Forschung, Wissenschaft

Crystallinity of Polymers and the Means to Influence the Crystallization Process *

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Abstract

One of the most important factors determining the properties of a solid polymer is the packing order. Crystallization is a means to control the degree and morphology of packing. There is a great difference between "free" and "induced" crystallization.

The "free" crystallization leads to quasi-isotropic products, which are strong and tough if the crystallites are small. This way of crystallization is rather well understood so that we are able to predict, with a fair amount of accuracy, the rate of crystallization and the average size of the spherulites. In spherulites the molecular chains are normally folded.

It is possible to carry out the crystallization in such a way that the molecular chains are partly extended.

Pressure-induced crystallization leads to extended chains, but the crystallites lie in random directions so that the products are very brittle.

Stress-induced crystallization leads to a completely different type of morphology: the micro-fibrillar structure with a row-nucleated core. Shear forces are far less important than tensile stresses. The rate of nucleation in this type of crystallization is some orders of magnitude higher than in spherulitic crystallization. Extremely high moduli can be obtained by superdrawing and similar techniques. These have no practical importance yet.

An interesting new phenomenon connected with stress-induced crystallization is the hard elastic fibre.

Contents

1. Introduction

1.1 Properties of polymers as a function of the packing order

The properties of polymers are strongly influenced by the "state of aggregation" in which the macromolecules occur.

A useful criterion in comparing the properties of different materials, notably the mechanical properties, is the modulus of elasticity, i.e. Young's modulus.

Table 1 gives a survey of some materials. It shows the practical and theoretical moduli of different types of polymers, and also compares polymers with inorganic materials in this respect.

Table 1: Elastic moduli of some materials

	Class of Materials			E-value 10^9 [N/m^2]
Polymers	*Elastomers* (Rubbers)			0.001
	Soft Plastics (e.g. low density PE)			0.2
	Isotropic Hard Plastics			
		Amorphous	Glassy	2.5–3
			Cross-linked	2.5–5
		Semicrystalline	$T_g < 275$ K	1–3
			$T_g > 325$ K	3
	High-tenacity fibres (in direction of orientation)			
		Normal Polymers (Nylon, PETP)		5–15
		Aromatic Polyamides (Aramides)		80–130
	Theoretical Modulus (in direction of orientation) *of fully ordered Material*			
		Extended zig-zag chains		120–350
		Extended helical chains		10–100
Inorganics	*Ceramics*			30
	Glass			60–100
	Steel			200
	Whiskers			1000–2000

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The theoretical values of the moduli of polymers have been calculated from the molecular force constants (bond stretching and valence angle deformation) of the polymer chains. These values are well supported by experiment, viz. by stress-strain measurements of crystal lattices using X-ray diffraction techniques (Sakurada et al., 1966–70; Treloar, 1960).

So the theoretical values are realistic, as possible maxima. From Table 1 we may draw the following conclusions:

1. Within the group of polymeric materials there are very great differences in modulus. Elastomers and hard plastics differ as much as about three decades in their E-values.
2. Between normal plastics and fibres on the one hand and fully aromatic poly-amide fibres on the other, there is again an E-difference of almost two decades!
3. Even in aramide fibres the modulus is still less than the theoretically possible value. In the usual high-tenacity yarns the modulus is only 5% of the theoretical one. For the normal plastics the value is still lower: of the order of 1% of the theoretical modulus only!
4. Even in completely ordered materials (theoretical situation) the modulus may vary considerably, depending on the "packing" of the molecular chains: the maximum modulus of polymers with fully extended chains (PE, Nylon, PETP) is roughly 5 times higher than that of polymers with helical chains (PP, PS, POM, PEO).
5. The theoretical values of polymer moduli are in the neighbourhood of the moduli of inorganic materials and steel. In the direction of chain orientation aramide is on the same level as steel.
6. Also for the inorganic materials the modulus is lower than that of ideally crystallized whiskers: these have E-values which are still higher by one decade.
7. The reason for the difference between organic and inorganic materials is, of course, the nature of their bonding forces. But the reason for the differences within the large group of polymers is the difference in "order" and "packing".

The general conclusion therefore is that order, and especially degree and nature of order, has a tremendous influence on the (mechanical) properties of a material. Completely ordered organic polymers may exhibit a modulus (and a tensile strength) comparable to that of steel—though in one direction only!

If we want to influence and improve the mechanical properties of a polymer, we will have to do this by improving the "order", using special ways of order perfection, i.e. of crystallization.

The purpose of this paper is to give a survey of the present knowledge of the influencing of polymer properties by crystallization.

Our approach will be in two directions:

a. Influencing the properties of quasi-isotropic semi-crystalline polymers by the crystallization process.

b. Influencing the properties of semi-crystalline polymers by orientation or oriented crystallization in one direction.

Before doing so, we must, however, consider the basic concepts of crystallinity and crystallization.

1.2 The concept "Polymer Crystallinity"

1.2.1 Degree of crystallinity

Polymers are called partly crystalline or semi-crystalline when the molecular chains are ordered in crystallites or aggregates of crystallites such as spherulites or fibrils. It is extremely difficult to define the concept "crystallinity" in an exact way, since the methods of measuring it (density measurements, X-ray diffraction measurements, infra-red determinations, etc.) have a different basis and lead to somewhat different values.

Anyhow, the important parameters are clear:

1. the degree of crystallinity (x_c)
2. the number of crystalline unities (originating from the number of crystalline nuclei) per unit of volume (N)
3. the average diameter or size of the crystallite or crystallite aggregate ($\bar{a}$)
4. the average distance between the crystalline unities ($\bar{d}$)

These parameters are, as a matter of course, interdependent: if we introduce a packing factor f, which—dependent on the shape of the crystalline units—varies from 0.5 to 1.0, it is easy to derive the following relationship:

$$x_c = N \cdot \bar{a}^3 \cdot f \qquad (1)$$

$$\bar{d} = \bar{a}\left[\left(\frac{f}{x_c}\right)^{1/3} - 1\right] \qquad (2)$$

1.2.2 Morphology

The second aspect in polymer crystallinity is that of *morphology*, ranging from molecular to supramolecular morphology.

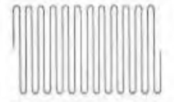
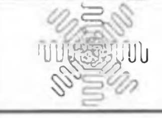
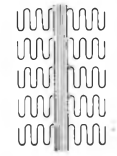
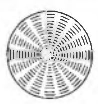
The *molecular morphology* or *conformation* is determined by the chemical structure of the molecular chains: a flexible chain may form a random coil and may fold; a rigid chain cannot.

Superposed on the chain morphology is the *morphology of the microstructural crystalline unit*.

Rigid chains will form rodlets or bundles of rodlets. Flexible chains may fold and form *microlamellar plates;* or they may *align in rows* to form microthreads.

The lamellar microstructure will normally lead to a *spherulitic macrostructure* since it will grow in three directions. The threadlike microstructure will normally develop into a *hybrid* macrostructure: the *row-nucleated lamellar structure*, consisting of a fully fibrillar core (with partly extended chains) and a lamellar peripheral growth structure.

The ideal form of the lamellar structure is the *plate-like single crystal* which may be obtained by crystal-

TYPE OF MACROMOLECULE	CONFORMATION	MICROSTRUCTURAL UNIT	CONDITIONS	MACROSTRUCTURE	PATTERN (CROSS-SECTION)
FLEXIBLE MACROMOLECULE IN QUIESCENT CONDITIONS	RANDOM COIL	FOLDED CHAIN LAMELLAE	VERY DILUTE QUESCENT SOLUTION	SINGLE GRYSTAL	
			MELT	SPHERULITE	
FLEXIBLE MACROMOLECULE IN FIELDS OF FORCE (FLOW)	DEFORMED COIL	CORE OF ALIGNED CRYSTALS (ROW) + LAMELLAR "SIDE PLATES"	DILUTE STIRRED SOLUTION	SHISH–KEBAB	
			EXTRUDED "MELT"	ROW NUCLEATED STRUCTURE	
RIGID MACROMOLECULE	ROD (LIQUID CRYSTAL)	MICRO-FIBRIL (RODLET)	SPINNING FROM SOLUTION WITHOUT SPECIAL PRECAUTIONS	MOZAIC OF RANDOMLY ORIENTED MICROFIBRILS	
			SPINNING WITH MAINTENANCE OF FULL ORIENTATION	HIGHLY AND SYMMETRICALLY ORDERED MICROFIBRILS	

Scheme 1: Morphology of cristallites in polymers.

lization from very dilute quiescent solutions. The ideal form of the row-nucleated macrostructure is the "*shis-kebab*", also obtained by crystallization from dilute, but in this case stirred solutions.

Scheme 1 gives a survey of the possibilities.

The "normal" macrostructures in practice are the *spherulitic* and the *row-nucleated* structure (the latter in stretched fibres). In both cases the basic microstructural unit seems to be the plate-like crystallite with folded chains.

The lamellae are aligned *radially* in the spherulites and *at right angles* to the direction of stretch (or flow) in the row-nucleated structures.

Structures with fully extended chains are normally observed in the case of rigid rod-like macromolecules. However, they may also be formed from flexible molecules, viz. under very high pressures. In this instance one finds mozaics of crystallites with fully extended chains.

1.2.3 Tie Molecules

Before ending this short introduction on crystallinity, I want to say a few words on a very important item as regards cohesive properties, viz. the *tie molecules*. They are parts of chains or bundles of chains extending from one plate (lamella) to another. They concentrate and distribute stresses throughout the material and are therefore particularly important for the mechanical properties of the semi-crystalline polymers [37].

Small amounts of tie molecules give a tremendous increase in the strength and a decrease in brittleness.

1.3 *Nucleation and growth*

The question: "how to influence polymer crystallization" can only be answered if we understand the basic parameters which determine the crystallization.

The crystallization phenomenon can be devided into two fundamental processes: nucleation and growth.

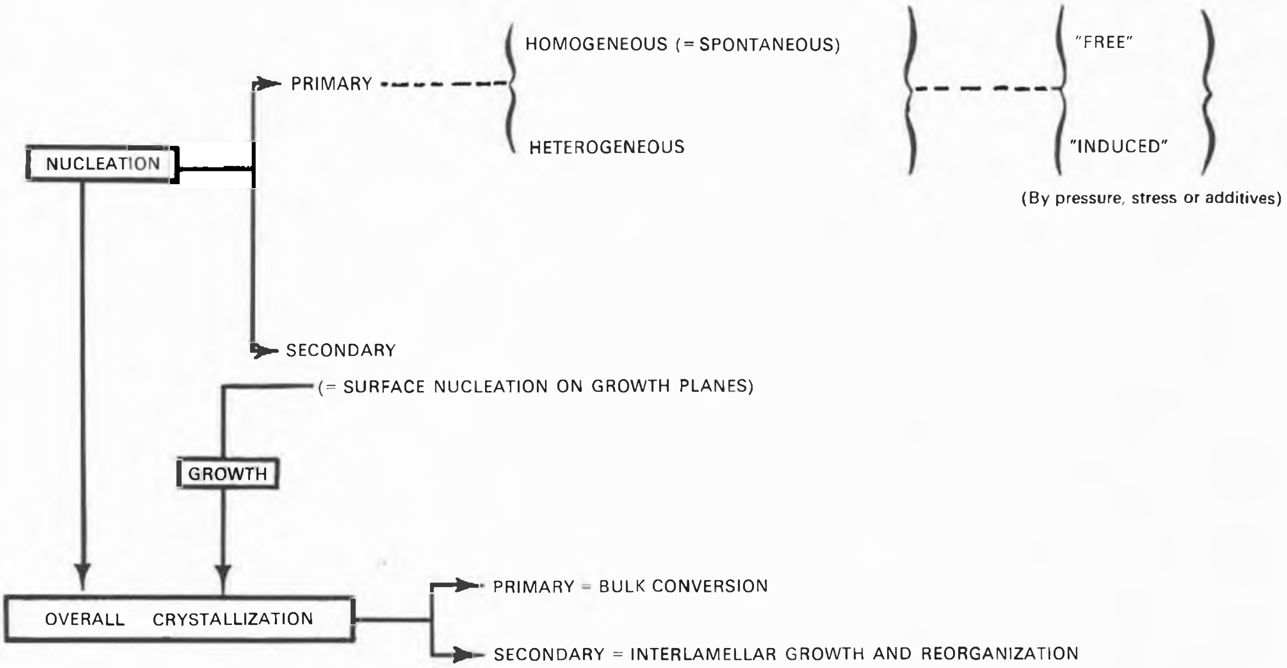
Nucleation is the initiation of a very small amount of crystalline material emerging from the parent phase by fluctuation processes (in density and ordering). It determines the morphology of the subsequently growing crystallites or aggregates of crystallites.

The number of crystallization centres determines the fineness of the crystallization pattern.

Growth proceeds again by a nucleation mechanism, viz. by surface nucleation on a growth plane. This is called *secondary nucleation*, as distinct from the *primary nucleation*, which occurs in the absence of the newly growing phase. Furthermore the nucleation may be *homogeneous* or *heterogeneous*. Homogeneous nucleation occurs in the absence of a second phase, spontaneously, by supercooling only. Heterogeneous nucleation is due to the presence of a second phase and occurs on the interphase of it. In normal practice heterogeneous nucleation is the rule, since all polymer melts contain heterogeneities (impurities, residues of incomplete melting, nucleating agents, etc.).

The primary nucleation may be "*free*", i.e. only dependent on temperature gradients, or "*induced*", by *pressure* or by *stress*.

Also in the *crystallization process as a whole* two phe-



Scheme 2: Basic concepts of polymer crystallization.

nomena may be discerned, viz. *primary and secondary crystallization*. Primary crystallization causes the bulk of the melt to be converted into solid material. But when the polymer has crystallized completely with respect to its volume, the crystallinity will increase still further because of secondary crystallization (thickening of the freshly grown lamellae, reorganization to a higher degree of lattice perfection, slow crystallization in inclusions).

Scheme 2 gives a survey of what we have discussed.

The whole crystallization process is a continuous interplay between nucleation (three- and two-dimensional) and diffusive transport of matter to a surface.

The rate of the overall crystallization depends on the number of available nuclei and on the rate of transport of molecules; nucleation and transport are in a certain sense "consecutive reactions".

2. "Free" crystallization under quasi-isotropic conditions

2.1 Basic considerations

In unstrained (quasi-isotropic) crystallization processes the crystallization starts from a number of point-nuclei, and progresses in all directions at an equal linear rate (v). In the case of isothermal crystallization the radius of the crystallized regions increases by an equal amount per unit of time (v = constant). The rate of growth is very much dependent, however, on the temperature of crystallization.

At the melting point (T_m) and at the glass transition point (T_g) its value is nearly zero; in the intermediate region a maximum (v_{max}) is observed at a temperature T_k. *Gandica* and *Magill* [12] have derived a master curve, valid for all "normal" polymers, in which the ratio v/v_{max} is plotted versus a dimensionless crystallization temperature:

$$\Theta = \frac{T - T_\infty}{T_m - T_\infty} \quad \text{where } T_\infty \approx (T_g - 50)$$

This master curve is shown in fig. 1. The top of the curve is reached at $\Theta \approx 0.635$, corresponding roughly with the empirical relationship:

$$T_k \approx 0.5(T_m + T_g) \tag{3}$$

The quantitative theory of crystallization has been developed by *Becker* and *Döring* [3], *Turnbull* and *Fisher* [47] and *Hoffman* and collaborators [13–17].

The theory starts with the following basic expressions:

$$\text{Rate of nucleation } \dot{N} = \dot{N}_0 \cdot e^{-\frac{E_D}{RT}} \cdot e^{-\frac{\Delta G_n^*}{kT}} \tag{4}$$

$$\text{Rate of growth } v = v_0 \cdot e^{-\frac{E_D}{RT}} \cdot e^{-\frac{\Delta G_2^*}{kT}} \tag{5}$$

The common term exp. $(-E_D/RT)$ is the temperature dependence of the rate of diffusive transport of the molecules in the melt. ΔG_n^* means the free energy of a nucleus with an n-dimensional growth.

2.2 The transport factor

Let us first look at the factor exp. $(-E_D/RT)$.

Hoffman supposed that E_D was not a constant, but that the diffusive transport in a melt could be described by a WLF function*, in the same way as visco-elastic deformations in a glassy polymer melt *near* T_g may be described by it.

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* WLF = Williams-Landel-Ferry

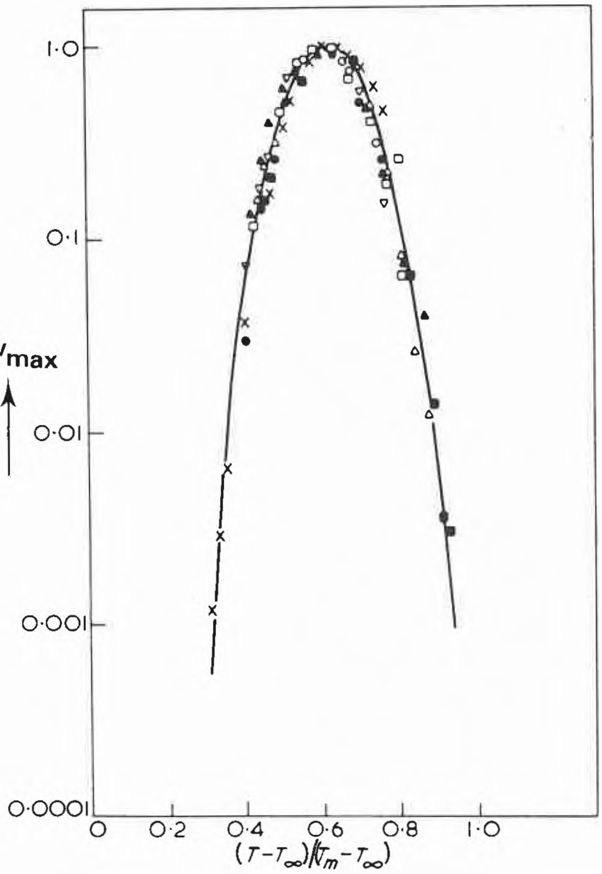

Fig. 1: Dimensionless master curve of the rate of growth, suggested by *Gandica* and *Magill*.

He therefore posed:

$$\frac{E_D}{RT} \approx \frac{C_1}{R(C_2 + T - T_g)} \tag{6}$$

where $C_1 \approx 17{,}2$ kJ/mol and $C_2 \approx 51{,}6$ K.

This, however, though approximately true in the neighbourhood of the glass-transition temperature, does not hold in the region of the optimum rate of crystallization, as has been shown by Mandelkern et al. [27] in experiments on crystal growth, and by *Van Krevelen* and *Hoftyzer* [51] for the viscous flow (which is also determined by E_D).

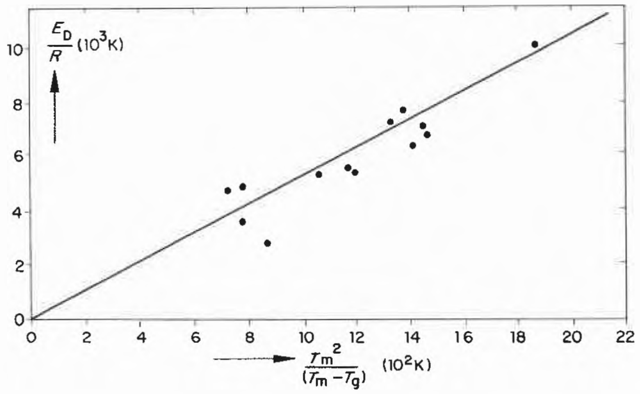

Fig. 2: Correlation between the activation energy of diffusive transport (E_D) and the characteristic transition temperatures of the polymer (*Van Krevelen*).

In the undercooled melt far from T_g, E_D *is* constant for a given polymer.

Mandelkern determined activation energies for a series of polymers and found that E_D for different polymers increases monotonically with T_g, in first approximation.

I myself, analysing *Mandelkern*'s data, came to the following semi-empirical correlation, which fits the data well:

$$\frac{E_D}{R} \approx C_D \frac{T_m^2}{T_m - T_g} \tag{7}$$

where $C_D \approx 5$.

Fig. 2 shows this correlation.

2.3 *The nucleation factor*

Let us now look at the nucleation factor exp. $(-\Delta G_n^*/kT)$. An enormous amount of theoretical work has been done in this subject and elaborate theories have been worked out, leading to complicated nucleation equations.

Close examination of these theories, however, reveals that they incorporate a major incorrectness, resulting from over-idealized assumptions and invalid generalizations, as *Binsbergen* [4] has shown.

The only really certain fact is that $\Delta G_n^*/kT$ has the following form:

$$\frac{\Delta G_n^*}{kT_x} = \frac{C}{T_x}\left(\frac{T_m}{T_x}\right)^{n-1}\left(\frac{T_m}{\Delta T}\right)^{n-1} \approx \frac{C}{T_x}\left(\frac{T_m}{\Delta T}\right)^{n-1} \tag{8}$$

where: T_x = crystallization temperature
$\Delta T = T_m - T_x$ = undercooling
n = the "dimensionality" of the nucleation process.
As mentioned before, the nucleation in practice is nearly always a surface process, so $n \approx 2$.
C = a characteristic constant for every polymer, (with the dimension temperature). It contains the ratio

$$\frac{\text{surface energy of the nucleus}}{\text{lattice energy of the crystal}}$$

For a number of polymers investigated the average value is: $C \approx 265$ K.

2.4 *The linear growth rate*

So we come to a rather simple semi-empirical expression for the *linear growth rate:*

$$\ln v = \ln v_0 - \frac{E_D}{RT_x} - \frac{265}{T_x}\frac{T_m}{\Delta T} \tag{9}$$

where $v_0 \approx 10^{12}$ nm/s

Substituting (7) resp. (6) into (9) and introducing the variables $\xi = T_m/T_x$ and $\delta = T_g/T_m$ one gets after some transformation:

for $T_x \geq T_k$

$$\log v = \log v_0 - 2.3\frac{\xi}{1-\delta} - \frac{115}{T_m}\frac{\xi^2}{\xi - 1} \tag{10}$$

for $T_x \ll T_k$

$$\log v = \log v_0 - \frac{895\,\xi}{51{,}6\,\xi + T_m(1-\delta\xi)} - \frac{115}{T_m}\frac{\xi^2}{\xi - 1} \tag{11}$$

Fig. 3 presents these equations in a graphical form. As

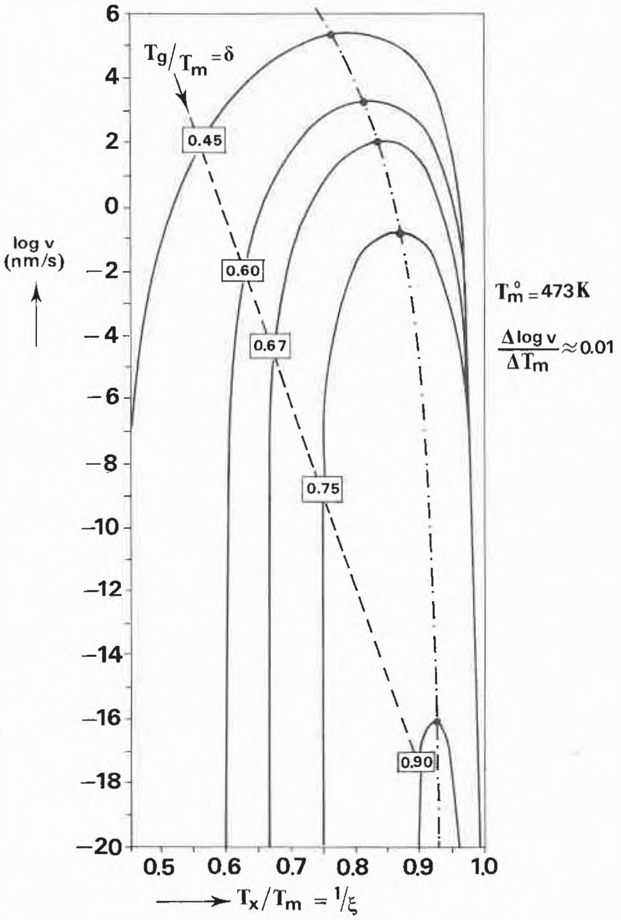

Fig. 3: Universal master curve of the rate of growth of spherulites as a function of the dimensionless parameters T_x/T_m and T_g/T_m (*Van Krevelen*).

a fixed standard value for T_m, necessary to represent the equations in a two-dimensional graph, the value 473 K was chosen. For every 10 °C that T_m is higher or lower, log v will be about 0,1 higher or lower then given in the graph.

Fig. 3 enables us to predict the value of v under experimental conditions for all "normal" polymers.

It is clear from fig. 3 that the ratio T_g/T_m has a very great influence on the absolute value of v.

Very simple and symmetrical polymers such as PE show high rates of crystallization, (their T_g/T_m ratio is about 0,5) whereas unsymmetrical polymers such as isot.-polystyrene with $\delta \approx 0{,}75$ have low v-values.

Some numerical values of the growth rate are interesting; they are presented in Table 2.

It is easy to calculate the time necessary to fill up a sphere of a radius of 10 cm with crystalline material, starting from one nucleus in the middle:

for PE	about 1 hour
for Nylon	about a day
for PETP	about a month
for PS	about 1 year

Table 2: Some maximum growth rates

Polymer	T_g/T_m [−]	Max. Growth rate [nm/s]
Polyethylene (PE-HD)	0.47	$3 \cdot 10^4$
Nylon 6	(0.6)	$3 \cdot 10^3$
Polyester (PETP)	0.64	10^2
isot. Polystyrene (iPS)	0.73	$3 \cdot 10^0$

As already mentioned v_0 is a temperature-independent constant. My collaborator Dr. *Van Antwerpen* [48,49] has shown that v_0 is a function of the molecular weight of the polymer, of the general form:

$$v_{0,M} = v_0 + \frac{\text{const.}}{\bar{M}_n} \xrightarrow{(\bar{M}_n \to \infty)} v_0 \qquad (12)$$

2.5 *The overall rate of crystallization*

Let us now consider the crystallinity as a function of time, which can be described by *Avrami*'s equation:

$$\alpha = 1 - \exp(-Kt^n) \qquad (13)$$

where:

α = volume fraction transformed into the spherulitic state. It may be determined from the density

$$\alpha = \frac{\varrho - \varrho_a}{\varrho_s - \varrho_a}$$

(with ϱ_a = amorphous density, ϱ_s = limiting spherulitic density), or by means of optical methods.

n is a constant, which in practice is always in the neighbourhood of 3,

$$\text{so } \alpha = 1 - \exp(-Kt^3) \qquad (14)$$

K is the overall rate constant of crystallization, directly related to the half-time of crystallization:

$$t_{1/2} = \left(\frac{\ln 2}{K}\right)^{1/3} \qquad (15)$$

Theoretically K is determined by the number of nuclei and the linear growth rate:

$$K \approx \frac{4}{3}\pi \cdot N \cdot v^3 \qquad (16)$$

The latter equation provides a means to derive N, if v and K (from α) have been determined experimentally.

2.6 *The number of nuclei N*

My collaborator Dr. *Boon* [5,6] investigated the kinetics of crystallization of isotactic polystyrene. This polymer is extremely interesting as a model substance for crystallization work. Its rate of growth is so low that the crystallization can be studied in the whole region from T_g to T_m. Due to the low growth rate the fundamental processes of nucleation and growth can be studied almost separately.

Boon determined the number of nuclei in the two extreme cases:

a. starting from a superheated melt and quenching to the crystallization temperature,

b. starting from the solid state and heating to the crystallization temperature.

His results are presented in fig. 4.

After heating above T_m for some time the number of nuclei is extremely small ($N < 10^5$ cm^{-3}). By quenching the number increases, attaining a maximum at T_g (N > 10^{12} cm^{-3}). By heating from T_g to higher temperatures the number of nuclei diminishes, reaching very low values at the melting point.

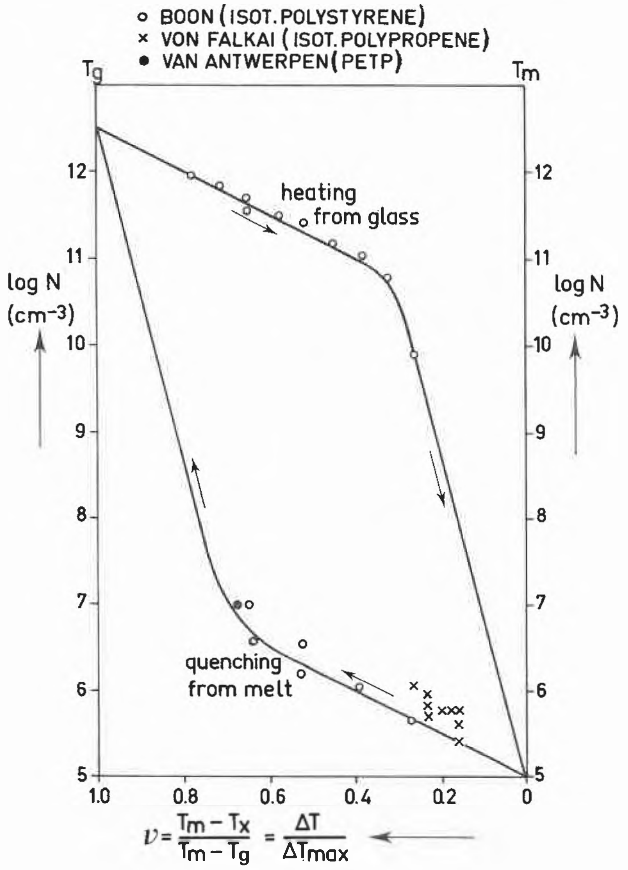

Fig. 4: Number of nuclei per unit volume after quenching and after reheating from the solid state.

Fig. 4 contains *Boon's* data as a function of the dimensionless parameter ν $[= (T_m - T_x)/(T_m - T_g)]$, the "relative undercooling".

In this master-form the graph also fits with the data of *Von Falkai* [52] for isotactic polypropene and with those of *Van Antwerpen* [48, 49] on PETP.

Generally speaking we may say that for all crystallizing polymers the number of nuclei will be of the following order of magnitude:

starting from the melt and quenched to T_x: $\sim 3 \cdot 10^6$ cm^{-3}

starting from the solid state and heated to T_x: $\sim 3 \cdot 10^{11}$ cm^{-3}

Since 1 cm^3 contains about 10^{19} molecules, the number of nuclei as a fraction of the molecules is extremely small!; viz:

starting from the melt: 3 in 10^{13} molecules
starting from the solid state: 3 in 10^8 molecules

This result is more or less surprising!

N will of course determine the maximum size of the spherulites after conversion of the whole melt into crystalline material.

It can easily be seen that

$$\frac{4}{3}\pi \bar{R}_{\mathrm{max}}{}^3 N = x_c \tag{17}$$

so that, if $x_c \approx 1$

$$\bar{R}_{\mathrm{max}} \cdot N^{1/3} \approx 0.62 \tag{18}$$

2.7 *Influencing the spherulitic crystallization*

We now come to practical conclusions.

From equation (15) and (16) we immediately derive for the overall rate of crystallization:

$$r_c \approx (t_{1/2})^{-1} \approx 1.5 \cdot N^{1/3} \cdot \nu \tag{19}$$

This means that both N and ν are very important. We have seen that N is mainly determined by the thermal programme. Just undercooling a melt gives N-values of about $3 \cdot 10^6$ cm^{-3}; cooling to room temperature and heating up gives N-values of the order of $3 \cdot 10^{11}$ cm^{-3}. For $N^{1/3}$ this gives a range from $1.5 \cdot 10^2$ to $5 \cdot 10^3$.

The rate of growth is more important than the number of nuclei. According to equations (10) and (11) it depends on:

a. the ratio T/T_m $(= 1/\xi)$
b. the ratio T_g/T_m $(= \delta)$
c. the absolute value of T_m
d. the absolute value of ν_0

The growth rate shows a maximum at $T_K \approx 0.825\ T_m$. This therefore is the "optimum temperature" for a rapid crystallization.

T_g/T_m and T_m are determined by the constitution of the polymer and cannot be influenced by process parameters.

The parameter ν_0 may be influenced by the average molecular weight and by the addition of nucleation agents.

So the practical way to influence the "free" crystallization of polymers is by choosing:

a. the right temperature programme for an optimal nucleation (c.q. quenching and reheating).
b. the optimum crystallization temperature for a rapid growth rate.
c. an optimal nucleation agent in order to increase the temperature-independent factor.

2.8 *Properties of semicrystalline spherulitic polymers*

Since plastic materials are brittle when they consist of large spherulites, it is a great advantage if the spherulites are as small as possible. For this reason N must be large, and therefore undercooling by quenching must be deep and fast. The optimum conditions are obtained if quenching is followed by reheating to T_K, with thorough crystallization. In processes like vacuum-forming this can easily be done.

Quantitative data on the correlation between spherulite size and (mechanical) properties are scarce.

Sharples [42] mentions some data on the influence on the yield point in nylon 66. They are given in Table 3.

Table 3: Yield points in nylon 66

Spherulite size (S) $[\mu]$	Yield stress P_Y p.s.i.	10^6 [N/m²]
50	10,250	72
10	11,800	83
5	12,700	89
3	14,000	98

In formula: $\frac{P_y}{P_{y,\max}} = 1 - 0.18 \log \frac{S(\mu)}{0.35}$

3. Pressure-induced crystallization *

3.1 The influence of pressure

One method to form polymeric crystallites with (partly) extended chains is to apply very high pressures to the polymer melt, at temperatures at which the molecules are sufficiently mobile.

Pressure crystallization is a rather slow process; most authors report "annealing times" of several hours or even days.

The effect of high pressure on the crystallization process is threefold:

1. A high pressure enhances the formation of crystal modifications with a packing that is as dense as possible. Since extended chains have a denser packing than folded chains, an increase of pressure is favourable for chain extension.
2. A high pressure raises the temperature of melting (and solidification). According to Clapeyron; formula

$$\frac{dT_m}{dP} = T_m^o \frac{\Delta V_m}{\Delta H_m} \tag{20}$$

where T_m^o is the conventional melting point and ΔV_m and ΔH_m are the volume and enthalpy effects of the melting process.

For large pressure variations the change in the melting temperature is given by the Simon equation

$$P - P^o = a\left[\left(\frac{T_m}{T_m^o}\right)^c - 1\right] \tag{21}$$

where the symbol ^{o} indicates the standard condition (atmospheric pressure).

For polyethylene the values of the constants in this formula are: $T_m^o = 409\ K$ (136 °C), $a \approx 3$ kbar, $c \approx 4.5$. Fig. 5 is a graphical representation of this equation, which is fully confirmed by the experiments of *Osugi* and *Hara* [29]. It is obvious that the *melting region* may be raised by about 100 °C at pressures of about 5 kbar.

3. It is a well-known fact that the length of folds in crystal lamellae increases with temperature. Since the melting temperature (= solidification temperature) goes up as a result of the high pressure, also the fold length will increase (with the full molecular chain length as the limit).

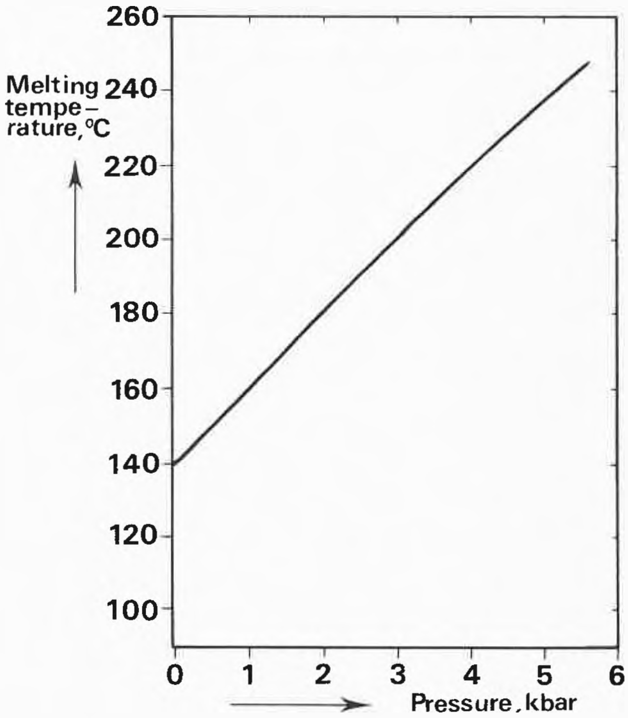

Fig. 5: Melting temperature of polyethylene as a function of pressure according to *Osugi* and *Hara* [29].

Of course the three effects are interrelated. From theoretical concepts as well as from experimental data it is obvious that crystallization with extended chains over a length of, say $> 10^{-7}$ m only takes place if the annealing temperature is in the melting region of extended chain crystals.

An extended chain of polyethylene melts (and solidifies) under a pressure of 5 kbar at 236 °C. So there is a region near this temperature where pressure crystallization at 5 kbar can be performed.

Mechanism

There has been much confusion about the mechanism of formation of extended chains. The most probable conception is that formation direct from the melt is the dominant mechanism; unfolding and subsequent lamella-thickening may also take place, especially at lower temperatures and long annealing times.

Some authors have reported that fractionation of chain molecules according to their chain length occurs during pressure crystallization. Crystals with fully extended molecules of uniform molecular mass (of about 10000 kg/kmol) have been observed.

3.2 Structure and high-pressure crystallization

Most of the pressure crystallization research has been done on polyethylene. Pressures of 3 kbar or higher are required to obtain crystallite thickenesses of 10^{-7} m. Some other polymers have a much stronger tendency

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* The most important investigations in this field have been made by *Wunderlich* [52–54] and *Basset* et al. [1,2].

towards extended chain formation. Poly(chloro-trifluoro-)ethylene shows this effect at about 1 kbar; poly(tetrafluoro)ethene already at about 0.3 kbar.

My former collaborator Dr. *Juyn* [21] suggested that there exists a relation between the tendency towards extended chain crystallization and the melting point dependence on pressure.

Since

$$\frac{dT_m}{dP} = T_m^o \frac{\Delta V_m}{\Delta H_m} = \varkappa \qquad (20)$$

a close relationship may be expected between $\varkappa$ and the minimum pressure required to form extended chains $> 10^{-7}$ m in the crystal.

Table 4 shows that this is the case indeed.

Table 4: Correlation between $\varkappa$ and $P^{\min}_{(>1000\,Å)}$

Polymer	$\varkappa$ [K/kbar]	$P^{\min}_{(>1000\,Å)}$ [kbar]
PE	25	~ 3
Nylon	15–40	~ 2 ?
PCTFE	65	~ 1
PTFE	140	~ 0.3

3.3 Properties

The mechanical properties of pressure-crystallized polymers are disappointing: they are very poor.

The main disadvantage of pressure crystallization is that it results in a quasi-isotropic brittle product, a mosaic of randomly oriented crystallites without much interconnection.

Wunderlich [53] reports that his polyethylene materials were so brittle that they could be easily powdered in a mortar.

4. Stress-induced crystallization

4.1 Basic considerations

In stress-induced crystallization the chain molecules are extended, prior to crystallization or during recrystallization. Chain extension as such requires a considerable stretching force in order to balance the entropic retracting force of the chains.

It is necessary that the extension time is of the same order as the relaxation time of the chains. This means that the following relationships should hold:

$$\left.\begin{array}{l} \dot{\varepsilon} \cdot \Theta \approx 1 \text{ for tensile stretch} \\ \dot{\gamma} \cdot \Theta \approx 1 \text{ for shear} \end{array}\right\} \qquad (22)$$

where:

$\dot{\varepsilon}$ = rate of elongation

$\dot{\gamma}$ = rate of shear

Θ = relaxation time

The relaxation time of polymer melts is of the order of 10^{-3} s.

According to Bueche the relaxation time (*at low rate of deformation*) is:

$$\Theta_0 = \frac{6}{\pi^2} \cdot \frac{\eta_0 \bar{M}}{\varrho RT} \qquad (23)$$

Chain extension under the influence of stretch or shear is therefore a function of molecular weight.

McHugh [28] has calculated the amount of extension as a function of deformation rate and molecular weight in polymer solutions. His results are presented in fig. 6.

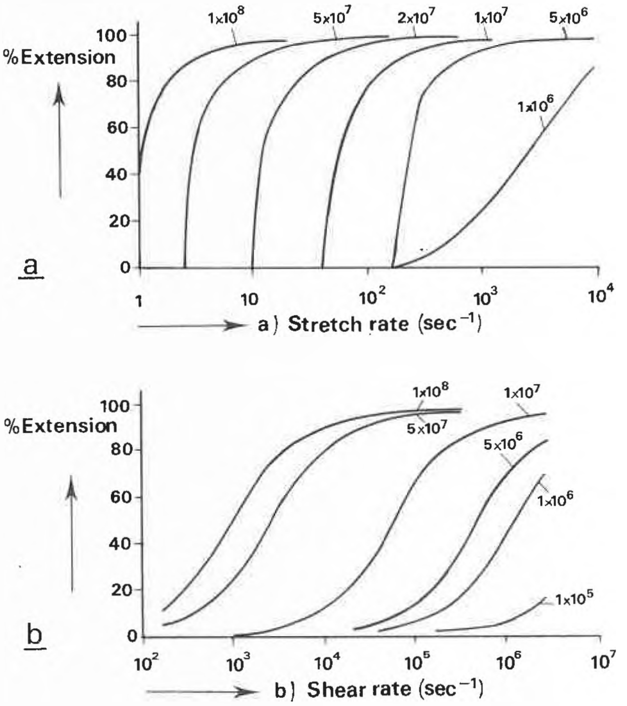

Fig. 6: Percentage extension of a polymer solution caused by different deformations (at 100 °C):
a. as a function of the stretch rate (for various molecular masses)
b. as a function of the shear rate (for various molecular masses)
(Calculations by *McHugh* [28]).

They illustrate the enormous difference between shear and stretch. Stretch forces are far more conducive to chain extension and hence to fibrous nucleation than shear forces.

It is clear that the extension must be maintained until the melt has solidified by crystallization. For spherulitic crystallization this would require residence times of 0,5–50 s (0,5 for PE and 50 for PETP), which excludes normal spherulitic crystallization for most polymers, since only fractions of seconds are available in practice.

It is therefore fortunate that another type of crystallization, that of the microfibrillar crystallite, is the dominant mode in stress-induced crystallization.

This is due to the fact that under tension threadlike row-nucleation is favoured.

The theory of stress-induced nucleation is not yet sufficiently developed but an interesting approach was made by *Kobayashi* and *Nagasawa* [24].

They calculated the acceleration of nucleation by means of simple elongation in the ideal case where there is no relaxation after elongation.

They found that the nucleation and hence the crystallization may be orders of magnitude higher than in spherulitic crystallization.

We shall now discuss the different forms of stress-induced nucleation. These are:

A. Starting from the liquid state:

1. Flow-induced crystallization from solutions
2. Spinning with high-speed winding from the melt

B. Starting from the solid state (in thread form)

1. Cold drawing of spun threads
2. Cold drawing followed by annealing under tension
3. "Superdrawing" of spun threads

Finnaly, some attention will be paid to a new phenomenon connected with stress-induced crystallization:

C. Hard-elastic fibres.

4.2 Stress-induced crystallization, starting from the liquid state

4.2.1 Flow-induced crystallization from solutions

My countryman *Pennings* [31–36] succeeded in producing threads of polyethylene, consisting of a core of highly extended chains; his technique was to induce extension forces by rotating a cylindrical rotor within a cylindrical stator. The polyethylene solution was between the two cylinders and the overall structure of the resulting yarn was the Shish-Kebab* (fig. 7, 8 and 9). In this process a similar fractionation according to molecular weight has been observed as in high-pressure crystallization.

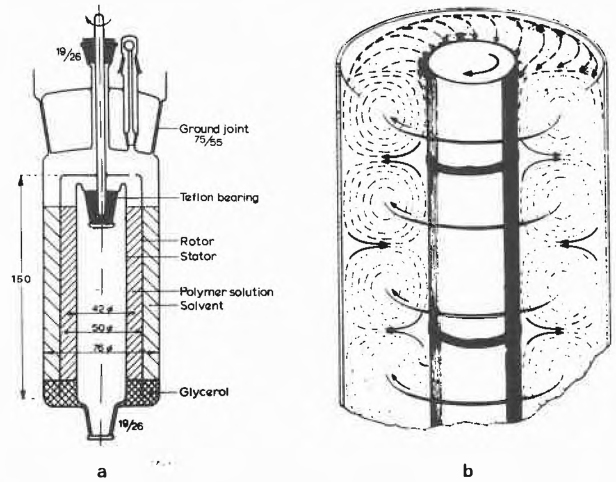

Fig. 7: Crystallization apparatus used by Pennings (1970)
a. Crystallization apparatus comprising a glas vessel, a stator and a rotor, used by *Pennings* for studying the effect on crystallization of simple shear flow and of *Taylor* vortices, with the polymer solution being confined between rotor and vessel wall, respectively.
b. Exploded view of the coaxial cylinders under the conditions of crystallization. The dashed lines represent the streamlines of the *Taylor* vortices. Fibrous rings revolving around the stirrer in the vortex cores are depicted by the solid lines. Fibrous rings are seen to have wrapped around the stirrer in two positions where the fluid moves towards the vessel wall.

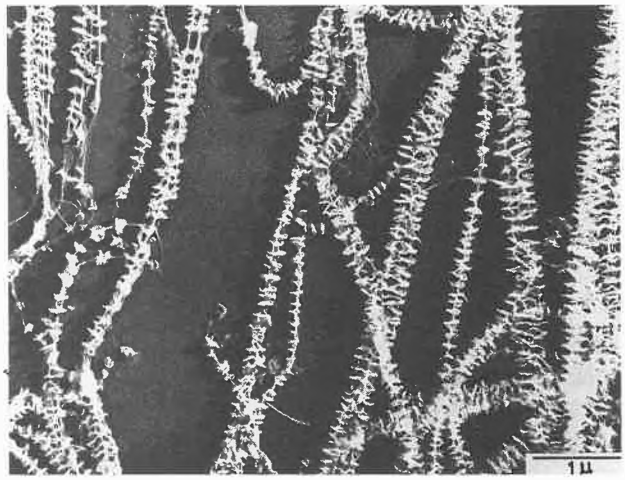

Fig. 8: Electron micrograph of polyethylene "Shish kebabs" *(Pennings* et al. [33]).

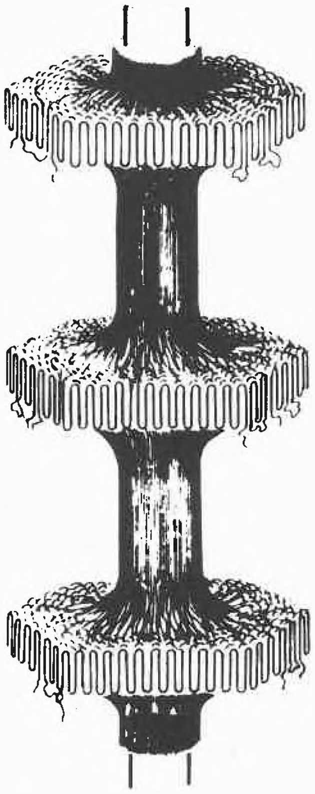

Fig. 9: Schematic representation of the "shish kebab" structure *(Pennings* et al. [33]).

In recent work, Pennings applied a technique to produce polyethylene fibres with a very high tensile modulus. In this method the thread grows continuously from a 0.4% solution of high-molecular mass polyethylene ($\approx 1.5 \cdot 10^6$ kg/kmol) at 120 °C; the fibrous crystal is wound on the rotor at a speed of up to 0.5 cm/s (0.3 m/min), and has a modulus of up to 50% of the theoretically attainable value, viz. 100 GN/m^2!

Other methods of flow-induced crystallization use extension forces between jets or within a symmetrical

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* Shish Kebabs have also been observed in experiments without any stirring. For example, by washing polyethylene powder with xylene *(Jamet* and *Perret* [20]) and by crystallizing nylon 4 from a glycerol/water mixture *(Sakaoku, Clark* and *Peterlin* [39]).

4-roller system first employed by Taylor (fig. 10). Important investigations in this area have been made by Frank and *Keller* et al. [22, 23] and *Torza* [45].

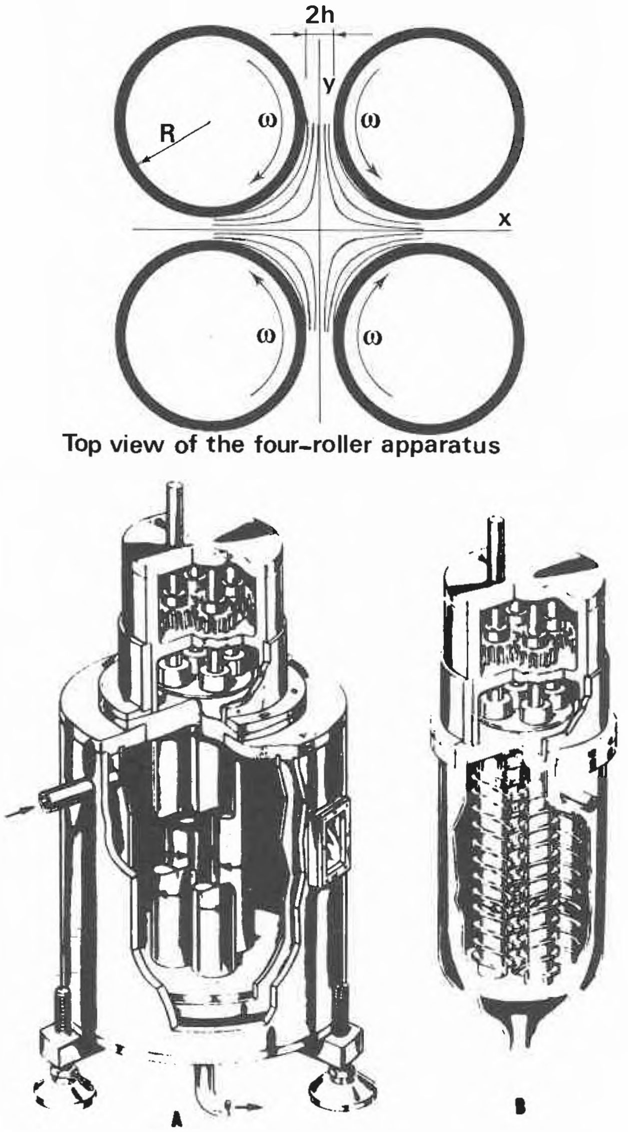


Fig. 10: The four-roller apparatus according to *Torza* [45]
a. Top view
b. Perspective view (A) and schematic representation of possible extruder head (B)

4.2.2 Spinning with high-speed winding

Especially polymers with a moderate rate of crystallization exhibit a very strong dependence of their physical structure on the rate of extension during spinning, i.e. on the winding speed.

Polyethylene terephthalate, PETP, is a good example. At winding speeds below 35 m/s (about 2000 m/min) the yarn as spun is nearly amorphous, whereas when wound at very high speeds of more than 100 m/s (e.g. at 7000 m/min) it contains well-developed crystallites of closely packed molecules. Fig. 11 presents the density, the sonic modulus (Young's modulus measured at a frequency of 10 kHz) and the crystallinity as a function of winding speed. These data were obtained by my former collaborators Drs. *Heuvel* and *Huisman* [18].

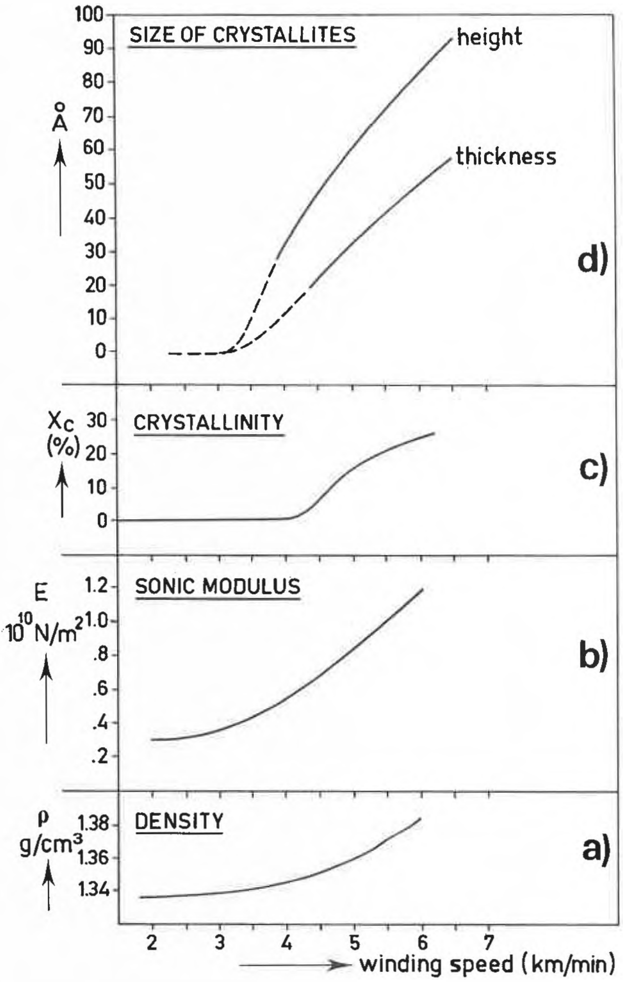


Fig. 11: Physical constants of PETP yarns wound at various speeds (Data of *Heuvel* and *Huisman* [18]).

Residence times of the real drawing are extremely short: some milliseconds; compared with the normal half-time of crystallization ($t_{1/2}$ of the order of 50 s) it is clear that the crystallization process during spinning with high-speed winding is many decades faster than that in the isotropic melt.

Fig. 11 d presents the size of the crystallites, as obtained by X-ray analysis, as a function of winding speed; a very schematic model of the chain structure based on these data is presented in fig. 12.

It is to be expected that (with respect to orientation) not only the winding speed but also the molecular weight, the molecular weight distribution, the temperature and pre-heating time of the melt, the shape of the spinneret, the way of cooling and other parameters will influence the crystalline structure.

4.3 Stress-induced crystallization starting from the solid state

4.3.1 "Cold"drawing of spun threads

The conventional way to effect stress-induced crystal-

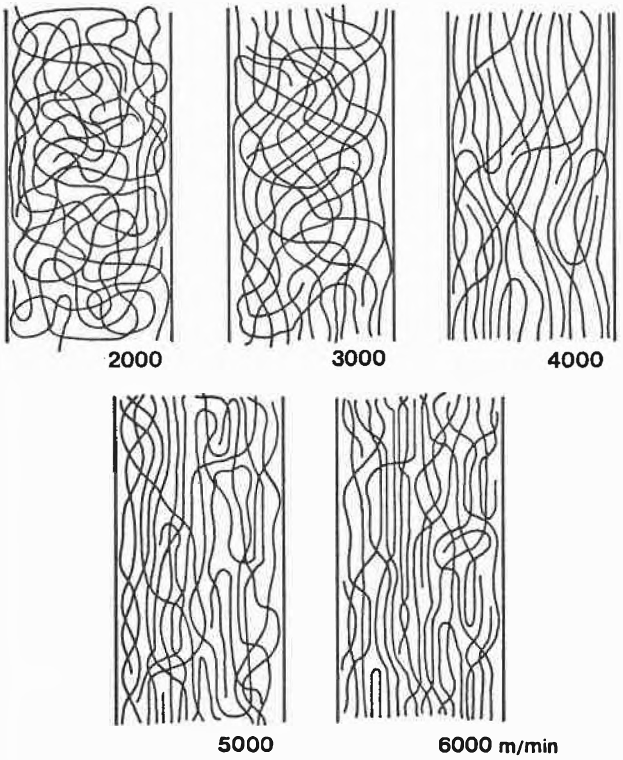


Fig. 12: Proposed molecular arrangements in yarns wound at various speeds as suggested by *Heuvel* and *Huisman* [18].

lization is "cold"drawing, i.e. drawing with the formation of a "neck". To achieve this, the yarn should have a temperature in the neighbourhood of T_g.

Some polymers, like PETP, are spun in a nearly amorphous state or show a low degree of crystallinity. In other polymers, such as nylon, the undrawn material is already semi-crystalline. In the latter case the impact of extension energy must be sufficient to "melt" the folded chain blocks (lamellae); in all cases unoriented material has to be converted into oriented crystalline material. In order to obtain high-tenacity yarns, the draw ratio must be high enough to transform a fraction of the chains in more or less extended state.

An interesting model of the possible structure of semicrystalline yarns is that given by *Prevorsek* et al. [38], and shown in fig. 13.

It consists of fibrils with a definite long period and thickness, consisting of crystallites characterized by a height of about 5 nm and a thickness of the order of 6 nm. Prevorsek supposes that along the fibrils a number of extended tie molecules are present, this number being responsible for the strength; at higher draw ratios the fraction of extended tie molecules increases.

My collaborator Dr. *Van der Meer* [50] made a systematic study of the influence of the applied draw ratio $\wedge$ on the properties of PETP yarns. Fig. 14 presents a survey of his results.

4.3.2 Cold drawing followed by annealing under tension

The "complete" conventional process to "steer" the

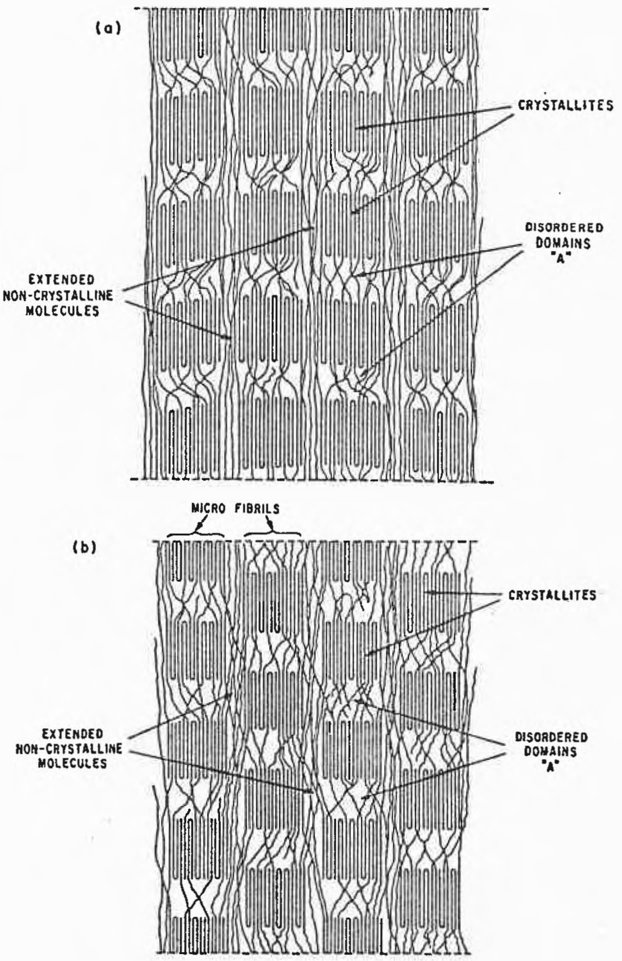


Fig. 13: Structure model of (a) nylon fibres; (b) PETP fibres (fibre axis vertical) as suggested by *Prevorsek* [38].

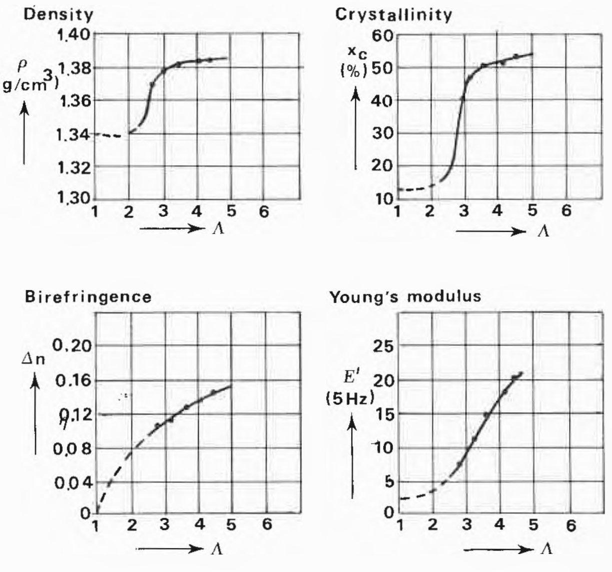


Fig. 14: Physical data of a polyester drawing series as a function of the drawing ratio (after *Van der Meer* [50]).

crystalline structure of a yarn involves the sequence: spinning—drawing—heat treatment (annealing).

As already mentioned, a PETP yarn, when spun at "usual" velocities (< 2000 m/min winding speed) is an almost amorphous body. After drawing (at about 75 °C) the crystallinity increases to about 0.2 and the size of the crystallites is about 3 nm in width and 5 nm in height. In order to increase the crystallinity these drawn yarns may be annealed under tension, the annealing taking place at temperatures varying from 125 to 225 °C (hot plate).

A remarkable problem manifests itself: in dyeing the annealed yarns a very characteristic minimum in dye uptake was found, corresponding to an annealing temperature of about 200 °C. With nylon yarns such a minimum has never been found! It was therefore interesting to investigate the structure morphology, also with respect to the interpretation of this dyeing behaviour.

Annealing under tension changes the values of the crystallinity and the crystallite sizes as shown in Fig. 15, constructed on the basis of data from a systematic investigation by *Huisman* and *Heuvel* [19].

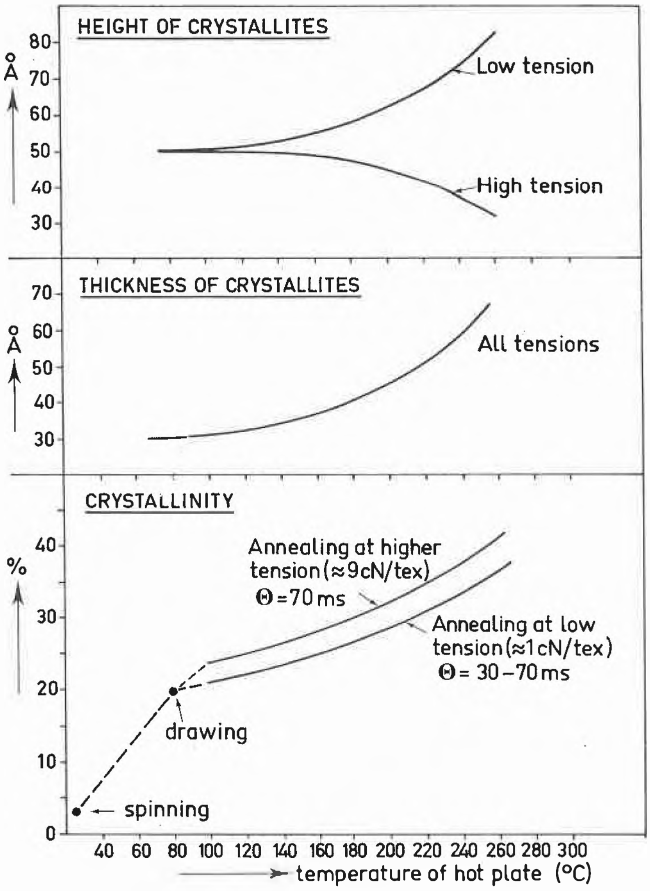


Fig. 15: Change of crystalline morphology of PETP yarns by annealing under tension (data from *Huisman* and *Heuvel* [19]).

Temperature proved to be by far the most important factor for the crystallization behaviour, but time and tension also influence the growth of crystals to a certain extent.

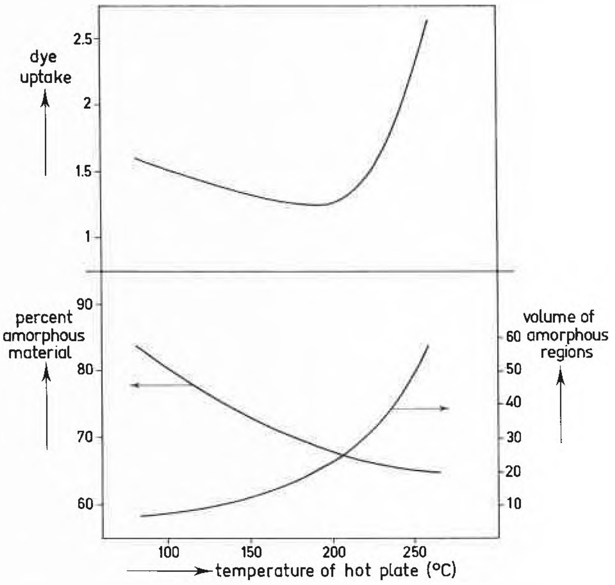


Fig. 16: Interpretation of the dye uptake of PETP yarns after annealing at various temperatures (suggested by *Huisman* and *Heuvel* [19]).

Generally speaking, PETP yarns (and yarns with a moderate rate of crystallization in general) show a low crystallinity which is built up of many small crystallites, if the yarns are annealed at low temperatures; if annealed at a high temperature, the yarns are composed of fewer but bigger crystallites, together with larger adjacent regions; the overall crystallinity becomes moderately high (about 40 %). So there clearly are two opposite and counter-acting factors in the annealing process as a function of temperature (fig. 16): a decrease of the fraction of amorphous material and at the same time an increase in the size of the individual amorphous regions. Fig. 17 presents a schematic picture. Since dyeing takes place in the amorphous regions, we now understand that there must be an annealing temperature where the dyestuff uptake passes through a minimum: the decrease of the amorphous content reduces the dye absorption, the increase of the acces-

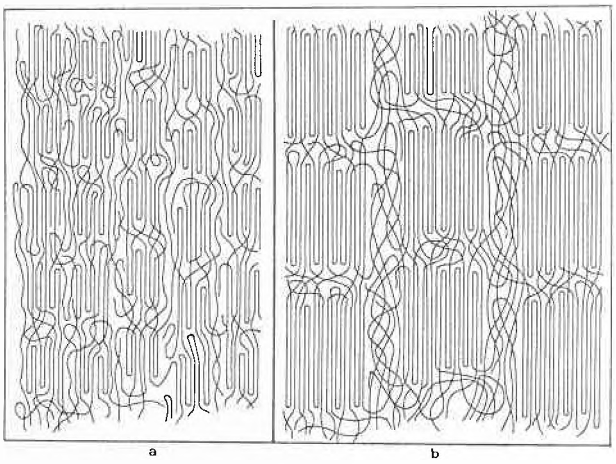


Fig. 17: Schematic yarn structures formed at:
a. low annealing temperatures
b. high annealing temperatures
(suggested by *Huisman* and *Heuvel* [19]).

sibility to the rather large dyestuff molecules facilitates the transport by diffusion.

This is a very important conclusion for practice. The fact that nylon yarns do not show this minimum results from their higher rate of crystallization; immediately after spinning and drawing the final degree of crystallinity is already obtained and annealing only increases the size of the crystalline and amorphous regions without changing the overall degree of crystallinity. So the accessibility increases with the annealing temperature.

4.3.3 "Superdrawing" of spun threads or films

As mentioned before, the conventional drawing process leads to the well-known fibrillar structure which still contains a majority of folded chains (fig. 13). In drawing above the "natural" draw ratio further unfolding takes place. Such a process at very high draw ratios must be conducted with the utmost care since critical concentrations of stress on the folded chain surface of the crystal blocks must be avoided: they lead to fracture. The superdrawing can be carried out in one and two stages.

The two-stage superdrawing consists of a normal fast drawing process as a first stage, followed by a second stage: a slow drawing process to very high draw ratios. Spectacular results have been obtained with two-stage drawing of polyoxymethylene by *Clark* and *Scott* [10]. In the first stage the polymer is drawn to the natural draw ratio of about 7. The second stage takes place at a very low velocity (50% elongation per minute) up to an ultimate draw ratio of about 20. The optimum temperature for the second step is about 30 °C below the standard melting point. A modulus of 35 GN/m^2, about 70% of the theoretical value has been obtained in this way. The drawn material did not show folded chain periodicity anymore.

Very high draw ratios can also be obtained by extremely careful one-stage drawing. *Capaccio* and *Ward* [7, 8] obtained with polyethylene draw ratios up to 30, and moduli up to 70 GN/m^2 have been reported.

Sheehan and *Cole* [43] drew polypropylene at a speed of 2 cm/s in a glycerol bath of 135 °C and obtained draw ratios up to 50 resulting in a modulus of about 15 GN/m^2 (30% of the theoretical value).

Up till now superdrawing has not been applied in practice.

4.4 Hard elastic fibres

A few words should be devoted to an interesting phenomenon connected with stress-induced crystallization: the so-called hard elastic fibres. They were discovered and explored during the last ten years and show a unique combination of rubber-like, high-elastic recovery from large deformations, with a relatively high modulus and tenacity as normally found in semi-crystalline fibres.

Statton and his coworkers [44] recently gave a comprehensive survey of this interesting new group of materials. They introduced the terms "springy polymers" and "springiness". The phenomenon has been discovered in the laboratories of Celanese and DuPont. Especially the polymers polyoxymethylene, polypivalolactone and polypropylene exhibit springiness.

It is remarkable that these are all polymers with a helical conformation in the extended state.

Under appropriate processing conditions stress-induced crystallization of these polymers results—after annealing—in springiness. The exact morphology necessary for springiness is extremely sensitive to the processing parameters such as spinning and quenching temperatures, shear rate, draw down ratio and annealing conditions (temperature and time). The elastic recovery behaviour is optimal if the spinning temperature is as low as possible and the annealing temperature as high as possible.

Fig. 18 presents a typical stress-strain curve. Springy materials are capable of maintaining their high-elastic recovery to low temperatures, e.g. below the glass transition. During extension the porosity of the material increases; obviously voids are created upon deformation, comparable with crazing in completely amorphous polymers.

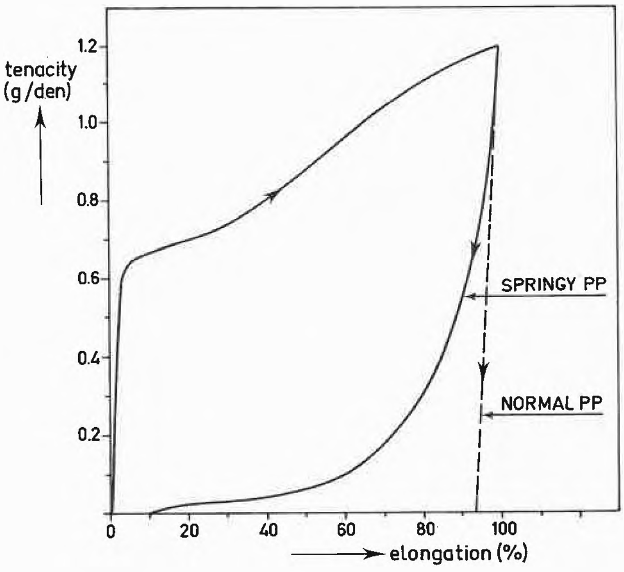


Fig. 18: Stress-strain diagram of "Springy" polypropylene.

Repeated extension lowers the yield point, but the material can be rehealed by allowing a certain recovery time. Extensive drawing finally destroys the springiness. Research on the kinetics of the retraction process revealed that both energetic and entropic contributions are present, although energetic retraction forces are dominant (in contra-distinction to what happens in elastomers).

The exact mechanism is still unknown. It is supposed that lamellar bowing takes place due to either bending of the crystallites or shearing of the chains within lamellae. All models developed to describe the springiness assume some sort of tie molecules or interlamellar connections.

Fig. 19a presents one of the most probable models based on interlamellar tie molecules. Fig. 19b gives virtually the same idea but now in the language of the paracrystalline model.

5. Concluding remarks

We are now in a position to summarize and conclude. It will be clear that the way of crystallization and its degree and morphology are factors that have an enormous influence on the properties of the final product.

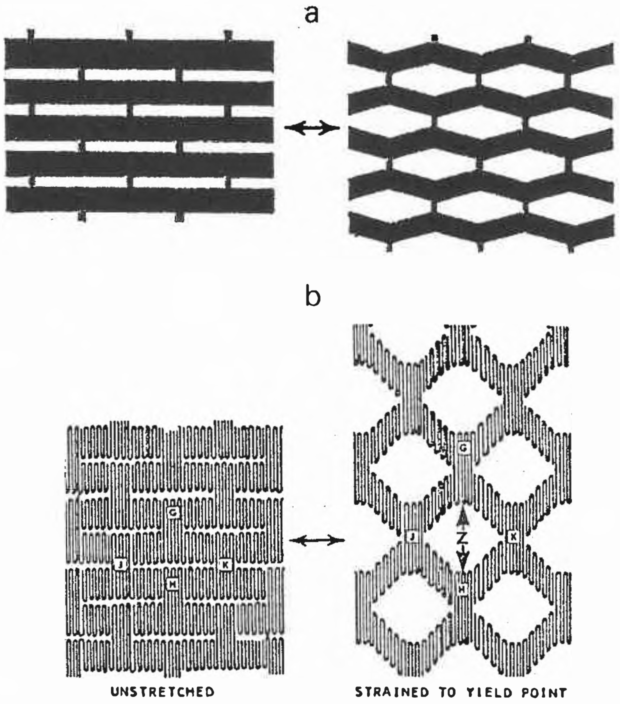


Fig. 19: Models for the interpretation of the elastic behaviour of hard elastic fibres as suggested by *E. S. Clark* [9] (from *Statton, Cannon* and *McKenna* [9]).

The "free", unstressed or quasi-isotropic crystallization leads to spherulitic products; they are strong and tough as long as the spherulites are very small, they are brittle if the spherulites become large.

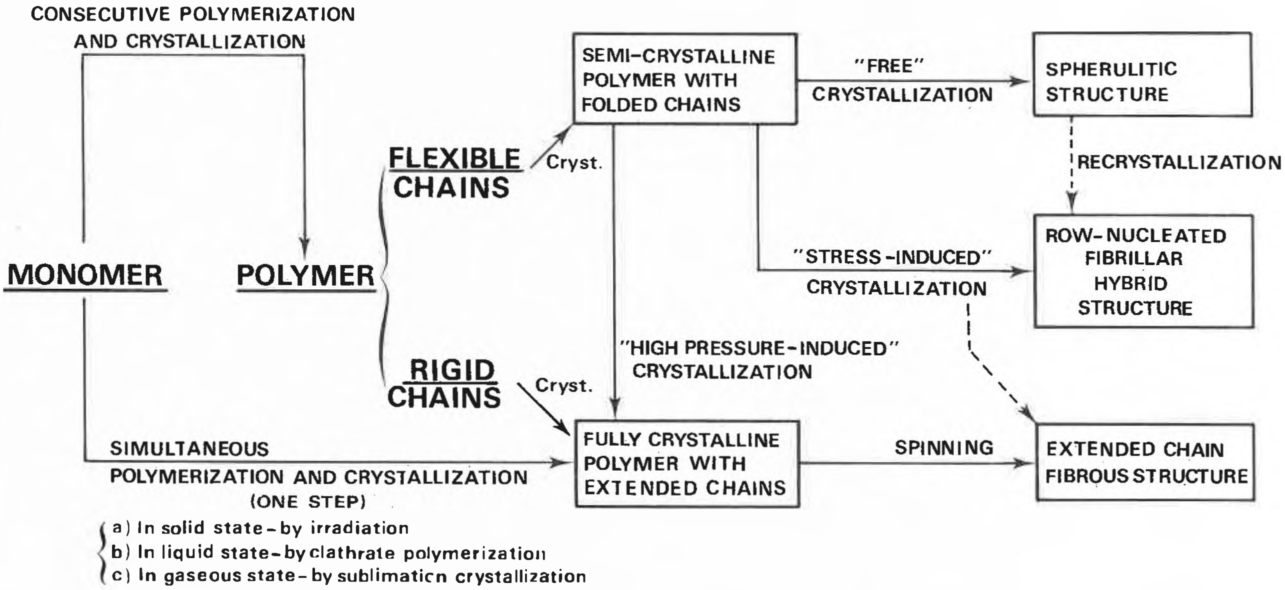
The understanding of this way of crystallization is rather well advanced, so that, for "normal" polymers we are able to predict with a fair amount of accuracy, the rate of crystallization and the approximate (average) size of the spherulites for an arbitrary set of operating conditions.

The "high pressure induced" crystallization leads to a structure of mosaic crystals in which the molecular chains are extended. Due to the random orientation these products are very brittle and have no commercial value. It would be interesting to start from oriented material and to maintain orientation by performing the pressure re-crystallization under tension.

The "stress induced" crystallization leads to a completely different type of morphology, viz. the microfibrillar structure, normally with a row-nucleated core. Tensile stresses are far more important than shear stresses.

Products with a fairly high modulus and high tenacity in the direction of orientation can be obtained. The rate of nucleation in this type of crystallization is some orders higher than in spherulitic crystallization.

The "high-speed spin-winding" and the "high speed (cold) draw-winding" processes of modern fibre technology belong to this group, although they do not yet provide products of very high modulus (i.e. in the neighbourhood of theoretical values). These extremely high moduli can only be obtained in laboratory techniques; for some polymers under extreme conditions (e.g. "superdrawing") moduli up to 50% of the theoretical values may be obtained.



Scheme 3: Ways of cristallization of polymers.

Scheme 3 presents a survey of all the available methods. The simultaneous polymerization and crystallization in one step has not been discussed here, since it is outside the theme of this paper.

It has not yet obtained technical and commercial interest.

The other methods of scheme 3 will be clear in themselves after my previous discussion of them.

Acknowledgement

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