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THE THEORY OF MOLECULAR ORIENTATION IN POLYMER SYSTEMS

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Synopsis

Theoretical study on the problem of molecular orientation in polymer systems is carried out. The mathematical treatments are made on general case, including earlier theories. Every stage of molecular orientation in practical cases can be regarded as a special case from this point of view. Macroscopic characteristics of orientation are calculated in terms of parameters of every special case according to the theory. Discussions are developed to the problems of molecular orientation during fiber spinning, drawing and heat-setting processes.

I. INTRODUCTION

It is commonly accepted to-day that molecular orientation, i.e. parallelization and extension of structural elements in fibers (molecular chains, crystallites, fibrils etc.) is the factor determining many physical characteristics of polymers first of all mechanical properties of fibers. The orientation of man-made fibers results mainly in the drawing operation, but is out unaffected by spinning and heat-setting. Therefore the mechanism of orientation in various steps of fiber formation is an important subject of interest of polymer physicists and fiber scientists.

The orientation in spinning of a polymer fluid and that in cold or hot-drawing of a solid polymer material differ in many aspects and are usually discussed in terms of separate theories. Such an approach was also involved in earlier papers by myself^{1,2)}. However, more recent theoretical considerations brought us up to the conclusion that both the spinning- and drawing orientation, as well as orientation changes during heat-treatment can be described as special cases of a unique, more general theory comprising also the streaming orientation of dilute polymer solutions and other situations. This theory will be formulated briefly in section II of this paper, followed by discussion of special cases for fiber spinning (section III), drawing (section IV) and heat-setting (section V). It should be noted that the theory can be also applied to other physical characteristics of polymer systems determined by configuration of structural elements.

II. GENERAL THEORY

1. Distribution function Ψ macroscopic characteristics and the orientation factor f

Molecular configuration of a polymer system (solution, melt, solid bulk polymer) can be described with the aid of a distribution density function $\Psi(t, \xi_1)$, where $\xi = (\xi_1, \xi_2, \dots, \xi_N)$ are configuration varia-

bles (e.g. orientations and deformations of various structural elements in the system) and t is time. The distribution function is normalized to the total concentration of structural elements in the system, ν

$$\int \dots \int \Psi dv = \nu(t) \quad (1)$$

where $dv = d\xi_1, d\xi_2, \dots, d\xi_N$ is a volume element in the N -dimensional configurational space.

Any macroscopic characteristic of the system which is determined by configuration of structural elements within the system can be represented as some function of the configurational variables $w(\xi)$ averaged over all configurations possible in the system

$$f(t) = \langle w(\xi) \rangle = \frac{1}{\nu(t)} \int \dots \int w(\xi) \Psi(t, \xi) dv \quad (2)$$

The configurational variables ξ , the distribution function Ψ and the function w are specific for the molecular system and the macroscopic characteristic involved. So, e.g. for a dilute suspension of rigid rods or ellipsoids the variables ξ denote orientation angles φ, θ of the asymmetry axes, $\Psi(t, \varphi, \theta)$ is the angular distribution function of axes, and the function w for uniaxial orientation factor is simply

$$w(\varphi, \theta) = 1 - \frac{3}{2} \sin^2 \theta \quad (3)$$

For dilute solutions containing flexible Gaussian chains, the configuration variables include coordinates x, y, z of a free chain end with respect to the other end fixed in the coordinate system. The axial orientation factor f is obtained by averaging of the function

$$w(x, y, z) = \text{const.} (z^2 - x^2) / h_0^2 \quad (4)$$

where z is directed along the flow (orientation) axis and h_0^2 is the average square of end-to-end distance at rest.

Similarly can be characterized other macroscopic characteristics, in particular the material functions in rheological constitutive equations (cf.⁹⁾). So, for instance, the stress tensor of a flowing system of Gaussians can be expressed as an average of dyadic

$$w(x, y, z) = \text{const.} (\mathbf{h}\mathbf{h}) \quad (5)$$

formed of the end-to-end vector $\mathbf{h} = (x, y, z)$.

In other systems more variables can be involved and the functions Ψ and w can be more complex.

The distribution function Ψ for any molecular system should satisfy the equation of continuity (in N -dimensional space)

$$\partial \Psi / \partial t = -\nabla \cdot (\Psi \cdot \dot{\xi}) + \dot{\Psi}_{\text{kin}} \quad (6)$$

∇ denotes the divergence operator acting on the total flux $(\Psi \cdot \dot{\xi})$ in an N -dimensional space, and $\dot{\Psi}_{\text{kin}}$ - the rate of production (or removal) of structural elements in the system due to some kinetic processes (e.g. dissociation and reformation of network chains in an energetic networks). The terms on the right hand side of eq. (6) are proportional either to the diffusion constant D (terms associated with intramolecular forces and fluxes), or to the velocity gradient $\mathbf{q}^*$ (effects of the superimposed external velocity field). Therefore we will write eq. (6) in the form:

$$\tau (\partial \Psi / \partial t) = L(\alpha) \cdot \Psi \quad (7)$$

where $\tau = (1/D)$ is a disorientation (relaxation) time, and $\alpha = \mathbf{q}^* \tau$ is a dimensionless parameter. $L(\alpha)$ is a differential (or integro-differential) operator in ξ .

There are two ways of finding the orientation factor f or anyother characteristics defined through eq. (2):

- i) to solve eq. (7) for $\Psi(t, \xi)$ and then integrate the proper function $w(\xi)$ as shown in eq. (2),
- ii) to multiply both sides of eq. (7) by $(w dv)$, integrate it term-by-term and then solve the resulting equation for $f(t)$.

Both methods were successfully applied to this purpose⁸⁻¹²⁾.

2. Orientation at constant α and τ

For more simple cases the equation of continuity is homogeneous and linear and the operator L does not involve time in an explicit form. In such a case the variables t and ξ can be separated and the solution for $\Psi(t, \xi)$ results in the form:

$$\Psi(t, \xi) = \Psi_{st}(\xi) + \sum_{k=1}^{\infty} \Psi_k(\xi) \exp(-\lambda_k t/\tau) \quad (8)$$

where $\lambda_k(\alpha)$ are eigenvalues, $\Psi_k(\alpha, \xi)$ are eigenfunctions, and $\Psi_{st}(\alpha, \xi)$ is the steady-state solution of the problem, i.e. solution of the equation:

$$L(\alpha) \cdot \Psi_{st} = 0 \quad (9)$$

The eigenvalues Ψ_k should satisfy the initial condition $[t=0, \Psi = \Psi_0]$

$$\Psi_{st} + \sum_k \Psi_k = \Psi_0 \quad (10)$$

Application of the definition of the macroscopic characteristic (eq. 2.) yields, after integration with the individual eigenfunction Ψ_k ,

$$f(t, \alpha) = f_{st}(\alpha) + \sum f_k(\alpha) \exp(-\lambda_k t/\tau) \quad (11)$$

$$f_{st} + \sum f_k = f_0 \quad (12)$$

Eq. (11) is a formal analogue of the phenomenological theory of linear viscoelasticity with a discrete relaxation times spectrum. It is to be noted however, that eq. (11) was derived without any phenomenological assumptions and all the eigenvalues and eigenfunctions possess clearly defined molecular sense for any given molecular system. Moreover, the linearity of eq. (11) does concern only the time variable, t , while functions $f_k(\alpha)$ and $\lambda_k(\alpha)$ are in general non-linear.

We will confine our considerations to the case when all λ_k are positive and their sequence is increasing rapidly enough for the sum in eq. (11) to be replaced by its first term alone. With the initial condition (eq. 12) this yields an approximate formula

$$f(t, \alpha) \approx f_{st}(\alpha) + (f_0 - f_{st}) \exp(-\lambda_1 t/\tau) \quad (13)$$

The approximation (eq. 13) is an exact solution of the problem when the operator $L(\alpha)$ in eq. (7) does satisfy the condition

$$\int \dots \int w L \Psi dv = F(\alpha) + G(\alpha) \int \dots \int w \Psi dv \quad (14)$$

According to eq. (13) the knowledge of three quantities is necessary and sufficient to determine the orientation factor f : the disorientation time τ (a temperature-dependent characteristic of the system), and two functions of α , λ_1 and f_{st} . These functions can be expanded in power series

$$f_{st}(\alpha) = \begin{matrix} a_1 \alpha + a_2 \alpha^2 + \dots & \text{for small } \alpha \\ 1 - a_1^* \alpha^{-1} - a_2^* \alpha^{-2} - \dots & \text{for large } \alpha \end{matrix} \quad (15a)$$

$$\quad \quad \quad 1 - a_1^* \alpha^{-1} - a_2^* \alpha^{-2} - \dots \quad (15b)$$

$$\lambda_1(\alpha) = \begin{matrix} 1 + b_1 \alpha + b_2 \alpha^2 + \dots & \text{for small } \alpha \\ \alpha(b_1^* + b_2^* \alpha^{-1} + \dots) & \text{for large } \alpha \end{matrix} \quad (16a)$$

$$\quad \quad \quad \alpha(b_1^* + b_2^* \alpha^{-1} + \dots) \quad (16b)$$

Fig. 1. Schematic plot of orientation factor f versus time t .
Increasing part: orientation at constant α
Decreasing part: disorientation at $\alpha=0$

Fig. 2. Orientation at zero disorientation time ($\tau=0$)

- a) orientation factor vs. time
b) steady-state orientation factor vs. α

Schematic plot of the orientation factor f vs. time t is shown in fig. 1.

We will consider now two asymptotic cases. For $\tau=0$ we have $\lambda_1=1$ and

$$f(t, \alpha) = f_{st}(\alpha) = \text{const.} \quad (17)$$

This corresponds to so-called "steady-state streaming orientation", a phenomenon commonly observed in low viscous polymer fluids subjected to a homogeneous, steady-state velocity field.

At $\tau=0$ the steady-state is reached instantaneously (see Fig. 2 a) and after the velocity field is switched off ($q^*=0$) also the disorientation proceeds instantaneously and completely ($f=0$). An invariant characteristic for this case is provided by the relation f_{st} vs. α as shown schematically in fig. 2 b.

Fig. 3. Molecular models used in the theory of streaming orientation.

- a) suspension of rigid particles^{6,7)}
- b) dilute solution of flexible chains⁸⁻¹⁰⁾
- c) "temporary" network with dissociating junctions^{11,12)}

Fig. 4. Orientation at infinite disorientation time ($\tau=\infty$)

- a) orientation factor vs. time
- b) asymptotic orientation factor vs. deformation.

The theory of streaming orientation in steady shear flow is widely exploited as a tool in the conformational investigations of dilute polymer solutions (cf. reviews^{4,6)}). The corresponding theory for steady elongational flow (i. e. that relevant for fiber spinning geometry) is available for several molecular models shown in fig. 3. Fig. 3 a presents a dilute suspension of rigid asymmetric particles (cf.^{6,7)}), fig. 3 b. - a dilute solution containing flexible, chain macromolecules⁸⁻¹⁰⁾ and fig. 3 c a "temporary" network formed of flexible chains with dissociating and reforming junctions^{11,12)}.

The other asymptotic case corresponds to the infinite disorientation time, $\tau=\infty$. As evident in eqs. (15 b) and (16 b) for this case: $f_{st}=1$, $\lambda_1=b_1^*\alpha$ and:

$$f(t) = 1 + (f_0 - 1) \exp(-b_1^* q^* t) \quad (18)$$

Replacing the variable t (time) by $\epsilon = q^* t$ (deformation), the orientation factor at any instant can be expressed as a function of ϵ alone:

$$f[\epsilon(t)] = 1 + (f_0 - 1) \exp(-b_1^* \epsilon) \quad (19)$$

or

$$f(\epsilon) = f_0 \exp(-b_1^* \epsilon) + f_\infty(\epsilon) \quad (20)$$

where

$$f_\infty(\epsilon) = 1 - \exp(-b_1^* \epsilon) \quad (21)$$

is an invariant characteristic of the system. The orientation in such a system develops with a rate equal to the rate of deformation is held constant ($\epsilon=\text{const}, q^*=0$) - fig. 4 a. An invariant characteristic f_∞ vs. ϵ is drawn schematically in fig.

4 b.

The above asymptotic case applies to the systems in which no molecular motions in the absence of external possible (no diffusion). The theory of such an "irrelaxational orientation" was developed for various molecular models: rigid, non-interacting ellipsoids (cf.^{7,13)}) or rods¹⁴⁾ (fig. 5 a), a system of rigid rods connected by joints into a chain ("second limiting case" by Kratky¹⁵⁾ - fig. 5 c, and an elastic deformable network with fixed, permanent junctions^{16,17)} (cf. fig. 5 c). In all theories some affinity of the displacement of

Fig. 5. Molecular models used in the theory of "irrelaxational" orientation.

- affine orientation of rigid particles embedded in a plastic medium ("first limiting case" by Kratky)^{13,14}
- deformation of a chain formed of rigid links connected with joints ("second limiting case" by Kratky)¹⁵
- affine deformation of an elastic network^{16,17}

of eq. (7) can be approximated by the first term in the expansion eq. (8), the non-isothermal equation, eq. (23), reduces to the form

$$\tau(t) \cdot (df/dt) = \lambda_1[\alpha(t)] \{f_{st}[\alpha(t)] - f\} \quad (24)$$

with a general solution, applicable to any given variation of α and τ :

$$f[t, \alpha(t)] = e^{-z} (f_0 + \int_0^t (\lambda_1 f_{st}/\tau) e^z dt) \quad (25)$$

with

$$z = \int_0^t (\lambda_1/\tau) dt \quad (26)$$

Eq. (25) reduces to eq. (13) when α and τ are constants. It is to note that an equation similar to eq. (24) was derived in a different way by Nishiumi¹⁸.

4. The range of applicability of the theory to particular molecular systems

There are several conditions required for the approximations eq. (13) and (25) to be applicable:

- the isothermal equation of continuity (eq. 7) should be separable, i. e. the operator L should be linear and independent of t ,
- the sequence of eigenvalues λ_k should be rapidly divergent, so that $\lambda_k \gg \lambda_1$ for $k=2, 3, \dots$
- or: iii) the integral condition (eq. 14) is satisfied, even if conditions i), ii) not fulfilled.

The condition i) alone is sufficient to present the isothermal solution in the form of eq. (8~11).

The conditions outlined above are satisfied by such molecular systems as suspensions of rigid, non-interacting particles^{6,7}, dilute solutions of flexible, Gaussian⁸ or non-Gaussian chains⁹ thus comprising a large variety of structures used for the description of fluid polymer systems. The applicability of the theory for "temporary" networks^{11,12,19} is problematic because of the kinetic term Ψ_{kin} in eq. (6). The theory does apply however, when $\dot{\Psi}_{kin}$ is assumed to have the form:

$$\dot{\Psi}_{kin} = H(\xi) + \text{const.} \Psi$$

Such a form was assumed by Lodge²⁰ in his theory of temporary energetic networks. The operator L in

structural elements was assumed (e.g. an affine transformation of orientation angles - model 5a - or an affine deformation of all network chains in model 5c). It should be noted here that the last two models shown in fig. 5 ("b" and "c") exceed beyond the limits of our theory, because they exclude infinitely large deformations (flow) and predict $f=1$ for finite deformations.

3. Orientation at variable α and τ

When the parameter α is a function of time (and this is most often the case in non-isothermal processes, since τ and α are strongly temperature-dependent) the equation resulting from eq. (7):

$$\tau(t) \cdot (\partial \Psi / \partial t) = L[\alpha(t)] \cdot \Psi \quad (22)$$

is no more separable. Multiplication of eq. (22) by $(w dv)$ with subsequent integration yields

$$\tau(t) \cdot (df/dt) = \frac{1}{\nu} \int \dots \int w L \Psi dv + (d \ln \nu / dt) f \quad (23)$$

an equation which sometimes can be solved for $f(t)$.

On the other hand, it can be shown that when the isothermal (i.e. that for τ and α constants) solution

the eq. (7) is no more linear and the eq. (6) is not separable, but integral condition (eq. 14) is fulfilled. It should also be noted that our theory is not applicable to systems with limited deformability, like permanent, chemically cross-linked networks etc. Such systems are similar to our asymptotic case for $\tau = \infty$, in that the orientation factor is a unique function of deformation; the shape of the orientation function, $f(\epsilon)$ and its asymptotic behavior, however, are different.

III. FIBER SPINNING

The deformation and molecular orientation accompanying fiber spinning (in any spinning technique) proceed in a fluid state with molecular mobility decreasing continuously, due to the solidification controlled by heat- and mass transfer. The disorientation time τ , in first approximation proportional to Newtonian viscosity, η , increases along spinning way, whereas the parallel velocity gradient $q^* = \partial V / \partial x$ first increases then decreases. The tensile stress involved, as proportional to the product (ηq^*) is rather small. In terms of our theory such conditions correspond to "non-isothermal" approximation (eq. 25) with f_{st} and λ_1 according to eqs. (15 a) and (16 a) respectively. Replacing in eq. (25) the variable t (time) by x (distance from spinneret measured along the filament axis)

$$t = \int (1/V) dx \quad (27)$$

where V - axial velocity of the filament, and putting $f_0 = 0$, one obtains, after simple rearrangements, the orientation factor f_L of an "as-spun", undrawn filament (L = the total spinning way) :

$$f_L = f(x=L) = f_{st}(\alpha_L) - \int_0^L \exp(u - u_L) (df_{st}/dx) dx \quad (27)$$

$$u(x) = \int_0^x (\lambda_1 / \tau V) dx; \quad \alpha_L = \alpha(x=L); \quad u_L = u(x=L)$$

Considering only first terms in eqs. (15 a) and (16 a) we have

$$f_L = a_1(\alpha_L - \int_0^L \exp(u - u_L) (d\alpha/dx) dx) \quad (29)$$

It is evident that the degree of orientation of an undrawn filament increases with (but is neither proportional to, nor uniquely determined by) the orientation parameter at $x=L$, α_L (and therefore proportional to the spinning stress σ_L). The other term in brackets is associated with variation of the parameters τ , q^* and V along spinning way. Generally speaking, the most important factors determining f_L are :

- velocity gradient along the spinning way $q^* = \partial V / \partial x$, dependent mainly on the spinning speed,
- molecular mobility and temperature as determining the disorientation time τ .
- solidification rate affecting the point values of q^* and τ as well as their distribution along the spinning way (second term in eq. 29).

The present author analyzed the kinetics of molecular orientation during melt-spinning²⁰ basing on equations similar to eq. (29). A simplified material- and force balance together with assumption that the disorientation time τ is proportional to the viscosity η of the polymer led to the following result :

$$f_L = \text{const.} \exp(1/\alpha_L) [E_i(-S/\alpha_L) - E_i(-1/\alpha_L)] \quad (30)$$

where $S = V_L/V_0$ is the deformation- (melt-draw) ratio. $E_i(x)$ - an integral exponential function. The above result explained several experimental observations: the non-linearity and non-uniqueness of the relation f_L vs. α_L (or: f_L vs. σ_L), and secondary importance of the melt-draw ratio S . The theoretically predicted orientational behavior in melt-spinning is qualitatively consistent with empirical data obtained for many various fiber-forming polymers. More detailed discussion of these data may be found in^{20,21}.

For dry- or wet-spinning processes the general relation eq. (29), remains true, but the variation and absolute values of τ and α are different. Usually in the solution-spinning techniques, tensile stress σ_L (and therefore the parameter α_L) is very small and the resulting orientation degree negligible. In some

conditions higher orientations were observed: e.g. in rapid spinning of PVA fibers in an aqueous salt bath considerably high f values were measured²²⁾. It was also observed that the degree of orientation increased with spinning velocity and velocity gradient q^* .

IV. DRAWING

Molecular orientation accompanying a cold- or hot-drawing process takes place in a solid system with very long disorientation times. In first approximation it can be considered an isothermal process although, due to the dissipation of mechanical energy, the actual temperature within the system is not necessarily equal to that of the surroundings. Therefore we will describe the drawing orientation with the aid of eq. (13) with f_{st} and λ_1 from eqs. (15 b) and (16 b) respectively.

Using first two terms only we have:

$$f(t) = 1 - a_1^*/\alpha - (1 - a_1^*/\alpha - f_0) \exp [-(b_1^*q^* + b_2^*/\tau)t] \quad (31)$$

After introduction of the variable $\epsilon = q^*t$,

$$f(\epsilon) = 1 - a_1^*/\alpha - (1 - a_1^*/\alpha - f_0) \exp [-(b_1^* + b_2^*/\alpha)\epsilon] \quad (32)$$

or:

$$f(\epsilon) = 1 - a_1^*/\alpha - (1 - a_1^*/\alpha - f_0) (1 - f_\infty) \exp (-b_2^*\epsilon/\alpha) \quad (33)$$

As evident in eqs. (32, 33) the orientation factor f resulting in drawing is not a unique function of deformation ϵ , but depends also on the deformation rate (q^*) and disorientation time τ . These factors play secondary, but not negligible role in the determination of fiber texture. It follows from the comparison of eqs. (32) and (28) that the mechanism of orientation during drawing and spinning is identical, viz. a "competition" between the orienting action of the hydrodynamic field and a disorienting effect of diffusion. The quantitative differences between spinning and drawing lie in the values of the disorientation time τ . In fiber spinning - τ is not very long and diffusion strongly affects the resulting orientation; in drawing - the hydrodynamic factor is dominant, relaxation being of secondary importance (very long τ).

So far all the molecular theories of drawing were confined to the "irrelaxational case" (cf. section II.2) and concerned only asymptotic relations f_∞ vs. ϵ . At the same time, experimental data on fiber drawing prove the existence of relaxational effects predicted by the more general theory.

Of course, in all cases the orientation factor of drawn fibers increases with deformation (draw-) ratio. Effects of diffusion manifest themselves in the dependence on the drawing speed (q^*), drawing temperature and molecular mobility of polymer, the latter two affecting the disorientation time, τ . The effect of drawing speed is complex. At constant temperature and constant ϵ , an increase of drawing speed in a non-crystallizing polymer should (according to eq. 33) to an increase of the orientation factor f . However, an increase of q^* is associated with increased rate of dissipation of energy and with increased temperature thus leading to some decrease of τ and α . When drawing is accompanied by polymer crystallization (a strongly temperature-dependent process) the effect of q^* is still more complex. Probably this explains why some authors observed an increase²³⁾, others a decrease²⁴⁾ of orientation factor with drawing speed.

In amorphous, non-crystallizing systems an increase of drawing temperature and/or molecular mobility, e.g. through swelling, decreased molecular weight etc.) invariably leads to the decrease of orientation factor f . So, drawing of fibers at elevated temperatures or in plasticizing baths (with shortened disorientation times τ) is associated with decreased "efficiency" of the orienting action of mechanical field. Typical effect of this kind may be noted in solution-spun fibers containing various amounts of solvent²⁵⁾ or having various degrees of solidification^{26, 27)}. Similar effect is due to the application of a plasticizing bath³⁰⁾ or to the increase of drawing temperature^{28, 29)}.

More complex is the situation with crystallizing polymers. A decrease of disorientation time τ usually facilitates crystallization of a supercooled system and the character of kinetic units in the system changes during drawing (macromolecules $\rightarrow$ crystallites). Typical example of such a behavior is provided by cross-linked

elastomers (rubbers) and polyamides (cf.^{28,31}). Phase transitions possibly accompanying orientation exceed the scope theory however. The theory considered in this paper does not allow the structural elements (particles, macromolecular chains, crystallites) to change during orientation and assumes the degree of crystallinity to be constant.

V. CONDITIONING AND HEAT-TREATMENT OF ORIENTED SYSTEMS

Conditioning (or heat-treatment) without any external stress of an oriented fiber is equivalent to putting $\alpha=0$ in eqs. (15) and (16). Orientation factor monotonically decreases according to the relation

$$f(t) = f_0 \exp(-t/\tau) \quad (34)$$

At room temperature the disorientation time τ is usually so long that no change of f is observed within days or weeks. An increase of temperature, possibly combined with a plasticization in a liquid bath, reduce τ considerably thus making some disorientation possible. Effects of heat-treatment at fixed length however, cannot be explained directly in terms of our formulas. Formally, the case $\varepsilon = \text{const.}$ ($q^* = 0$) corresponds to $\alpha = 0$ and leads to eq. (34). At the same time it is well known that heating at constant length sometimes leads to an increase of orientation rather than relaxation predicted by eq. (34). However, a solid, drawn fiber is a viscoelastic material with frozen internal stresses which manifest themselves in shrinkage at elevated temperatures. To maintain the length of fiber constant during heating one must actually apply an external tensile stress, σ_0 , equivalent to some parameter α_0 . Therefore it seems to be reasonable to consider the heating at fixed length as an orientation process occurring at a $\alpha = \alpha_0$ (σ_0) rather than at $\alpha = 0$. Since σ_0 (and α_0) is rather large we will write (eq. 16 b) :

$$f(t) = f_{st}(\alpha_0) - [f_{st}(\alpha_0) - f_0] \exp[-(b_1^* \alpha_0 + b_2^*)t/\tau] \quad (35)$$

instead of eq. (34). It is evident that when the initial (i.e. that produced during drawing) orientation factor f_0 is greater than the steady-state factor corresponding to α_0 , $f_0 > f_{st}(\alpha_0)$, heat treatment will lead to some disorientation, while for higher stresses, $f_0 < f_{st}(\alpha_0)$ and orientation will be improved. Both effects were observed in heat-setting of man-made fibers³²⁻³⁴.

* * *

We are now in a position to summarize the effects of orientation in all the operations of fiber formation. Scheme of these effects is shown in fig. 6.

Fig. 6. Scheme of the variation of orientation factor in various operations of fiber formation.

Spinning orientation is appreciable in melt-spinning and rather negligible in wet- or dry-spinning procedures. The direction of change in heat-treatment depends on stress conditions. In all cases the mechanism of molecular orientation is relaxational and factors like temperature and molecular mobility affect the degree of orientation.

Note

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