

Studies on Orientation Phenomena by Fiber Formation from Polymer Melts. Part II. Theoretical Considerations

ANDRZEJ ZIABICKI

Gorzowskie Zakłady Włókien Sztucznych-Physico-chemical Laboratory, Gorzów Wielkopolski, Poland

In the previous paper¹ it was shown that the main factors determining the orientation of macromolecules through fiber formation from polymer melt are the axial velocity gradient dV/dl and the relaxation rate as related to cooling conditions. From those results as well as from the x-ray investigations, it should be supposed that the mechanism of orientation through fiber-spinning is analogous to the streaming orientation observed in the flow of polymer solutions through capillaries or in a Couette apparatus. The conditions occurring in the both processes however are different in principle. In the present paper, those differences will be discussed and the equations derived to describe the unstationary process of orientation for two extreme molecular models.

CONDITIONS OF ORIENTING MACROMOLECULES BY MELT-SPINNING FIBERS

Velocity Field

The existent theories of "classical" streaming orientation and birefringence treat the velocity field of a viscous liquid flowing through a capillary or between rotating cylinders (Couette apparatus). In such a field, a transverse velocity gradient dV/dr exists perpendicular to flow direction. In the case of fiber-spinning, no transverse velocity gradient exists: the velocity distribution through the fiber cross-section is practically uniform. The velocity field is characterized by an axial velocity gradient dV/dl parallel to the direction of flow. The scheme of both velocity fields is shown in Figure 1.

The character of the velocity field determines the way in which asymmetrical molecules rotate in a flowing liquid. In the field with a transverse velocity gradient (Fig. 1a), the rotation rate depends upon the shape of the molecules and the velocity gradient, whereas in the second case (Fig.

1b), the rate of rotation is dependent on the velocity gradient alone. According to the model of W. Kuhn,² the angular velocity of a rotational ellipsoid with axial ratio $p = a/b$ in the transverse-gradient field amounts to:

$$d\phi/dt = -[G_{\perp}/(1 + p^{-2})](\sin^2\phi + p^{-2} \cos^2\phi) \quad (1a)$$

and in the parallel-gradient field to:

$$d\phi/dt = -(G_{\parallel}/2) \sin 2\phi \quad (1b)$$

where

$$\begin{aligned} G_{\perp} &= dV/dr = \text{transversal velocity gradient} \\ G_{\parallel} &= dV/dl = \text{axial velocity gradient} \\ d\phi/dt &= \text{angular velocity of rotation.} \end{aligned}$$

For the axial ratio $p = 1$ (a sphere), in both cases the rotation velocity becomes constant. For the first type of field, it amounts to $-G_{\perp}/2$, while for the second type, rotation wholly disappears: $d\phi/dt = 0$. The relations between rotation velocities and angles ϕ are demonstrated in Figures 2 and 3. From these figures, it is apparent that in the transverse-gradient field the rotation is always in the same direction and that the rotational velocity never falls to 0, but only tends to 0 at $\phi = 0$ for high values of p .

In fiber-spinning the velocity field has an axial gradient, and the velocity of rotation changes sign and reaches 0 at $\phi = 0$ for any $p > 1$. Consequently, the position of a macromolecule parallel to the fiber axis is characterized by stable equilibrium. In the transverse-gradient field, the axial position of a single molecule is metastable and only a statistical equilibrium for the system may be obtained. The least deviation from an axial position $\phi = 0$, (e.g., owing to Brownian motion), is always followed, in the parallel-gradient field, by a return to the equilibrium (axial) position. In the first type of field, however, such a deviation may be fol-

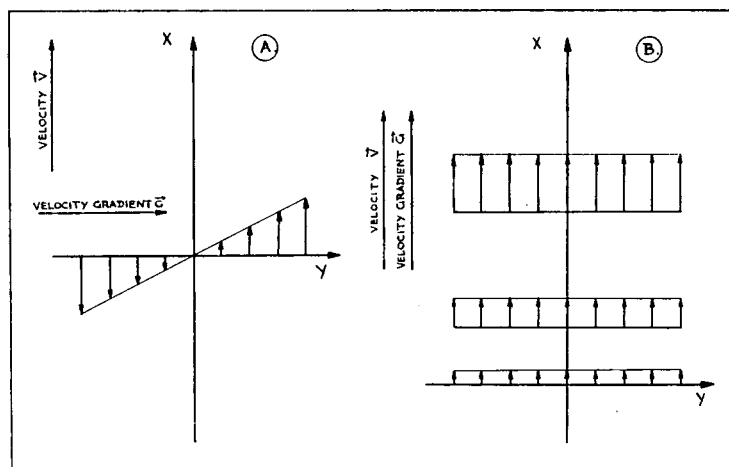


Fig. 1. Scheme of velocity fields: (A) field with transverse velocity gradient, (B) field with axial velocity gradient.

lowed either by a return or by a further rotation of the macromolecule.

Those differences are probably responsible for the differences between the rheological behavior of macromolecular liquids flowing through capillaries and those being spun into fibers. This seems to be confirmed by results of spinnability investigations carried out on polymer solutions by Nitschmann and Schrade.³

Molecular State

In the theories of streaming orientation and birefringence, the diluted polymer solutions have usu-

ally been considered to contain independent, single molecules free to move in the low-molecular-weight, solvent medium. In the case of fiber-formation from molten polymer, this assumption is no longer valid. The medium in which flowing proceeds consists of macromolecules alone, and the relatively small distances between them create very convenient conditions for macromolecular interactions, especially of long chains (tangle) and strongly polar polymers (hydrogen bonds, short range order). Those factors should be taken into account in exact interpretations of investigations carried out on polymers of different molecular structures.

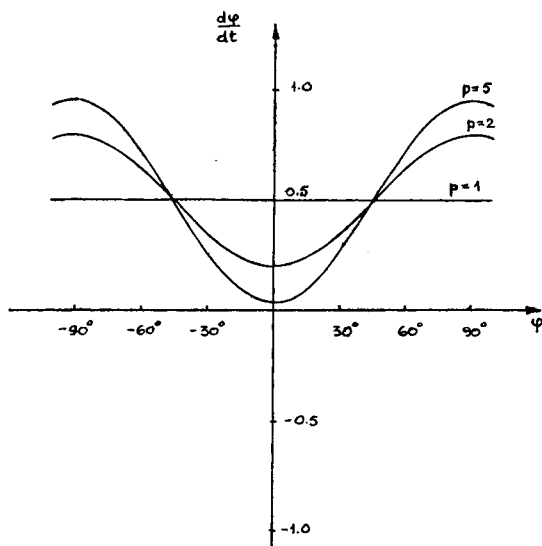


Fig. 2. Angular dependence of rotation velocity of ellipsoid in the field with transverse gradient.

$$d\phi/dt = -G_{\perp} [1/(1 + p^{-2})] (\sin^2 \phi + p^{-2} \cos^2 \phi)$$

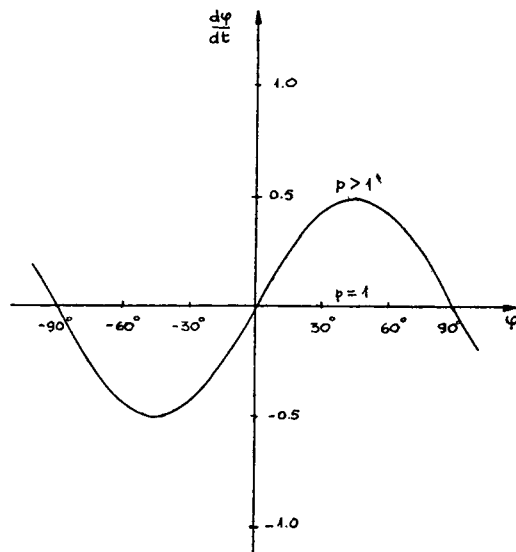


Fig. 3. Angular dependence of rotation velocity of ellipsoid in the field with axial gradient.

$$d\phi/dt = -G_{\parallel}/2 (\sin 2\phi)$$

Time Effects

In diluted or even moderately concentrated solutions of polymers which were objects of previous studies on streaming orientation, the rate of diffusion is so high that an equilibrium is reached almost instantly and time effects may be neglected. For that reason, the theories of streaming orientation regarded only stationary processes.

For molten polymers, in which viscosities are many orders higher than in solutions, time effects must be taken into account. An additional complicating factor is the variation of velocity gradients and diffusion rates with time, resulting from an increase of viscosity during cooling and solidification of polymer melt. Thus the ultimate degree of orientation is the result of simultaneous variation of velocity gradients and relaxation rates over the time t . In the further sections of this paper, the differential equations describing an unstationary orientation process will be derived for two extreme molecular models: rigid prolate ellipsoids and flexible, coiled chains.

DIFFERENTIAL EQUATIONS OF ORIENTATION

Model I. Rigid Ellipsoids

The model considered is identical with that described by Boeder⁴ and W. Kuhn² in papers regarding dispersions of rodlike particles.

The velocity field in the fiber-formation melt stream is given by equations:

$$\mathbf{V} = V_x \cdot \mathbf{i} \quad (2a)$$

$$dV_x/dx = G_{||} \quad (2b)$$

A prolate rotational ellipsoid of length l undergoes rotation under the influence of the difference between the velocities at its two ends (Fig. 4).

For a small length of the ellipsoid, the velocity difference may be written:

$$\Delta V \cong G_{||} \Delta x = G_{||} l \cos \phi \quad (3)$$

Hence, the angular velocity of rotation is:

$$\omega = d\phi/dt = -1/2 G_{||} \sin 2\phi \quad (4)$$

The orientation of rigid particles is described by a distribution function:

$$\rho(\phi) = \lim_{\Delta\phi \rightarrow 0} \frac{\Delta N}{\Delta\phi}$$

where ΔN is the number of particles which lie in the angle interval $[\phi, \phi + \Delta\phi]$. The increase of func-

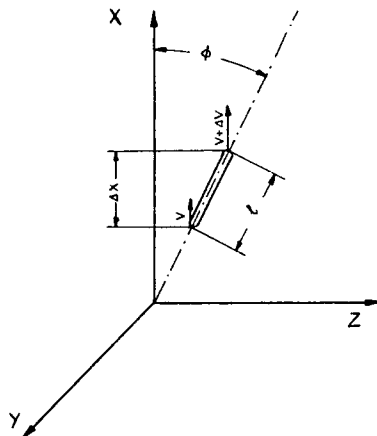


Fig. 4. Model I, rigid ellipsoid.

tion ρ in the time interval dt caused by an action of the velocity field amounts to:

$$(\partial\rho/\partial t)_G = -(\partial/\partial\phi)(\rho\omega) \quad (5)$$

Simultaneously, a disorientation due to diffusion proceeds according to the equation:

$$(\partial\rho/\partial t)_D = D_r(\partial^2\rho/\partial\phi^2) \quad (6)$$

where D_r = rotational diffusion rate constant.

The continuity flow equation has the form:

$$\partial\rho/\partial t = -(\partial/\partial\phi)(\rho\omega) + D_r(\partial^2\rho/\partial\phi^2) \quad (7)$$

For our considerations, the full form of eq. 7 for dynamic process will be of interest when parameters $G_{||}$ and D_r are allowed to vary in time. Putting the velocity of rotation (eq. 4) into eq. 7, the differential equation of orientation of rigid particles in the field of axial velocity gradient is obtained:

$$\begin{aligned} (\partial\rho/\partial t) - D_r(t)(\partial^2\rho/\partial\phi^2) - \frac{1}{2} G_{||}(t) \sin 2\phi (\partial\rho/\partial\phi) \\ - G_{||}(t) \cos 2\phi \cdot \rho(t, \phi) = 0 \end{aligned} \quad (8)$$

Model II. Flexible Coiled Chains

According to the conception of W. and H. Kuhn⁵ and J. J. Hermans,⁶ the orientation of a system of statistically coiled polymer chains may be described by the density distribution function of free chain ends:

$$F(x, y, z) = \lim_{\Delta V \rightarrow 0} (\Delta N/\Delta V)$$

where $dV = dx dy dz$. This concept assumes that the other ends of the chains are fixed in the origin of the coordinate system (Fig. 5).

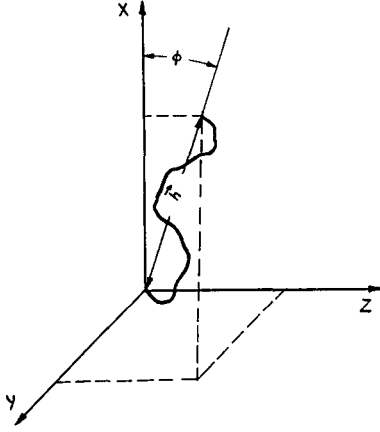


Fig. 5. Model II, flexible, coiled chain.

There are three factors which tend to change the position of free chain end:

- the velocity field with an axial velocity gradient $G_{||}$
- the diffusion with translational rate constant D_t
- the statistical reactionary force \mathbf{R} .

The density of stream of free chain ends amounts to:

regarding to velocity gradient:

$$\mathbf{j}_G = F\mathbf{V} = FG_{||}\mathbf{F} \quad (9a)$$

regarding to diffusion:

$$\mathbf{j}_D = D_t \text{grad } F \quad (9b)$$

regarding to reactionary force:

$$\mathbf{j}_R = FRD_t/kT \quad (9c)$$

For the statistically coiled chains the force \mathbf{R} , according to Kuhn and Gr \ddot{u} n,⁷ may be calculated as an inverse Langevin function of the ratio (end-to-end distance h : x-ray length of extended chain NA), or:

$$\mathbf{R} = (kT/A)L^{-1}[\mathbf{h}/NA] \quad (10)$$

For small extensions ($h \ll NA$), the following approximation is sufficient:

$$\mathbf{R} \cong kT3\mathbf{h}/NA^2 \quad (10a)$$

The stream density \mathbf{j}_R , after substituting \mathbf{R} from eq. 10, amounts to:

$$\mathbf{j}_R = -F \left(\frac{D_t}{A} \right) \cdot L^{-1} \left[\frac{h}{NA} \right] \quad (11)$$

and using approximation (10a):

$$\mathbf{j}_R \cong -FD_t3\mathbf{h}/NA^2 = -\beta^2FD_t\mathbf{h} \quad (11a)$$

where $\beta^2 = 3/NA^2$ is a constant dependent on the statistical segment length A and the number of segments N in the polymer chain.

The flow continuity equation:

$$\frac{\partial F}{\partial t} + \text{div}(\mathbf{V}F - D_t \text{grad } F - \beta^2 D_t F \mathbf{h}) = 0 \quad (12)$$

with all constituents written out has the form:

$$\begin{aligned} (\partial F / \partial t) - D_t \nabla^2 F + (G_{||} - \beta^2 D_t) x (\partial F / \partial x) - \\ \beta^2 D_t [y (\partial F / \partial y) + z (\partial F / \partial z)] \\ + (G_{||} - 3\beta^2 D_t) F = 0 \quad (12a) \end{aligned}$$

Because of the axial fiber symmetry, it is more convenient to apply the cylindrical coordinates x, r, ϑ in which:

$$\begin{aligned} x &= x \\ r &= (y^2 + z^2)^{1/2} \\ \vartheta &= \text{arc tan } (y/z) \end{aligned}$$

Considering the axial symmetry conditions:

$$\frac{\partial F}{\partial \vartheta} = \frac{\partial^2 F}{\partial \vartheta^2} = 0$$

the orientation equation written in Cartesian coordinates x, r (the coordinate ϑ has been eliminated) is obtained:

$$\begin{aligned} \frac{\partial F}{\partial t} - D_t \left[\frac{\partial^2 F}{\partial x^2} + \frac{\partial^2 F}{\partial r^2} \right] + (G_{||} - \beta^2 D_t) x \frac{\partial F}{\partial x} \\ - \left(\beta^2 r + \frac{1}{r} \right) D_t \frac{\partial F}{\partial r} + (G_{||} - 3\beta^2 D_t) F = 0 \quad (12b) \end{aligned}$$

For the interpretation of physical properties of the system of oriented chains, the further transformation of eq. (12b) into polar coordinates h, ϕ is necessary. Also, these coordinates have physical sense: h is the chain end-to-end distance and ϕ an angle formed by the vector \mathbf{h} with flow direction (fiber axis). The orientation equation may be written in the final form:

$$\begin{aligned} \frac{\partial F}{\partial t} - D_t \left[\frac{\partial^2 F}{\partial h^2} + \frac{1}{h^2} \frac{\partial^2 F}{\partial \phi^2} \right] \\ + \left[h(G_{||} \cos^2 \phi - \beta^2 D_t) - \frac{2D_t}{h} \right] \frac{\partial F}{\partial h} \\ - \left[G_{||} \sin \phi \cos \phi + D_t \frac{\cot \phi}{h^2} \right] \frac{\partial F}{\partial \phi} \\ + [G_{||} - 3\beta^2 D_t] F(t, h, \phi) = 0 \quad (13) \end{aligned}$$

Equations (8) and (13) are too complicated to be solved for their general solutions. The numerical solutions for particular cases and the discussion of such results are separate problems. The purpose of the present work is simply the mathematical formulation of the orientation. From the derived equations, it is apparent that the orientation is a complicated function of molecular parameters, velocity gradient, and diffusion rate, as well as the time variations of those factors.

COEFFICIENT OF FIBER ORIENTATION

Functions $F(h, \phi)$ and $\rho(\phi)$ describe a distribution of end-to-end distances and a distribution of directions in space of chains or rigid ellipsoids, respectively. For the calculation of anisotropic properties of the whole fiber, the introduction of a new parameter related to orientation is necessary, a parameter characterizing quantitatively the anisotropy of a macromolecular system. Such a parameter is called a coefficient of orientation.

The coefficient of axial (fiber) orientation has been defined in different ways by various authors. The following definition seems to be the most correct one:

“The coefficient of axial orientation is a ratio of the resultant polarization anisotropy of a given fibrous system to the theoretical polarization anisotropy of the system consisting of ideally extended and axially parallel macromolecules, where the adding-up of constituent polarization anisotropies of the individual structural elements is carried out geometrically, exclusively, neglecting the possible changes of internal field.”

The last restriction has an important methodical implication. The coefficient of orientation is a geometrical term and as such cannot depend on any physical factors. The known definition of the coefficient of fiber orientation after P. H. Hermans⁸ was based upon birefringence and density. That definition was often criticized with regard to its neglect of changes in the internal field caused by orientation and, consequently, of the related deviations of the observed from the expected birefringence. It is implied that this coefficient contains no physical factors (e.g., birefringence), and that the internal field does not affect the value. Further, it will be shown that the definition proposed in the present paper is free of such incorrectnesses; orientation coefficients derived below depend exclusively upon shape, dimensions, and arrangement of macromolecules in the fiber.

Model I. Rigid Ellipsoids

In the system of rigid ellipsoids each of which exhibits an anisotropy of polarization ($\sigma_1 - \sigma_2$), the coefficient of orientation depends only upon the spatial distribution of the ellipsoids' directions.

To describe such a distribution, a special construction called “Polanyi's sphere” is commonly used. It is a spherical surface on which all directions are projected. All directions pass simultaneously through the center of sphere (Fig. 6). The density of intersection points on the surface characterizes the spatial distribution of directions. In our case, this distribution has an axial symmetry.

It may be seen from Figure 6 that the number of ellipsoids whose axes form with the fiber axis an angle lying in the interval $(\phi, \phi + d\phi)$ amounts to:

$$dG_{\phi, \phi + d\phi} = 2\pi R\rho(\phi) \sin \phi d\phi \quad (14)$$

The constituent of fiber polarization anisotropy which proceeds from a single particle of anisotropy ($\sigma_1 - \sigma_2$) inclined to fiber axis at an angle ϕ is:⁹

$$(\alpha_{||} - \alpha_{\perp})_{\phi} = (\sigma_1 - \sigma_2)[1 - (3/2) \sin^2 \phi] \quad (15)$$

The mean polarization anisotropy of the whole fiber consisting of rigid particles distributed according to the function $\rho(\phi)$ amounts to:

$$(\alpha_{||} - \alpha_{\perp})_{\phi} = \int (\alpha_{||} - \alpha_{\perp})_{\phi} dG / \int dG \quad (16)$$

Substituting dG from eq. (14) and $(\alpha_{||} - \alpha_{\perp})_{\phi}$

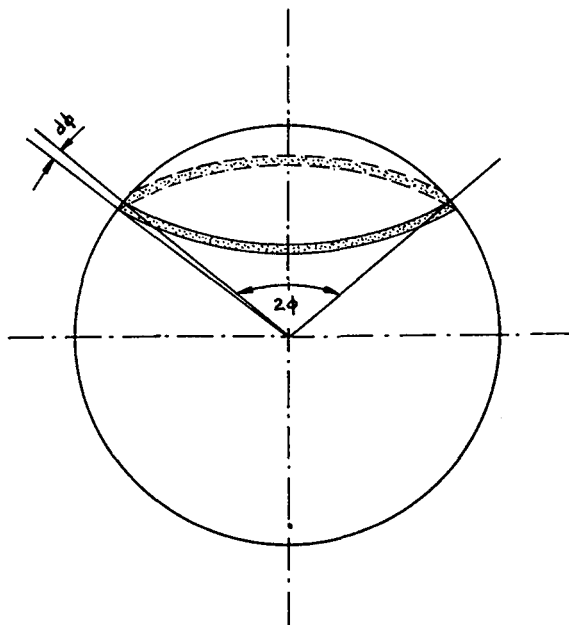


Fig. 6. Polanyi's sphere.

from eq. (15) into eq. (16), we obtain the coefficient of orientation f :

$$f = \frac{\overline{(\alpha_{||} - \alpha_{\perp})}}{(\sigma_1 - \sigma_2)} = 1 - \frac{3 \int_0^{\pi/2} \rho(\phi) \sin^3 \phi d\phi}{2 \int_0^{\pi/2} \rho(\phi) \sin \phi d\phi} \quad (17)$$

Model II. Flexible, Coiled Chains

A polarization anisotropy in the direction of vector \mathbf{h} of the single macromolecular chain consisting of N statistical segments, each having an anisotropy of polarization $(\alpha_1 - \alpha_2)$, amounts to, according to Kuhn and Gr \ddot{u} n,⁷

$$(\gamma_1 - \gamma_2) = N(\alpha_1 - \alpha_2) \left[1 - \frac{3h/NA}{L^{-1}(h/NA)} \right] \quad (18)$$

For small extensions ($h \ll NA$), the following approximation may be used:

$$(\gamma_1 - \gamma_2) \cong (3/5)(\alpha_1 - \alpha_2)(h^2/NA^2) \quad (18a)$$

The mean polarization anisotropy of a fiber depends on the degree of chain extension as well as on the angular distribution of the directions of vector \mathbf{h} . The constituent of fiber polarization anisotropy proceeding from the chains of end-to-end distance h directed at an angle ϕ to the fiber axis is:

$$(\alpha_{||} - \alpha_{\perp})_{h,\phi} = (\gamma_1 - \gamma_2) [1 - (3/2) \sin^2 \phi] \quad (19)$$

and, considering approximation (18a) instead of (18) for $(\gamma_1 - \gamma_2)$:

$$(\alpha_{||} - \alpha_{\perp})_{h,\phi} \cong (3/5)(\alpha_1 - \alpha_2)(h^2/NA^2) (1 - (3/2) \sin^2 \phi) \quad (19a)$$

To describe the spatial distribution of free chain ends according to the function $F(h, \phi)$, a new construction has been built which in fact is a three-dimensional Polanyi's sphere. The construction is a spherical solid; in the center of sphere, one end of each chain is fixed, whereas all the other free ends determine the density of the solid. Chain ends at an equal distance h form a spherical surface (Polanyi's sphere) of radius h . The whole construction consists of an infinite number of Polanyi's spheres (Fig. 7). The number of chain ends included in the angular interval $(\phi, \phi + d\phi)$ and length interval $(h, h + dh)$ amounts to:

$$dG_{\phi, \phi + d\phi, h, h + dh} = 2\pi h F(h, \phi) \sin \phi d\phi dh \quad (20)$$

Hence, the mean polarization anisotropy of a fiber is:

$$\overline{(\alpha_{||} - \alpha_{\perp})} = \int \int (\alpha_{||} - \alpha_{\perp})_{h,\phi} dG / \int \int dG \quad (21)$$

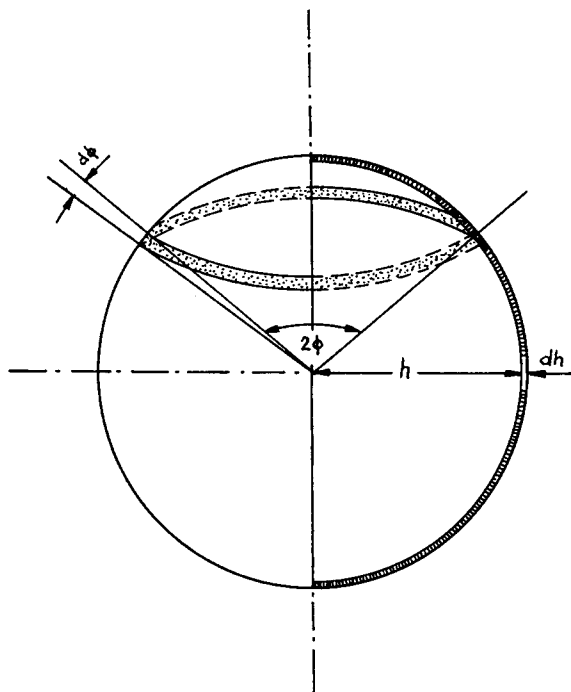


Fig. 7. Three-dimensional Polanyi's sphere.

For the system of ideally oriented ($\phi = 0$) and fully extended ($h = NA$) chains, the anisotropy is:

$$\begin{aligned} (\alpha_{||} - \alpha_{\perp})_{\phi=0, h=NA} &= N(\alpha_1 - \alpha_2) \left[1 - \frac{3}{L^{-1}(1)} \right] \\ &= N(\alpha_1 - \alpha_2) \end{aligned} \quad (22)$$

Thus the coefficient of fiber orientation is:

$$\begin{aligned} f &= \frac{\overline{(\alpha_{||} - \alpha_{\perp})}}{N(\alpha_1 - \alpha_2)} = \frac{3}{5N^2A^2} \\ &= \frac{\int_{h=0}^{NA} \int_{\phi=0}^{\pi/2} F(h, \phi) h^3 \sin \phi \left(1 - \frac{3}{2} \sin^2 \phi \right) dh d\phi}{\int_{h=0}^{NA} \int_{\phi=0}^{\pi/2} F(h, \phi) h \sin \phi dh d\phi} \end{aligned} \quad (23)$$

It should be noted that in the formulas (17) and (23) only those factors occur which are related to the shape and spatial arrangement of macromolecules. This agrees with the postulation given in our definition. Those physical factors (polarization anisotropies) used in the derivation of formulas (17) and (23) have been further eliminated; so the orientation coefficient contains exclusively geometrical parameters.

THE INTERPRETATION OF SPINNING EXPERIMENTS

From the theories of streaming birefringence, it is possible to determine the shape and deformability of a macromolecule *in solution*. Besides the Maxwell constant, the extinction angle and the relation of birefringence vs. velocity gradient are important. For rigid, rodlike particles, where the birefringence is determined by an orientation effect alone, the last relation corresponds to the saturation curve. In the case of flexible, light-deformable coils, the increase of birefringence with velocity gradient is linear or even more rapid (a concave curve). The shape of the curve Δn vs. G_{\perp} may then be a comparative measure of so-called "internal viscosity" and deformability of macromolecules.

It is a question, whether similar information about macromolecules *in the molten state* can be obtained from the relationship of birefringence vs. velocity difference in spinning experiments. Such a curve would have a form similar to that mentioned above. The solution and molten state relationships cannot, of course, be identified one with another, and one should take into account the specific conditions described in the first sections of this paper. These conditions cause some deformation of the curve Δn vs. ΔV .

In the preceding paper,¹ it has been shown that as the velocity difference (and mean velocity gradient) increase, the cooling rate increases, changing the viscosity and relaxation time of polymer stream. In this case, the birefringence is not (as in classical streaming orientation) determined by an equilibrium between the action of *constant* velocity gradient and *constant* diffusion rate, but is a resultant of an action over time t of *continuously varying* velocity gradients and rates of diffusion.

In Figure 8, a scheme of an experimental bire-

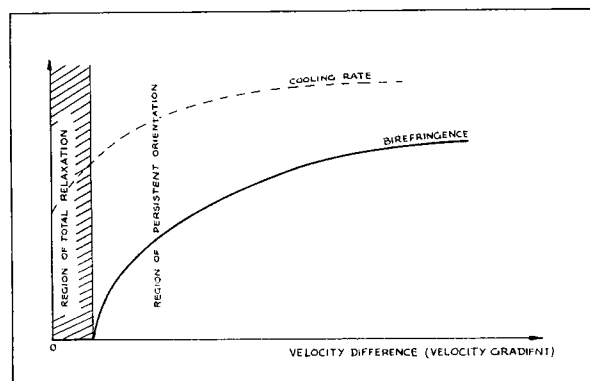


Fig. 8. Schematic diagram of spinning orientation.

fringence vs. velocity difference curve for polycapronamide fiber is shown.

Above the birefringence curve in Figure 8, the simultaneous changes of cooling rate are demonstrated (dotted line). It is apparent that an increase in spinning velocity is accompanied by an increase in cooling rate, and hence a decrease of diffusion intensity. It is characteristic that the birefringence curve does not pass through the origin of the coordinate system, but over some interval of velocity differences retains value 0. Such an effect did not occur in streaming orientation experiments under isothermal conditions ("classical" streaming birefringence). This "anomalous" behavior of fibers results from the specific conditions of experiment. At low spinning velocities and simultaneously low cooling rates, the thermal relaxation is so strong that it completely eliminates the orienting action of the velocity field. The region of persistent orientation is thus shifted into higher velocity differences.

In spite of the above-mentioned difficulties in the exact interpretation of spinning experiments, it may be expected that the shape of the fiber birefringence vs. velocity difference curve, obtained under standard conditions, will give worthwhile information about the behavior of macromolecules in fiber-spinning and about the character of macromolecules in the molten state. The comparative investigations of various polymers will be reported in one of the next papers.

References

1. A. Ziabicki and K. Kedzierska, *J. Appl. Polymer Sci.*, **2**, 14 (1959).
2. W. Kuhn, *Kolloid-Z.*, **62**, 269 (1933); *Z. physik. Chem. (Leipzig)*, **A161**, 1 (1932).
3. H. Nitschmann and S. Schrade, *Helv. Chim. Acta*, **31**, 297 (1948).
4. P. Boeder, *Z. Physik.*, **75**, 258 (1932).
5. W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **26**, 1394 (1943).
6. J. J. Hermans, *Physica*, **10**, 777 (1942).
7. W. Kuhn and F. Grün, *Kolloid-Z.*, **101**, 248 (1942).
8. P. H. Hermans, *Physics and Chemistry of Cellulose Fibers*, Elsevier, New York, 1949.
9. J. J. Hermans in P. H. Hermans, *Contribution to the Physics of Cellulose Fibers*, Elsevier, Amsterdam, 1946.

Synopsis

The mechanism for orientation of macromolecules through the melt-spinning of synthetic fibers is analogous to that in polymer solutions flowing in capillaries or in a Couette apparatus. The differences between the two processes, with regard to the velocity field, molecular state, and time de-

pendencies, have been discussed and the differential equations derived to describe the orientation of two extreme molecular models. The coefficients of orientation for fibers consisting of rigid particles (model I) and flexible, coiled chains (model II) have been defined. The specific conditions occurring in fiber-spinning experiments have been shown, as well as the possibility of applying such experiments to the study of the behavior of macromolecules in the molten state.

Résumé

Le mécanisme d'orientation des macromolécules par filage à la fusion de fibres synthétiques est analogue à celui ayant lieu au cours du passage de solutions de polymères au travers de capillaires ou dans l'appareil de Couette. On discute la différence des processus due au gradient de vitesse, à l'état moléculaire et à l'influence du temps et on a dérivé l'équation différentielle pour décrire l'orientation de deux modèles moléculaires extrêmes. On a défini le coefficient d'orientation pour des fibres constituées de particules rigides (modèle I) et des chaînes flexibles accolées. (modèle II) On a exposé les conditions spécifiques dans lesquelles ont

lieu les expériences de filage des fibres ainsi que la possibilité d'appliquer de telles expériences à l'étude du comportement des macromolécules à l'état fondu.

Zusammenfassung

Der Mechanismus der Orientierung von Makromolekülen beim Schmelzspinnverfahren ist dem beim Fließen von Polymerlösungen in Kapillaren oder im Couetteapparat auftretenden analog. Die Unterschiede zwischen den beiden Vorgängen in bezug auf Geschwindigkeitsfeld, Molekularzustand und Zeiteffekte wurden diskutiert und Differentialgleichungen zur Beschreibung der Orientierung zweier extrem verschiedener Molekülmodelle abgeleitet. Es wurden Orientierungskoeffizienten für Fasern, die aus starren Partikeln bestehen (Modell I) und solche aus biegsamen, verknäuelten Ketten (Modell II) definiert. Die spezifischen Bedingungen, die bei Faserspinnversuchen auftreten wurden aufgezeigt und ebenso die Möglichkeit, solche Versuche zur Untersuchung des Verhaltens von Makromolekülen im geschmolzenen Zustand anzuwenden.

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