Those 5-carbons in 2-alkylated end phenol rings and 2,4-disubstituted phenol rings appear at 127.4–128.4 ppm. Those 3,5-carbons in 2,6-disubstituted phenol rings are between 128.9 and 129.3 ppm, whereas 3-carbons in 2,4-disubstituted phenol rings are between 131.7 and 132.2 ppm.

All unsubstituted aromatic carbons in the 2 or the 6 position resonate in a very narrow spectral region, between 115.4 and 116.0 ppm. This was independent of the position of the phenol ring in the molecule and its substitution pattern. Likewise all unsubstituted aromatic carbons in the 4 position are between 119.9 and 120.9 ppm, irrespective of position of the phenol ring in the molecule.

The chemical shift trends noted above are tabulated in Table II for easy reference. With these results as background, the interpretation of more complex resin systems may be attempted with the view of obtaining very intimate structural and compositional detail. We intend to expand this data base by examining larger oligomers and by investigating the effects of ^{13}C chemical shifts caused by branching centers (trialkylated phenol rings).

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A New Theoretical Approach of the Secondary Nucleation at High Supercooling

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ABSTRACT: A new model for lamellar crystallization is presented. It ensures a finite crystal thickness at every supercooling. The result comes from a detailed description of the buildup of a secondary nucleus in which the segmental nature of the linear macromolecules is explicitly considered. The potentialities of the new model are illustrated by detailed calculations of the dependence of the lamellar thickness on the crystallization temperature and by considering the dependence of the crystal thickness of polyamides on the length of their repeating unit.

The dependence of the thickness of lamellar crystals, L, of polymers on the crystallization temperature, T_c, was the subject of numerous experimental and theoretical studies. In this paper, our main concern will be the overall shape of the L vs. T_c curves. It is well-known that the following general dependence of L on T_c is observed; it consists of an inverse dependence on the undercooling ΔT, at low ΔT values, tending to an invariant value beyond a certain ΔT. At low undercooling, the situation is known from the very beginning.[1] At high undercooling, the presence of the long horizontal plateau instead of an upswing in L is first observed for polyamides and polystyrene[2] and is now appreciated as generally valid.

Various suggestions were made in order to explain these experimental observations. One of these suggestions seems to be successful and leads to the well-known theory of Lauritzen and Hoffman.[3] These authors consider the effect of a physical adsorption on the surface, prior to actual crystallographic attachment onto the substrate. Such an hypothesis leads to a decrease in the driving force for the crystallization and to an increase in the critical undercooling, ΔT_c. The choice of the parameter ψ used to express the amount of the reduction of the driving force for the crystallization is critical. Decreasing ψ allowed the taking into account of a higher ΔT_c. A 0.382 value gives the best fit for the L vs. ΔT curve of the polystyrene at a supercooling as high as 190 °C. A 0.7 value gives the best fit for polyethylene at a supercooling as high as 80 °C. The choice of these ψ values is not clearly related to the chemical nature of the polymer. Lower values of ψ do not permit the avoidance of the δl catastrophe. Higher values lead to a continuous decrease in L with an increase in ΔT instead of the observed long plateau. In conclusion, it is not obvious that the Lauritzen–Hoffman theory, in this form, is the best explanation of a situation which, on experimental grounds, seems to be quite general. Therefore, we are searching for alternative explanations.

In the discussion of their results on polystyrene, Jones, Latham, Keller, and Girolamo[2a] questioned the steady state approximation, intrinsic of the usual derivation of the kinetic theory. But when the crystallization is rather slow, as in the case of polystyrene, departures from the steady state are considered as being of little significance (as noted by Jones[2a]). Moreover, it can be shown, on a theoretical basis, that the time constants involved are short and that the steady state approximation is readily usable. This particular point is to be discussed in a forthcoming paper with J. K. Platten.

A more complete discussion of the complexity of such a process as the attachment of a long fold stem of flexible molecular chain to the crystal seems to be another important point. The question was raised by Frank and Tosi[4] (see also Jones[2a]) a long time ago. Frank and Tosi established more clearly the distinction between two situations. In the first situation, a range of configurations, corresponding to the partial attachment of a stem, is considered as belonging to one stage. In the second situation, they assume that in the attachment process of a

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stem of, say, 100 CH_2 units on the crystal, such a stem attaches in successive segments (or "flexibility units") of, for instance, 10 CH_2 groups. In the work of Frank and Tosi, the primary object of the comparison between the coarse and fine grained way of deposition of a stem was the comparison of the height and the shape of the free energy barriers.

In the following discussion, the idea of attachment of segments shorter than the full fold stem but longer than a single chain member is kept. However, the objective is not to consider the shape and the height of the free energy barrier but to emphasize the opportunity for the molecule to fold back at the end of each stage of deposition. So, when the deposition of the first stem of the secondary nucleus is considered, the molecule does not anticipate the final length L of the full fold stem. The surface nucleus starts with a segment of length Δl coming into the crystallographic register with the substrate. Then, either the molecule folds back on itself and starts to crystallize, in a position adjacent to the first stem, or the crystallization of a further segment of Δl (in the direction of the first one and without folding) occurs. The same alternative is considered at the end of the deposition of every segment of the first stem.

In our model, the attachment of the next stem proceeds by deposition of consecutive segments. However, we can consider two versions of the theory. In the first version, we consider the opportunity for the molecule to fold back at the end of every stage. Therefore, the possibility of variation of the stem length in one secondary nucleus is taken into account. In the second version of our model, to be given here, the idea of Lauritzen and Hoffman is maintained; there is no change in stem length after the first folding occurs. This does not imply that the deposition of the second (and further) stem proceeds in one stage but only that the final length of the stems is determined by the effective length of the first one. The problem of fluctuation of the fold periods in a layer has been dealt with by a number of authors (cf. ref 5), but, in order to be clear, it seems useful to deal first with the second version of our model.

The Model

Let us consider the number n_i of nuclei made of one straight molecular stem made of i segments. These nuclei may lead to the following: (a) nuclei of the $(i + 1)$ species (by further attachment of one segment); (b) nuclei of the $(i - 1)$ species (by detachment of one segment); and (c) two-dimensional nuclei by folding and subsequent crystallization. Let A and B be the rate constants of the forward and backward reactions a and b. Let C be the overall net rate constant, for the folding reaction, in steady state. Within the framework of the well-known theory of crystallization (see for instance ref 5), we assume the following:

(1) The driving force of the forward reaction (a) contains a positive term arising from the free enthalpy of crystallization and a negative term pertaining to the lateral surface free energy, and the inequality $A < B$ is invalid beyond a critical supercooling approximated by $\Delta T_c = 2\sigma T_m{}^0/\psi\Delta h_f a$ (σ, $T_m{}^0$, Δh_f, and a, as usual, denote the lateral surface free energy, the equilibrium melting temperature, the heat of fusion, and the molecular width).

(2) The forward rate constant for folding, C_{i+}, results from a positive driving force arising from the free enthalpy of crystallization and a reverse driving force pertaining to the work of chain folding. The overall net rates for folding, C_i, are different from zero only if the fold length exceeds a critical value approximated by $l_c = (2\sigma_e T_m{}^0)/(\Delta h_f \Delta T)$. Moreover, C_i increases with the length, $l = i\Delta l$, of the stem.

In the steady state, we obtain[17]

$$A n_{i-1} - (A + B + C_i)n_i + B n_{i+1} = 0 \qquad (1)$$

The general solution of the recurrence relation 1 cannot be given in a closed form because of the dependence of C_i upon i. We will first examine the fictitious case with C constant, because, in this case, the mean value of $\langle i \rangle$ is obtained in a closed form. Moreover, the analysis of this simple situation clarifies the mechanism by which, at every supercooling, $\langle i \rangle$ remains finite and leads to the conclusion that in the actual case (where C_i is not constant) the δl catastrophe is, a fortiori, avoided. This last conclusion is further substantiated by analysis of the physical situation, where C_i is rapidly increasing along with i. Finally, we will obtain, by numerical calculations, a good fit of experimental results pertaining to the dependence of l on T_c.

The Basic Mechanism of Limitation of Fold Length

To clarify the mechanism by which the δl catastrophe may be avoided, let us examine the fictitious case where C_i does not depend upon i. In this particular case, the general solution of recurrence 1 is a linear combination of the two particular solutions

$$n_i = r_1{}^i, \qquad n_2 = r_2{}^i \qquad (2)$$

where r_1 and r_2 are the solutions of the characteristic equation

$$A - (A + B + C)x + Bx^2 = 0 \qquad (3)$$

$$r_1, r_2 = (1/2B)\{(A + B + C) \pm [(A + B + C)^2 - 4AB]^{1/2}\} \qquad (4)$$

But when C is positive, the values of r_1 and r_2 are positive, and the lowest value r_2 is less than 1 (even when the inequality $A < B$ is not fulfilled). This ensures the existence of a steady state solution where the n_i are in a decreasing geometrical progression: $n_i = \rho r_2{}^i$ (where ρ is some constant). The mean value of i is

$$\langle i \rangle = \sum_{i=i_{\min}}^{\infty} i n_i C_i \Big/ \sum_{i=i_{\min}}^{\infty} n_i C_i = \sum_{i=i_{\min}}^{\infty} i\rho r_2{}^i C \Big/ \sum_{i=i_{\min}}^{\infty} \rho r_2{}^i C \qquad (5)$$

In this expression, $i_{\min} = E(l_c/\Delta l) + 1$, where $E(x)$ denotes the integer part of the x. Under the assumption of constant C_i, the mean value of i

$$\langle i \rangle = \sum_{i_{\min}}^{\infty} i r_2{}^i \Big/ \sum_{i_{\min}}^{\infty} r_2{}^i \qquad (6)$$

is finite at every supercooling.

The basic mechanism which permits the avoidance of the δl catastrophe is thus the following. The first stems of prohibitive length have so many opportunities of folding back, before being formed, that they are unlikely to appear. Before dealing with the case where C depends upon i, let us consider the case where C, already constant, has a very low value. Neglecting C in (4) (but this is not readily allowed) would lead to $r_1 = A/B$ and $r_2 = 1$. If the supercooling ΔT is higher than the critical one

$$\Delta T > \Delta T_c = 2\sigma T_m{}^0/\psi \Delta h_f a \qquad (7)$$

r_1 and r_2 are higher or equal to 1, and under the assumption of constant C, the mean value of i (see eq 6) goes to infinity, and the δl catastrophe is predicted as usual.

The Physical Case Where C_i Depends upon i

In fact, it is not enough to show that $\langle i \rangle$ or $\langle l \rangle$ is finite. For low and constant values of C and $A > B$, the values of n_i are slowly decreasing with i. High values of i are to be considered in (6), and actual calculations show that $\langle l \rangle$, though finite, increases when ΔT increases beyond ΔT_c. Fortunately, C_i is not constant but is rapidly increasing with i.

We consider the following. (a) Expressions of the rate constants are

$$C_i = \beta 2 \sinh \{(\Delta h_f a b i \Delta l \Delta T / 2 T_m{}^0 - \sigma_e a b)/kT\}$$
$$A = \beta \exp\{(+\Delta h_f a b \Delta l \Delta T / 2 T_m{}^0 - \sigma b \Delta l)/kT\} \qquad (8)$$
$$B = \beta \exp(-\Delta h_f a b \Delta l \Delta T / 2 T_m{}^0 + \sigma b \Delta l)/kT$$

where b is the thickness of a stem and β some retardation factor.

(b) Acceptable values of the various parameters (for instance in the case of the crystallization of polyethylene[5]) are $a = 4.15$ Å, $b = 4.55$ Å, $\Delta l = 10$ Å, $\sigma/k = 5.7$ K Å^{-2}, $\sigma_e/k = 70.2$ Å^{-2}, $\Delta h_f/k = 20.5$ K Å^{-3}, $T_m{}^0 = 416$ K.

(c) We choose i^* integer a few units higher than $i_{\min}$, then for $i \geq i^*$ we obtain, for sufficiently high undercooling,

$$C_i \gg (A + B) \qquad (9)$$

$$C_i \simeq C_{i+} \qquad (10)$$

where C_{i+} denotes the forward rate constant for the folding reaction and by virtue of (1)

$$n_{i-1} \ll n_i \ll n_{i+1} \qquad (11)$$

Various alterations can be made to expressions 7 and 8 (taking into account the possible asymmetry of the free-energy barrier or by introducing a ψ adsorption parameter) without destroying the validity of inequalities 9 and 11 and of condition 10. By virtue of eq 9, 10, and 11, the recurrence relation 1 gives

$$n_i/n_{i-1} = A/C_i \simeq A/C_{i+} = \exp(-\alpha i + \delta) \text{ if } i \geq i^* \qquad (12)$$

with $C_{i+} = \exp(\alpha i - \gamma)$. For instance, if the crystallization of polyethylene from dilute solution is considered with a temperature of dissolution $T_d = 387$ K and at supercooling, $\Delta T = 60$ K, it comes from the hypothesis that $\alpha \simeq 0.854$, $\delta \simeq 4.11$, $\gamma \simeq 4.05$, $i_{\min} = 5$. For $i \geq i^* = 10$, the approximations in eq 9, 10, 11 are readily acceptable. A repeated application of (12) gives, if $i > i^*$:

$$n_i C_i \simeq n_i C_{i+} = \exp[-(\alpha/2)(i - \delta/\alpha + 0.5)^2 + \epsilon]$$

where ϵ is some constant.

The mean thickness calculated for the population of the lamellae, the thickness of which is higher than $i^* \Delta l$, is

$$\langle l' \rangle = \Delta l \sum_{i=i^*}^{\infty} i n_i C_i \Big/ \sum_{i=i^*}^{\infty} n_i C_i$$

or

$$\langle l' \rangle = \Delta l (\delta/\alpha + 0.5) + \Delta l \sum_{u=u^*}^{\infty} u \exp(-\alpha u^2/2) \Big/ \sum_{u=u^*}^{\infty} \exp(-\alpha u^2/2)$$

$$u^* = i^* - \delta/\alpha + 0.5$$

If the sums are approximated by integrals, we get

$$\langle l' \rangle / \Delta l = \delta/\alpha + 0.5 + (2/\alpha)^{1/2} [\exp(-t^2)/\pi \operatorname{erfc}(t)]$$

where erfc is the complementary error function and t takes the value

$$t = (\alpha/2)^{1/2} u^*$$

Exact values of $1/\pi \exp(-t^2)/\operatorname{erfc}(t)$ can be taken from ref 6, and representative values are given in Table I. In fact, this function can be approximated as slightly higher than its argument. It turns out that $\langle l' \rangle \simeq i^* \Delta l$. In other words, in the calculation of

$$\langle l \rangle = \Delta l \left(\sum_{i=i_{\min}}^{\infty} i n_i C_i \Big/ \sum_{i=i_{\min}}^{\infty} n_i C_i \right)$$

only the first few terms of each sum are to be considered.

Table I

t	$\exp(-t^2)/\pi \operatorname{erfc}(t)$
0	0.564
1	1.319
2	2.209
5	5.096
10	10.050

Actual Calculation of the Lamellar Thickness

Now, we intend to show that, on the basis of rather simple assumptions about the rate constants, a good fit to experimental results can be readily obtained. For this purpose, we assume that σ and σ_e are independent of temperature, and we do not introduce an adjustable ψ parameter. The object of these simplifications is to show that the present model allows for the accounting of the experimental results, even when using a very few adjustable parameters. In order to avoid any explicit formulation of the rate constants A and B, we rewrite expression 1, dividing both members by $(AB)^{1/2}$

$$X n_{i-1} + (X + 1/X + D) n_i + (1/X) n_{i+1} = 0 \qquad (13)$$

where the expressions for X and D are

$$X = (A/B)^{1/2} = \exp(-b \Delta l \sigma / kT + a b \Delta l \Delta g / 2kT)$$

$$D = \beta^* [\exp(-2 a b \sigma_e / kT + a b l \Delta g / 2kT) - \exp(-a b l \Delta g / 2kT)]$$

$$\Delta g = \Delta h_f \Delta T / T_m{}^0$$

The value of β^* depends upon the symmetry of the free-energy barriers (which under the assumption $\beta^* = 1$ differs from that considered in eq 8 and as usual may contain a retardation factor). For the actual calculation of $\langle l \rangle$, we proceed by iteration from

$$i_\infty \gg i_{\min} \qquad (14)$$

We take $n_{i_\infty+1} = 0$ and n_{i_∞} = an arbitrary value. Then, the repeated application of (13) gives the values of $n_{i_\infty-1}$, $n_{i_\infty-2}$, ..., $n_{i_{\min}}$. These values allow $\langle l \rangle$ to be determined. Moreover as demonstrated before, the result is insensitive to the value of i_∞ chosen, provided inequality 14 is satisfied.

Taking $\beta^* = 1$ and using Δl, σ_e/k, and σ/k as adjustable parameters, it is possible, as shown in Figure 1, to reproduce experimental results pertaining to the crystallization of polyethylene[7] from dilute solution in xylene. The values adopted for Δl, σ_e/k, and σ/k are 13.3 Å, 70.2 K/Å^2, and 5.7 K/Å^2, respectively.

Similar adjustments[8] are made to account for the results obtained from polystyrene and Nylon 6.6.[8] If the symmetry of the free-energy barriers is modified (by changing the expression for D), a similar agreement is obtained,[8] but slightly different values for the adjustable parameters have to be chosen.

Discussion

It is easy to illustrate the differences between the classical mechanism of nucleation and the one considered here. For this purpose, we use the graph of ΔG vs. the length and the width of a two-dimensional nucleus, as presented by Wunderlich,[9] and we superimpose on this

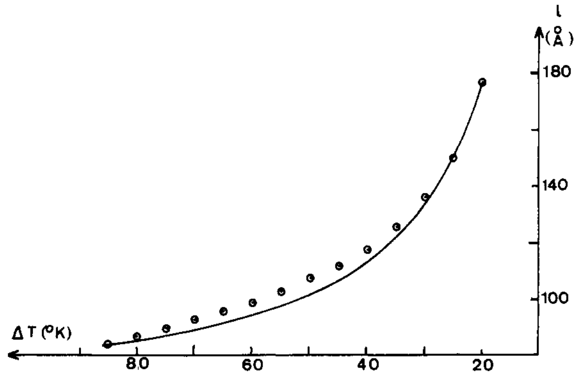

Figure 1. Mean thickness of polyethylene lamellae from dilute xylene solution as a function of undercooling. The continuous curve is from data in the literature according to ref 5; dots indicate the present calculation. Assumed parameters are $\Delta l = 13.3 \times 10^{-8}$ cm; $\sigma/k = 5.7$ K/Å^2; $\sigma_e/k = 70.2$ K/Å^2; $\Delta h_f/k = 20.5$ K/Å^3; $b = 4.15 \times 10^{-8}$ cm; $a = 4.55\ 10^{-8}$ cm; $T_m{}^0 = 416$ K; $T_d = 387$ K; and $\beta^* = 1$.

graph the various paths considered for the crystal growth (Figure 2). In Figures 2a and 2b the undercooling ΔT is supposed lower than ΔT_c. In Figures 2c and 2d the undercooling ΔT is supposed larger than ΔT_c (eq 7).

In Figures 2a and 2c, we have drawn the reaction paths usually considered. Growths along paths u, v, ... are not possible because in either case ($\Delta T > \Delta T_c$ or $\Delta T < \Delta T_c$) negative values of ΔG are never obtained. Growths along the paths x, y, z, ... are possible because, in either case, they all lead ultimately to a decrease of ΔG. For ΔT lower than ΔT_c (Figure 2a), ΔG increases along the first stage of the various paths 4, 5, ..., and the larger the length of the stem, the larger the increase in ΔG. Thus along the various paths x, y, z, ... the rate constants for the first stage are decreasing functions of l, while the rate constants for the subsequent stages are increasing functions of l. As a result, a limitation of fold length is obtained. At undercooling larger than ΔT_c (Figure 2c), along the first stage of the various paths x, y, ..., the larger the length of the stem, the larger the *decrease* in ΔG. Thus, the rate constants of all the stages, including the first, are increasing functions of l. This results in the δl catastrophe.

Figures 2b and 2d show, at undercoolings respectively lower and higher than the critical one, the paths considered in this work; the deposition of the first stem proceeds by crystallization of successive segments (flexibility units), and at every stage the opportunity of lateral growth is considered, but the lateral growth is only possible when it permits a decrease of the free enthalpy; as before, growth along the paths u, v, ... is not possible. Consider now growth with stem length l_Z higher than l_c. In fact, state Z is reached along a path which goes through the states X and Y (and not directly from the melt). The decrease of the occupation numbers of the various states, along the path X, Y, Z, ..., results from the opportunity of lateral growth from each of the intermediate states X, Y, Z, ... Provided that the rate constant for lateral growth increases rapidly with the length of the stem, this second scheme automatically ensures the limitation of the crystallite thickness. The primary aim of this note was to establish this fact.

However, this prescribed condition can be met by many different expressions for the rate constant. Only a few adjustable parameters are needed. This is the reason why we refrained from using many parameters. This also explains why, when only dependence on thickness of the crystal vs. the temperature of crystallization is considered, it is difficult to assign definite values to the physical

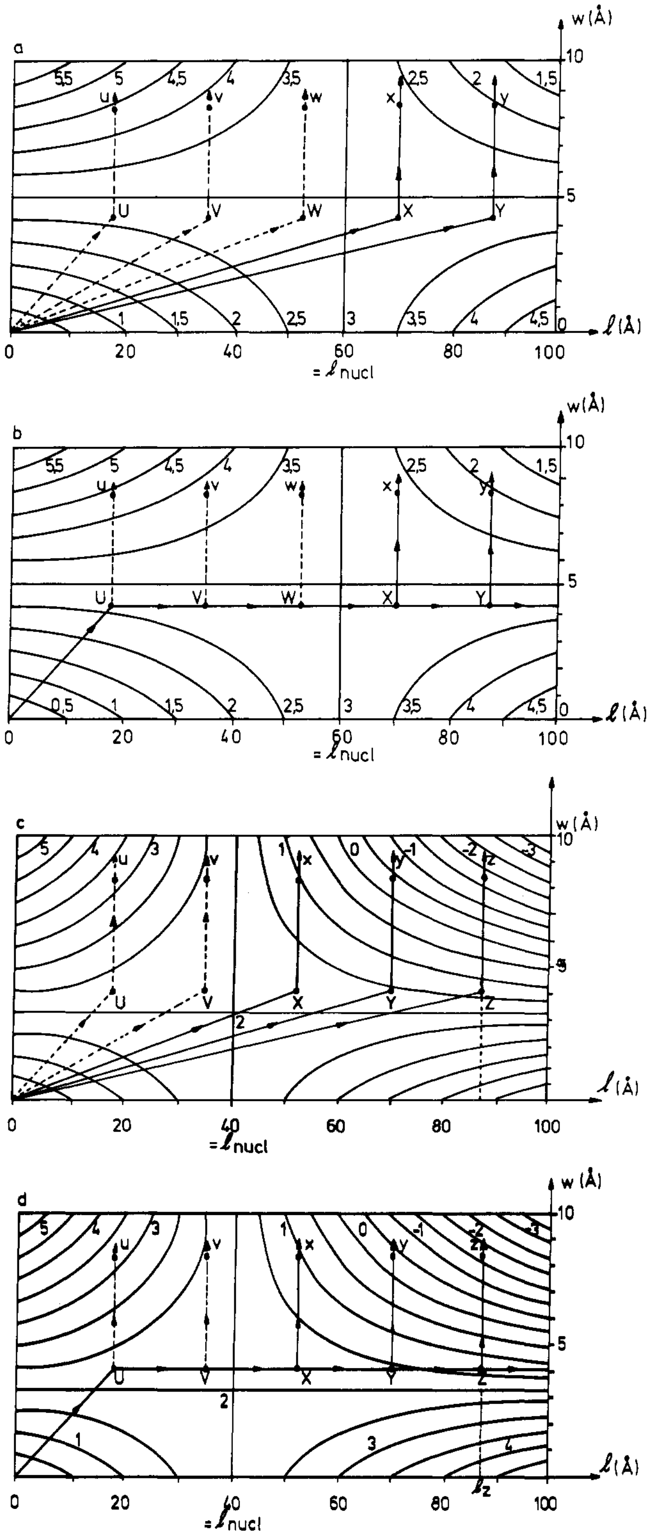

Figure 2. Paths for secondary nucleation from the classical model (a and c) and from the present work (b and d). In a and b, the undercooling is lower than the critical one. In c and d, the undercooling is higher than the critical one. The curves are hyperboles of iso-free enthalpy of formation of the nucleus in units 10^{-13} ergs. Values of the parameters used in the calculation are: $\sigma_e = 60$ erg/cm^2; $\sigma = 5$ erg/cm^2; $b = 5\ 10^{-8}$ cm; $a = 4.15 \times 10^{-8}$ cm; $\Delta g = 2 \times 10^8$ erg/cm^3 (a and b); $\Delta g = 3 \times 10^8$ erg/cm^3 (c and d). The figures are drawn as are those in ref 9, p 80.

constants involved. In fact in this study, it is possible to account for the L vs. ΔT changes, using values of σ or σ_e in the conventional range. In a similar way, with the same values of σ and σ_e, it is also possible to obtain reasonable values for the rate of crystal growth.[8] But alterations of the shape of the free-energy barrier change the "optimum values" of σ, σ_e, and Δl. We do not think that the comparison between the values of σ and σ_e, obtained from interpretation of different data, can be used to justify a definite choice of the expression for the rate constants. Unfortunately, exhaustive data on a single system are not available, even for polyethylene. For instance, in works on the kinetics of crystal growth from the melt, no precise estimation of the lamellar thickness[11] and/or the molecular length[12] is claimed.

In principle, the dependence on T of the rate of primary nucleation leads to an estimate of the product $\sigma^2\sigma_e$. However, the critical nucleus, as described by the theory, is a long thin rod. We further note that the so-called σ (see ref 5 for the conventional nature of σ) used in the theory of secondary nucleation pertains to the deposition of one molecule on a plane substrate. As a result, there is no theoretical reason for equating this σ with the σ involved in the theory of primary nucleation which is related to a bundle made of a few molecular stems.

Possible Extension of the Model

Thus we need exhaustive data on a single system, as a basis for further discussion. In our opinion, the PEO system extensively studied by Kovacs and co-workers[14] is the sole system in which (1) adjacent reentry can be assumed with reasonable certainty, (2) precise values of crystal thickness are readily obtained, and (3) extensive data on the rate of crystal growth are available. The present theory can be extended to that system, with some success. But so many problems are linked with the finite length of the molecules that a comprehensive discussion is outside the scope of the present paper and is to be dealt with in a forthcoming paper, with A. J. Kovacs.

Moreover, considering the work on neutron diffraction (see for instance Sadler and Keller[13]), adjacent reentry, explicitly implied both in the work of Hoffman and Lauritzen and in the present work, cannot be assumed with any certainty when crystallization of high molecular weight material from the melt is considered. However, in the model described here, the difference between the sign of the change in ΔG implied by the deposition of the first and further stems is not relevant. The mechanism, described here, of molecule deposition, segment by segment, seems of general applicability and could, in principle, lead to widely different configurations; lamellar crystals with sharp reentry and crystals in which the chains have an overall random coil configuration represent in this view the limiting cases in which respectively the molecules are deposited slowly or rapidly.

Correlation between the Molecular Structure and the Thickness of the Lamellae

Another advantage of the model is to allow a discussion of the correlation between the molecular structure and the thickness of the lamellae. We shall treat briefly the case of the polyamides. In the paper of Dreyfuss and Keller,[15] a correlation between the length of the polyamide repeating unit and the thickness of the crystal is emphasized. These authors define the R ratio between the lamellar thickness (for crystal obtained from dilute solution) and the length of the repeating unit. It is reported that the R values are between 4 and 3 and are decreasing slightly with the increase of the length of the repeating unit. Similar results are observed in the case of crystals grown from the melt.[16]

Using our model, we have determined the value of the R^* ratio between the lamellar thickness and the length of the flexibility unit. With constant values for $\Delta h_f/k$, σ_e/k, a, and b (values directly chosen to be acceptable for Nylon 6.6), the dependence of R^* on Δl is obtained and reported in Figure 3. It can be observed that for Δl in the 10–20 Å range values between 4.5 and 2.5 are obtained. These values decrease as Δl increases.

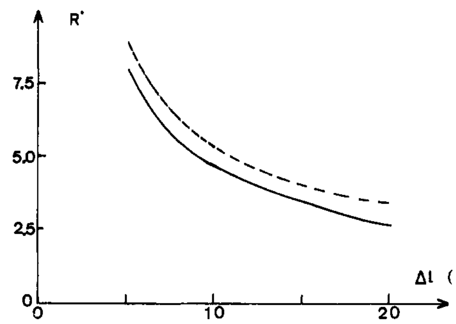

Figure 3. R^* ratio of the mean lamellar thickness, at high undercooling, vs. the length, Δl, of the flexibility units, as a function of Δl. Values of the parameters used in the calculation are: $\sigma_e/k = 20\ \mathrm{K/Å^2}$; $\Delta h_f/k = 6.65\ \mathrm{K/Å^3}$; $b = 5.5 \times 10^{-8}$ cm; $a = 12.8 \times 10^{-8}$ cm; $T_d = 478$ K; and for the curve (—) $\sigma/k = 9\ k/\mathrm{Å^2}$ and for the curve (---) $\sigma/k = 1\ \mathrm{K/Å^2}$.

Summary

A model is presented for lamellar crystallization. The first stem of a secondary nucleus is assumed to be constructed by successive attachment of segments shorter than the full fold stem and longer than a single chain member (the "flexibility units" assumed by Frank and Tosi a long time ago). The following innovation is introduced here. At the end of each stage of deposition the molecule faces a decision: either to pursue its deposition in the initial chosen direction or to fold back on itself. No detailed description of the deposition of the next stems is assumed, and the growth of a secondary nucleus proceeds by successive crystallization of stems of the same length as the first one (as in the classical theory of Hoffman and Lauritzen).

Whichever reasonable choice is made for the expression of the rate constants, this model ensures a finite crystal thickness even at undercoolings higher than the critical one

$$\Delta T > \Delta T_c = 2\sigma T_m{}^0/\Delta h_f a$$

This is illustrated by detailed calculation in the case of polyethylene. Reasonable values are obtained for the surface free energy, length of the "flexibility units", and rate of crystal growth.

The present model introduces the concept of the segmental nature of the macromolecules into the theory of crystallization. Its potential to establish correlations between the molecular structure and the crystal thickness is illustrated in the calculation of an R^* ratio, corresponding to the R ratio defined by Keller and Dreyfuss in the case of the polyamides.

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(17) If n_i', n_i'', and n_i''' denote the occupation numbers for nuclei of length $i\Delta l$, made of 2, 3, ... stems, their rates of change are given by $\mathrm{d}n_i/\mathrm{d}t = An_{i-1} - (A + B + C_{i+})n_i + Bn_{i+1} + C_{i-}n_i'$, $\mathrm{d}n_i'/\mathrm{d}t = C_{i+}n_i - (C_{i+} + C_{i-})n_i' + C_{i-}n_i''$, and $\mathrm{d}n_i''/\mathrm{d}t = ...$, where C_{i+} and C_{i-} denote the rate constant for folding and unfolding, respectively. In the steady state, we obtain, under the assumption $C_{i+} > C_{i-}$, $n_i = n_i' = n_i'' = n_i'''$ and eq 1, where $C_i = C_{i+} - C_{i-}$.

Carbon-13 Magnetic Relaxation Study of the Internal Motions of Poly(4-vinyl-*N*-*n*-alkylpyridinium bromides) in Methanol Solutions

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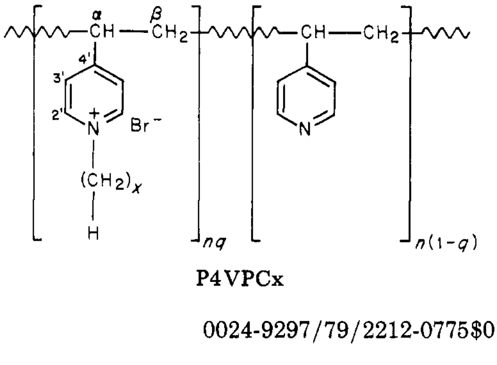
ABSTRACT: The dynamical behavior of poly(4-vinylpyridine) quaternized by *n*-alkyl bromides of different chain length (x = 2, 4, 6, 8, 10) in methanol solution has been investigated by ^{13}C longitudinal relaxation at 25 MHz with some subsidiary T_1 and NOE measurements at 63 MHz. As in the case of poly(4-vinylpyridine) neutral or quaternized by HBr, the T_1's in the macromolecular chain and in the pyridyl rings have been interpreted by a quasi-isotropic segmental motion and a jump oscillation about the C(α)–C(4′) axis, respectively, assuming a distribution of correlation times. The influence of the coulombic and steric effects on the internal motions of these polymers has been examined by varying the length of alkyl side chains and the degree of quaternization. Both of these parameters have a marked effect on the flexibility of the main chain and side chains but not on the axial motion of pyridyl rings. For the internal motion of alkyl side chains, we have considered three basic models of rotation about N–C or C–C bonds and some of their combinations: rotational diffusion (A), jump among three equivalent sites corresponding to the t, g^+, and g^- conformers (B), and same as (B) with t unequivalent to g^+, g^- (C). The consistency between the T_1 and NOE observed and computed for 25 and 63 MHz is achieved only for model C with $W(g^+ \rightleftarrows g^-) < W(t \rightarrow g^\pm) \leq 0.5W(g^\pm \rightarrow t)$.

The understanding of the dynamical behavior of hydrocarbon chains is important in many physicochemical problems, in particular those dealing with micellar solutions and membranes. In the last few years, several models have been proposed for the segmental motion of these chains,[1-8] but an unequivocal selection among them has not been achieved up to now. This problem prompted us to investigate the ^{13}C relaxation in poly(4-vinylpyridine), quaternized at different degree q by n-alkyl bromides of various chain length, the general formula of which is



P4VPCx

We have previously interpreted the ^{13}C relaxation in alkyl side chains, either by a diffusional motion about C–C bonds[9] using a semiempirical treatment proposed by Levine et al.[1] or by random jumps of the methylene group among three unequivalent sites by means of the Monte-Carlo method.[7] These two different models lead to a satisfactory agreement with experiment at a single spectrometer frequency; we have reexamined this problem by means of a more general treatment[10] allowing for computation of the ^{13}C relaxation for several models of motion about the successive C–C bonds of an alkyl chain. In the present work, the ^{13}C longitudinal relaxation times and the ^{13}C {^{1}H} nuclear overhauser enhancement (NOE), computed at two different spectrometer frequencies (25 and 63 MHz), are compared to experimental data in order to select the most suitable model for the internal motions of the alkyl side chains.

We have also examined the influence of the degree of quaternization and of the length of alkyl side chains on the segmental motion of the macromolecular chain and on the rotational motion of pyridyl rings, assuming a dis-

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