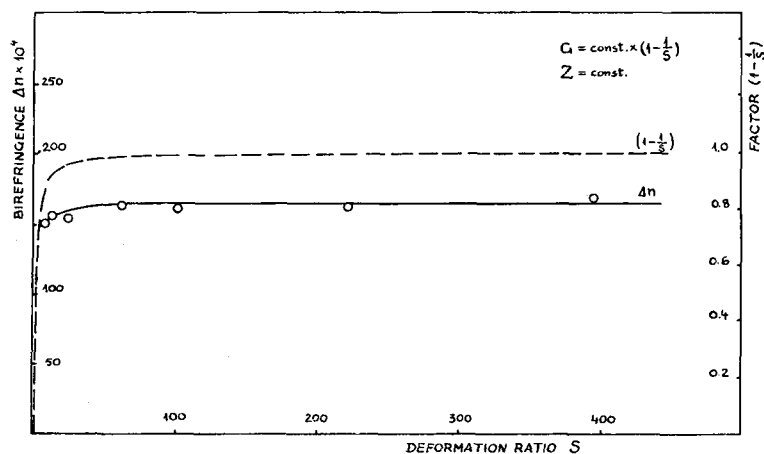


Fig. 4. The dependence of fiber birefringence on deformation ratio S .

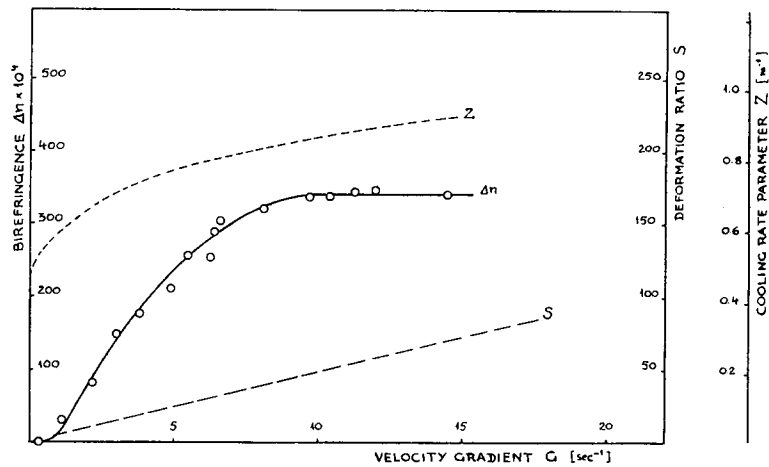


Fig. 5. The dependence of fiber birefringence on velocity gradient.

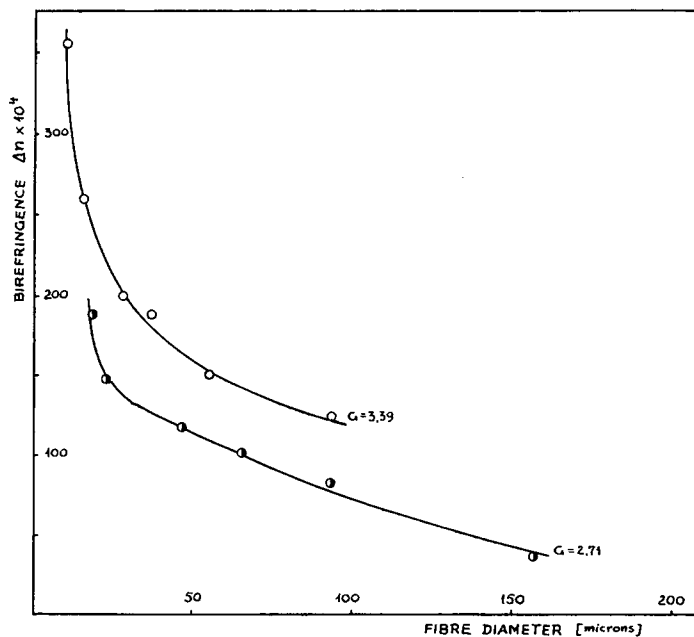


Fig. 6. The dependence of fiber birefringence on fiber diameter (velocity gradients indicated).

ments (see Table I) are shown in Figure 4. From the diagram, it is evident that except at low values of S , the birefringence is practically constant. The deformation ratios S (reaching nearly 400 in the series shown and over 1000 in another experiment) are two orders of magnitude higher than the maximal draw ratios found for rubberlike or crystalline polymers. In Figure 4 it may be observed that for the small values of S (below $S = 20$) the birefringence decreases. This deviation becomes clear when it is considered that in the 1st series of ex-

periments, the mean velocity gradient G written in the form:

$$G = (V_E/l_E)[1 - (1/S)]$$

is not *strictly* constant, but is practically fixed at higher values of S . The decrease of birefringence occurring at S below 20 may be caused by the simultaneously occurring decrease in the parameter G . The factor $[1 - (1/S)]$ determining the deviation of velocity gradient G from the constant is shown in Figure 4 by a dotted line.

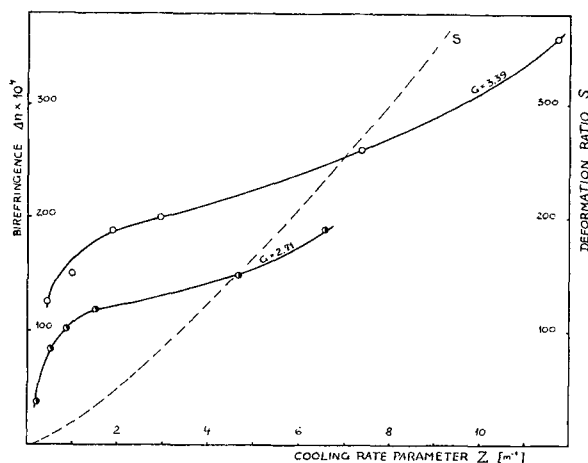


Fig. 7. The dependence of fiber birefringence on the cooling rate parameter Z (velocity gradients indicated).

The velocity gradient G is closely bound up with the parameters S and Z . The 2nd series of experiments (see Table I) contains the change of velocity gradient by simultaneous increase of parameters S and Z . In Figure 5, fiber birefringence is plotted vs. velocity gradient G . The simultaneously changing parameters S and Z are drawn with dotted lines. The relationship of birefringence vs. velocity gradient has the character of a "saturation curve" with a limiting value of about 350×10^{-4} . It is also significant that birefringence retains the value 0 in the region of G below 0.5 sec.^{-1} . In the same region of G , a strong decrease in Z is observed (thick fibers, slow cooling). It should therefore be assumed that the region of zero birefringence corresponds to conditions in which the thermal relaxation overwhelms the action of velocity field. In order to separate the influence of G from the possible influences of parameters S and Z , a 3rd series of experiments was carried out in which the deformation ratio S remained constant while the cooling rate parameter Z decreased with velocity gradient G . The results of this series are given in Table II.

TABLE II

The Influence of Velocity Gradient G on Fiber Birefringence at constant S^a and decreasing Z

Velocity gradient G , sec.^{-1}	Cooling-rate parameter Z , meters $^{-1}$	Fiber birefringence, $\Delta n \times 10^4$
1.21	0.657	32
2.18	0.464	82
3.50	0.362	172

^a $S = \text{const.} = 80.4 \pm 1.5$.

TABLE III

The Influence of Cooling Rate Z on Fiber Birefringence at Constant^a S and G

Cooling rate parameter Z , meters $^{-1}$	Fiber birefringence, $\Delta n \times 10^4$
0.282	105
1.820	161
2.512	170
5.523	210

^a $G = \text{const.} = 3.08 \text{ sec.}^{-1}$; $S = \text{const.} = 12.2$.

The comparison of the results of series 2 (Fig. 5) with those of series 3 (Table II) shows that birefringence of fibers evidently increases under the influence of velocity gradient G itself. It should be also expected that the relationship $\Delta n(G)$ at constant S and Z will yield a flatter "saturation curve" than the one observed by simultaneous increase of S and Z , as in series 2 (Fig. 5).

The cooling rate described by the parameter Z can be changed simply through the decrease of fiber diameter φ_E . In the 4th series of experiments, the diameter of fiber was changed between wide limits while the velocity gradient G remained constant. The deformation ratio S increased with decreasing φ_E . The birefringence of fibers from series 4 is plotted vs. fiber diameter in Figure 6. Figure 7 shows the dependence of fiber birefringence on the parameter Z . From Figures 6 and 7, it may be seen that the birefringence decreases with increasing fiber diameter, i.e., it increases with cooling rate Z . In order to eliminate the influence of deformation ratio S , in the 5th series the fiber diameter was changed at constant G and S . The results are given in Table III.

From the results shown in Figures 6 and 7 and those given in Table III, it is evident that the birefringence increases with increasing cooling rate. The variations in birefringence are caused by the changes of the cooling rate itself, while the velocity gradient and deformation ratio remain constant.

Spinning Stress

The variation of spinning stress under the influence of spinning conditions is similar to that observed for birefringence. The spinning stress, like the birefringence, is practically independent of the deformation ratio S . The relationships of the spinning stress to the velocity gradient G (in series 2) as well as to the cooling rate Z (in series 4) are shown in Figures 8 and 9. It must be noted that

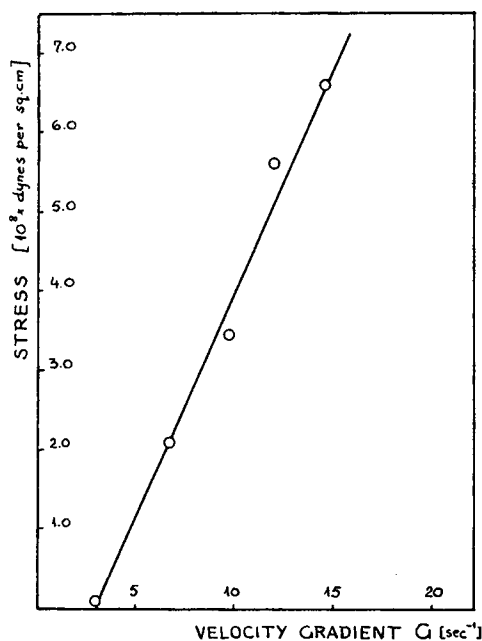


Fig. 8. The dependence of spinning stress on velocity gradient G .

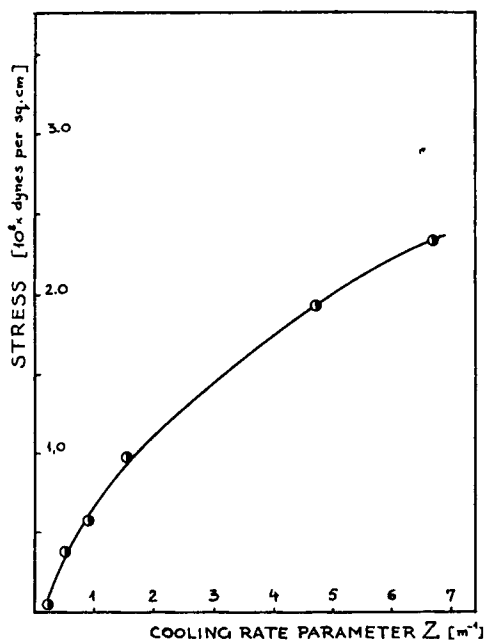


Fig. 9. The dependence of spinning stress on cooling rate parameter Z .

the observed increase of spinning stress with decrease of fiber diameter (series 4 in Figure 9, shown as a function of parameter Z) could be caused also by surface tension of the molten polymer. The measurements carried out on polycapronamide melt at 270°C . show a surface tension on the order of 70

dynes/cm. The force corresponding to this value lies about two orders of magnitude lower than that observed in spinning. Therefore the influence of surface tension on the spinning stress may be neglected.

It is significant that the spinning stress, depending on spinning conditions, amounts to 0.05×10^8 – 6.6×10^8 dynes/cm. 2 , while the stress involved in cold-drawing polycapronamide fibers, calculated on the final cross-section, is of the order 20×10^8 – 50×10^8 dynes/cm. 2 at the draw ratio 3.5. 8

X-ray Structures

The x-ray diffraction patterns of the polycapronamide quenched from the molten state show the appearance of two diffuse rings with corresponding maxima 4.2 and 8.4 Å. which relate to the frozen high-temperature modification β , the structure of which has not yet been thoroughly explained. Cold-drawing or hot-water treatment leads to the transformation to the crystalline α -modification of monoclinic elementary cells with parameters: 9

$$a = 9.56 \text{ \AA.}$$

$$b = 17.24 \text{ \AA.}$$

$$c = 8.01 \text{ \AA.}$$

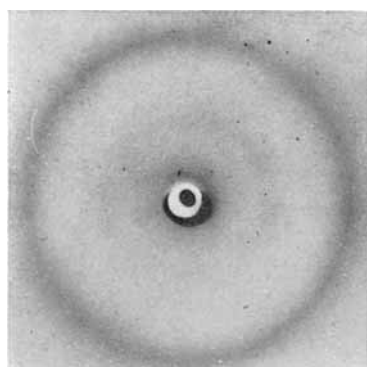
$$\text{angle } \beta = 67.5^\circ$$

The x-ray patterns of cold-drawn polycapronamide fibers show the presence of two strong equatorial reflexes (200) and $\begin{pmatrix} 002 \\ 202 \end{pmatrix}$ the distinct layer lines, and the absence, or only traces of, the meridional reflex (020).

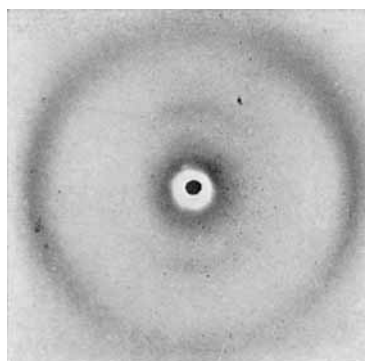
Figures 10, 11, and 12 are x-ray diffraction patterns of unstretched fibers spun with different velocity gradients G . Figure 13 shows the x-ray pattern of a cold-drawn fiber and Figure 14, that of the fiber corresponding to Figure 12, treated with boiling water.

From the comparison of patterns, it is evident that the orientation by fiber formation from melt proceeds in the unchanged modification β which is distinctly different from the modification α existing in cold-drawn fibers. The broad equatorial reflex $d = 4.2$ Å. in Figures 10–12 splits into two reflexes 4.42 Å. and 3.85 Å. after cold drawing (Fig. 13). At the same time, the strong meridional reflex $d = 8.4$ Å. disappears. The pattern of the water-treated β -oriented fiber (Fig. 14) shows the presence of reflexes characteristic for both modifications.

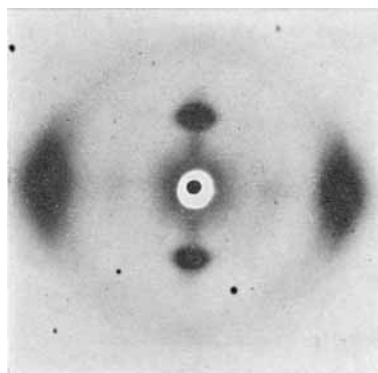
In Fig. 15 the azimuthal photometric curves for



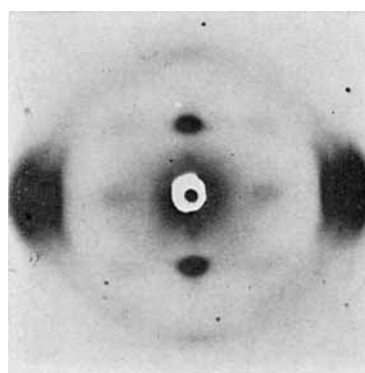
(10)



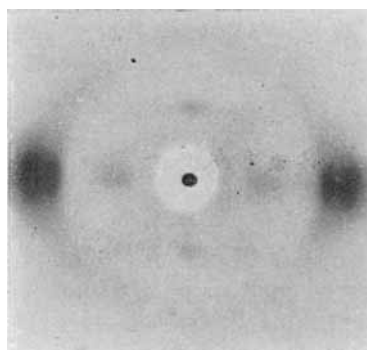
(11)



(12)



(13)



(14)

patterns 10-14 are shown. For the samples oriented in the β -form (Figs. 10-12) and for that of α -form (Fig. 13) the equatorial reflex $d = 4.2$ A. and the reflex (202) $d = 3.85$ A., respectively, were photometered.

Table IV contains the spinning parameters, the half-angles of crystallite orientation $\beta_{0.5}$, estimated from photometric curves, and the birefringence of fibers, x-ray patterns of which are shown in Figures 10-13.

The half-angle of crystallite orientation $\beta_{0.5}$ for sample F1/2a spun at the high velocity gradient of $G = 15.0$ sec.⁻¹ is nearly equal to that of the cold-drawn fiber R1, though the birefringence of the last

Fig. 10-Fig. 14. The x-ray patterns of polycapronamide fibers. For sample characteristics, see Table IV. CuK α Ni-filtered radiation, object-film distance 50 mm., fiber axis vertical.

TABLE IV
The Influence of Spinning Conditions on the Orientation Characteristics of Fibers

Sample	X-ray pattern	S	G , sec. ⁻¹	Z , meters ⁻¹	$\beta_{0.5}$, °	$\frac{\Delta n}{\lambda}$ $\times 10^4$
KA1	Fig. 10	20	1.12	2.090	40	50
F1/K	Fig. 11	7	2.76	0.491	32.5	150
F1/2a	Fig. 12	31	15.0	0.720	11.0	386
R1	Fig. 13		cold-drawn in the ratio 4:1		9.0	503

is considerably higher. This difference may be explained by the various lattice structures of the samples, as well as by the considerably higher de-

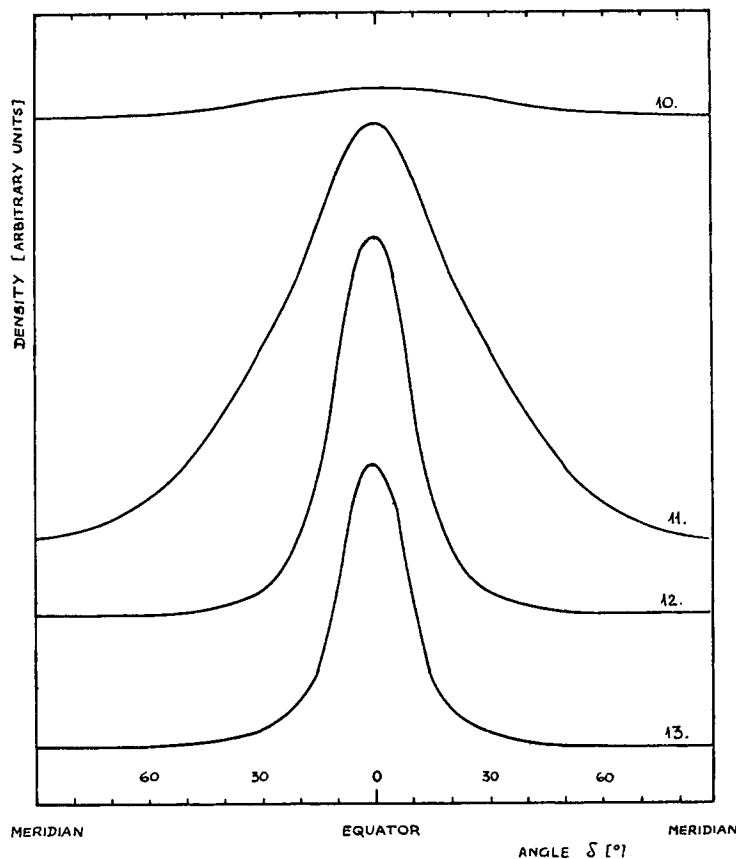


Fig. 15. The azimuthal photometric curves for x-ray patterns (pattern numbers indicated).

gree of crystallinity and dimensions of the ordered regions in the cold-drawn sample.

The examination of highly oriented samples of β -polycapronamide throws a little light upon their structure. The small number of distinct reflexes as well as their diffusivity leads to an assumption that the modification β is not a crystalline structure *sensu stricto*, but an intermediate one between the liquid of so-called "short range order" and the polycrystalline solid. The definitive explanation of this problem, however, requires more detailed investigations.

CONCLUSIONS

According to the results obtained, the main factors determining the orientation of macromolecules by fiber-formation from polymer melts are:

- (1) parallel velocity gradient dV/dl
- (2) relaxation factors.

The deformation ratio $S = V_E/V_0$ which, as a rule, is considerably higher than that attained

through cold-drawing, does not affect the orientation. It has been established that in opposition to cold-drawing where the orientation is accompanied by the structural transformation $\beta \rightarrow \alpha$, the orientation by melt-spinning proceeds in the unchanged modification β . The results obtained from experiments are in full agreement with the expectations regarding the second mechanism of orientation. The orientation thus proceeds in the liquid region of polymer (melt stream) as a result of the simultaneous action of velocity gradient and thermal relaxation.

The character of the relationship birefringence vs. velocity gradient ("saturation curve") leads us to suppose that the structural units undergoing orientation in the molten polycapronamide are rigid particles. This assumption seems to be confirmed by the presence of some order in the quenched samples (β -modification), and probably also of short range order in the melt. The verification of that hypothesis should be brought about by our further investigations carried out on another polymer.

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Synopsis

The problem of the mechanism of macromolecule orientation occurring in the formation of fibers from polymer melts has been qualitatively analyzed. As a result of birefringence, x-ray, and spinning stress investigations carried out on polycapronamide fibers, the main parameters determining orientation have been established. They are the parallel velocity gradient along the spinning length, $G = dV/dl$, and the relaxation factors. The deformation ratio S (the ratio of final to original linear velocity), analogous to the draw ratio $\lambda = l/l_0$ in the cold-drawing process, has no influence on the degree of orientation. The orientation by spinning is not accompanied by any such structural transformations as occur through cold-drawing. The fibers spun at high velocity gradients consist of well-oriented β -polycapronamide. It is thus assumed that the orientation proceeds in the region of the liquid melt-stream as a result of simultaneous action of velocity gradient and thermal relaxation. This mechanism, analogous to that causing the familiar streaming orientation of polymer solutions in capillaries or in a Couette apparatus, is different in principle from that of the cold-drawing process.

Résumé

Le problème du mécanisme de l'orientation qui se produit lors de la formation de fibres à partir de polymères fondus a été analysé qualitativement. A partir des mesures de biréfringence, rayons X et tension d'étirement effectuées

sur des fibres de polycapronamide les principaux paramètres déterminant l'orientation ont été établis. Ce sont; le gradient de vitesse parallèle à la direction d'étirement $G = dV/dl$ et les facteurs de relaxation. Le rapport de déformation S (étant le rapport de la vitesse linéaire finale et initiale) analogue au rapport d'étirement $\lambda = l/l_0$ dans le procédé d'étirement à froid n'a pas d'influence sur le degré d'orientation. Par filage l'orientation n'est accompagnée d'aucune transformation de structure ainsi que cela se passe dans le procédé d'étirement à froid. Le filage de fibres à gradient de vitesse élevée est constitué de β -polycapronamide bien orientée. On suppose donc que l'orientation s'effectue dans la région du courant fondu liquide, résultat de l'action simultanée du gradient de vitesse et de la relaxation thermique. Ce mécanisme, analogue à l'orientation bien connue due à l'écoulement de solutions polymériques dans des capillaires ou dans l'appareillage de Couette, est essentiellement différent du mécanisme dans le procédé d'étirement à froid.

Zusammenfassung

Das Problem des Mechanismus der bei der Fadenbildung aus Polymerschmelzen auftretenden Orientierung wurde einer qualitativen Analyse unterzogen. An Hand von Ergebnissen von Doppelbrechungs-, Röntgen- und Spannungsuntersuchungen, die an Polycapronamidfasern ausgeführt waren, wurden die für die Orientierung wichtigen Parameter festgestellt. Diese sind das Geschwindigkeitsgefälle parallel zur Spinnlänge $G = dV/dl$ und die Relaxationsfaktoren. Das Deformationsverhältnis S (nämlich das Verhältnis der linearen End- zur Anfangsgeschwindigkeit), gebildet in Analogie zum Dehnungsverhältnis $\lambda = l/l_0$ bei der Kaltver Streckung, hat keinen Einfluss auf den Orientierungsgrad. Die durch den Spinprozess hervorgerufene Orientierung wird nicht von Strukturumwandlungen, wie sie durch die Kaltver Streckung hervorgerufen werden begleitet. Die bei hohen Geschwindigkeitsgefällen gesponnenen Fasern bestehen aus gut orientiertem β -Polycapronamid. Es wird daher angenommen, dass die Orientierung in Bereiche der strömenden flüssigen Schmelze als Ergebnis der gleichzeitigen Wirkung des Geschwindigkeitsgradienten und der thermischen Relaxation erfolgt. Diesen Mechanismus, der der bekannten Strömungsorientierung von Polymerlösungen in Kapillaren oder im Couette-Apparat analog ist, unterscheidet sich grundsätzlich von dem der Kaltver Streckung.

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