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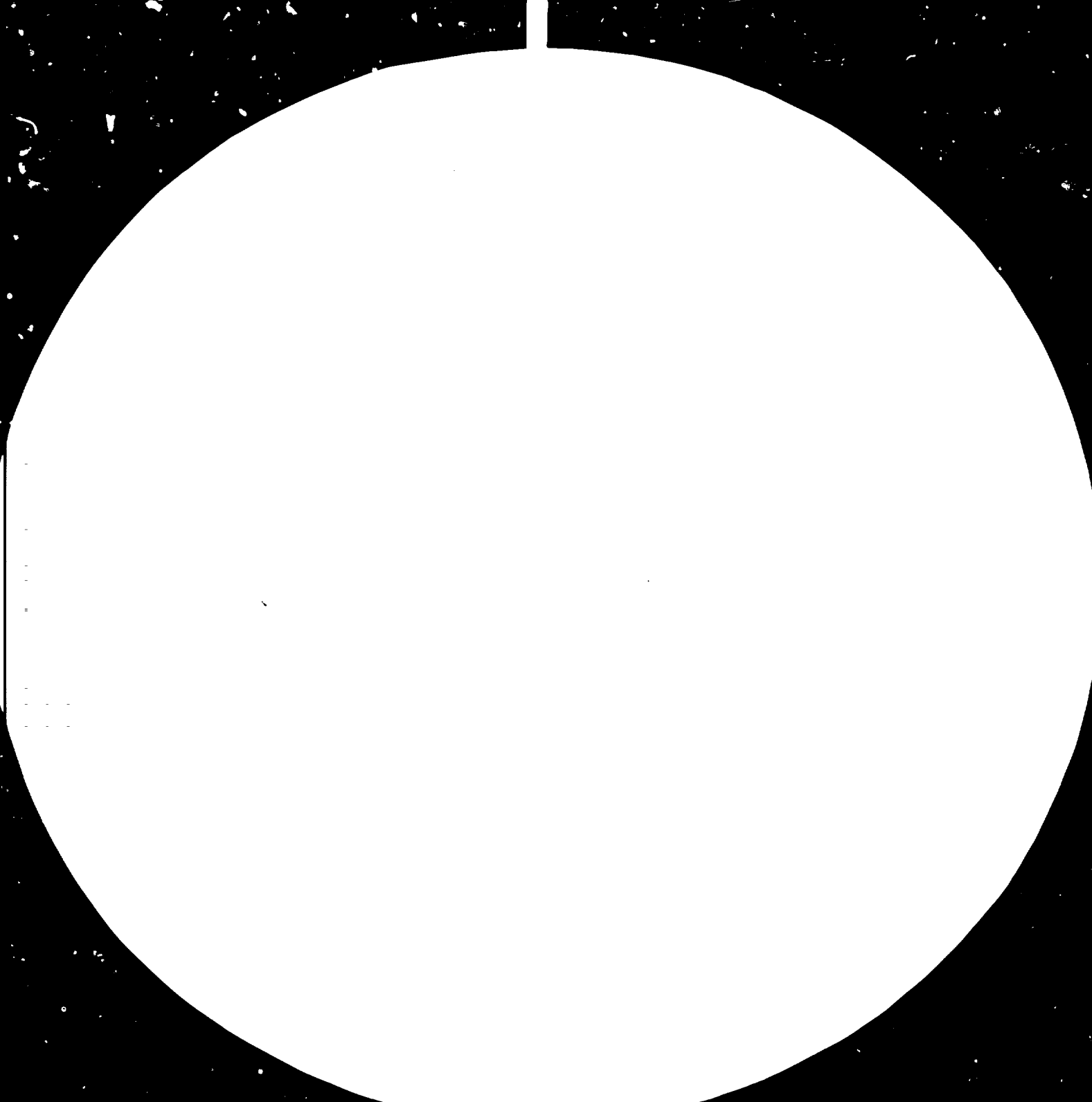
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(IV)

Polymer Chemistry and Polymer Physics
in the Relation to Synthetic Fibers

Dr. Walter Lebensaft

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Polymer Chemistry and Polymer Physics in the Relation to Synthetic Fibers

1. Introduction

Fibers are characterized by fineness, flexibility, and high ratio of length to thickness.

Fibers consist of partially crystalline, partially oriented linear polymer materials. In order to be useful. Fibers have to meet certain physical and chemical requirements.

These are

mechanical properties: tensile strength, torsion, bending, resistance to deformation, recovery after deformation, intermediate elastic extensibility

thermal properties: heat absorption, heat conduction, transition, melting, decomposition

moisture absorption: swelling, extent of weight change, change of properties, comfort (moisture absorption from body - moisture acts as heat reservoir, prevents sudden shock to body)

frictional properties: smooth but not slippery

chemical stability: laundering, dry cleaning

dyeability

These properties are determined by the chemistry and the fine structure of the fiber.

2. Structure of Polymers

In order to arrive at fiber forming polymers several structural prerequisites are necessary. These will be discussed in the following.

2.1. Definitions

Polymers are composed of covalent structures many times greater in extent than those occurring in simple compounds. This feature alone accounts for their characteristic properties which set them apart from other form of matter. They are synthesized out of monomers by polymerization, polycondensation or polyaddition.

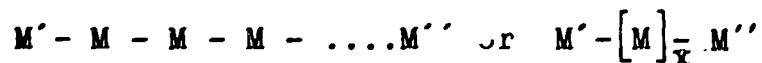
monomer - one unit
oligomer - few units
polymer - many units

Structural units are groups having a valency of two or more. The terminal units possess a valency of one.

The structural units are connected to one another in any conceivable pattern.

2.1.1. Linear Polymers

The structural units are connected in linear sequence



x = degree of polymerization, expresses the number of structural units in a given polymer molecule.

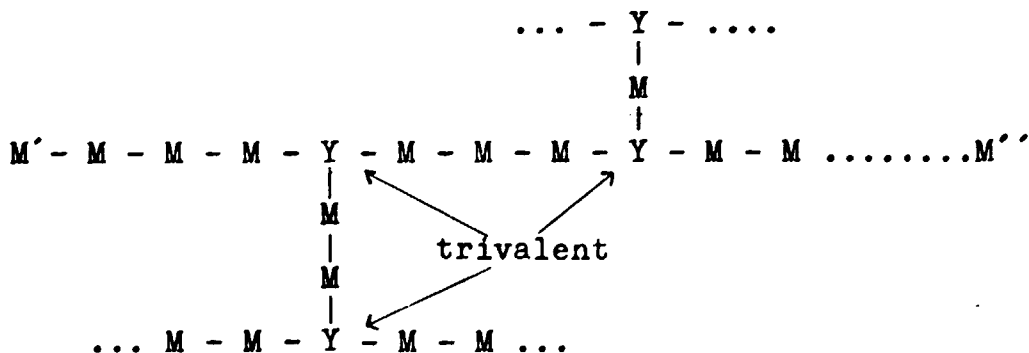
The structural units must be bivalent except the terminal units M' and M''. The group M' may or may not be identical with M'' but neither may be identical with M. In many cases the terminal units have the same composition as the principal units, but their structures must differ inasmuch as the former are monovalent.

A polymer containing a single repeating unit is a homopolymer. A polymer composed of two different kinds of bifunctional units is referred to as copolymer. According to the arrangement of the different units within the polymer chain one can distinguish:

Random copolymers	- A - B - B - A - A - A - B -
Alternating copolymers	- A - B - A - B - A - B - A -
Block copolymers	- A - A - A - A - B - B - B -
Graft copolymers	- A - A - A - A - A - A - A -
	B
	B

2.1.2. Nonlinear Polymers (branched structures)

Some of the structural units must have a valency greater than two



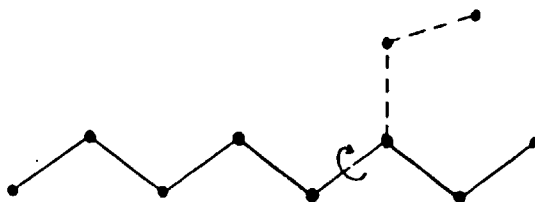
2.2. Structure and Properties

Fiber substances consist of polymer molecules characterized by shape, length, flexibility and attractive forces.

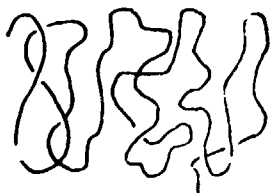
The most important classes of substances for the production of synthetic fibers are polyamide, polyester, polyacrylonitrile, polypropylene.

2.2.1. Molecular Mobility

In spite of their chemical differences all of these substances consist of unbranched flexible polymer chains. The backbone of the polymer chain consists mainly of C-atoms, in some substances also N or O. The bonds between the backbone atoms are not in opposite direction but in an angle of about 110° (tetrahedral angle). A bond rotation causes a change in shape.



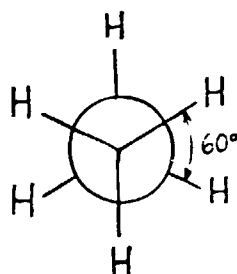
With a free polymer chain rotations can occur within the whole molecule. Therefore not only a zig-zag form is possible but also a cluster like spaghetti.



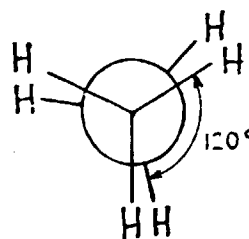
Bond rotation can be restricted by

steric interference
polar interactions
electronic structure

Steric interference is due to certain energy barriers. Even the so called "free rotations" postulated in organic chemistry have to overcome energy barriers. The energetic situation of groups which rotate about a carbon-carbon bond is not the same with each position, e.g. ethane



staggered



eclipsed

The staggered arrangement is more stable. Eclipsing leads to strain because of repulsion between the H - atoms due to their shorter interatomic distance. However, the passage of two hydrogens through their eclipsing position contributes little to a barrier ($8\text{kJ} = 2\text{ kcal}$). Already at room temperature rotations can be realized. The barrier becomes more pronounced with bigger groups.

Groups with dipoles increase the barrier by polar interactions.

The energy barrier to rotation about a carbon-carbon double bond is high enough to hold the four attached

substituents in a rigid configuration except at high temperatures. The π molecular orbital has to be destroyed.

With the long polymer molecules which do have substituents, steric and polar interactions are frequently encountered. In practice it is found that rotations of the bonds in the backbones of linear polymers almost always sets in sharply at some temperature which corresponds to energy barriers of about 40 to 80 kJ (10 to 20 kcal). These sharp transitions are accompanied by a marked change in physical properties. This change is called "second order transition" or "glass transition". Below this temperature the polymer is in a glassy state where segmental rotations are frozen.

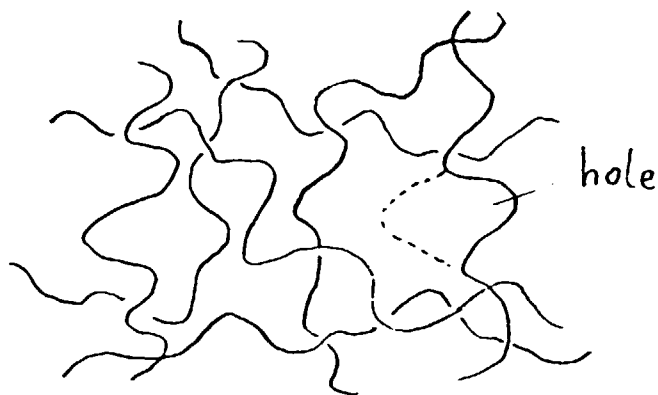
2.2.2. The Mechanism of Flow and Deformation

The easy deformation of low molecular weight liquids known as flow is possible because of the ease with which their small molecules can slide past each other. The higher viscous glycerol has restricted sliding properties because of intermolecular hydrogen bonds, with sodium silicate there are ionic bonds between the molecules.

The deformation of polymers is much more difficult because of the strong covalent bonds which tie the monomers together forming long chains. Deformation can occur only by local motion of a small chain segment at a time. Segments of neighbouring chains are situated closely together. Therefore macroscopic deformation can occur only by a number of segmental motions. Flexibility of chain segments is essential for such motions, and it is precisely the rotability of their backbone bonds that

confer flexibility on the segments.

In amorphous polymers the degree of order in the arrangement of the polymer chains is low. This facilitates segmental motions because a "free volume" is present in the form of holes.



Such a hole can move through the structure of a chain polymer. By such segmental rotation jumps, the holes normally diffuse randomly through the structure in all directions. If a stress is applied, certain directions will be preferred and the segments will lead to macroscopic and visible deformation of the polymer sample.

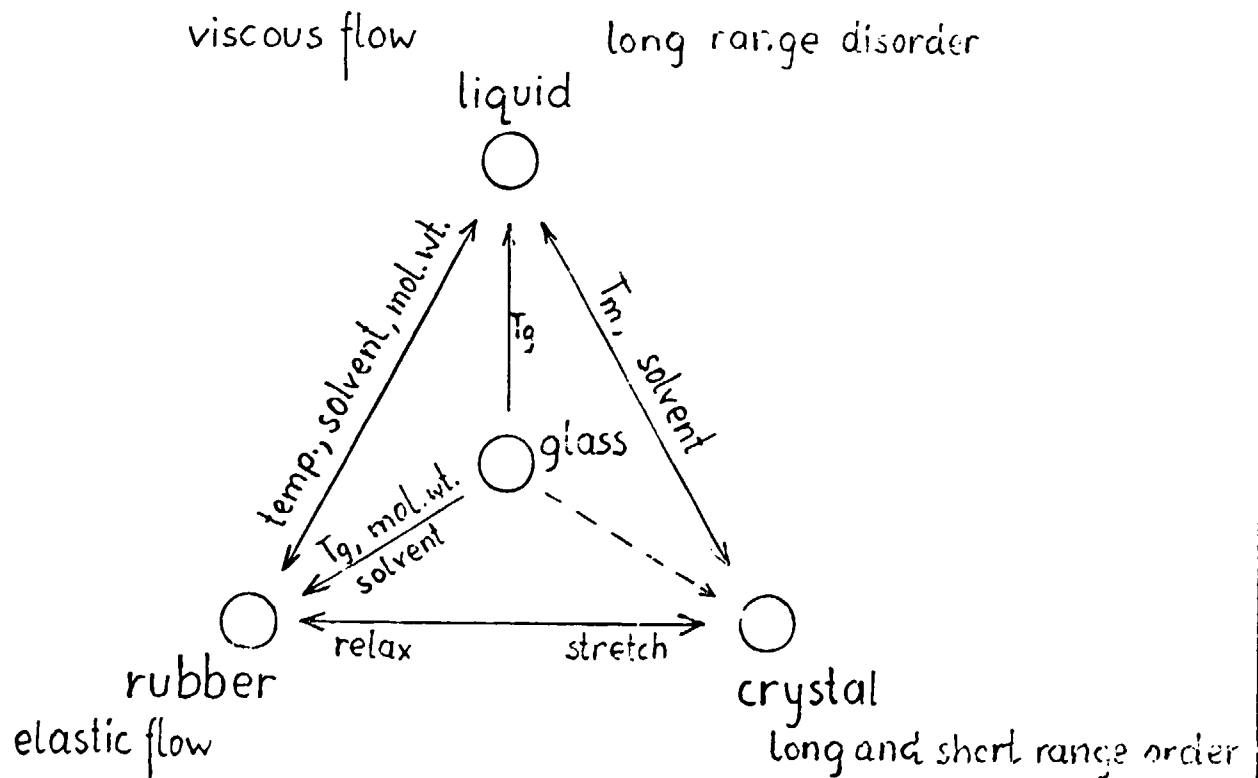
Among the deformations depending on segmental rotation jumps, the following are important:

- a) mechanical stretching and relaxing (forces applied externally)
- b) swelling in solvents (deformation under osmotic forces)
- c) shrinking due to crystallization (deformation due to lattice forces)
- d) volume changing with temperature (deformation under creation of new holes).

The average frequency at which rotational jumps of molecular chain segments occur is referred to as segmental relaxation rate. The average time occupied by a single jump is called relaxation time.

In rubbery polymers the segmental relaxation rates tend to zero as the specimen is cooled down to the glass temperature, where rotations are frozen.

2.2.3. States of Aggregation and Their Interconversion



The interconversion of crystal to liquid is determined by a sharp and reversible melting point. This melting point is an example for a first order transition temperature (T_m)

with which the primary thermodynamic variables like specific volume, heat content, undergo a jump (discontinuity). The sharpness of the melting point suffers somewhat with larger molecules. Of course a normal crystal-liquid transformation is also possible at constant temperature below melting point by addition or removal of solvent.

The interconversion of a liquid to rubber is always gradual and normally reversible. Three ways can be used:

- a) a rubbery polymer can be gradually transformed to a liquid by heating over a large temperature range. This process should not be called "melting", since this term is reserved for crystals. During the transformation the rubber passes gradually through the state of viscoelastic liquid which shows both, slow liquid flow and weak rubbery elasticity to a liquid which is highly viscous but without rubber elasticity, until finally the viscosity is reduced to the range of an ordinary liquid. With cooling the transformation takes place in the opposite direction.
- b) The same sequence can be obtained with addition or removal of solvent at constant temperature.
- c) The same sequence can also be obtained by polymerization (or depolymerization) of a liquid.

Conversely, when rubber is liquefied all three effects can contribute.

Interconversion of crystal to rubber: typical natural or synthetic rubbers are microcrystalline, i.e. minute crystals are embedded in a matrix of amorphous (noncrystalline) polymer. Melting or freezing of these small crystallites

can be obtained by changing two variables: temperature or degree of mechanical stretching.

Transformations involving the glassy state of polymers:

The transformation of a glassy polymer to a crystalline state is so slow as to be of negligible importance. The change of a crystalline polymer to a glassy polymer is not observed.

All non-crystalline polymers at sufficiently low temperature are relatively hard, glass-like solids. As the temperature is increased, at a high enough temperature they become soft, flexible and rubberlike.

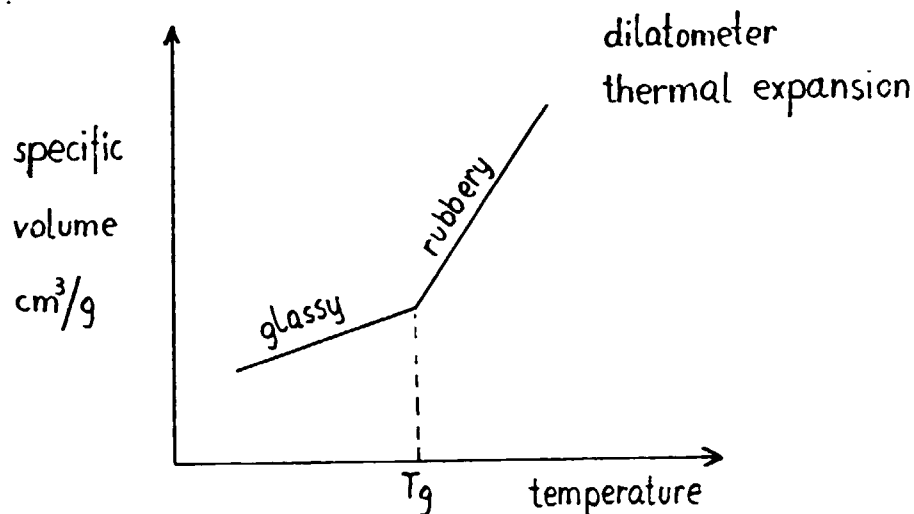
At the glass temperature T_g (or second order transition) the noncrystalline polymer changes from a rubbery liquid to a glassy solid. It is the point at which the segmental motions depending on rotation become frozen.

The glass temperature is a very important feature for fibers.

T_g above room temperature: fibers, plastics
 T_g below room temperature: rubbers

Methods for locating T_g : thermal expansion (specific volume)
refractive index
specific heat
other physical variables

The rate of expansion $\frac{dV}{dT}$ with temperature is always higher in the rubbery state than in the glassy state because expansion forces can expand the structure by creating holes when the chains become flexible. The T_g is therefore marked by a kink in the V/T curve.



2.2.4. Requirements for Crystallinity

In fiber substances the polymer chains are not free to move, they are frozen. The properties of fibers are determined by the variety of possible arrangements of the polymer chains. Within the molecular chain strong chemical bonds are effective which cause the stability of this molecule. Between the molecular chains, however, there are only weak intermolecular forces. These forces are holding the chains together and offer resistance to chain slippage. In most cases intermolecular forces are additive but effective only over short distances. Thus, the attraction between the molecular chains becomes stronger, when the chains are aligned parallel to each other forming crystals.

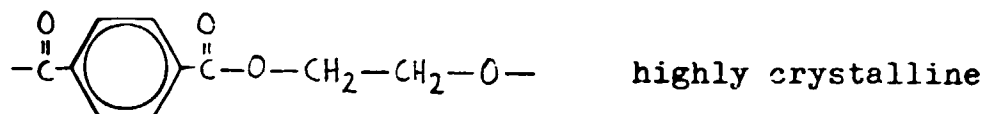
Actually fibers exhibit a two phase system. They are partially crystalline and partially amorphous. The most

important contribution of the crystalline portion is tensile strength, that of the amorphous portion is flexibility, dyeability etc. The percent crystallinity characterizes a polymer.

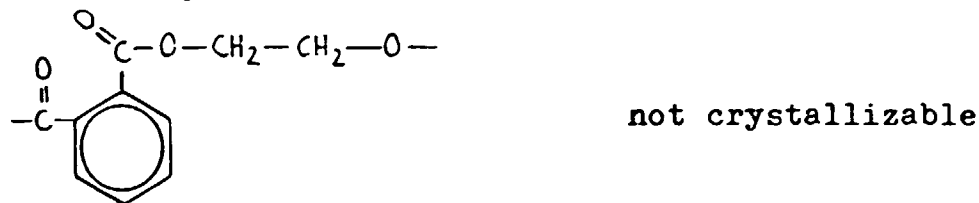
For polymer crystallinity 2 factors are of importance:

- a) Regularity of the structure
- b) Chemical nature of the chain

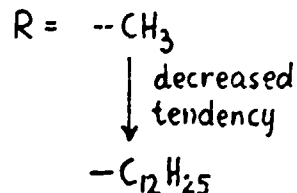
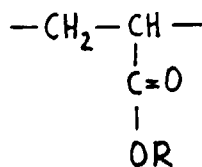
Polymer chains should be linear, e.g. a polyester made with terephthalic acid and ethyleneglycol is highly crystalline



whereas a polyester made with phthalic acid and ethyleneglycol is not crystallizable



Bulky side groups or chain branches should be avoided otherwise there is no crystallization or a decreased tendency



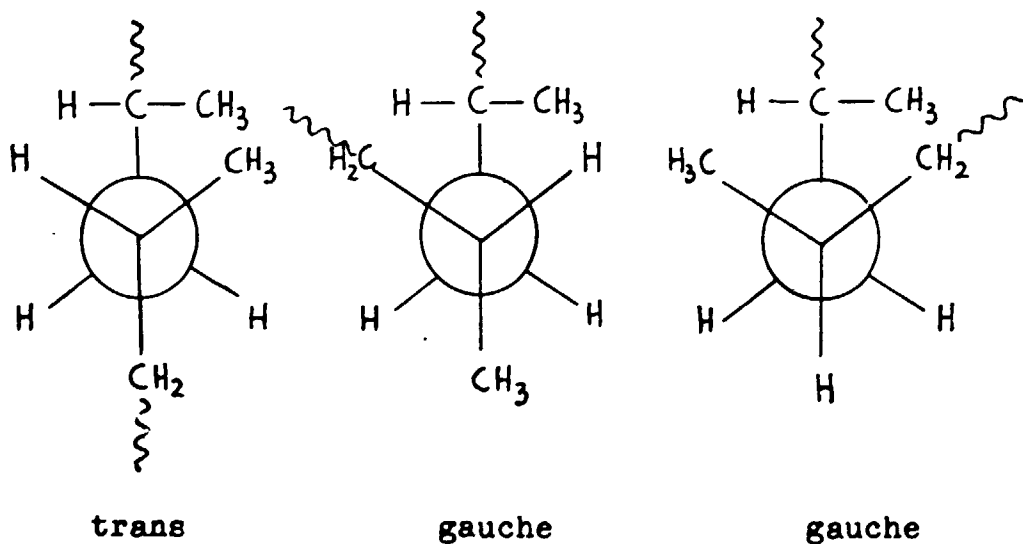
The chemical nature of groups in the chain is of importance. Polar groups or groups which are capable of forming hydrogen bonds favor crystallization.

Polymer molecules can pack with three-dimensional regularity only when the molecules exhibit a high degree of configurational and conformational regularity.

With polypropylene the stereoregularity (tacticity) is important.

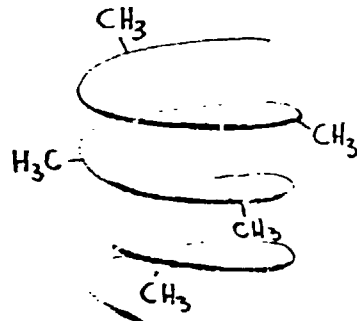
d d d d d	isotactic	}	crystalline
l l l l l			
d l d l d l	syndiotactic	}	amorphous
d l l d l l	atactic		

Considering polypropylene conformations:



The preferred conformation is the one with the lowest potential or free energy.

For isotactic polypropylene the helical form has the least crowding in the methyl groups.



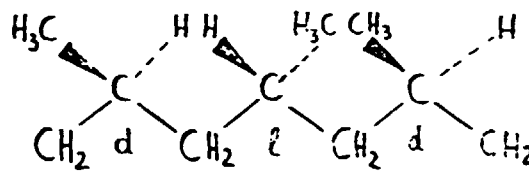
trans - gauche - trans

120° 3 monomers necessary to make the turn

crystals are known to have screw axis

Isotactic polypropylene is successfully used in the fiber field.

Syndiotactic polypropylene is trans - trans - trans

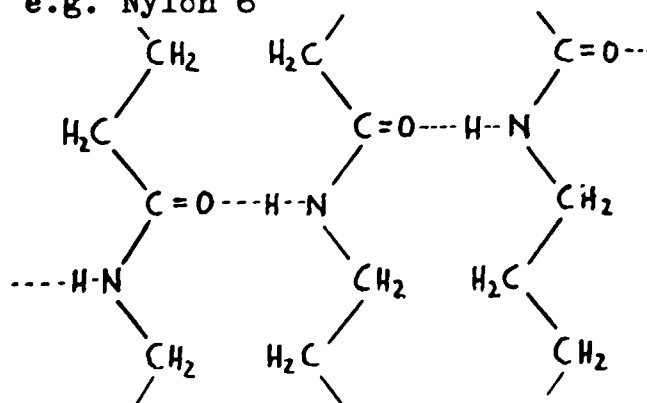


glide plans

Polyethylene terephthalate has helical conformation. successive ester groups are trans.

Polyamides have extended chains (zig zag)

e.g. Nylon 6



all conditions for crystallinity are present

3. Preparation

Polymers can be classified according to the chemistry of their preparation. There are three broad categories: polymers made by polycondensation, by polymerization and by polyaddition.

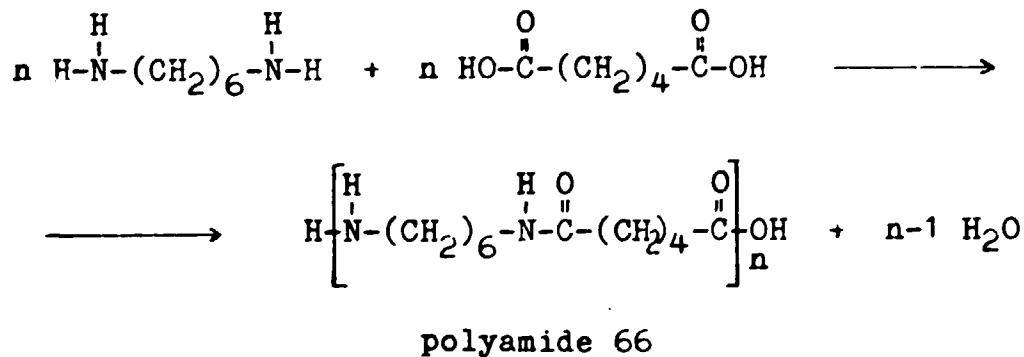
3.1. Condensation Polymers

Polymers prepared by condensation reaction whereby a simple molecule (in most cases water) is eliminated.

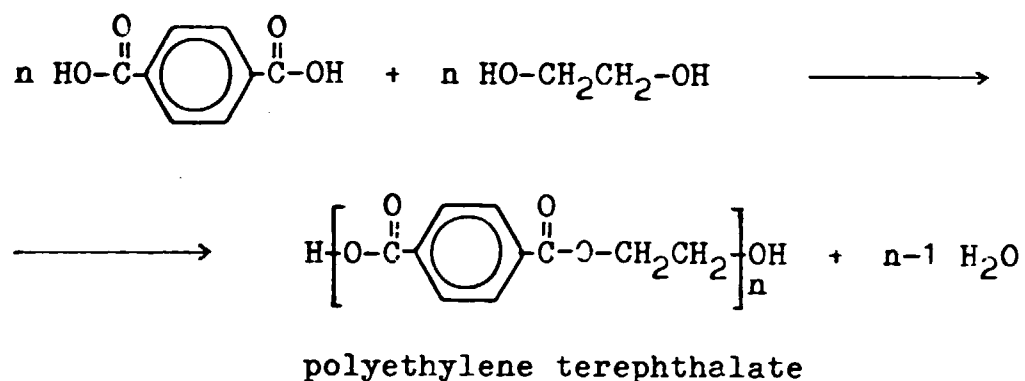
The structural units are joined by interunit functional groups (ester or amide), thus they possess polar groups at regularly spaced intervals which are responsible for characteristic chemical and physical properties.

Polyamides and polyesters are the most important fiber forming condensation polymers, e.g.

Polyamide resulting from condensation of hexamethylene diamine and adipic acid



Polyester formed by condensation of terephthalic acid and ethylene glycol



3.1.1. Formation

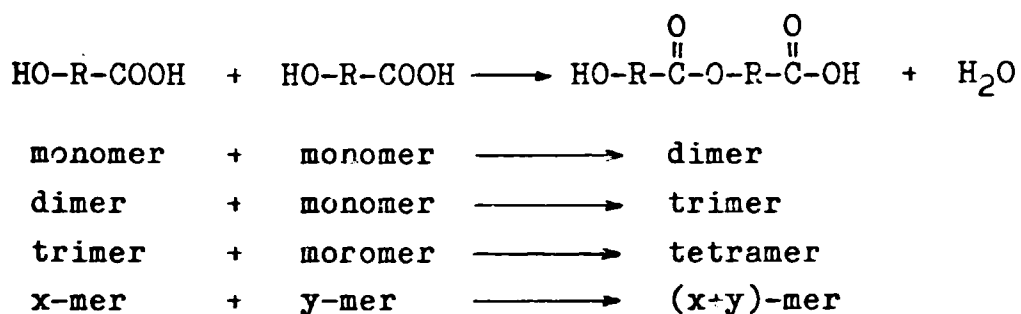
Characteristic features of condensation polymerization:

- a) Proceeds by stepwise intermolecular condensation of functional groups.
- b) Monomer disappears almost completely during initial phase of polymerization.
- c) Degree of polymerization (DP) changes considerably during reaction. Reaction must be carried essentially to completion in order to obtain a high molecular weight. Purpose of increasing reaction time is increasing the molecular weight.

The primary requisite is a monomer, or a pair of monomers bearing two condensable groups. Each step is actually a simple condensation reaction.

Polyesterification -OH + HOOC-

Polyamidation -NH₂ + HOOC-



The various steps in the process need not to be differentiated. All involve the same process, e.g. esterification, each step can be described by the same bimolecular rate constant. The entire process can be regarded as a reaction between functional groups, e.g. OH and COOH which leads to products of finite molecular weight.

The influence of molecular size on the chemical reactivity of the functional groups may be disregarded.

Flory's concept:

The intrinsic reactivity of a functional group remains independent of molecular size except when the molecule is quite small. Ordinarily the reactivity of a given functional group in a polyfunctional molecule can be assigned a definite value that does not change during the course of reaction.

According to the principle of equal reactivity, at every stage of the polymerization process an equal opportunity for reaction is available to each functional group of a

given chemical type, irrespective of the size of the molecule to which it is attached.

That does not mean that the chemical reactivity has to remain constant throughout the course of the polymerization. Reason: large molecules diffuse slowly, but diffusion rate must not be confused with the collision rate. The longer diffusion period of the large molecule is compensated by the longer collision period. The collision rate for functional groups on large molecules is approximately the same as for functional groups on small molecules.

The average degree of polymerization and hence the average molecular weight of a linear condensation polymer depends:

- a) on the degree of completion achieved in the condensation reaction
- b) reaction must be reasonable free of side reactions
- c) monomers must be pure
- d) in polymerizations of the A-A + B-B type the reactants must be used in precise as possible stoichiometrically equivalents
- e) reaction should be one which may be carried very nearly to completion.

Under optimum conditions, average molecular weights exceeding 25 000 may be obtained.

3.1.2. Kinetics of Condensation Polymerization

The basic data necessary for a kinetic study can be obtained by measurements of the progress of the reaction in predetermined intervals of time. With e.g. polyester-forming reactions between glycols and dibasic acids this can be done by titrating the unreacted carboxyl groups. The number of unreacted carboxyl groups must equal the number of molecules present in the system if the hydroxyl and carboxyl groups being present in equal numbers.

Simple esterification reactions are known to be acid catalyzed.

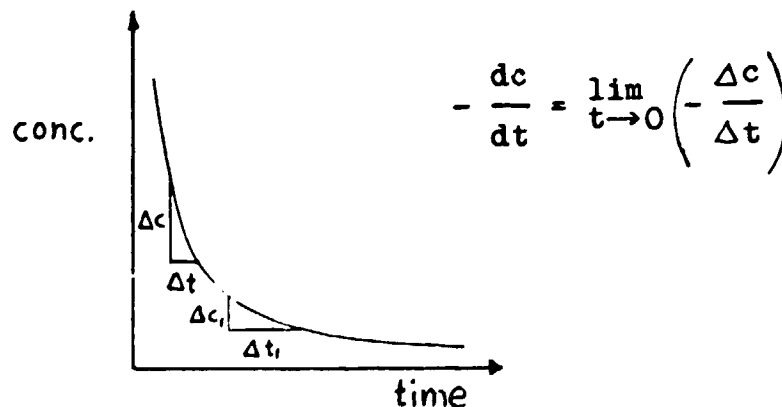
Rate of disappearance:

$$-\frac{d[\text{COOH}]}{dt} = k[\text{COOH}][\text{OH}][\text{H}^+]$$

k = specific rate constant

$$k = \frac{\text{rate}}{\text{conc. of reactants}} = \text{characteristic of a specific reaction}$$

Rate changes during the course of reaction as a result of changing concentration of the reactants



In presence of a strong acid $[H^+] = \text{constant}$

$$-\frac{d[\text{COOH}]}{dt} = k' [\text{COOH}] [\text{OH}] \quad \begin{array}{l} 2^{\text{nd}} \text{ order reaction} \\ \text{in presence of strong acid} \\ k' = k[H^+] \end{array}$$

The concentrations are expressed as equivalents.

Overall rate of consumption of COOH groups is the sum of rates of each step in the process.

Since $c = [\text{OH}]$ equals $c = [\text{COOH}]$ the rate equation can be rewritten

$$-\frac{dc}{dt} = k' c^2 \quad \int_c^{c_0} -\frac{dc}{c^2} = k' \int_{t_0}^t dt$$

c_0 = initial concentration

c = concentration at any time

$$\frac{1}{c} - \frac{1}{c_0} = k' t$$

In the absence of an added strong acid a second carboxylic acid acts as a catalyst

$$-\frac{d[\text{COOH}]}{dt} = k_1 [\text{COOH}]^2 [\text{OH}] \quad 3^{\text{rd}} \text{ order reaction}$$

$$-\frac{dc}{dt} = k_1 c^3 \quad \text{integrated}$$

$$\frac{1}{c^2} - \frac{1}{c_0^2} = 2 k_1 t$$

However, it is more convenient to express the results in terms of extent of the reaction rather than in terms of concentration. The extent of the reaction p is the fraction of functional groups which have reacted at time t .

$$p = \frac{c_0 - c}{c_0} \quad p \cdot c_0 = c_0 - c$$

$$c = c_0(1 - p)$$

Introducing this expression into the rate equation for catalyzed condensation:

$$k't = \frac{1}{c} - \frac{1}{c_0}$$

$$k't = \frac{1}{c_0(1 - p)} - \frac{1}{c_0}$$

$$\boxed{c_0 k't = \frac{1}{1 - p} - 1}$$

m
 y
 x
 b

a straight line equation is obtained: $y = mx + b$

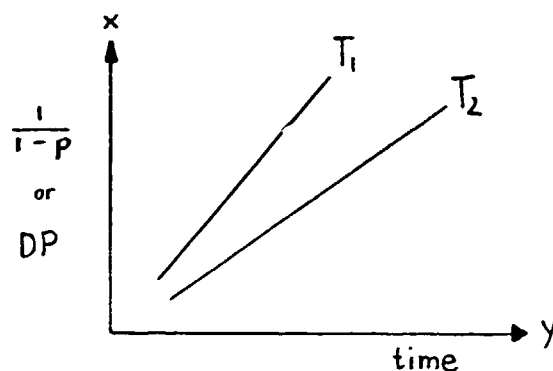
$$m = \text{slope } \frac{\Delta y}{\Delta x}$$

$b = \text{y-intercept}$

The data for catalyzed esterification of a glycol with adipic acid plotted in a diagram show that the system follows the second order kinetics, following the above

equation up to high molecular weight, confirming the hypothesis of independence of reactivity on molecular size.

The catalyzed formation of polyamides also follows second order law.



catalyzed condensation polymerization

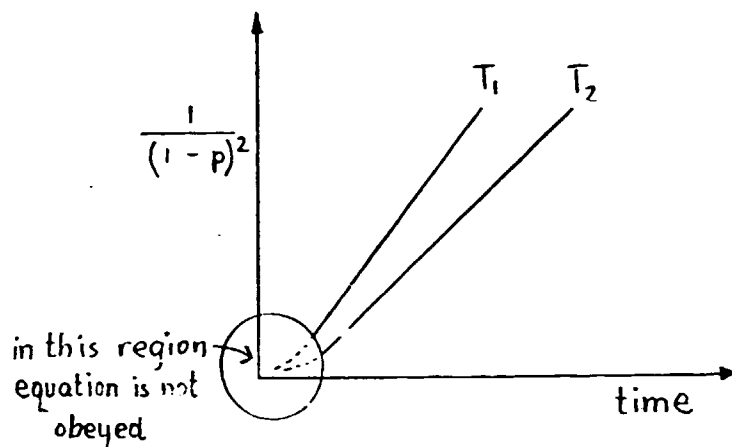
Uncatalyzed systems:

$$2 k_1 t = \frac{1}{c^2} - \frac{1}{c_0^2}$$

$$2 k_1 t = \frac{1}{c_0^2 (1-p)^2} - \frac{1}{c_0^2}$$

$$2 c_0^2 k_1 t = \frac{1}{(1-p)^2} - 1$$

The graph with data for uncatalyzed esterification of a glycol with adipic acid shows straight lines after the reaction has proceeded a certain time.



uncatalyzed condensation polymerization

The number of molecules in moles per unit volume is equal

$$c = c_0(1 - p)$$

Total number of structural units = c_0 = total number of bifunctional molecules initially employed.

The number average degree of polymerization \bar{x}_n

$$\bar{x}_n = \frac{\text{number of units}}{\text{number of molecules}}$$

$$\bar{x}_n = \frac{c_0}{c_0(1 - p)} = \frac{1}{1 - p}$$

With the 2nd order reaction:

$$c_0 k' t = \frac{1}{1 - p} - 1$$

$$\bar{x}_n = (1 + c_0 k' t)$$

$$\bar{x}_n \propto t$$

The number average DP is proportional to reaction time.

With the 3rd order reaction:

$$2 c_0^2 k_1 t = \frac{1}{(1-p)^2} - 1$$

$$\bar{x}_n = (1 + 2 c_0^2 k_1 t)^{1/2}$$

$$\bar{x}_n \propto t^{1/2}$$

The number average DP is proportional to the square root of reaction time

3.2. Molecular Weight

The molecules of a polymer have different molecular weights. Polymers are heterogeneous, they consist of mixtures of chain molecules having different chain length. Accordingly the molecular weight of any polymer is an average molecular weight. Also the degrees of polymerization (DP) are average values.

There are two kinds of average molecular weights, the "number average molecular weight" and the "weight average molecular weight".

3.2.1. Number Average Molecular Weight \bar{M}_n

This average is based on the number of molecules.

The average DP is given by the total number of molecules at the beginning of the reaction N_0 divided by the number at time t . N_0/N .

The number of molecules can be obtained by titrating the unreacted end groups.

In terms of p:

$$\bar{x}_n = \frac{1}{1 - p}$$

$$\bar{M}_n = M_0 \cdot \bar{x}_n$$

$$\bar{M}_n = \frac{M_0}{1 - p}$$

M_0 = molecular weight of a structural unit.

$$\bar{M}_n = \frac{\text{total weight of polymer}}{\text{total number of molecules}}$$

Considering the individual molecules:

The polymer contains molecules of various DP

$$n = 1, 2, 3, \dots, i$$

$$\text{Total number of molecules} = N_1 + N_2 + N_3 + \dots + N_i = \sum N_i$$

Total weight of polymer = total number of molecules times molecular weight of molecules

$$= \sum N_i M_i$$

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

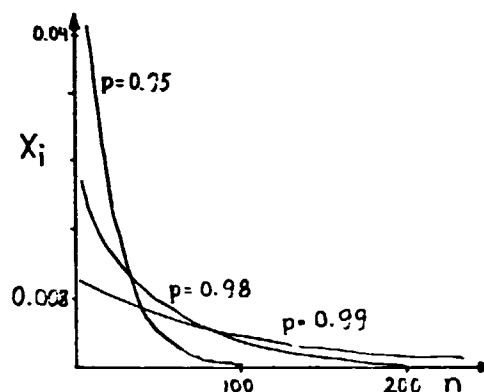
X_i = mole fraction of species i

$$X_i = \frac{\text{number of molecules of species } i}{\text{total number of molecules in polymer}} = \frac{N_i}{\sum N_i}$$

$$\bar{M}_n = \sum X_i M_i$$

The distribution of molecular weights can vary widely. Mechanical properties of the resulting polymer depend on this distribution.

Number distribution curve:



Mole fraction distribution
for several extents of reaction p

Number average molecular weight is obtained by end-group analysis and by methods involving depression of freezing point, elevation of boiling point, osmotic pressure.

3.2.2. Weight Average Molecular Weight \bar{M}_w

This can be computed by summing up the contributions on a weight basis of each molecular species i and its molecular weight M_i :

$$\bar{M}_w = \frac{\sum w_i M_i}{\sum w_i}$$

w_i = weight of molecular species $w_i = N_i M_i$

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

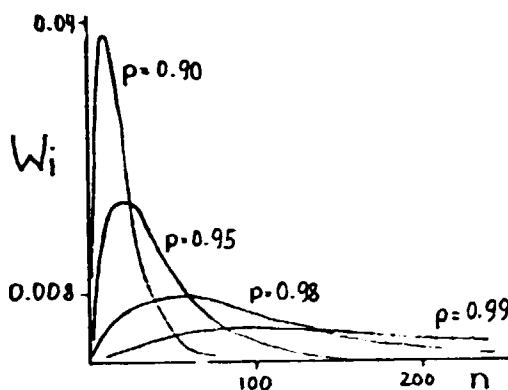
This can also be described in terms of weight fraction W_i

$$W_i = \frac{\text{total weight of species } i}{\text{total weight of polymer}} = \frac{w_i}{\sum w_i}$$

then

$$\bar{M}_w = \sum W_i M_i$$

Weight distribution curve:



Weight fraction distribution
for several extents of reaction p

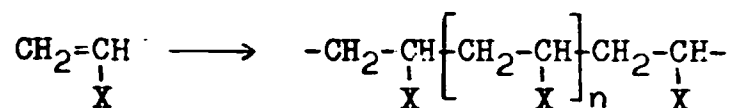
\bar{M}_w is sensitiv to high molecular weight material.

Weight average molecular weight is obtained by light scattering techniques.

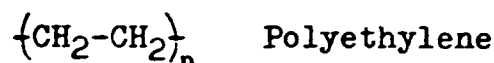
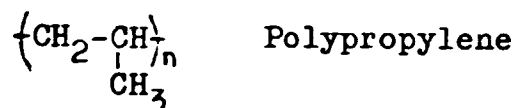
Methods involving viscosity depend on the size of the solute molecules relative to the solvent molecules. Thus the viscosity average molecular weight \bar{M}_v is a special one.

3.3. Polymerization Polymers

Unsaturated monomers are converted to polymers of high molecular weight. The molecular formula of the structural unit(s) is identical with that of the monomer.



e.g.



Polymerization polymers do not possess functional groups within the polymer chain, they may be present in side groups. The backbone usually consists exclusively of carbon atoms.

3.3.1. Formation

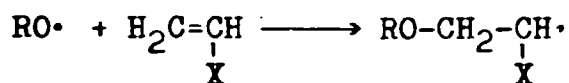
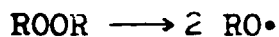
Characteristic features of ~~addition~~ polymerization:

- a) Proceeds by chain mechanism involving active centers of some sort.
- b) Only a small number of actively growing chains present at any instant. Reaction mixture of any given time consists of unreacted monomer and polymer.
- c) Polymer molecule is synthesized in few seconds. The overall conversion of monomer to polymer may require hours.

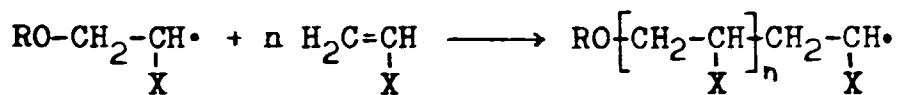
- d) As percentage conversion of monomer to polymer increases, average DP of polymerized portion remains almost unchanged. Purpose of increasing reaction time is to increase the yield and not the molecular weight.

The primary activation (initiation) of a monomer is followed by the addition of other monomers in rapid succession until the growing chain is deactivated.

Initiation:

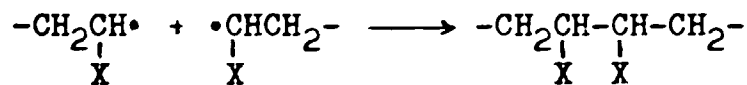


Propagation:



Termination:

- a) by combination



- b) by disproportionation (transfer of hydrogen atom)



- c) by chain transfer

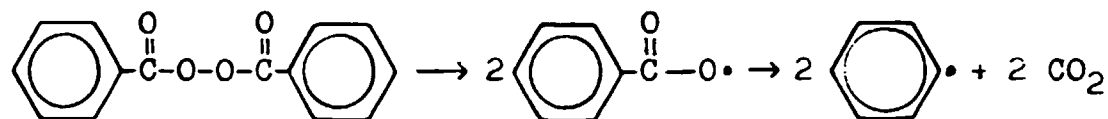


The polymerization is initiated through the presence of an activated molecule introduced into the system by

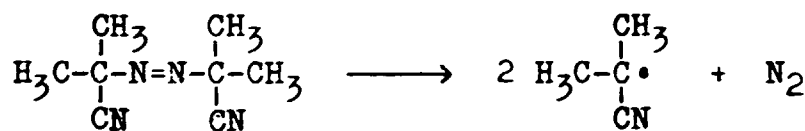
thermal means
free radical initiation
light
ionic catalysts

The free radical initiation is the most important. Compounds which generate free radicals are e.g.

benzoyl peroxide



aliphatic azo compounds



3.3.2. Kinetics

The kinetics of polymerization depends on the chemical character of the monomer as well as on the conditions of polymerization. Polymerization can be performed under heterogeneous conditions as it is with bulk polymerization or in emulsion polymerization. These systems are more complicated than polymerization under homogeneous conditions. Here, the latter one is considered only.

3.3.2.1. Initiation

First step: decomposition of the initiator I to yield a pair of free radicals R•



The rate of generation of free radicals:

$$\frac{d[R\bullet]}{dt} = 2 k_i [I]$$

The factor 2 takes care that the radicals must be produced in pairs.

Second step: addition of a monomer M to a primary radical R• to yield a chain radical



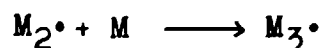
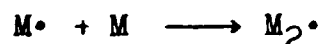
Under normal conditions each R• starts a chain radical.

Rate of initiation of chain radicals = rate of formation of growing polymer chains:

$$R_i = \frac{d[M\bullet]}{dt} = 2 k_i [I]$$

3.3.2.2. Propagation

The growth of polymer molecules by successive addition of monomers to the radicals



$M_n\bullet$ = chain carrier of
n units

The disappearance of monomer is a measure of the rate of propagation:

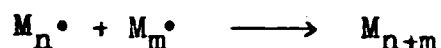
$$R_p = - \frac{d[M]}{dt} = k_p [M] [M\cdot]$$

[M] = monomer concentration
in mole/l

[M•] = radical concentration
in mole/l

Assumption: radical reactivity is independent of chain length.

3.3.2.3. Termination



The loss of radicals is a measure of the rate of termination by combination:

$$R_t = - \frac{d[M\cdot]}{dt} = 2 k_t [M\cdot]^2$$

The rate of termination is independent of molecular weight when the viscosity is low.

With higher viscosity, i.e. higher molecular weight, a point is reached when termination is diffusion controlled. The rate of termination is decreased but rate of initiation and propagation is not cut down. This can happen by using a high initial monomer concentration. A marked acceleration in rate can occur at an advanced state of the polymerization. Simultaneously the average molecular weight of the polymer being formed increases sharply.

3.3.2.4. Steady State

The steady state condition is reached when

$$R_i = R_t$$

Chain radicals are created and destroyed at equal rates.

$$\frac{d[M\cdot]}{dt} = 0$$

$$k_t [M\cdot]^2 = k_i [I]$$

$$[M\cdot] = \left(\frac{k_i [I]}{k_t} \right)^{1/2} \quad \text{steady state conc. of chain radicals}$$

Substituted in R_p -expression: $R_p = [M][M\cdot]$

$$R_p = k_p [M] \left(\frac{k_i}{k_t} \right)^{1/2} [I]^{1/2}$$

Thus the rate of polymerization is dependent upon

k_p = rate constant of propagation

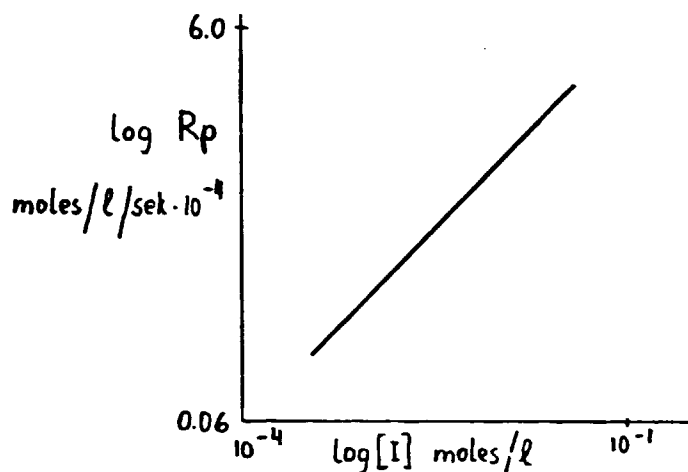
$\frac{k_i}{k_t}$ = ratio of rate constants of initiat. and termin.

$[M]$ = monomer concentration

$[I]$ = initiator concentration

At a given monomer concentration the rate of polymerization is proportional to the square root of initiator concentration

$$R_p = \text{const. } [I]^{1/2} [M]$$



Rate of polymerization against initiator conc.

3.3.2.5. Degree of Polymerization

The kinetic chain length ν represents the average number of monomers reacting with a given active center from its initiation to its termination. This quantity is given by the ratio of the rate of propagation R_p to the rate of initiation R_i . Under steady state conditions R_i must equal R_t .

$$\nu = \frac{R_p}{R_i} = \frac{R_p}{R_t}$$

$$\nu = \frac{k_p [M] [M^\bullet]}{2 k_t [M^\bullet]^2} = \frac{k_p [M]}{2 k_t [M^\bullet]}$$

The radical concentration may be eliminated in terms of rate of propagation

$$R_p = k_p [M] [M^\bullet] \quad [M^\bullet] = \frac{R_p}{k_p [M]}$$

$$\nu = \frac{k_p^2 [M]^2}{2 k_t R_p}$$

The kinetic chain length is calculable from a knowledge of the constants, monomer concentration and rate of propagation.

\bar{x}_n versus ν :

When the termination step is by combination

$$\bar{x}_n = 2\nu$$

With disproportionation

$$\bar{x}_n = \nu$$

3.3.2.6. Inhibition and Retardation

The degree of polymerization can be reduced by a retarder. These substances lower the ability of chain radicals to react with the monomer. If the substance suppresses the reaction completely it is referred to as inhibitor.

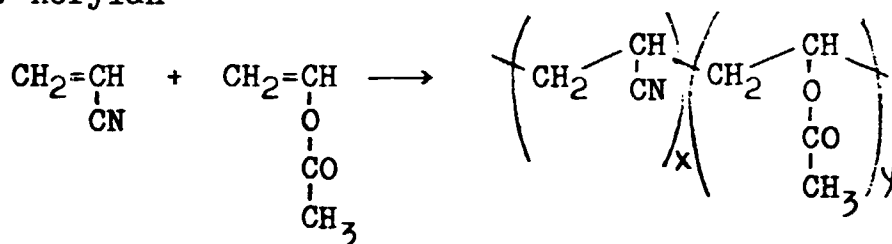
3.4. Copolymers

Although there are examples of condensation copolymers, the most important ones are made by free radical polymerization.

Fibers made from acrylonitrile as a homopolymer are lacking solubility in common solvents and dyeability. To overcome these difficulties a certain amount of comonomers are used in the polymerization. For lowering crystallinity and thus for increasing diffusion rate, nonionic comonomers are used. For introducing dyeability ionic comonomers are used. The properties of copolymers depend not only on the chemical nature of the comonomer but also on their relative proportions in the product.

Acrylics contain at least 85% acrylonitrile and a maximum of 15% comonomers. Fibers with less than 85% but at least 35% acrylonitrile are called modacrylics.

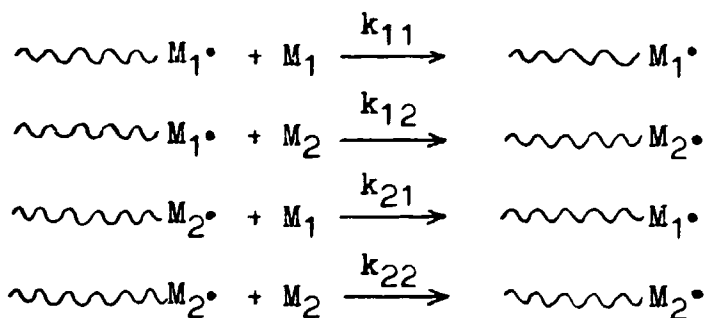
e.g. Acrylan



vinylacetate

The composition of the copolymer and the arrangement of units along the chain are determined by the relative rates of the various chain propagation reactions. The rate of polymerization depends also on the rates of termination reactions.

With two monomers M_1 and M_2 the following chain propagation reaction occur:



Radicals of type M_1^\bullet are formed by primary initiation
by reaction 21

M_1^\bullet are destroyed by reaction 12
by termination reactions

At steady state, the rates of generation and of disappearance of these radicals are equal. Considering long chains the state conditions approximate

$$k_{21}[M_2^\bullet][M_1] = k_{12}[M_1^\bullet][M_2]$$

The rates of consumption of monomers M_1 and M_2 at steady state are

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^\bullet][M_1] + k_{21}[M_2^\bullet][M_1]$$

$$-\frac{d[M_2]}{dt} = k_{12}[M_1^\bullet][M_2] + k_{22}[M_2^\bullet][M_2]$$

Dividing these two equations and eliminating the concentration of radicals by the former expression, the copolymerisation equation is obtained.

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1 \frac{[M_1]}{[M_2]} + 1}{\frac{[M_1]}{[M_2]} + r_2}$$

This equation gives the composition of the copolymer formed at any instant.

r_1 & r_2 = monomer reactivity ratios

$$r_1 = \frac{k_{11}}{k_{12}} \quad r_2 = \frac{k_{22}}{k_{21}}$$

$d[M_1]$ = mole fraction of M_1 in copolymer

$d[M_2]$ = mole fraction of M_2 in copolymer

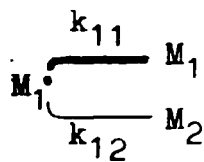
$[M_1]$ = mole fraction of M_1 in monomer feed

$[M_2]$ = mole fraction of M_2 in monomer feed

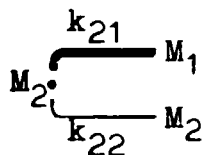
The composition of the copolymer depends on:

- a) composition of the monomer feed
- b) reactivity of the chain terminal unit
- c) relative reactivity of the monomers with this terminal unit.

With "ideal copolymerization" the two radicals have the same preference for one of the monomers over the other



e.g. M_1 is preferred

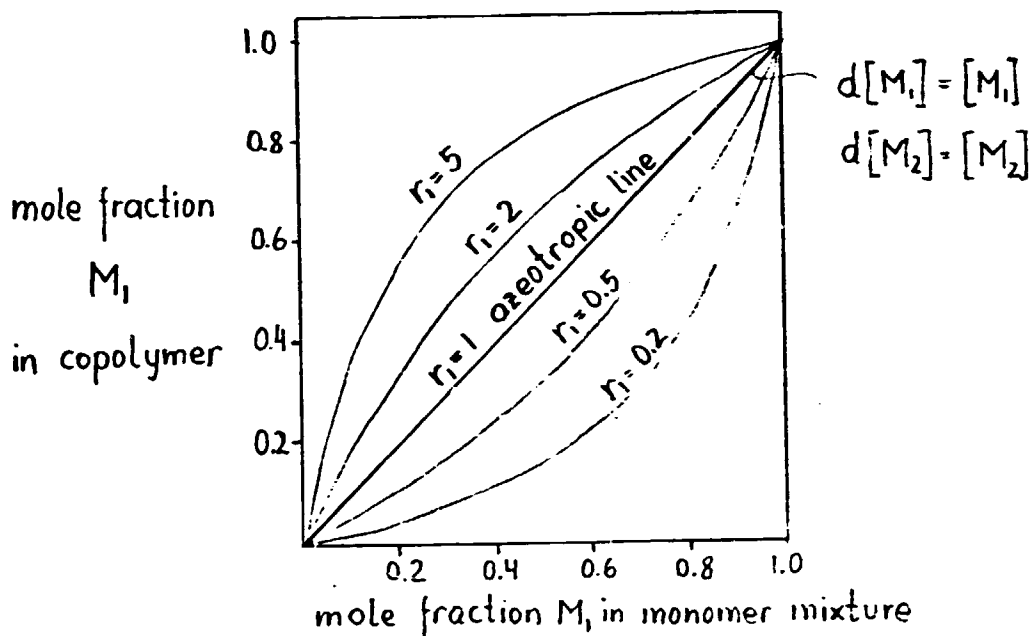


$$\frac{k_{11}}{k_{12}} = \frac{k_{21}}{k_{22}}$$

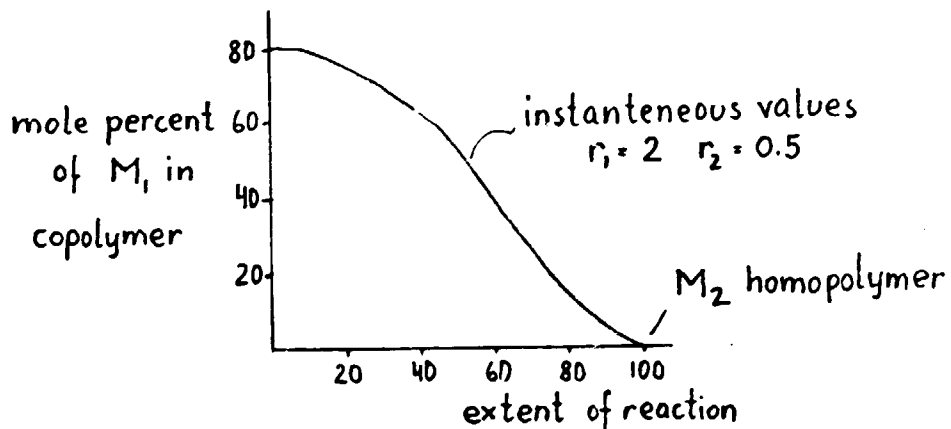
$$r_1 \cdot r_2 = 1$$

In this case the copolymerization equation reduces to

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]}$$



If $r_1 > 1$ ($r_2 < 1$) Monomer M_1 is more reactive than monomer M_2 with both growing free radicals



If $r_1 < 1$ ($r_2 > 1$) monomer M_2 is more reactive than M_1

Non-ideal copolymerization is the usual case.

$r_1 \cdot r_2 \neq 1$, the two radicals display different selectivities in their choice of monomer.

In most cases $r_1 \cdot r_2 < 1$

$$\frac{k_{11}}{k_{12}} \cdot \frac{k_{22}}{k_{21}} < 1$$

(k₁₂) (k₂₁)
 preferred

The cross monomer addition dominate additions of a like monomer to a radical.

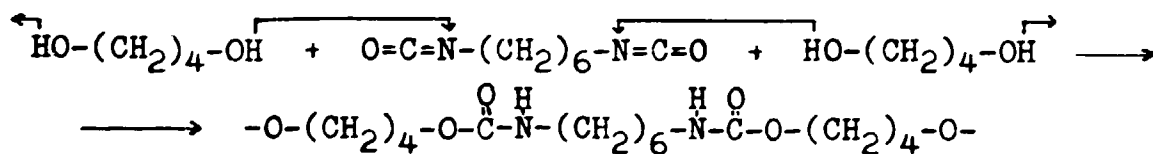
If both r_1 & r_2 have very small values approaching zero, a copolymer is obtained in which the monomers alternate with near perfect regularity along the chain $M_1M_2M_1M_2M_1$ etc.

If one of the monomers is very much more reactive than the other, the two monomers tend to polymerize consecutively.

3.5. Addition Polymers

Polymers prepared by addition polymerization proceed without elimination of simple molecules but with a transfer of H-atoms.

Polyurethane is formed by polyaddition of a dihydric alcohol and a diisocyanate



Polyurethans are used in the fiber field as a stiff fiber for brushes etc., but also to produce elastomeric fibers.

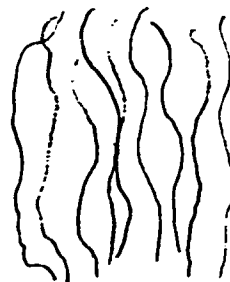
4. Orientation and Crystallinity

Not only crystallinity is a very important factor for successful fiber performance but also the orientation of chain molecules.

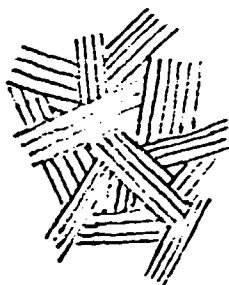
One can distinguish the following patterns:



minimum order
zero orientation



low order
high orientation



high order
zero orientation



perfect order
perfect orientation

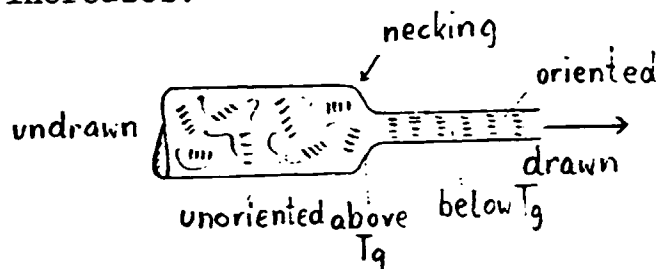
Since a fiber has to be strong in the length direction and flexible in the width direction, the chain molecules must be oriented in length direction.

With the spinning process the molten or dissolved polymer becomes extruded through a spinneret (jet) and solidified by cooling or by running through a coagulation bath.

The filament emerging from the spinneret orifice has no orientation. So far it does not exhibit fiber properties yet.

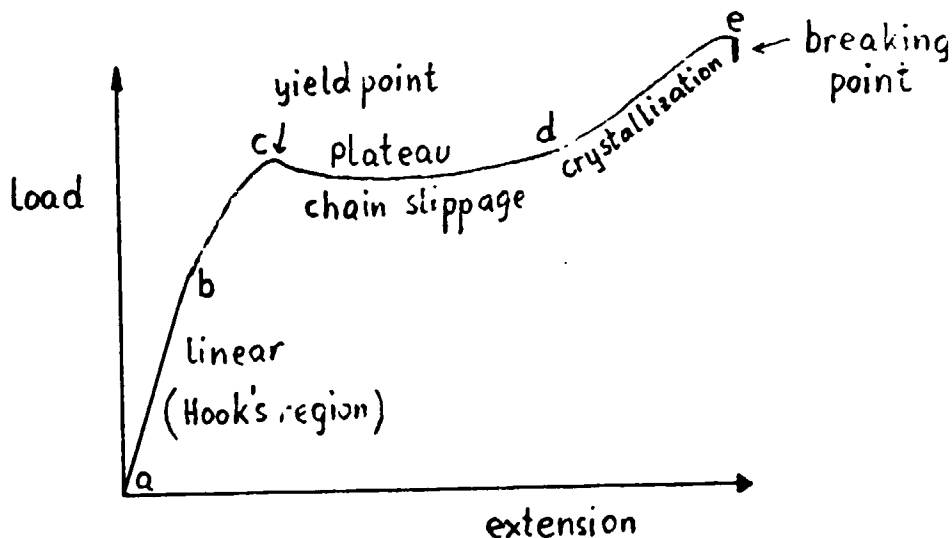
The orientation of the chain molecules in the direction of the fiber axis is accomplished by stretching or drawing. Drawing is carried out on a machine with which the yarn is wrapped around two rollers, one running faster than the other.

With drawing the filament on extension necks down at one position to a smaller cross-section, the length of the filament increases.

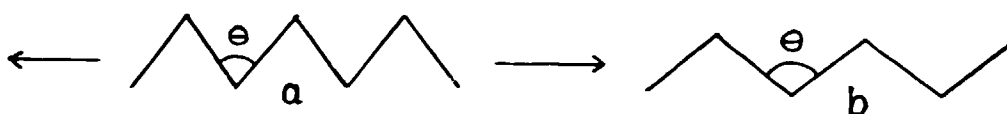


The drawing orients the crystallites as well as the amorphous material.

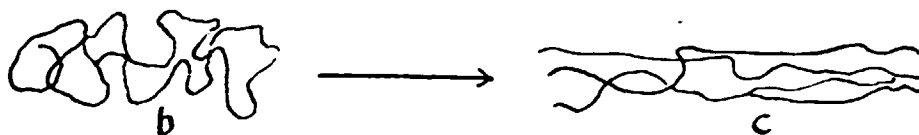
The load extension curve gives some information about what is going on:



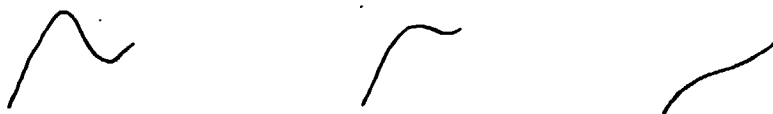
From a to b the load is proportional to extension, it is completely recoverable. This elastic range is due to a change in valence angle θ



From b to c is still elastic range, but some set is introduced. This is due to rotation of chain segments which is not reversible



At the yield point necking occurs. The shape of the yield point region reflects the crystallinity of the drawn polymer

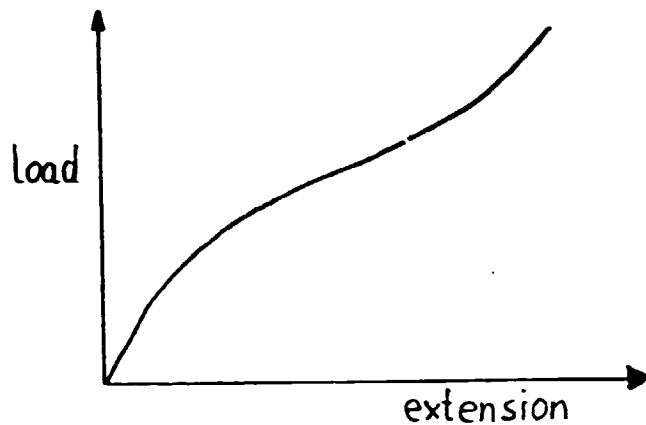


highly crystalline more amorphous amorphous

From c to d almost no increased load is needed. Chain slippage occurs which is highly time dependent.

From d to e there is an increased resistance to elongation probably because of occurring crystallization.

The load-extension curve of a drawn fiber:



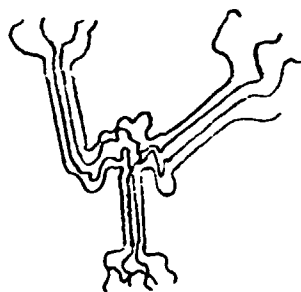
The influence of major structural parameters on physical properties of fibers are as follows:

- a higher degree of crystallinity
 - increases strength, dimensional stability, initial modulus, density, stiffness,
 - decreases flexibility, extensibility, toughness,
- a higher degree of orientation
 - stiffens the material in preferred direction, increases strength,
- a larger size of units
 - weakens the structure,
- a larger molecular extent
 - strengthens the structure.

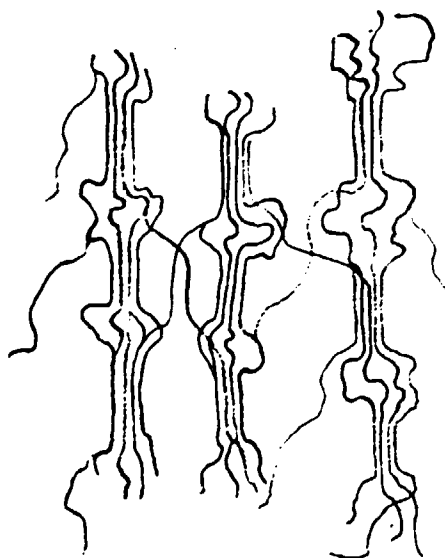
Properties depending on amorphous regions are moisture regain, swelling, heat absorption, dyeing.

The existence of the two phase structure of fibrous polymers has been proven by several means. The detailed picture is still a matter of discussion. X-ray experiments show that the crystalline regions vary in size and perfection.

A very useful model is the fringe micelle theory. In this the micelles as regions of high order are statistically distributed in regions of lower order. The transition from regions of high order to regions of low order is gradual. One chain passes through several crystallites.

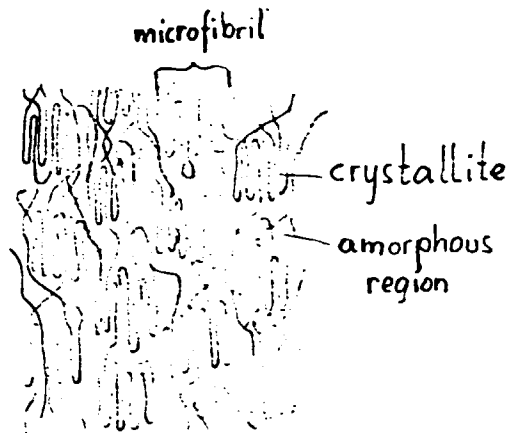


unoriented specimen



oriented specimen

Another model is the folded chain theory



The arrangement of chains is also dependent upon annealing.
Many other theories have been put forward, e.g. shish kebab
from Bill Statton

