

THEORY OF NUCLEATION AND CRYSTAL GROWTH OF POLYMERS IN CONCENTRATED SOLUTIONS

H. G. ZACHMANN

*Institut für Physikalische Chemie der Universität Mainz,
Mainz, BRD*

ABSTRACT

The process of crystallization in concentrated solutions depends strongly on the rate of crystallization and the rate of long range diffusion of the polymer chains. If the crystallization proceeds slowly compared to diffusion, this type of crystal nucleus will be formed for which the free energy of nucleation is smallest. By taking into account entropy effects which are characteristic for chain molecules one can show that the crystal with smallest free energy of nucleation is a crystal with almost regular chain folds on the surfaces. The influence of supercooling, concentration and molecular weight on the thickness and growth rate of such crystals is discussed.

If the crystallization proceeds rapidly compared to the large range diffusion each part of the chain will crystallize as far as possible at the same place where it is lying in the solution. The nucleation process is not governed by thermodynamics. The type of crystal which is formed depends in this case on the concentration and the order of the chains in solution. A single parameter has to be introduced in the theory: the probability p that a new molecule is incorporated into the crystal. If p is large, crystals with loose loops with comparatively large end-to-end distances will be formed. With decreasing p the case of short regular folds with adjacent reentry is approached. In dilute solutions small values of p can be expected. With increasing concentration p increases, provided that the polymer molecules penetrate each other.

A. INTRODUCTION

Experiments have shown that polymers crystallize from dilute solutions in the form of lamellae. The lamellae have a uniform thickness of about 100 Å. The molecules are oriented perpendicular to the basal plane of each lamella and fold back at the upper and lower surface of the lamella. Possible models for the arrangement of the chains in the crystals are shown in *Figure 1*. Some investigators¹ assume that the folds are regular and as short as possible as indicated in *Figure 1a* (adjacent reentry model), others^{2,3} think of loose loops as shown in *Figure 1b* ('switch-board' model). In addition to the folds or loose loops chains with one free end ('cilia') have also to be assumed⁴.

Lamellar crystals are also formed in concentrated solutions. Here however the crystals are often bound together forming bigger units which, in some cases, show a structure more or less similar to that of the spherulites obtained from the melt⁵. As a consequence, in addition to loops, folds and chains with free

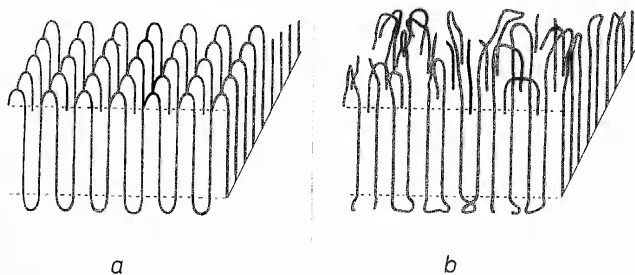


Figure 1. Possible models for the arrangement of the molecules in single crystals grown from solutions¹⁵.

ends, tie molecules connecting two different crystals may also emerge from the crystal surfaces.

How can these results be explained? The theory of the crystallization of polymers has been developed in a number of papers. The first investigations were published by Hoffman and Lauritzen⁶. These authors *assumed* that crystals with regular folds are formed. With the help of this assumption they showed that the crystals must have uniform thickness, namely the thickness of the critical nucleus. A more refined calculation of crystal thickness, taking into account variation in the thickness as well, was performed later by Frank and Tosi⁷, Price⁸, and Lauritzen, Di Marzio and Passaglia⁹. Quite recently, Sanchez and Di Marzio¹⁰⁻¹² extended the theory to polymers of finite molecular weight and calculated the influence of molecular weight, as well as of the concentration, on the crystal growth rate. But none of these theories explains chain folding: they are theories on crystal growth rates, distribution of crystal thickness, etc. under the assumption that folding of the chains occurs.

How can chain folding itself be explained? In dilute solutions, chain folding results simply from the fact that the molecules crystallize one by one. If a single molecule forms a crystal it *has* to fold more or less regularly. This is not true, however, for concentrated solutions. Here, allowance must be made for two or more molecules crystallizing at the same location. As a consequence, the formation of bundle-like crystals is possible and seems quite probable. Are there also thermodynamic or kinetic reasons which favour chain folding in a system of concentrated chain molecules? If so, what is the most probable distribution of the lengths and the end-to-end distances of the loops?

These questions have been investigated extensively in our laboratory in recent years. It has been shown that chain folding can occur under certain conditions both in concentrated solutions and in the melt. It is a consequence of entropy effects which are characteristic for chain molecules. One has to distinguish between two cases:

(1) Crystallization proceeds slowly compared to long range diffusion. In this case crystals with regular folds are formed because such crystals have a minimum of free enthalpy of nucleation^{13, 14}.

(2) Crystallization proceeds rapidly compared to long range diffusion. In this case each part of a molecule is crystallizing near the place where it is lying in the solution or melt respectively. In dilute solutions, again, crystals with regular folds are formed. In concentrated solutions and in the melt, however,

regular folds are formed only if the molecules do not penetrate each other before crystallization¹⁵, otherwise mainly loose loops and tie molecules are found.

In the following we will review more extensively all the theories mentioned. We shall not discuss them in historical order but shall combine them in such a way that we obtain a systematic theory for the crystallization of concentrated solutions.

B. THEORY OF SLOW CRYSTALLIZATION

1. Which type of crystal is formed?

In a concentrated solution, in principle different types of crystals can be formed: bundle-like crystals (*Figure 2a*), crystals with irregular loose loops (*Figure 2b*), crystals with regular folds (*Figure 2c*), and crystals which are connected to other crystals by tie molecules (*Figure 2d*). Of course, a mixture

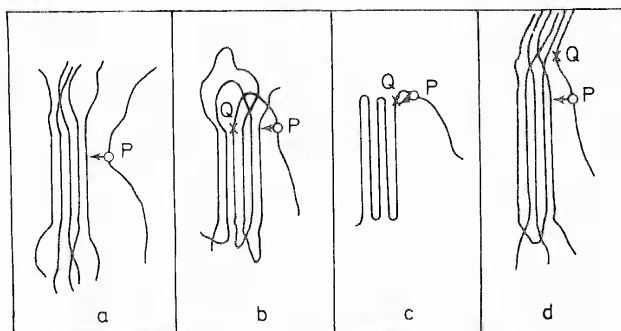


Figure 2. Different types of crystals which may be formed in a concentrated solution.

of all these types can also occur. Which type will actually be formed?

In order to answer this question we have to apply the theory of nucleation. The number of crystal nuclei formed in unit time is given¹⁶ by

$$I = \text{const.} \exp(-\Delta G_A^*/kT) \quad (1)$$

ΔG_A^* is the free enthalpy of nucleation, k is the Boltzmann constant and T is the temperature. We will first calculate ΔG_A^* for a cylindrical crystal of small molecules. The free enthalpy necessary to form such a crystal is given by⁶

$$\Delta G = \pi \rho^2 l \rho_k \Delta G^\circ + 2\pi \rho^2 \sigma_c + 2\pi \rho l \sigma_t \quad (2)$$

ρ is the radius of the base, l the height, ρ_k the density, σ_t and σ_c the free surface energy at the lateral surface and the two other surfaces respectively. ΔG° is the difference in bulk free enthalpy between the crystal and the melt per unit of mass. ΔG as a function of l and ρ is represented by a plane with a saddle point (see *Figure 3*). For small crystals ΔG increases with increasing l and ρ due to the formation of additional surface, crystal growth is not favoured thermodynamically. After having reached a critical size, ΔG decreases with further growth, and further crystallization is thermodynamically favoured. The amount of free enthalpy ΔG_A , which is necessary to reach the critical size so

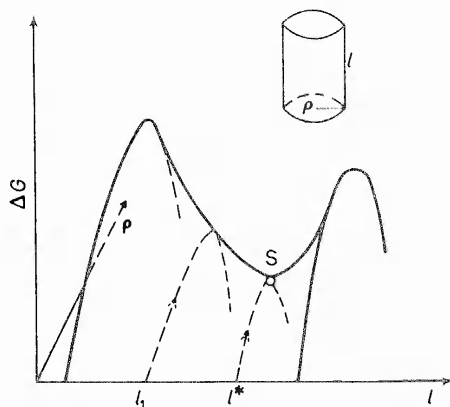


Figure 3. Amount of free enthalpy ΔG for formation of a cylindrical crystal as a function of the crystal dimensions l and ρ .

that further growth is favoured, depends on l . For a certain value of l , denoted by l^* , ΔG_A assumes a minimum ΔG_A^* , called free enthalpy of nucleation. ΔG_A^* , l^* and ρ^* are the values corresponding to the saddle point S. One obtains^{6, 17}

$$\Delta G_A^* = \frac{8\pi\sigma_l^2\sigma_c}{\rho_k(\Delta G^\circ)^2} \quad (3)$$

$$l^* = -\frac{4\sigma_c}{\rho_k\Delta G^\circ} \quad (4)$$

and

$$\rho^* = -\frac{2\sigma_l}{\rho_k\Delta G^\circ} \quad (5)$$

In the case of long chain molecules the situation is more complicated. The essential difference between the crystallization of small molecules and of long chain molecules is illustrated in *Figure 4*. With small molecules, in an elementary step of crystallization, it is always a complete molecule which passes from the solution into the crystal (left side of *Figure 4*). The entropy change caused by crystallization is the same for each molecule. With polymers, in an elementary step of crystallization only a small part of the molecule, say a monomer unit, crystallizes (see *Figure 4*, right side). The change of entropy connected with this process is different from unit to unit. This is due to the fact that not only the entropy of the crystallizing unit is changed but usually also the entropy of the rest of the chain which is not crystallized. This can be seen very clearly in the process indicated in *Figure 2b*. When the unit P crystallizes the chain between Q and P becomes a chain with two fixed ends. Before this process it had one end, namely P, free. Therefore the number of conformations and the entropy of the chain QP decrease markedly when P crystallizes.

The entropy change mentioned, ΔS_k , of the part of the chain which is not crystallized but is hanging out of the crystal, varies for different types of

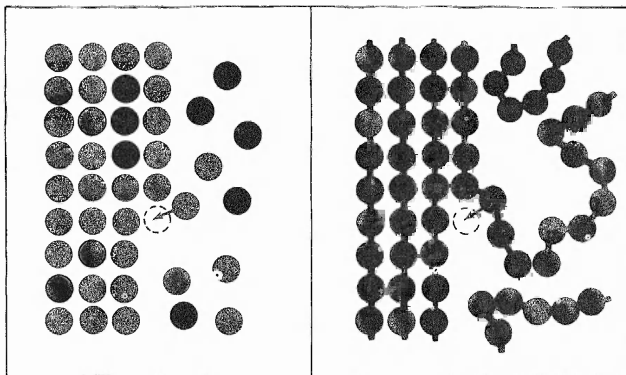


Figure 4. Elementary step of crystallization in a low molecular weight substance and in a polymer.

crystals*. In order to take this effect into account, equations 2–5 have to be modified^{13, 14}. If ΔS_k is the same for each chain the total additional change of entropy during formation of a crystal is proportional to the number of chains coming out of the surface of the cylinder. Therefore this entropy acts in the same way as an additional contribution to the surface free energy σ_e . If we denote this additional contribution by σ'_e we can write

$$\sigma'_e = v_0 k T \Delta S_k \quad (6)$$

where v_0 is the number of chains emerging from the unit area. Therefore, in order to take the entropy effect mentioned into account we have simply to replace σ_e by $\sigma_e + \sigma'_e$ in equations 2–5. In particular, for the free enthalpy of nucleation we obtain¹³

$$\Delta G_A^* = \frac{8\pi\sigma_e^2(\sigma_e + \sigma'_e)}{\rho_k (\Delta G^\circ)^2} \quad (7)$$

We will now show that for various types of nuclei σ'_e is different¹⁴. Therefore according to equations 7 and 1 ΔG_A^* and the nucleation rate I are different. This type of crystal, which has the lowest value of σ'_e and therewith the largest value of I , will be formed most quickly and therefore will dominate.

We consider at first the growing of a bundle-like crystal composed of chains hanging out of another crystal. Such a process is indicated in *Figure 2d*. Every time a chain is added to the growing crystal, a chain with two fixed ends (tie molecule) is created, for example the chain QP in *Figure 2d*. The fixing of the chain end is connected with a big loss in entropy ΔS_k . *Figure 5* gives this entropy change as a function of chain length measured in number of units of the chain. The parameter h is the end-to-end distance. When one assumes for example an end-to-end distance of 100 nm and a chain length of 600 nm one obtains $\Delta S_k = 25 k$. This corresponds in the case of polyethylene to an additional surface free energy $\sigma'_e = 700 \text{ erg cm}^{-2}$.

We consider next a crystal with loose loops and nonadjacent reentry (*Figure 2b*). Here also, during the growth process, chains with fixed ends are

* The considered change of entropy of the part of the molecule which is not crystallized is always negative. Therefore the introduced decrease of entropy, ΔS_k , is always positive.

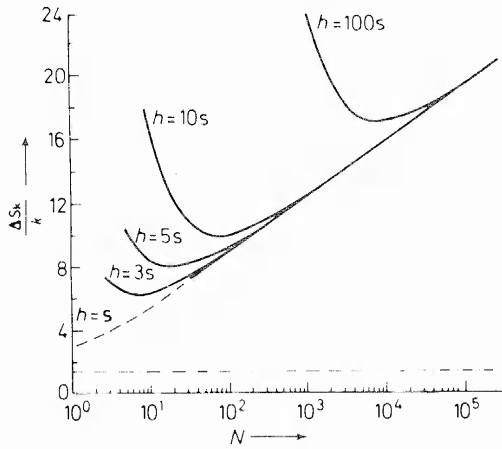


Figure 5. Decrease of entropy occurring with fixing the ends of a chain in a distance h as a function of the number N of monomer units of the chain¹³.

created at the crystal surfaces, namely the loops. However, the end-to-end distance of the chain-loops can be considerably smaller than in the first case. Therefore σ'_c also is not so large. When $h = 10$ and $N = 50$ one obtains $\Delta S_k = 9k$ and $\sigma'_c \approx 400 \text{ erg cm}^{-2}$. σ'_c decreases further with decreasing values of h .

If the loop length N and end-to-end distance h assume the smallest possible values, the loose loop model goes over into the adjacent reentry model shown in Figure 2c. The shortest loop with adjacent reentry consists in the case of polyethylene of 4 CH_2 -units which are outside the crystal lattice. The fixing of the chain end, in this case, gives rise¹⁸ to a surface free energy of only 30 erg cm^{-2} . We have also to consider that there is an increased number of gauche-conformations in such a short loop, which corresponds to about 70 erg cm^{-2} . Therefore the total additional surface free energy σ'_c is about 100 erg cm^{-2} . A slight increase of loop length and end-to-end distance might decrease σ'_c a little. This cannot be calculated exactly because the chain statistics applied in our calculations are not valid for very short chains. In any event, however, comparatively large loops and end-to-end distances lead to much higher values of σ'_c , as shown above. Therefore one can say that in the case of chain folding the smallest value of σ'_c is obtained for comparatively short loops with adjacent or almost adjacent reentry.

Lastly we consider a bundle-like crystal formed of molecules which were completely amorphous before they were incorporated into the crystal (Figure 2a). In this case, on both surfaces chains with one free end hang out of the crystal. Each of these chains loses entropy when the molecule to which it belongs is attached to the crystal. There are two reasons for the entropy loss: (i) The number of conformations of the chain considered is reduced because the volume available to this chain is limited by the crystal. Owing to this effect conformations like that shown in Figure 6 are no longer possible. Figure 7 shows the loss of entropy ΔS_k as a function of chain length. If, for example, the

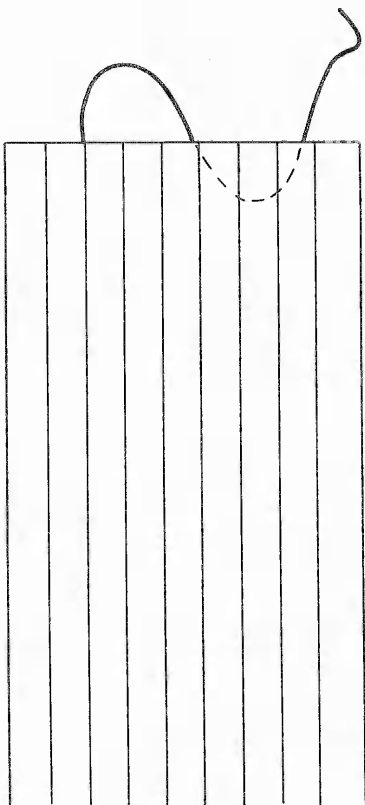


Figure 6. Example of an impossible conformation of a chain hanging out of a crystal¹⁹.

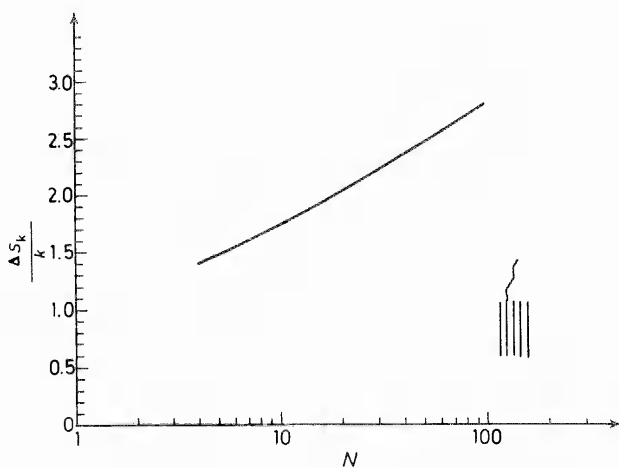


Figure 7. Decrease of the entropy of a chain with one free end caused by the limitation of the volume as a function of the number of units of the chain²⁰.

chain hanging out of the crystal consists of 1000 units, the loss of entropy $\Delta S_k = 4k$ corresponding to an additional surface free energy of 120 erg cm^{-2} . (ii) The chain as a whole can no longer perform a translational diffusion after part of it is incorporated into the crystal. The entropy caused by diffusion is small compared to the conformational entropy of the whole chain. It is not small however compared to the conformational entropy of a few units which are incorporated into the crystal. Therefore it cannot be neglected in nucleation processes. The considered entropy change is given according to Flory-Huggins theory by²¹

$$\Delta S_i = k \ln N_0/v_2 \quad (8)$$

where N_0 is the number of units of the chain and v_2 the mole fraction of polymer. For $N_0 = 2000$ and concentrated solution the factor v_2 can be neglected and one obtains $\Delta S_i/2 = 3.80 k$. This value corresponds to an additional surface free energy of $\sigma'_e \approx 120 \text{ erg cm}^{-2}$. Both effects together give a value of $\sigma'_e = 240 \text{ erg cm}^{-2}$. According to Hoffman and Lauritzen²² one has to consider also a third contribution of about 100 erg cm^{-2} from the special packing conditions.

The results obtained are summarized in *Figure 8*. Here again one can see

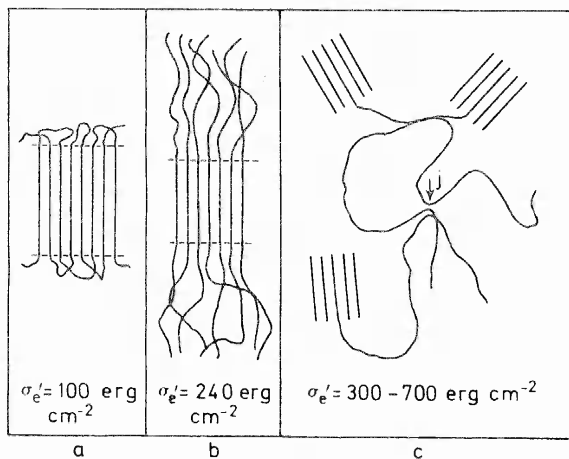


Figure 8. Additional surface free energies for different types of crystals¹⁴.

the crystal with short loops and almost adjacent reentry, the bundle-like crystal formed of chains which were completely amorphous before incorporation into the crystal, and a crystal which is formed of chains hanging out of another crystal. The corresponding additional surface free energies σ'_e are given below each crystal type. One sees that the crystal with folds has the smallest value of σ'_e . We have to stress here, that in our estimation of the σ'_e values we have already got an upper limit for the folded chain crystal and lower limits for the other types of crystals. From this result we conclude that the crystal with short folds with almost adjacent reentry is thermodynamically favoured.

2. Crystal thickness

After having seen that crystals with almost regular folds are also formed in concentrated solution, we can apply the theories developed for folded chain crystallization. We will first calculate the thickness of the crystals according to the theory of Lauritzen and Hoffman⁶. The theory starts with the statement that crystals with chain folds can grow only in a lateral direction; an increase in thickness is combined with difficult diffusion and is very slow. Therefore during crystal growth l is constant and ρ is increased. The change in free enthalpy during crystal growth with a constant value of l is indicated for some values of l by the dashed lines in *Figure 3*. One sees that the amount ΔG_A of free enthalpy which is necessary to create a stable crystal varies with l . ΔG_A assumes the minimum value ΔG_A^* if l equals the thickness l^* of the critical nucleus defined by the saddle point. In principle crystals with all values of l will be formed. But according to equation 1 the nucleation rate for crystals of different thickness l is given by

$$I = \text{const. exp}(-\Delta G_A/kT) \quad (9)$$

Therefore the overwhelming number of crystals will have the thickness l^* for which ΔG_A is at a minimum and I at a maximum.

As mentioned in the Introduction, this theory has been refined by considering also variations in thickness during growth. Without going into details, we show only some results. The curves in *Figure 9* show the calculated thickness

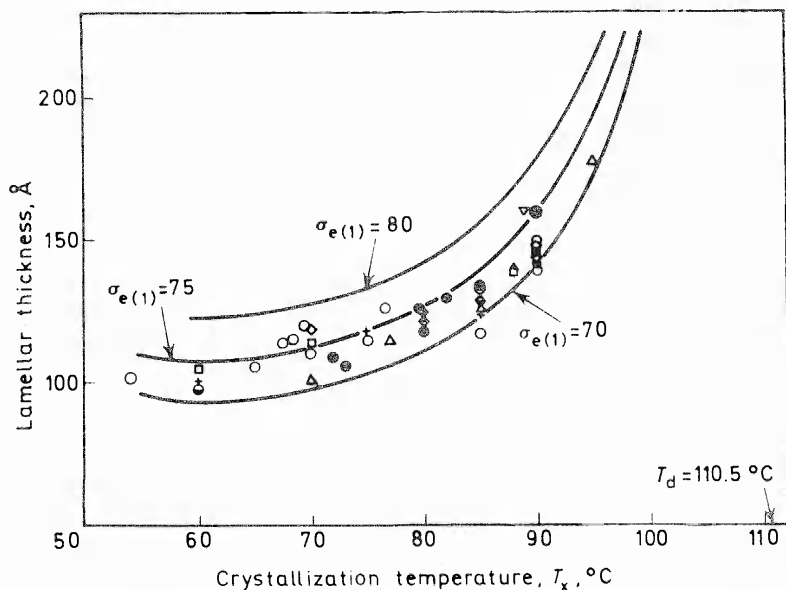


Figure 9. Lamellar thickness of chain-folded polyethylene single crystals as a function of crystallization temperature. The curves represent calculated values for different values of surface free energy σ_e . The points represent the measured values²³.

of the lamellae as a function of crystallization temperature for different values of the surface free energy. The points have been obtained experimentally for

crystallizations from dilute solutions. No experimental results are known for concentrated solutions.

3. Growth rate

Assuming chain folding, the theory of Sanchez and DiMarzio¹⁰⁻¹² for crystal growth rates can also be applied. Growth rate is governed mainly by the rate of secondary nucleation. Sanchez and DiMarzio distinguish between two different nucleation mechanisms: nucleation by cilia, that is by chain ends hanging out of the crystal, and nucleation by chains which lie completely in the melt. If S^c and S^s are the two nucleation rates respectively, and w^c and w^s the probabilities for the two processes, the total nucleation rate is given by

$$S = w^c S^c + w^s S^s \quad (10)$$

S^c and S^s have been calculated separately as a function of molecular weight and concentration for the case of polyethylene in *p*-xylene. The results are shown in Figure 10. One sees that both S^c and S^s increase with increasing

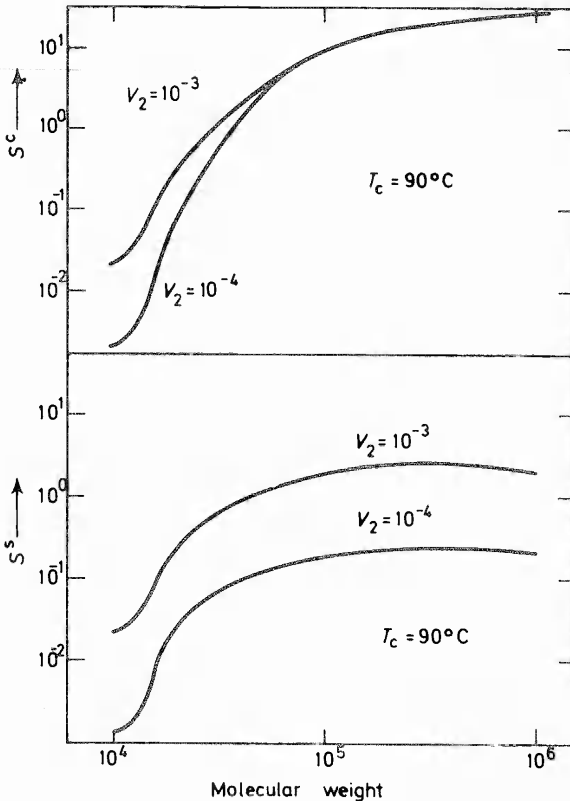


Figure 10. The relative effect of concentration on nucleation rate of solution molecules S^s and cilia S^c as a function of molecular weight¹¹.

molecular weight. The influence of concentration on S^c is not the same as on S^s . S^s increases with concentration, S^c however is almost independent of

concentration. Unfortunately only very low concentrations have been considered in the calculation.

The values w^s and w^f have not been calculated by Sanchez and DiMarzio. According to our considerations in part 1, w^s has to be much smaller than w^f .

C. THEORY OF RAPID CRYSTALLIZATION

We will next assume that crystallization proceeds rapidly compared to long range diffusion¹⁵. In this case a part of the molecule which is reached by the crystal surface will be incorporated by the crystal, independently of whether the thermodynamically most favoured configuration is reached by this process. In *Figure 11* we see two molecules penetrating each other, before

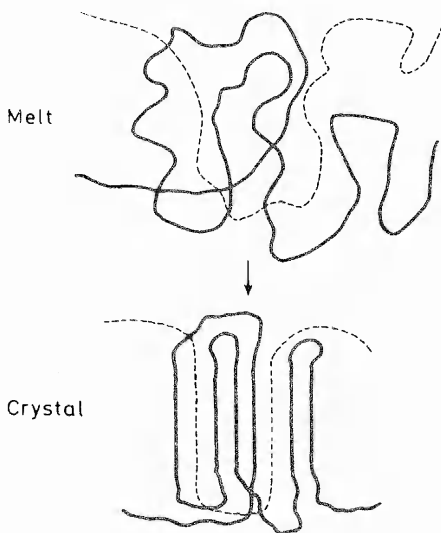


Figure 11. Schematic representation of the crystallization process if crystallization proceeds rapidly compared to long range diffusion¹⁵.

crystallization (above) and after crystallization (below). Generally, those parts of the molecules which are neighbours in the concentrated solution remain also neighbours in the crystal.

Figure 12 illustrates the different crystallization processes we have to consider. Crystal growth has proceeded so far that at location P a chain has to be added. In any stage of crystallization one will find on the crystal surface sharp folds, loops with nonadjacent reentry and chains with one free end. The amounts of the different types of chains may vary but in principle all these types have to be considered. We have to distinguish between four possible processes:

- (a) A part of a new chain, which before lay completely in the melt, is incorporated in the crystal. In this case a chain with one free end is created both in the upper and in the lower surface.
- (b) A part of a chain hanging out of the upper surface can be incorporated in

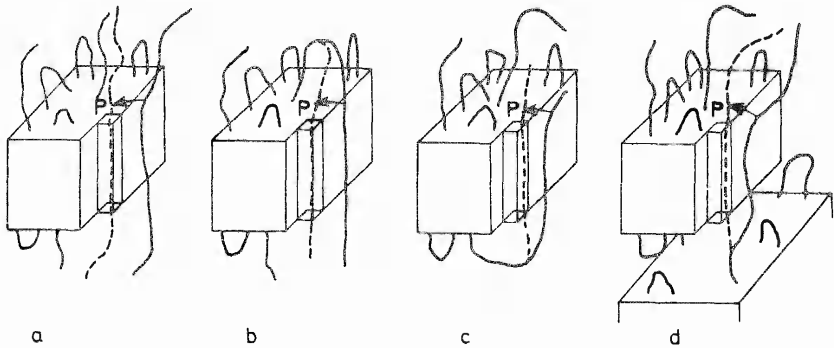


Figure 12. The different processes during crystal growth¹⁵.

the crystal. In this case a loop is formed at the upper surface and a chain with one end free at the lower surface.

(c) A part of a chain hanging out of the lower surface can be incorporated, thus forming a loop in the lower surface and a chain with a free end in the upper surface.

(d) A chain hanging out of another crystal can be crystallized, thus creating a tie molecule and a chain with one free end.

For the following calculation we need only one parameter for the characterization of the system, which we will call p : p is given by

$$p = p_1 + \frac{1}{2}p_2 \quad (11)$$

where p_1 is the probability that a new molecule, previously lying completely in the solution, is added to the crystal, and p_2 is the probability that a tie molecule is formed. In the case of dilute solutions p will be almost zero because no other molecule is in the vicinity of the molecule considered. In the case of concentrated solutions p increases with increasing concentration, provided that the molecules penetrate each other. If the molecules do not penetrate each other p is also small for concentrated solutions. Using this parameter we will derive the end-to-end distance distribution function $\omega(h)$ of the loops, that is, the number of loops which have an end-to-end distance between h and $h + 1$. The meaning of h can be seen in Figure 13.

For the calculations the following assumption is made: the probability that a loop of end-to-end distance h is formed at a certain point P is given by the number of possibilities of forming such a loop divided by the number of possibilities of forming a loop of any end-to-end distance. If $\tilde{\mu}(h)$ denotes the density of chains with one end free in distance h from point P one can write

$$\omega(h) = \frac{\tilde{\mu}(h) h \sum_N Z^*(N, h)}{\int_a^{h_{\max}} \tilde{\mu}(h) \sum_N Z^*(N, h) dh} \quad (12)$$

$Z^*(N, h)$ is the number of conformations of a chain of length N and end-to-end distance h . h_{\max} is the average length of chains with one free end and a the

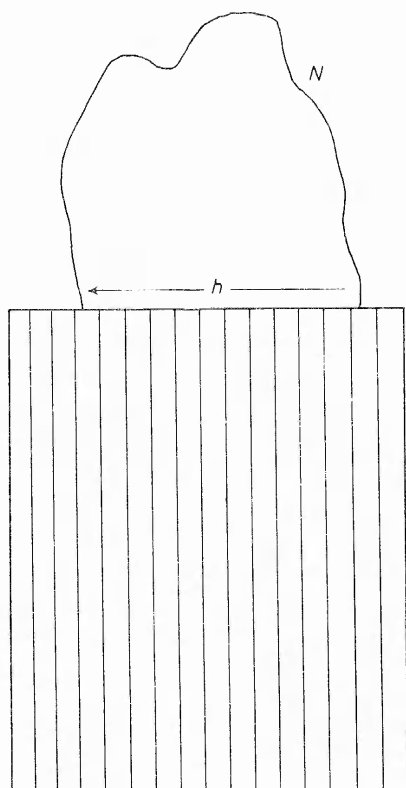


Figure 13. Definition of h and N for a loop¹⁵.

distance of neighbouring chains in the crystal. The function $\tilde{\mu}(h)$ is not known. It can be derived however from the condition that the numbers of chain ends which disappear must be equal to the number of loops formed. This condition yields a differential equation

$$\tilde{\mu}'(h) + \beta(1 - p) \sum_N Z^*(N, h) \tilde{\mu}(h) = 0 \quad (13)$$

with

$$\beta = v \left[Z \tilde{a} b \pi \int_a^{h_{\max}} \tilde{\mu}(h) h \sum_N Z^*(N, h) dh \right] \quad (14)$$

By solving this equation $\tilde{\mu}(h)$ is determined and then with help of equation 12 the function $\omega(h)$ is obtained.

The influence of the probability p on the end-to-end distribution function $\omega(h)$ for molecules consisting of $N_0 = 2000$ units is shown in Figure 14. If p has a very small value, for example 10^{-10} , which is the case in a dilute solution or in a concentrated solution in which the molecules do not penetrate each other, almost all molecules have an end-to-end distance which is smaller than

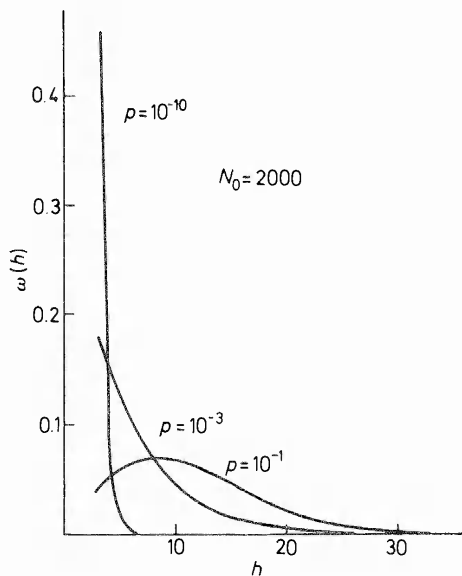


Figure 14. End-to-end distance distribution function $\omega(h)$ for different values of the probability p . N_0 = number of monomer units of a molecule.

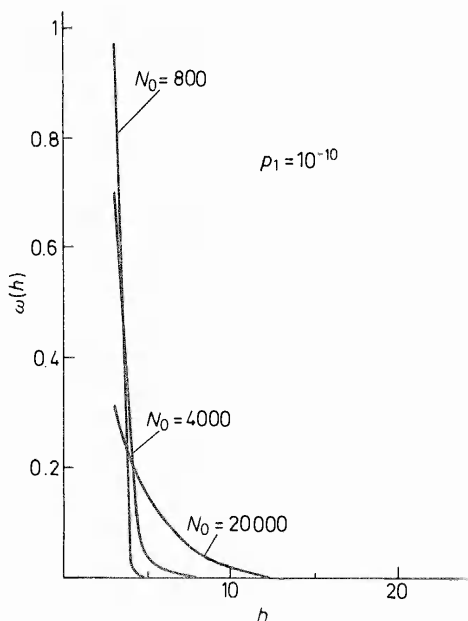


Figure 15. End-to-end distance distribution function $\omega(h)$ for molecules of different length N_0 when $p = 10^{-10}$. The length N_0 is measured in monomer units¹⁵.

5. This means that one has almost adjacent reentry. With larger values of p the distribution becomes broader and loops with greater and greater end-to-end distances occur. p increases when the concentration increases and the molecules penetrate each other. As the molecules actually penetrate each other under usual conditions, one can conclude that, with increasing concentration of the solution, the end-to-end distances of the loops become larger.

The end-to-end distance distribution is also influenced by the length of the molecules, that is by the molecular weight. *Figure 15* shows $\omega(h)$ for molecules of different lengths N_0 when p equals 10^{-10} . With increasing lengths the end-to-end distances become larger. The same is true also for other values of p as shown in *Figure 16*.

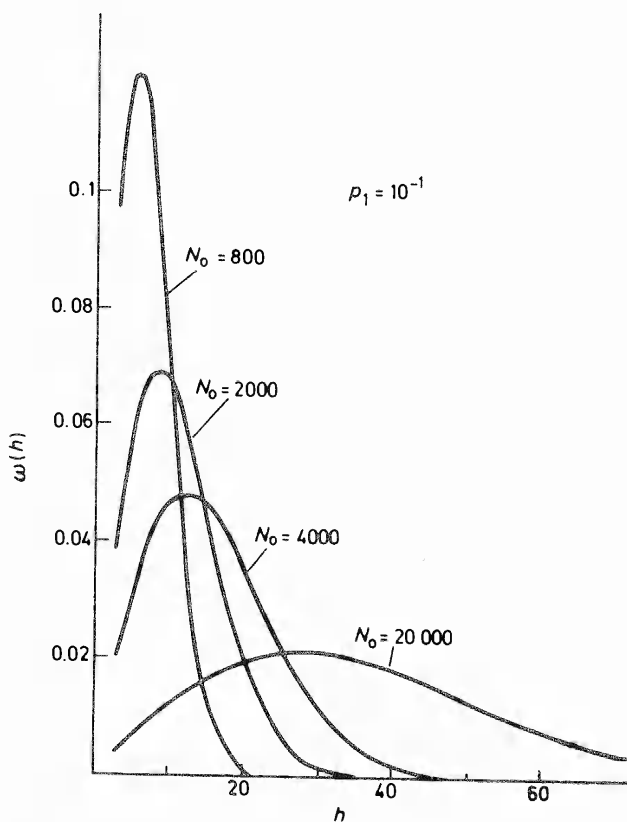


Figure 16. End-to-end distance distribution function $\omega(h)$ for molecules of different length N_0 when $p = 10^{-1}$. The length N_0 is measured in monomer units¹⁵.

Up to now, we have discussed only the end-to-end distances. The loop lengths have not been calculated. This is because the kinetic factors during crystallization do not influence the final loop lengths. The end-to-end distance

distribution established during crystallization cannot be changed later without melting the whole crystal. The loop lengths however can always be changed by comparatively simple diffusion processes and the melting of small surface layers of the crystal. Therefore the final loop lengths are not determined by kinetic but by thermodynamic factors. The kinetic parameter p influences the loop length only as far as it determines the end-to-end distances of the loops.

Calculations of the average equilibrium loop length assuming fixed ends of the loops* have been performed by methods described elsewhere^{15,18,24}. Some results are shown in *Figures 17 and 18*. The average loop length $\langle N \rangle$ increases with increasing temperature because of partial melting. Compared at the same temperature, $\langle N \rangle$ increases with increasing p and N_0 . From these results we can conclude that the loop lengths and the melting range of the crystals will increase with increasing concentration of the solution in which the crystals were grown.

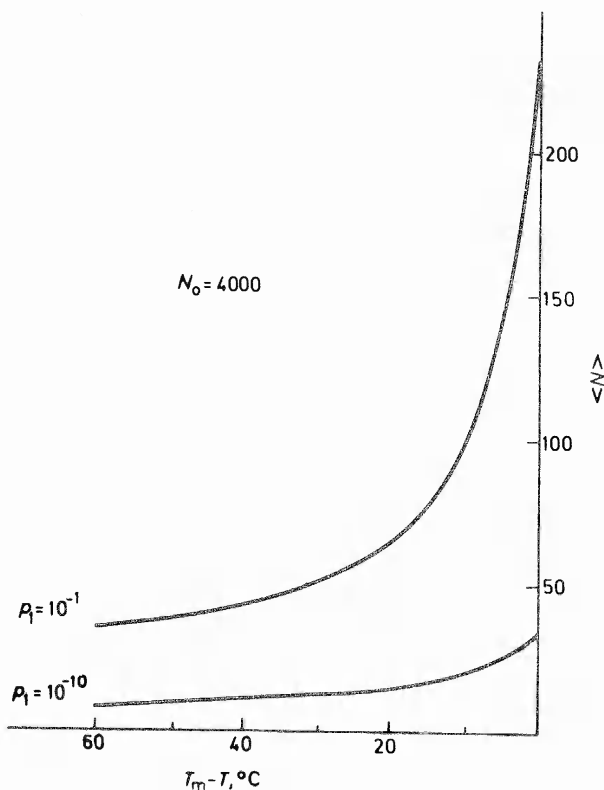


Figure 17. Average loop length $\langle N \rangle$ as a function of temperature for molecules consisting of $N_0 = 4000$ monomer units¹⁵.

* Calculations of the end-to-end distance distribution functions and the lengths of the loops when the end-to-end distance of each loop may vary, have been performed by Roe²⁵ as well as by Zachmann and Peterlin²⁴. We do not think, however, that the assumption of various end-to-end distances is fulfilled under usual experimental conditions (see discussion in Ref. 25).

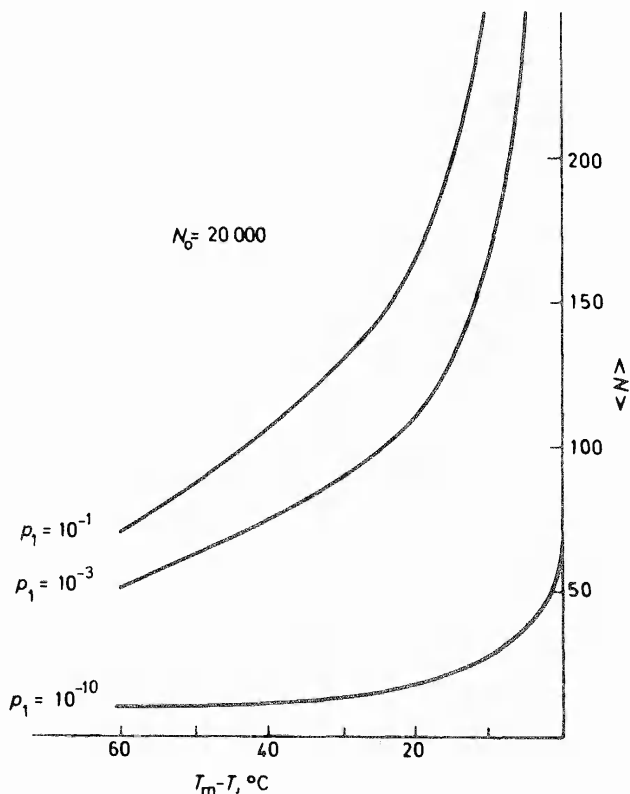


Figure 18. Average loop length $\langle N \rangle$ as a function of temperature for molecules consisting of $N_0 = 20000$ monomer units¹⁵.

REFERENCES

- ¹ A. Keller, *Phil. Mag.* **2**, 1171 (1957).
- ² P. I. Flory, *J. Amer. Chem. Soc.* **84**, 2857 (1962).
- ³ E. W. Fischer and R. Lorenz, *Kolloid-Z. Z. Polymere* **189**, 97 (1963).
- ⁴ P. H. Lindenmayer, *Kolloid-Z. Z. Polymere* **231**, 593 (1969).
- ⁵ F. Khoury, *J. Res. Nat. Bur. Standards* **70A**, 29 (1966); I. Heber, *Kolloid-Z. Z. Polymere* **189**, 112-114 (1963).
- ⁶ J. I. Lauritzen Jr and J. D. Hoffman, *J. Res. Nat. Bur. Standards* **64A**, 73 (1960).
- ⁷ F. C. Frank and M. Tosi, *Proc. Roy. Soc. (London)* **A263**, 323 (1961).
- ⁸ F. P. Price, *J. Chem. Phys.* **35**, 1884 (1961).
- ⁹ J. I. Lauritzen Jr, E. A. Di Marzio and E. Passaglia, *J. Chem. Phys.* **45**, 4444 (1969); J. I. Lauritzen Jr and E. Passaglia, *J. Res. Nat. Bur. Standards* **71A**, 261 (1967).
- ¹⁰ I. C. Sanchez and E. A. Di Marzio, *J. Chem. Phys.* **55**, 893 (1971).
- ¹¹ I. C. Sanchez and E. A. Di Marzio, *Macromolecules* **4**, 677 (1971).
- ¹² I. C. Sanchez and E. A. Di Marzio, *J. Res. Nat. Bur. Standards* **76A**, 231 (1972).
- ¹³ H. G. Zachmann, *Z. Naturforschung*, **20a**, 719 (1965).
- ¹⁴ H. G. Zachmann, *Kolloid-Z. Z. Polymere*, **216-217**, 180 (1967).
- ¹⁵ W. M. Ewers, H. G. Zachmann and A. Peterlin, *Kolloid-Z. Z. Polymere*, **250**, 1187 (1972).
- ¹⁶ D. Turnbull and J. C. Fisher, *J. Chem. Phys.* **17**, 71 (1949).
- ¹⁷ H. G. Zachmann, *Fortschr. Hochpolym. Forsch.* **3**, 581 (1964).
- ¹⁸ H. G. Zachmann and A. Peterlin, *J. Macromol. Sci.* **B3(3)**, 495 (1969).

H. G. ZACHMANN

- ¹⁹ H. G. Zachmann, *Kolloid-Z. Z. Polymere*, **231**, 504 (1969).
²⁰ H. G. Zachmann and P. Spellucci, *Kolloid. Z. Z. Polymere*, **213**, 39 (1966).
²¹ H. G. Zachmann, to be published.
²² J. D. Hoffman and J. I. Lauritzen Jr, *J. Res. Nat. Bur. Standards*, **65A**, 297 (1961).
²³ J. D. Hoffman, J. I. Lauritzen Jr, E. Passaglia, G. S. Ross, L. J. Frolen and J. J. Weeks, *Kolloid-Z. Z. Polymere*, **231**, 564 (1969).
²⁴ W. M. Ewers, H. G. Zachmann and A. Peterlin, *J. Macromol. Sci.* **B6**, 695 (1972).
²⁵ R. J. Roe, *J. Chem. Phys.* **53**, 3026 (1970).