II POLYMER AS RAW MATERIAL

II.1 Structure and Character

The majority of polymers used for the manufacture of fibers are of organic nature. The physical behavior of polymers differs from the behavior of the *ordinary*, low molecular mass, substances. The differences are caused principally by the large and nonuniform size of the polymer molecules. In organic chemistry, this is known as the notion of *homolog series.* Polymers, however, may be considered rather as mixtures of homologs.

In the case of ordinary compounds, we speak of molecular mass, while in the case of polymers, we may speak only about an average molecular mass, since the molecules are of uneven size. The molecular mass may have various distributions, and here one needs the help of statistics to describe them. The commonly used averages, presented in a mathematical form, are:

$$\langle M_n \rangle = \frac{\sum_i n_i M_i}{\sum_i n_i} \tag{II.1}$$

$$\langle M_w \rangle = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} \tag{II.2}$$

$$\langle M_z \rangle = \frac{\sum_i n_i M_i^3}{\sum_i n_i M_i^2} \tag{II.3}$$

$$\langle M_{z+1} \rangle = \frac{\sum_i n_i M_i^4}{\sum_i n_i M_i^3} \tag{II.4}$$

In equations II.1 through II.4 n_i denotes the number of molecules of mass M, $\langle M \rangle$ is average molecular mass (colloquially molecular weight). The subscripts mean:

- n represents *number average* molecular mass, where species of each molecular mass are represented by their number or mole fraction.
- w represents *mass average* (or weight average) molecular mass. Here, molecular mass of each of the species is represented by its weight.
- z represents the so called *z-average molecular mass.* This average has primarily mathematical meaning, while physically, it is related to some volume dependence, *e.g.* like radius of gyration in light scattering experiments.
- $z + 1$ is called $z + 1$ - *average*; it has only mathematical significance.

There is one more – perhaps the most commonly used average: the *viscosity average* molecular mass. Particularly until the advent of newer instrumental methods, like the gel permeation (or size exclusion) chromatography this has been the most commonly used average, since the viscosity measurements are easier than other techniques for molecular mass determination.. The unquestionable problem connected with viscosity average is that it is not really constant: its relation to other averages depends on the solvent used. In limiting cases it may equal the weight average. Otherwise it is smaller, down to a minimum reaching about half the difference between the weight and number averages. Mathematically the viscosity average molecular mass may be presented as

$$\langle M_\eta \rangle = \left(\sum_{i=0}^{n} w_i M_i^a \right)^{1/a} \tag{II.5}$$

Here, w_i is weight fraction of species of molecular mass M_i, a is the Mark-Houwink exponent in the intrinsic viscosity equation $[\eta] = KM^a$, which may vary from 0.5 for *theta solvent* to 1.0 for a very good solvent. As the a coefficient approaches unity, the viscosity average approaches the weight average molecular mass, though this occurs rarely. [3,4]

The Gauss distribution is, perhaps, the most fundamental and common in statistics. Its mathematical formulation in relation to molecular mass is:

$$W(M) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[\frac{(M - M_m)^2}{2\sigma^2}\right] \tag{II.6}$$

where M_m is the median value of molecular mass, around which the curve is symmetric, and at the same time it represents the number average molecular mass; σ describes the breadth of the distribution, it corresponds to the standard deviation in statistics. The value of standard deviation, σ_n, may be expressed in terms of the average of molecular masses of different type:

$$\sigma_n = \sqrt{\langle M_w \rangle \langle M_n \rangle - \langle M_n \rangle^2} \tag{II.7}$$

The molar fraction of 0.6826 lies within the limits of $\pm\sigma$. Figure II.1 shows a Gaussian distribution of molecular mass. Unfortunately, there are few polymers which have Gaussian distribution. The normal logarithmic distribution seems to be more common. The mathematical form of the *"log-normal"* distribution, as it is called for short, is the Gaussian distribution, where the molecular mass fraction in the exponent is substituted by its natural logarithm. The standard deviation, σ_w*, for the distribution where the number of molecules is substituted with a weight fraction, is

$$\exp(\sigma_w^*)^2 = \frac{\langle M_w \rangle}{\langle M_n \rangle} = \frac{\langle M_z \rangle}{\langle M_w \rangle} \tag{II.8}$$

An example of the *log-normal* distribution curve is presented in Figure II.2. In the normal distribution the maximum of the curve coincides with the number average molecular mass. In log-normal distribution this is not the case: log-normal distribution is characterized by a larger fraction of smaller molecules. The distribution curves encountered experimentally often resemble log-normal distribution,

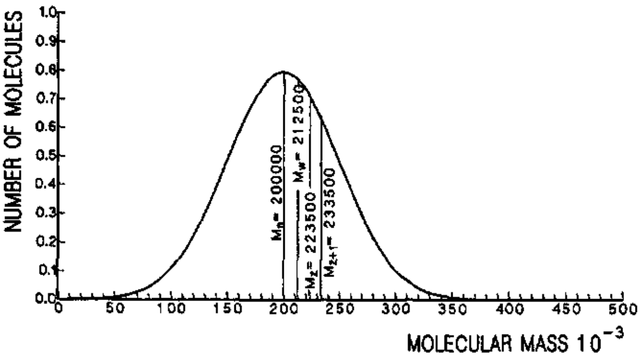


Figure II.1: *Gaussian distribution of molecular masses.*

though they do not fit exactly into its mathematical form. Therefore, a number of modifications to the log-normal distribution equation have been suggested to accommodate the discrepancies. For details on these distributions the reader is referred to the polymer textbooks.[1,2]

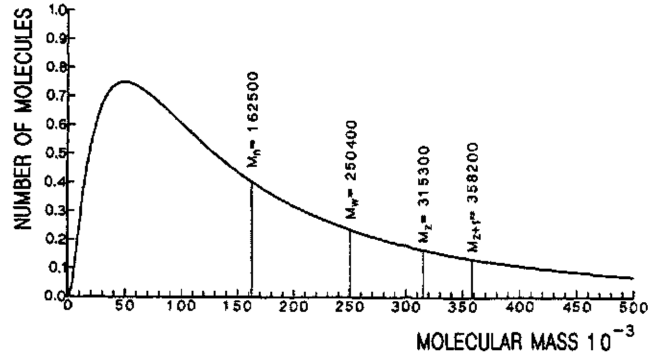


Figure II.2: *Example of a normal logarithmic type of molecular mass distribution.*

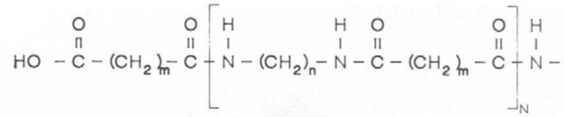
Experimentally, molecular mass distribution and all the averages are commonly determined by the size exclusion chromatography. Other methods are used less frequently as they are experimentally more difficult. These methods usually yield molecular mass averages of different type. Particularly troublesome are other methods for determination of mass distributions. However, from the direct specialized methods like osmometry for number average, light scattering for weight average, and ultra centrifuge for weight and z-average, more accurate data may be obtained. The size exclusion chromatography requires calibration, which is based on the direct methods.

Polydispersity of polymers, as expressed by the weight average over number average ratio, rarely is less then 2 and in some cases may reach as high as ten or twelve. This is true both for commercial and for experimental polymers. The lower values are more typical for condensation type polymers, the higher values occur primarily with some vinyl-type polymers. Polymers of higher average molecular mass have a tendency toward having a somewhat broader mass distribution.[5]

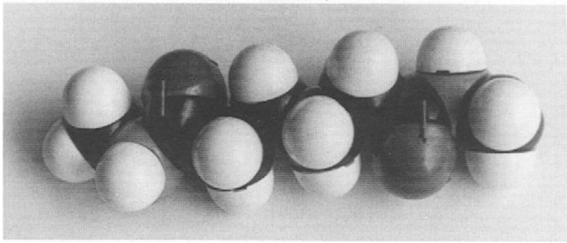
Polydispersity may be high also due to the blending of different polymer batches, or as a result of not very stable continuous polymerization processes. In such cases one may encounter bimodal, or even multimodal distributions which do not have any general mathematical representations given *a priori*.

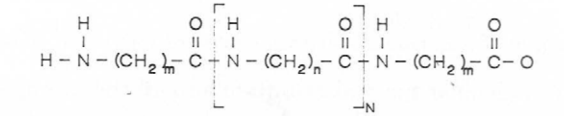
Practically, all the fiber forming polymers known currently have linear chain structure. The molecular formulas predict such linearity quite clearly.

The group of polyamides **polyamides**, is based either on $\alpha - \omega$ difunctional acids and $\alpha - \omega$ iamines or on $\alpha - \omega$ aminoacids. Aromatic diacids or diamines make the melting point very high and may increase the strength substantially. Examples of structural formula of an $\alpha - \omega$ diacid and $\alpha - \omega$ diamine, as well as Stuart-Briegleb models of single mer of nylon 6 and a segment of nylon 66 with amid bonds and with one CH2 group on each side, respectively, are:

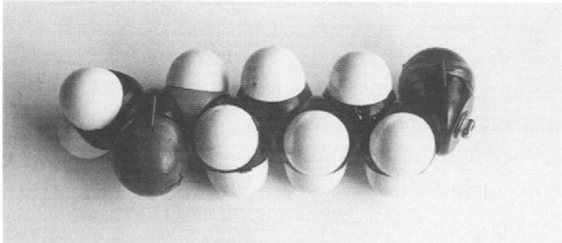


$$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_m-\overset{O}{\overset{\|}{C}}-\left[\overset{H}{\overset{|}{N}}-(CH_2)_n-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_m-\overset{O}{\overset{\|}{C}}\right]_N-\overset{H}{\overset{|}{N}}-$$

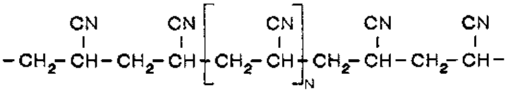




$$H-\overset{H}{\overset{|}{N}}-(CH_2)_m-\overset{O}{\overset{\|}{C}}-\left[\overset{H}{\overset{|}{N}}-(CH_2)_n-\overset{O}{\overset{\|}{C}}\right]_N-\overset{H}{\overset{|}{N}}-(CH_2)_m-\overset{O}{\overset{\|}{C}}-O$$

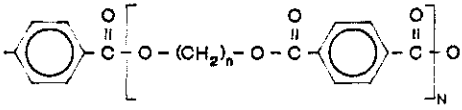


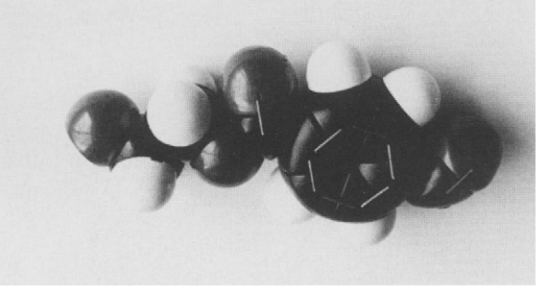
Poly(acrylonitrile) (usually called *acrylic fiber*) has an irregular stereo configuration, often containing small amounts of comonomers, does not melt and is processed from solution:



$$-CH_2-\overset{CN}{\overset{|}{CH}}-CH_2-\overset{CN}{\overset{|}{CH}}\left[-CH_2-\overset{CN}{\overset{|}{CH}}-\right]_N CH_2-\overset{CN}{\overset{|}{CH}}-CH_2-\overset{CN}{\overset{|}{CH}}-$$

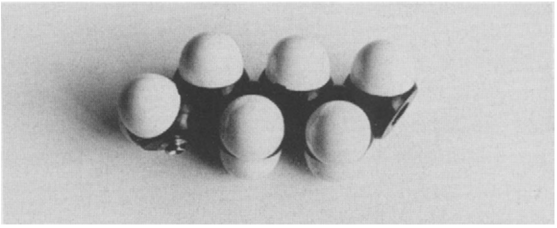
Polyesters in their most common version are based on terephthalic acid and glycols of different length, most often ethylene glycol. Structural formula and Stuart-Briegleb model of one mer of poly(ethylene terephthalate) are:



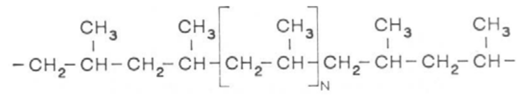


Polyethylene (or *polymethylene*, if it has a most regular structure), is a polymer of high theoretical interest due to the structure simplicity, commercially it is less attractive due to low melting. Structural formula and Stuart - Briegleb model of three mer segment are:

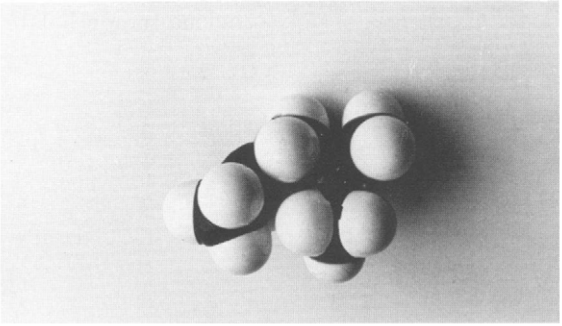
$$-CH_2-CH_2-CH_2-CH_2\left[-CH_2-CH_2-\right]_N CH_2-CH_2-CH_2-CH_2-$$



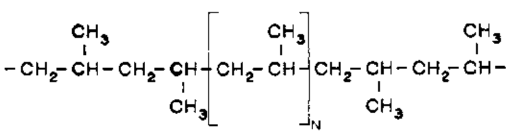
Isotactic **polypropylene**, which cannot assume a planar *zig - zag* but instead has a helical conformation as found in crystals. Structural formula and Stuart-Briegleb model of a two mer segment are:



$$-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-\left[CH_2-\overset{CH_3}{\overset{|}{CH}}\right]_N-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-$$



Syndiotactic-**polypropylene**, has planar conformation but usually melts lower than its isotactic counterpart:



$$-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-\left[CH_2-\overset{CH_3}{\overset{|}{CH}}\right]_N-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-$$

Naturally, the list of polymers used for manufacturing of fibers is substantially longer, especially when one takes into consideration the so-called high performance fibers and modifications of naturally occurring polymers. If any of the useful polymers, from the fiber formation point of view, have chain branching synthesized intentionally, then the side chains are rather short. Unfortunately, almost all polymers contain some fraction of chains with long branches built in unintentionally, as imperfections, as a result of side reactions. In the case of low molecular mass compounds, products of side reactions are removed during purification processes; in the case of polymers, such purification is impossible, particularly if the side products are built into the chains. It must be stressed that long chain branching, particularly when it is severe enough to form cross linked, gel molecules, is most detrimental to the polymer quality, to the ease of processing, and potentially to the polymer usefulness.[6,8] Doubtlessly, in commercial operations such chain imperfections often represent a strong economic factor.

In melts and in solutions, the polymer molecules are coiled into what looks like a little balls. How tightly a polymer coils depends on the flexibility of chain, and in the case of solutions, the quality of the solvent.[9,10] It is indeed difficult to imagine a rod with length to diameter ratio of several thousands staying fully extended, or close to it, especially when one considers interaction with other molecules. Conditions like this may be met only in cases of very rigid molecule structure (e.g. liquid crystal polymers).

In concentrated solutions and in the melts, the coiled polymer molecules are not entirely independent. To some degree, the coils are interpenetrated and the chains entangled. A fully quantitative description of the chain morphology in concentrated solutions and in the melts is currently impossible. The problem of chain conformation in solid state is also not less important; it will be discussed in the next sections.

As the molecules lack full freedom of motion, they cannot always assume such spatial positions as would correspond to a minimum of free energy in the system. Thus, polymers belong to the systems which are not in thermodynamic equilibrium.[11] This fact is of great theoretical and practical importance:[12] it is the basis for the phenomenon that the very same polymer can have different properties in solid state. The same specimen may be crystallized to different degrees, and many of the crystalline forms will be in a *meta*-stable state for practically an indefinite time under normal service conditions. The same specimen may also be crystallized to the same degree, but if the crystalline morphology is different, the properties will be different also. Mostly the physical properties will differ to a larger degree, e.g. tensile strength, Young's modulus, creep, etc. The non-equilibrium character of polymers is responsible for the influence of processing on the product properties. Full knowledge of the appropriate relationships is necessary to fully utilize all the possibilities that any type of processing offers.

Molecular structure, regardless of whether it is more or less ideal, has an obviously quite dominant role in determining fiber properties. So, the presence or absence of polar forces, as well as their strength, determine many properties. Poly(acrylonitrile), which has very strong polar groups, is able to form good and strong fibers even at low levels of crystallinity; the polar forces hold the supermolecular structure together. Polyolefines, with no polar forces to speak of, need much higher levels of crystallinity and higher molecular mass to form sufficiently stable, low creeping fibers.[13] If well crystallizing polymers have, in addition, strong polar forces or hydrogen bonds, or both,[14,15] like poly(ethylene terephthalate), the resulting fibers have excellent mechanical properties. On the other hand, the dense crystalline morphology of the fibers may create problems with diffusion related properties such as dyeability and water absorption. The last two properties are important, particularly in fibers aimed at applications in garments, sanitary materials, or insulating materials. Nonpolar polymers, like polyethylene or polypropylene, are used for such applications where dyeing is not important or may be substituted with pigmenting the polymer in bulk.

The chemical structure of polymers also accounts for such properties as stability against heat, oxidation, microorganisms, and different kinds of radiation, as well as resistance to hydrolysis, to attacks of different solvents, etc.[16-18]

In essence, the polymer presents a certain potential range of obtainable fiber properties. Exactly which properties are utilized depends on the processing. The degree of development and the level of sophistication of the process are reflected in the utilized fraction of the potential a polymer offers.

II.2 Polymer Crystals

II.2.a Crystal Structure

Some polymers have been found to be able to crystallize. Those polymers which are able to crystallize give X-ray diffractograms typical of crystalline structure superposed on a halo obtained normally from amorphous materials. The "crystalline part" of polymer diffractograms is similar to powder diffractograms of low molecular mass crystalline compounds. Fibers give usually diffractograms similar to single crystal, indicating presence of orientation.

The duality of x-ray diffraction patterns suggests the notion of semicrystallinity in polymers. Although the first x-ray observations were made in the late twenties or early thirties, the crystallography of polymers is still open for a development effort.

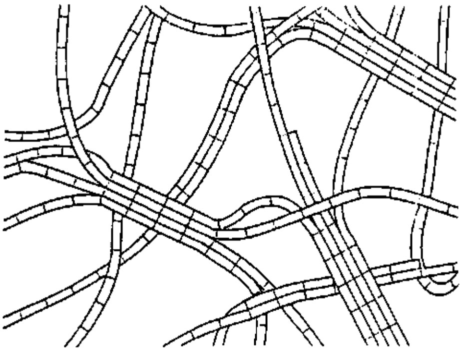


Figure II.3: *First depiction of crystalline structure in polymers after Hermann, Gerngross, and Abitz.*[19-21]

The first attempts to describe the structure of polymer crystals were published

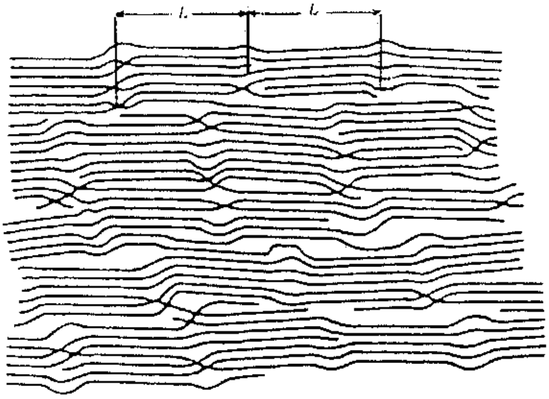


Figure II.4: *Model of polymer crystallinity by Hess and Kiessig.*[24,25] *Reproduced by permission of the copyrights owner, Dietrich Steinkopf Verlag.*

by Hermann and Gerngross[19–21] in 1932. Their model is presented schematically in Figure II.3. With only minor modifications, Statton reactivated the model in 1959.[22] This interpretation of polymer crystals is usually referred to as the *fringed micelle model.* Based on the low angle X-ray scattering obtained from fibers, Hess and Kiessig[23,24] developed in 1942 another model, which was characterized by substantially more order and alternating arrangement of areas of crystalline - non-crystalline material (see Figure II.4). None of the models, though, was able to provide explanation of the material properties, particularly, the properties of fibers.

In 1957, three different laboratories reported the discovery of polymer single crystals.[25–27] Electron microscopic investigations of single crystals revealed that the crystal dimensions were incompatible with dimensions of fully extended polymer chains – *ergo* – the chains in the crystal must be folded. The folds were found to be around 100 Å in size. The large surfaces of the single crystals, though they physically belong to the crystal, contain the molecule folds. The folds do not have the packing regularity of a crystal, hence they may then be considered noncrystalline. The thickness of single crystal was found to be variable and dependent on the growth conditions: temperature and medium, e.g. solvent or melt. Thickness of the crystal lamellae, as they have been named, has been found to coincide with the long periodicity, as determined by low angle X-ray scattering. Table II.1 presents, as an example, the relationship between the growth conditions of polyethylene crystals and corresponding long periods.[28] Later investigations indicated that at large supercoolings, the long periods reach a constant value independent of the crystallization temperature.[29–31] Further, it has been found that the long period grows also during isothermal crystallization beginning from some minimum. This minimum value of long period corresponds also to the long period obtained in crystallization from solution.[38] The most recent investigations[39] show that during crystallization of monodisperse polyethylene, the long period grows in steps, doubling, tripling, and quadrupling the minimum long period, l^*. Figure II.5 presents a proposed mechanism of the jump changes of chain folding,[39] which

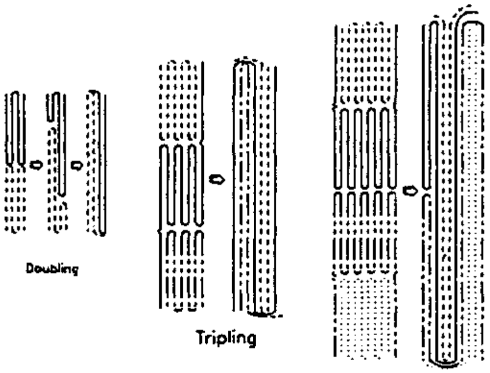


Figure II.5: *Sketch illustrating a scheme for refolding which leads to multiplication of the minimum fold size. Reproduced from P. J. Barham and A. Keller*[39] *by permission of the copyrights holder, John Wiley & Sons, Inc.*

is observable irrespectively of the crystallization medium, but in the melt it proceeds at substantially higher rates.

Table II.1.
Long Period of Polyethylene Crystals
in Relation to Growth Conditions.

Medium	Temperature, ^{o}C	Long Period, Å
o-Xylene	50	92.5
o-Xylene	60	102.0
o-Xylene	70	111.5
o-Xylene	80	120.5
o-Xylene	90	150.0
Polyethylene melt	120	190.0
Polyethylene melt	125	223.0
Polyethylene melt	130	355.0

A number of investigators[40–42] have suggested that one molecule may be involved in more than one lamella, creating *tie molecules*. The tie molecules connect different lamellae with stronger bonds than might be provided by the poorly ordered fold planes. E. W. Fischer and co-workers[43] have shown that in general, one molecule, $l*$,[32–37] crystallizes in more than one lamella. In the same paper Fischer describes an X-ray based method of detailed quantitative analysis of the molecule involvement in lamellae.

Based on thermodynamic considerations,[44–48] it was predicted that stability of polymer crystal has two maxima: one at a limited thickness – which depends on crystallization temperature and is realized in folded chain crystals, the other maximum of stability corresponds to fully extended chain conformation. Crystals with fully extended chains have been obtained experimentally. Namely, polyethylene crystallizes with extended chains when the crystallization process is carried out at pressures in excess of 2300 *atm.*[49] Also, polymers with very rigid chains are unable to coil. Therefore, their normal mode of crystallization is with extended chains. Some of the so-called *high performance* fibers are based on such, or similar, polymers.

What makes polymers crystallize? This is an important question. The answer may be: the tendency to give up an excess of energy which may be achieved by entering into proper positions in relation to other chains. Why is it then that some polymers crystallize and other do not? Regularity of crystalline lattices requires some minimum of regularity in polymer chain. At some point it was believed that the regularity needed is very high,[50] so high that the chains would need to be nearly perfectly stereoregular. Such rigid requirements may be correct if "perfect" crystals are to be obtained. Commonly, however, crystals are not so "perfect" and are able to accommodate chain imperfections. Polypropylene with four to five chlorine atoms per hundred carbon chain atoms shows only relatively minor deformation of crystalline lattice.[51] The degree of crystallinity of polyethylene decreases gradually with the increasing number of "foreign" substituents, like chlorine, methyl, isopropyl.[52] Copolymers with three or five percent of a comonomer are quite well able to form crystalline materials. Different stereoisomers, in comparison to copolymers, represent only a minor disturbance of the chain regularity.[53,54] The feature most detrimental to crystallization is chain branching, particularly long chain and frequent branching. There is evidence that, despite the imperfections, polymers do crystallize, but the imperfections influence the resulting crystal morphology, as well as the crystallization rate.[140]

Great progress in evaluation of X-ray diffraction data made by Hosemann and collaborators[55,56] in the early 1950's led to the formulation of the notion of *paracrystallinity*. Crystalline structure ceased to be treated in terms of "black and white", it moved into the "grey" area. Crystal structure may range from perfection down, through *paracrystals* distinguishing *smectic* and *nematic* morphologies, all the way to an amorphous state. The nematic form describes some degree of lateral order between the molecules, though distances are not fully regular. The smectic form is somewhat more ordered, the chain elements or groups become ordered laterally, though still not in the constraints of a regular crystalline lattice. Methods to analyze the imperfections became known, though the reasons for the imperfections would not be determined equally precisely. Generally, the causes of imperfections are believed to belong to two categories:

primo – those resulting from the irregularities in chain conformation, and

secundo – imperfections of the geometry of the polymer chain itself.

The first category includes improper alignment of the chain in the lattice, unusual configuration of folds, incorporation of chain ends in the lattice, inversion of helix turns, etc. The second category includes steric imperfections, chain branches, comonomer units, chemical imperfections built into the chains, end groups of different chemical nature, etc.[53,57]

It has been shown that even well developed polymer crystals, including single

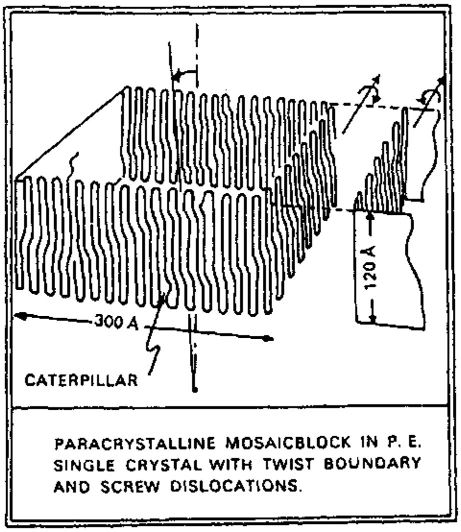


Figure II.6: *Schematic drawing of a mosaic block boundaries, according to R. Hosemann et al.*[58] *Reproduced by permission of the copyright owner, International Union of Crystallography.*

crystals, do not have a completely homogeneous structure. If a single polymer crystal is analyzed by X-ray diffraction, one obtains values for the size of the crystal substantially smaller than the whole crystal mat, usually only around 100 Å. The same is true with any other polymer crystals. Crystals, including single crystals, are built of small blocks which have been given the name *paracrystalline mosaic blocks*.[58,59] The size of the small blocks is strongly related to the paracrystalline lattice distortions:

$$\bar{D} = \frac{\alpha^2 \bar{a}}{g^2} \qquad \text{(II.9)}$$

Here, a is distance between the lattice planes, $\bar{D}$ represents the average size of the paracrystalline particle in a direction perpendicular to the considered lattice plane, g is the paracrystalline lattice distortion factor, and α characterizes the forces binding the network planes. For many polymers, including polyethylene, the value of α is around 0.15. This relationship indicates that the distortions in crystalline lattice are additive, they superimpose in some way. Therefore the distortions are effectively growing with the growth of the crystal. Depending on the magnitude of the distortions, what is reflected by the g-factor, depends the number of crystalline unit cells grown to the point where the distortion becomes large enough to create a discontinuity of the total structure. The local distortion of the order becomes so large that the area appears to X-ray diffraction as noncrystalline (Figure II.6). The question of lattice distortions has been further refined and related to particular lattices by Blöchl and Bonart.[139] Under the influence of relatively small forces, a single crystal mat or lamella breaks down along the distorted and weak boundaries between mosaic blocks.[60,61]

It has been suggested[89,90,130] that the process of crystallization is preceded by precipitation of the molecules in their coiled form. Subsequently, the molecules crystallize to a large extent within the coils. It has been suggested even that at the conditions close to crystallization, the chain segments within a coil are already largely parallel to obtain the maximum packing.[58] The connections between the lamellae are suggested to originate in the chain entanglements. From a mechanistic point of view these suggestions appear quite plausible.

At the current state of knowledge it is easy to realize that the notion of crystallinity is quite ill-defined. Should the fold planes be considered as crystalline or not? They belong, though, to a single crystal. Even a single crystal is not viewed as hundred per cent crystalline by X-ray. Density and heat of fusion must vary with the degree of crystal perfection. The only solution to the problem appears to be adherence to the concept of paracrystallinity and observation of the necessity to indicate the method of analysis by which the degree of crystallinity has been deduced. Naturally, closer description of the structural features, like the g-factor, type of distortions,[62] long period, etc., additionally clarifies the meaning, but the analyses may be time consuming and expensive. Thus, very often we must remain satisfied with the more or less approximate description of the order in the polymer solid state.[63,64]

II.2.b Melting of Crystals

If a thermodynamic equilibrium would exist in a partially crystalline system, then the change in free energy during the melting of a small crystal layer would equal:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = 0 \qquad \text{(II.10)}$$

Here ΔG^0 is change in free energy, and ΔH^0, ΔS^0 are changes of melting enthalpy and melting entropy, respectively. All the values are calculated per mole. From equation II.10 one may find the equilibrium temperature:

$$T' = \Delta H^0 / \Delta S^0 \qquad \text{(II.11)}$$

If the actual temperature of a specimen would become greater than T', then ΔG^0 would become negative and the crystal would melt. If, on the other hand, the specimen temperature would decrease below T', then ΔG^0 would become positive and further crystallization would proceed.

In case of low molecular mass compounds, when the crystals are sufficiently large, ΔG^0 and ΔS^0 are material constants which do not change. In such cases, equation II.11 defines the melting point. For high molecular mass compounds, both enthalpy and entropy change during melting. The enthalpy of melting depends quite strongly on the crystallization temperature and on the molecular mass of the polymer. The value of enthalpy increases with increasing crystallization temperature and decreases with increasing molecular mass to reach an equilibrium point for infinitely long polymer chains at the melting temperature.[104]

The total entropy, S, of a polymeric system consists of:

1. Transition entropy, S_t, which is connected with vibrations of the center of gravity of the entire molecule.
2. Entropy of internal vibrations, S_w, which is related to the vibrations of different segments of a molecule, while the center of gravity does not shift.
3. Configurational entropy, S_c, which arises from changes of form and spatial arrangement of the molecule.

In effect one may write:

$$S = S_t + S_\nu + S_c$$

During the melting of polymers, the configurational entropy, S_c, undergoes changes and because of this the equilibrium temperature, T' changes also. This complicates an adequate description of the melting phenomena in polymers. In addition, the degree of crystallinity may also be affected by the crystallization temperature.[64] Polymer melting may be described adequately only in the form of a relationship between the crystallization temperature and the corresponding melting temperature, as it is shown in Figure II.7. The slope of melting temperature, T_m, against crystallization temperature, T_c, is usually around 0.5.[1] In practice, however, the values range from 0.3 to 0.8. The large deviations from the expected value of 0.5 may be partially due to the fact that experimental determination of the relationship is rather difficult. Also, at larger supercoolings the melting temperature becomes constant and independent of the crystallization temperature.[29–31] If the point is not well defined, the experimental points may become confused, leading to an incorrect slope. The slope, on the other hand, is of utmost importance, as it determines the point where the temperature of melting equals the temperature of crystallization, $T_m = T_c$, that is the ***equilibrium melting point***, T_m^0. Practically, this point is determined by the point of intersection of the line of T_m *versus* T_c with the line of slope equal one. The thermodynamic equilibrium melting pint is defined as the temperature at which the free energy of an infinite crystal, consisting of fully extended chains, is equal to that of a liquid polymer.[28] Equilibrium melting point is a material constant, barring any alterations resulting from polymer chain imperfections. However, such cases are rather common. Polyethylene crystallized under high pressure does melt at the equilibrium melting temperature, or close to it.

Molecular mass has an influence on melting point.[1,66,104]

$$T_m = T_m^0 \cdot \frac{2RT_mT_m^0}{(\Delta H_m)_u} \cdot \frac{lnX}{X} + f(x) \qquad \text{(II.12)}$$

Here $(\Delta H_m)_u$ is the melting enthalpy of a monomer unit, R is, as usual, the gas constant, and X is degree of polymerization. $f(X)$ represents a long expression, but its numerical value is normally negligibly small. This influence is primarily a reflection of different chain end groups acting as impurities. Consequently, the

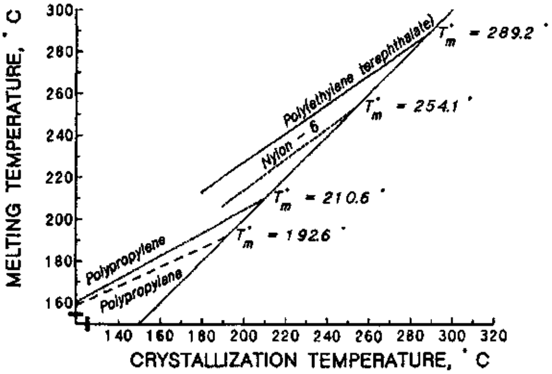


Figure II.7: *Relationship between crystallization and melting temperatures: poly(ethylene terephthalate):*[95] $T_m = 0.694\,T_c{+}88.43$; *nylon-6:*[132] $T_m = 0.7445\,T_c{+}64.91$; *polypropylene:*[131] $T_m = 0.4644\ T_c + 103.13$ *and* $T_m = 0.5501\ T_c + 97.74$.

influence decreases strongly with increasing molecular mass, so for the majority of common cases it may be neglected. Recently, it has been also reported[67] that molecular mass has some effect on the lamella growth, and this would, naturally, influence melting temperature. However, the influence becomes negligible already above degree of polymerization of 500, and its influence decreases further with increasing degree of polymerization.

As has been mentioned above, the crystalline long period depends on crystallization temperature. Now we see that melting point depends on the size of long period; thus, melting temperature depends on crystallization temperature. The logic of structure and behavior is complete. However, one needs to take into account the medium in which crystallization proceeds, and whether refolding is possible or not. This may modify the melting point.

Polymers do not usually have sharp melting points. It is still not entirely clear what are the thermodynamic reasons underlying this fact. The ratio of the fold surface area to the crystal size depends on long period:[68]

$$T_m = T_m^0 \left[\frac{1 - 2\sigma}{(L \Delta H_f)} \right] \tag{II.13}$$

where σ is surface free energy of the fold surfaces, ΔH_f heat of fusion, and L is long period. It is claimed[69,70] that heat of fusion decreases with molecular mass. On the other hand, melting temperature is sensitive to molecular mass only at low molecular masses (*e.g.* for polyethylene below $2 \cdot 10^4$)[71]

The theory of partial melting[42,72,94] treats the fold sites differently. It assumes that a polymer below its melting point reaches its absolute minimum of free energy when it is almost completely crystalline. The steric hindrances do not allow the minimum of free energy to be reached. Only a relative, metastable equilibrium between the crystalline and unordered layers may be achieved. The length of the unordered chains reflects a temperature dependent equilibrium, and this explains the broad melting of polymers, as well as some decrease in crystallinity. The latter is accompanied by an increase of the thickness of interlamellar layers as temperature increases. In addition, surface melting results in an increase of specific heat. Taking these into account, the great influence of long periodicity on the thermal behavior of polymers becomes obvious. The dependence of the degree of crystallinity on temperature is:[42]

$$\alpha(T) = \left(1 + dT \cdot \frac{\rho_a}{L\rho_\alpha \pi}\right)^{-1} \tag{II.14}$$

Here ρ_a is density of the unordered layer, ρ_α is density of the crystalline layer, L is thickness of the crystalline layer, and d stands for the thickness of the unordered layer.

Partial melting may take place only when the unordered molecules have both ends tied to the crystal surface. Figure II.8 shows such situations as cases A and B. Case D, with only one end tied in the crystal, does not aid the surface melting. In cases of typical tie molecules, like case C, partial melting should not be expected, since the distance between the tied points is affected by melting. Cases like E are not very likely to occur, but should they happen, melting may be affected. Significant experimental support, based on X-ray analyses, for the partial melting theory has been reported by Kavesh and Schultz.[73]

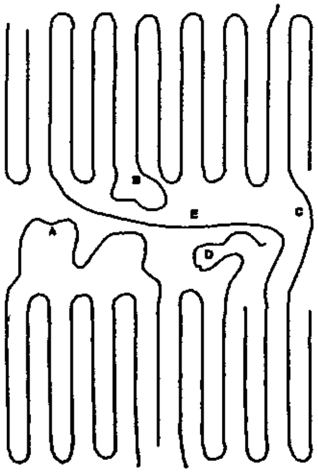


Figure II.8: *Possible chain arrangements, other than adjacent reentry, between crystalline lamellae. After Fischer.*[42]

Newer investigations[137] show that partial melting is due also to the "wandering" of paracrystalline portions between crystalline ↔ paracrystalline (*intermediate*) ↔ amorphous. Partial melting involves not only the chain folds; a large role is played by the distribution of long period sizes.[138]

Besides surface melting, there are several other reasons why melting may be broadened:

- Small temperature gradients during crystallization may cause small differences in the size of long period, and furthermore in melting temperature.
- Imperfections in the crystalline lattice.[12,28]
- Impurities lower the melting points of crystals, as in the case of low molecular mass compounds.
- Chain branching has a very complex influence on melting point, much more complex than formulated by Flory.[74,75]

The great number of possible combinations of length, frequency, and distribution of branches along the chains give a basis for the complexity.[71] The true reasons for melting point broadening are, most likely, of very complex nature and attributable to many factors,[76] including the broadening effect of the instruments used.

If a polymer crystal is subjected to elevated temperature, though still substantially below its actual melting temperature, the melting temperature may increase. This process is called *annealing*. The annealing effect is observable above a certain temperature, T_α, which coincides with a transition in the viscoelastic spectrum, the so called α_c transition. In terms of structure, long period grows exponentially with time to an asymptotic value.[28,77–82] Macroscopic density of the crystal also increases. There is no linearity in the relationship between the long period growth and temperature. Density increases show a linear relationship with the reciprocal value of the long period for a given constant temperature. When the annealing temperature exceeds a certain maximum that is close to the melting point of the specimen, the long period does not reach an equilibrium.[82]

Newer investigations[141 & ref] show that not all crystals have equally strong α_c relaxation, which is related to the translational chain motions. The translation may proceed through various mechanisms, like chain rotation, helical jumps, "crankshaft" jumps. The translation is obviously more difficult, if possible, for polymers with large side groups, rigid chains, and extensive chain entanglements. Some polymers do not have the α_c transition; they form *nonductile crystals* , or according to other terminology, are *crystal fixed*. The rate of growth of long period is considered dependent on molecular mass,[83] which is usually connected with higher degree of chain entanglement. The growth of long period during annealing is accomplished by a mechanism similar to refolding during crystallization: by longitudinal translation of the chains within the crystalline lattice after the lattice has been softened sufficiently for such a process to take place. The softening is possible within the temperature interval beginning with T_α and upwards to some temperature close, but not reaching, the actual melting point of the specimen.[80,81] It is also possible that partial melting is involved in the process.[76,78] There are conflicting views regarding the influence of annealing on the crystal perfection: some authors believe that the perfection increases,[82] others claim the opposite effect to be true.[28]

Annealing processes are accompanied by macroscopic changes of the sample shape, *e.g.* shrinking when a sample was previously oriented, or formation of holes during annealing of single crystal mats. These changes of shape may occur only when a sample is annealed without a restraint imposed on its dimensions. All of the description given above concerns only such cases. During isometric annealing, polymers behave differently. Such cases will be discussed in other sections.

It is not without significance whether a sample is annealed in air or in a liquid. Annealing in liquids is much more effective, the new equilibrium is reached faster even when using liquids which do not interact physicochemically with the polymer. A more intense heat transfer must be responsible for the accelerating effect.[84]

In experimental practice, the measured melting temperature often depends on the heating rate during the experiment. This effect may be related to the partial annealing.[85]

Heat treatment, sometimes even at relatively low temperature, can have an influence on the entropy of some noncrystalline elements of the structure. Stresses on noncrystalline molecules imposed by crystallization of other molecule segments may gain a chance of relaxation. Such a relaxation would result in a change of configurational entropy. Even without noticeable change in long periodicity, melting point may be affected,[86] but certainly the macroscopic shape of the specimen will be altered.

There are known cases when annealing caused changes of the crystallographic form.[87,88] Such change, if it takes place, is responsible for the most serious changes of melting behavior. Other properties may be affected also, and quite strongly at that.

II.2.c Crystallization Kinetics

It is generally accepted that the kinetics of polymer crystallization follows the Avrami equation originally developed for low molecular mass compounds and for metals in particular:[91–95]

$$1 - \alpha = \exp(-Kt^n) \tag{II.15}$$

In this equation α represents the degree of crystallinity, t is time, n is constant, depending on the process of nucleation and assuming values $1 \leq n \leq 4$, which according to the original development must be integers. K is here a rate constant. The majority of polymers seem to follow the equation fairly well, but n is almost always fractional. The equation reflects neither the influence of molecular mass on the kinetics, nor the temperature dependence of the process.

Another approach to crystallization kinetics is also based on thermodynamic considerations. The earliest notions go as far back as Gibbs.[96] R. Becker[97] formulated the nucleation rate in a condensed phase, $n*$, as:

$$n^* = n_0 \exp\left(-\frac{\Delta F^* + \Delta\phi^*}{kT}\right) \tag{II.16}$$

Here n_0 is an unspecified constant, ΔF^* is the free energy of activation for the transport of a molecule across the phase boundary, k is Boltzmann's constant, and

T is temperature. $\Delta\phi^*$ is the greatest contributor in the equation and represents a "barrier" which is inversely proportional to temperature. Fisher and Turnbull[98] reformulated the equation:

$$\Delta\phi^* = \frac{4\ b_0\ \sigma_1\ \sigma_2}{\Delta f} \tag{II.17}$$

where b_0 is thickness of the crystallizing entity, and is assumed constant; σ_1 and σ_2 are the interfacial free energies per unit area for the nucleus faces $a\,b_0$ and $c\,b_0$; Δf represents the free energy of fusion per unit of volume of the macroscopic crystal:

$$\Delta f = \frac{[\Delta h_f(T_m^0 - T)]}{T_m^0} \tag{II.18}$$

In equation II.18 Δh_f is the heat of fusion per unit volume of the crystal, T_m^0 is the equilibrium melting point, T is crystallization temperature. Thus, equation II.16 in the Fisher and Turnbull version may assume the following form:

$$n^* = \left(\frac{NkT}{h}\right)\exp\left(-\frac{\Delta F^*}{kT}\right)\exp\left[-\frac{4\ c_0\ \sigma_1\sigma_2\ T_m^0}{\Delta h_f \times \Delta T \times kT}\right] \tag{II.19}$$

The additional notation in equation II.19 has the usual meaning: N is Avogadro's number, h is Planck constant, $\Delta T = T_m^0 - T$.

Hoffman and co-workers[99] have modified the Fisher-Turnbull equation and for three dimensional homogeneous nucleation of polymer crystal they suggest:

$$I^* = \left(\frac{NkT}{hV_m}\right)\exp\left(-\frac{\Delta F^*}{RT}\right)\exp\left\{-\frac{32\ \sigma^2\ \sigma_e(T_m^0)^2}{[\ \Delta h_f \times \Delta T \times kT]^2}\right\} \tag{II.20}$$

Here V_m represents " *molar volume of the order of magnitude of that associated with a chain length of the fold period*"; as the free energy of activation for transport. WLF equation for activation energy of flow (see chapter on rheology) is used to describe the transport,[12] $\Delta F^* = \Delta F^*_{WLF} = 4120T/(51.6 + T - T_g)$, where T_g is the glass transition temperature. To improve the agreement between the results calculated from equation II.20 and those obtained from experiment, the authors[99] add to the denominator of the last segment of the equation a correcting factor y^2, with the value of y close to unity.

There were attempts made to improve the agreement between equation II.20 and experimental data by dividing the problem into three "regimes". Definition of the "regimes" is based approximately on the degree of supercooling.[113–117] These attempts appear to be somewhat artificial however, and the entire Hoffman-Lauritzen theory has been subjected to very severe criticism.[118–123] Improvements of the equation, as well as new solutions of the problem have been suggested by many authors,[118–130] many of the solutions are based on extension of the Avrami equation to nonisothermal conditions. These efforts offer some small improvements, but none of them is significant, so far. A detailed review of the efforts may be found in a paper by Di Lorenzo and Silvestre.[142]

Confrontations of experimental results with equation II.20 show some agreement, though it is not complete. Figure II.9 presents a superposition of the experimental crystallization rate against temperature with the least square fit of the data into equation II.20. This happens to be one of the closest results obtainable. Least square fits give a coefficient for the nucleation term very close to the values

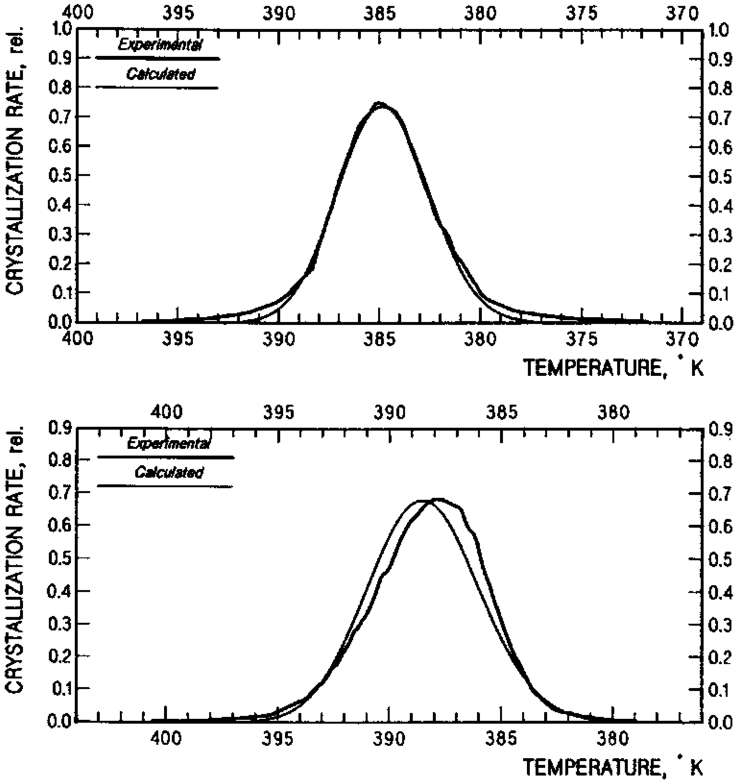


Figure II.9: *Experimental crystallization rate (heavy line) in comparison with a least square fit into Equation II.20. Experimentally determined activation energy of flow was used in the calculation. Two different polypropylenes.*

expected from the theory. However, the "flow" term with the WLF activation energy calls for coefficients ranging between 50 and 60. Thus the model of this segment must be deemed incorrect. The WLF equation is valid for temperature close to glass transition, and by no means higher than 40 or 50 ° K. Crystallization, on the other hand takes place usually at much more than 100 ° K above glass transition temperature. Similar reservations have been voiced earlier by Mandelkern. The shape of the rate curve with the WLF energy indicates that the crystal growth tends to lag behind the nucleation, but for quiescent crystallization the discrepancies are not large and are usually taken as experimental error. If, instead of the WLF activation energy, activation energy determined experimentally from polymer melt flow is used, (see section III.8) the agreement between the equation II.20 and experiment improves only marginally. There is still a coefficient substantially different from unity. Use of the rheologic shift factor, instead of activation energy, also improves the fit a little, though not enough. These observations lead to the suspicion that the assumption that the overall rate of crystallization is solely governed by the nucleation rate may be incorrect, at least as far as polymers are involved. The subject is discussed somewhat further in section IV.5. As imperfect as it may be, equation II.20 by Hoffman and co-workers remains for the time being the most convenient way to describe crystallization kinetics.[120]

A very significant finding, based on atomic force microscopic studies, has been reported lately:[131] growth of lamellae does not proceed at a constant rate. Authors of the paper suggest that besides the primary nucleation rate, I_0, there is a secondary nucleation on the growth surfaces. The combined nucleation rate is described as follows.

$$I = I_0 \exp\left[-\frac{4l_0\sigma_a\sigma_b}{(\Delta H)kT}\right] \times \left[-\frac{8\sigma_e\sigma_a\sigma_b}{(\Delta H)kT}\right] \times \left[-\frac{\Delta E_{act}}{R(T-T_g)}\right] \qquad \text{(II.21)}$$

where I_0 is the rate of formation of the initial nucleation, l_0 is the fold period of the initial nucleus, which may or may not be identical with the lamellae fold length, depending on the growth conditions, E_{act} actvation energy for molecular motion. The remaining notation is as in equation II.20.

The authors[131] present an excellent agreement of their experimental data with the equation. The work seems to represent a movement in a good direction, however, it is somewhat too early to estimate generality of the solution; probably, it is still incomplete.

It is well known that the rate of crystallization is affected by molecular mass. An example of experimental demonstration of such a dependence is presented in Figure II.10.[100]

In the case of polydisperse systems (in industrial practice we have always to deal with such polymers) the crystallization rate is proportional to the number average molecular mass.[101,104] It has been also reported[105,106] that the relationship between crystallization half-time and number average molecular mass goes through a minimum, tion of which varies with the temperature of crystallization.

For a lower crystallization temperature, the minimum in the rate of crytallization shifts toward lower molecular masses. These reports, however, did not find any additional confirmations. On the other hand, it has been found[35,40] that fractionation according to molecular mass may take place during crystallization of polydisperse polymers. This indicates that the molecular mass influence is strong indeed. In equation II.20 the molecular mass is reflected only indirectly through its influence on the surface energy, which increases with increasing molecular mass. For polyethylene this relationship is given in table II.2.[122]

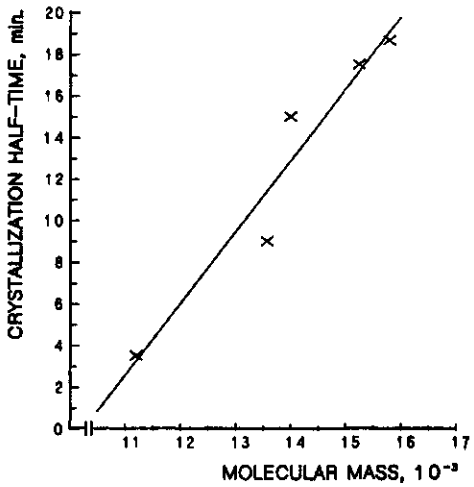


Figure II.10: *Half-time of crystallization of poly(ethylene terephthalate) in relation to the number average molecular mass.*[100]

For the sake of illustration, crystallization half-time for several polymers, as obtained from isothermal crystallization interpreted according to the Avrami equation (II.15), is quoted in Figure II.11.

Table II.2
Relationship Between Surface Free Energy
and Molecular Mass[122]

M_w	$\frac{M_w}{M_n}$	$\sigma, \frac{erg}{cm^2}$
15,700	1.10	13.1
17,000	1.11	16.0
25,200	1.08	15.3
61,600	1.09	16.3
83,900	1.10	17.4
115,000	1.15	19.4
195,000	1.11	17.9

The descriptions of crystallization kinetics do not take into account the new developments in the area of crystal structure. All the solutions suggested so far assume that polymers crystallize with the chains folded, the fold size depending on the temperature — at equilibrium melting temperature the fold size equals the size of the extended chain (it is infinite). Newer suggestions of the relationship between molecule coils in the melt, or solution, and crystallization into mosaic blocks have many logical connections with other facts, but it would be very difficult to interpret

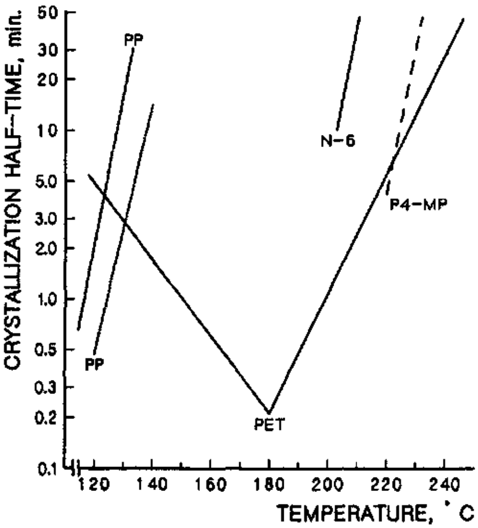


Figure II.11: *Influence of crystallization temperature on crystallization half-time.*[95,132,133] *PET - Poly(ethylene terephthalate), PP – polypropylene, N-6 – poly(aminocaprolacam) (nylon-6), P4-MP – poly(4-methylopentene).*

these in any quantitative terms. Also, the suggestion of parallelization of chains already in the coils[130] connects well with the mosaic blocks, but it also has the flavor of predetermined nucleation, and this may be difficult to reconcile with the available evidence on kinetics.

Another aspect that might have substantially larger influence than admitted so far in kinetics is rheology, especially chain entanglements and relaxation processes.

II.3 Polymer Solutions

Even though macromolecules dissolve more slowly, with more difficulty, and usually solutions of relatively low concentration are obtained, there are similarities between them and the solutions of low molecular mass compounds. If a polymer has cross linked structure, which usually forms a tridimensional grid, the molecules cannot be fully separated and a solution cannot be formed. If under such circumstances a solvent penetrates into the network, it swells it: a *polymer gel* is formed.

The similarity between solutions of polymers and of low molecular mass compounds permits that the classic general thermodynamics of solutions may be applied also for polymer solutions, though with qualified success.[134–136] In agreement with the second law of thermodynamics, the Gibbs' free energy G is related to enthalpy, H, entropy, S, and temperature by the following equation:

$$G = H - T\,S = U + p\,V - T\,S \tag{II.22}$$

where U is internal energy, p represents pressure, and V stands for volume.

The change of Gibbs' energy resulting from the addition of one mole of a component i to an infinite volume of a solution is named partial molar Gibbs' energy, or *chemical potential*, μ_I:

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_i} = \bar{G}_i = \mu_i \tag{II.23}$$

After some mathematical manipulations which are described in the textbooks of polymer physics or thermodynamics one may arrive at the relationship:

$$G = H - T\ S = U + p\ V - T\ S \tag{II.24}$$

where U is internal energy, p represents pressure, and V stands for volume.

Mathematical manipulations lead further to the relationship:

$$\mu_i = \mu_i^o + R\ T\ ln a_i = \mu_i^o + R\ T\ ln(x_i \gamma_i) \tag{II.25}$$

where μ_i^o is the chemical potential of a pure substance. The relative activity, a, may be separated into the mole fraction, x_i, and the coefficient of activity, γ_i. While the contribution of the mole fraction is called the ideal component, the contribution resulting from the coefficient of activity is called the *excess function*:

$$\Delta\mu_1 = \mu_i - \mu_i^o = R\ T\ \ x_i + R\ T\ ln c_i = \Delta\mu_i^i + \Delta\mu_i^e \tag{II.26}$$

According to the magnitude and sign of the excess function the solutions may be classified into four types: ideal, athermal, regular, and real (irregular). If a solution is ideal then the contribution to Gibbs' energy results from the ideal entropy of mixing, the enthalpy is zero. In athermal solutions the enthalpy of mixing is equal zero but the entropy of mixing is different than the ideal. In regular solutions, enthalpy of mixing is not zero, and there is no excess of entropy of mixing. For irregular solutions the enthalpy of mixing and the excess entropy of mixing are different from zero.

In macromolecular science we have the notion of θ-solutions. These are pseudoideal solutions where the enthalpy of mixing and the excess of entropy of mixing compensate each other. The exact compensations usually take place at some temperature, specific for the system, which is called the *theta temperature*. The θ-solutions behave like ideal solutions, though by definition they are not ideal, as the enthalpy of mixing and excess entropy of mixing are different from zero. Also, ideal solutions are independent from temperature, while the behavior of θ-solutions is temperature dependent.

An amount of energy equal to $N\ z\ \epsilon/2$ per one mole is needed to separate molecules at an infinite distance; here z is the number of neighbors, and ϵ is the energy per bond, N is Avogadro's number. This energy equals the internal molar energy of evaporation, ΔE_{vap}, and in relation to the molar volume, V , one may write:

$$e_j = \frac{\Delta\ E_{vap}}{V_j} = -0.5\frac{N\ \epsilon\ z}{V_j} \tag{II.27}$$

The quantity e is called *cohesive energy density* and the square root of the cohesive energy density is called *solubility parameter*: δ:

$$\delta_j \equiv e_j^{\frac{1}{2}} \tag{II.28}$$

Mixing of solvent, s, and polymer, p, produces two polymer - solvent bonds at the expense of one solvent - solvent bond and one polymer - polymer bond. The energy change is then:

$$2\ \Delta\ \epsilon = 2\ \epsilon_{ps} - (\epsilon_{ss} + \epsilon_{pp}) \tag{II.29}$$

In accordance with quantum mechanics considerations, the interaction of two different spherical molecules on the basis of dispersion forces is equal to the geometric mean of the interaction energies of the involved molecules between themselves. One may write then:

$$\epsilon_{ps} = -\left(\epsilon_{ss} \cdot \epsilon_{pp}\right) \tag{II.30}$$

Equation II.29 may be rewritten as:

$$-2\ \Delta\epsilon = (\epsilon_{ss}^{\frac{1}{2}})^2 - 2\ \epsilon_{ps} + \epsilon_{pp}^{\frac{1}{2}})^2 \tag{$II.29\,a$}$$

And from equations II.29a and II.30 in relation to the molar volume

$$\Delta\ \epsilon = -\frac{1}{2}\ \left(|e_s s|^{\frac{1}{2}} - |e_{pp}|^{\frac{1}{2}}\right)^2 \tag{II.31}$$

By the definition of the solubility parameter and in relation to the molar volume one may write :

$$\Delta\epsilon = -\frac{1}{2}\,(\delta_s - \delta_p)^2 \tag{II.32}$$

Equation II.32 represents the basis of the frequently used practical system of predicting expected solubility. If there is a large difference in the absolute value of the cohesive energy densities, then there will be essentially no interaction, and no dissolution will take place. The same is true in relation to the solubility parameters. If, on the other hand, the difference between the two solubility parameters (or cohesive energy densities) is zero, then the polymer will be well soluble. The question arises: How large a range around zero still allows for dissolution to take place? The empirically found answer is: between ±0.8 and ±3.4. The uncertainty of the answer lies in the fact that the solubility parameter is considered to consist of three components: $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$, related to dispersion, dipole, and hydrogen bonding forces, respectively. Dispersion forces do not vary appreciably, but the other components do. Consequently, the solubility parameters are classified for polarity and hydrogen bonding. Even with this differentiation, the system is not fool-proof, it gives only orientational predictions. The old rule that "like dissolves like" is not to be forgotten in practical considerations of solubility.

The solubility parameters may be calculated from equation II.27, and the necessary data for solvents are tabulated in literature. Since polymers cannot be brought into vapor state, the solubility parameters may be determined only indirectly. It is important to stress that polymer solubility is very "sensitive", it may be affected by differences seemingly as small as distribution of substituents along the chain, not to speak of stereoregularity of the chain, and the like.

With the help of statistical thermodynamics; the equation for molar enthalpy of mixing has been derived as:[1]

$$\Delta\ H = R\ T\ x_s\ \phi_p\ (\chi_0 + \sigma\ \phi_p) \tag{II.33}$$

where

$$\chi = \frac{z\ X_s\ \Delta\epsilon}{k\ T} \tag{II.34}$$

and

$$\chi = \chi_0 + \sigma\phi_p \tag{II.35}$$

The designations in equations II.32 to II.34 are: x is mole fraction, ϕ is volume fraction, X is number of segment units, z stands for the number of neighbors, N is the number of molecules, χ represents the Flory - Huggins polymer solvent interaction parameter k, T, R, have the conventional meaning. The Flory - Huggins interaction parameter, χ , is assumed to have a linear dependence on the volume fraction of polymer with the slope of σ. This is correct for some polymers, and with some approximation for the others; for lower concentration the assumption is mostly correct. The reduced molar Gibbs energy of mixing, in view of the above, may be given as

$$\frac{\Delta\bar{G}}{RT} = \frac{\phi_s\phi_p\chi_0 + \phi_s\vartheta_p^2\sigma + \phi_s \ln\phi_s + X_sX_p^{-1}\phi_p\ln\phi_p}{X_s} \tag{II.36}$$

Figure II.12 represents the reduced molar energy of mixing as a function of the volume fraction of a polymer. The different curves are calculated for the degree of polymerization of 100 and solvent of $X_s = 1$. The interaction parameter is as given on the graph. The temperature slope, σ, is taken as zero. For the sake of comparison, an additional curve for the degree of polymerization of one (it is for the monomer) is given with $\chi = 0.5$. From the graph one may easily appreciate what an increase in the degree of polymerization does to solubility, not to speak of the influence of the interaction parameter.

Along similar lines of statistical thermodynamic reasoning, one may give formulations for the chemical potential of solvent:

$$\Delta\mu_s = RT\left[(\chi_0 - \sigma + 2\sigma\chi_p)\,\phi_p^2 + ln\,(1-\phi_p) + (1 - X_s/X_p)\,\phi_p\right] \tag{II.37}$$

and chemical potential for polymer:

$$\Delta\mu_p = RT\left[(\chi_0\phi_s + 2\sigma\phi_p\phi_s - 1) \times \times\phi_sX_p/X_s + \phi_s + \ln\phi_p\right] \tag{II.38}$$

Figure II.13 presents the chemical potential of a solvent with degree of polymerization of one ($X_s = 1$) as a function of volume fraction of polymer, ϕ_p, of

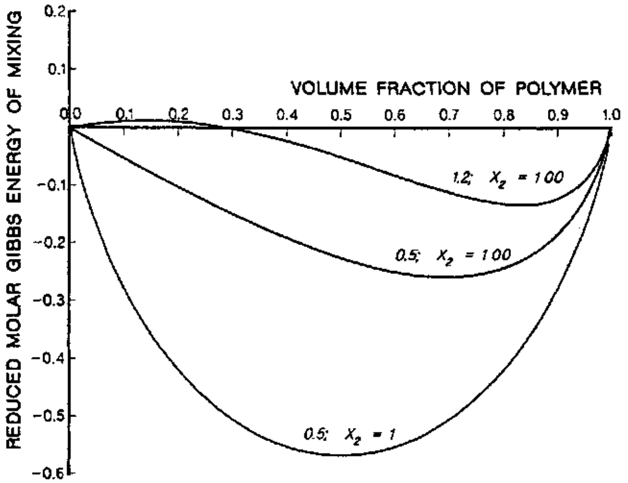


Figure II.12: *Reduced molar Gibbs energy of mixing as a function of volume fraction of a polymer. Data for the degree of polymerization of 100 and various values of the interaction parameter.*

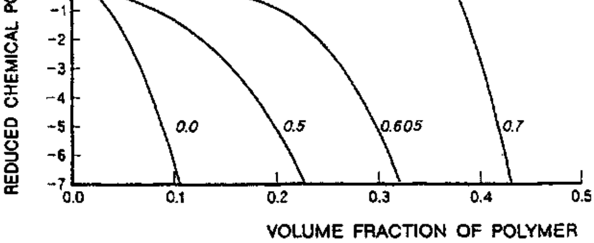


Figure II.13: *Reduced chemical potential of solvent* ($X_s = 1$) *as a function of the volume fraction of a polymer of degree of polymerization* (X_p) *of* 100. *Parameter: polymer - solvent interaction,* χ.

degree of polymerization of 100 · ($X_p = 100$). The calculations for different polymer - solvent interaction parameters have been performed using equation II.36 with slope $\sigma = 0$. With the increasing value of the interaction parameter, the initial portion of the curve becomes more extended and seemingly flatter, though a minimum, initially insignificant, forms. At higher values than some critical χ, a small minimum and a large maximum form.

The chemical potentials, $\Delta\,\mu_s$ and $\Delta\,\mu_p$, may be obtained by extrapolation of the line tangent to the function $\Delta\,G\,/\,R\,T = f|;(\phi_p)$. The equation of the tangent line is

$$Y = A + B\phi_p \tag{II.39}$$

where

$$B = N_p\,X_p\,\left[\left(\frac{\Delta\,\mu_p}{X_p}\right) - \left(\frac{\Delta\,\mu_s}{X_s}\right)\right]\phi_p^{-1} \tag{II.39 a}$$

and

$$A = \frac{N_p\,X_p\,\Delta\,\mu_s}{\phi_p\,X_s} \tag{II.39 b}$$

The final relationships are then

$$\lim_{\phi\to 0} Y = \frac{N_p\,X_p\,\Delta\,\mu_s}{X_s\,\phi_p} \tag{II.40}$$

$$\lim_{\phi\to 1} Y = \frac{N_p\,\Delta\,\mu_p}{\phi_p} \tag{II.40 a}$$

There is no theory which would describe solubility adequately, completely, and with few exceptions. For this reason, development of a good solution system requires a great deal of experimental work; detailed thermodynamic measurements are to be highly recommended, despite the fact that they are so laborious. However, it is still good to remember the old rule that *"like dissolves like"*.

Some polymers are capable of association in solution. The association is usually due to some specific groups, often end groups. Hydrogen bonding is one of the strongest and most common, but other types of associating forces may be involved. Some stereoregular polymers are capable of the formation of mutually complementary stereo structures – stereo complexes. The associated solutions behave, naturally, like solutions of polymers of appropriately higher molecular mass.

One of the more important and characteristic properties of polymer solutions is viscosity. This topic is treated briefly in section III.7.

II.4 References

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