

# Kinetic phase diagram for crystallization of bimodal mixtures of oligomers as predicted by computer simulations

Jens-Uwe Sommer

*Institut de Chimie des Surfaces et Interfaces, CNRS, 15 rue Jean Starcky, B.P. 2488, 68057 Mulhouse Cedex, France*

Received 19 March 2001; received in revised form 15 June 2001; accepted 26 June 2001

## Abstract

We analyze the crystallization process of mixtures of long and short oligomers such as *n*-alkanes using a Sadler–Gilmer-type growth algorithm. The short chains are assumed to crystallize only in a fully stretched conformation, while the long chains take a pathway over a folded state. Increasing the concentration of long chains from zero to unity, the zero-growth temperature, which separates the stable growing phase from the non-growing phase, first decreases for low concentrations of long chains, reaching a minimum value at intermediate concentrations, and increases again for higher concentrations, as a result a growth-gap appears. Here, mixing long chains into the short chain liquid stops the growth process completely until it resumes at higher concentrations of long chains. This effect is explained by the particular kinetic pathway, the long chains take into the crystalline state. Since the folded state has to be passed at first, long chains are more likely to be desorbed again. At low concentrations, the long chains thus effectively dilute the short chain liquid leading to a decrease of the zero-growth temperature. At higher concentrations, the transition into the stretched state of the long chains leads more frequently to bonded pairs, which stabilizes the growth again due to the higher binding energy among fully stretched long chains. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Oligomers; Computer simulations; Zero-growth temperature

## 1. Introduction

Polymer chains crystallize in form of lamellae which are usually much thinner compared to the length of the fully stretched individual chains [1]. The description of polymer crystallization from a theoretical point of view is a formidable task since the resulting polymer lamellae are generally out of equilibrium structures and therefore the standard methods of equilibrium thermodynamics and statistical mechanics can a priori not be applied. For conventional polymers, various effects such as polydispersity and entanglements can influence the crystallization process and hence the resulting morphology. Furthermore, long polymer chains usually fold many times in the crystal state implying possible configurational disorders, such as loops, cilia, bridges between different lamellae, and the formation of rather rough and disordered folding surfaces. Therefore, the most simple system which can provide understanding of the process of polymer crystallization is given by relatively short, exactly mono-disperse oligomers such as *n*-alkanes [2–4]. If the chains are shorter than typically 15 nm, only the fully stretched state S has been observed in experiments, while long oligomers appear also

in a folded state F [5]. For simplicity, we will consider here long oligomers, which can fold only once.

Before we start to describe the model at hand, it is in order to point out some general aspects regarding the simulation of polymer crystallization processes. The typical growth rate of a few  $\mu\text{m/s}$  indicates that the molecular organization process is very slow. Assuming a few Å for the typical dimension of a crystalline cell, one obtains a time scale of  $10^{-4}$  s to build up one crystalline stem, i.e. to add one elementary cell to the growth front. Let us further assume a typical time unit of  $10^{-10}$  s which characterizes the motion of monomers in the liquid state on the scale of the crystal cell. Hence,  $10^6$  time units are necessary just for one elementary step in the growth process. This illustrates that the rearrangements of the polymer conformations at the growth front are a longsome process, which involves many trial events together with interactions among the chains at the growth front. Therefore, first-principle simulations will face serious difficulties in modeling the process of polymer crystallization. On the other hand, experiments on short chains reveal only a few discrete values for the lamellar thickness. This indicates that the individual chains also obtain only a few rather well defined states in the crystalline

structure, usually denoted as regularly folded states. Respecting the fact that only the fully extended state of the chains corresponds to the thermodynamic equilibrium of the crystal, we denote the folded chain states generally as intermediate states in a thermodynamic sense. These intermediate states form an extremely small subset in the statistical phase space of chain conformations.

Now, the idea is appealing to establish a kinetic model which takes into account these few intermediate states only [5]. Though the kinetic pathways in between these states are formed by time-consuming and quite complex chain rearrangements, the latter enter the model only via their characteristic time-scales expressed by corresponding transition rates. The transition rates themselves, which we call kinetic parameters here, cannot be calculated directly but are adjustable values of the model. In previous work, we have developed a simulation model along this lines, which is able to describe the crystallization process in thin polymer films [6]. Here, many different morphological phase could be predicted and experimentally verified [7,8]. The aim of this paper is to simplify the model once again to understand the essential processes during crystallization of short oligomers.

## 2. Simulation model

A modified variant of the Sadler–Gilmer (SG) model is used [9–11]. Here, lateral correlations along with the growth front of the crystal are neglected and a cut through the growing crystal in the direction perpendicular to the front represents a one-dimensional growth model. The different folded states of an individual chain are considered as internal variables, which correspond directly to the thickness of the crystal. For a more recent reconsideration of this model, see Ref. [12]. In the present case, we have to consider two types of chains: short chains, which can only crystallize in the stretched state S, and long chains, which can adopt a once-folded state F. This requires some modifications of the original model as described in the following.

### 2.1. Simple growth law for short chains, which can only be in the stretched state

Since the short chains crystallize only in the fully stretched state, one obtains a simple and completely solvable growth kinetics. In order to join the crystal, a chain of length  $N_S$  from the liquid phase must overcome some ‘entropic’ barrier  $s$ , involving stretching of the conformation in the first place but also the loss of translational entropy. Therefore, the probability for a new chain to enter the crystal is given by

$$p_{\text{entr}} = e^{-s}. \quad (1)$$

Note that the exponential representation of  $p_{\text{entr}}$  does not indicate an equilibrium nature of  $s$ , but is only made for convenience. For the sake of simplicity, we set the time

constant for an attempt to enter the crystal to unity. Furthermore, we choose  $k = 1$  for the unit of entropy. In order to remove a chain at the growth front, a corresponding binding energy  $\epsilon_{\text{bind}}$  among the crystallized units must be surmounted. The probability for outgoing events is thus

$$p_{\text{out}} = e^{-\epsilon_{\text{bind}}/T}. \quad (2)$$

As a combined effect of entropic and energetic barriers one obtains for the steady state growth rate

$$\begin{aligned} G &= p_{\text{entr}} - p_{\text{out}} = e^{-s}(1 - e^{-\epsilon_{\text{bind}}/T+s}) \\ &= e^{-s}(1 - e^{-\epsilon_{\text{bind}}\Delta T/TT_0^S}), \end{aligned} \quad (3)$$

where we made use of  $G(T_0^S) = 0$ , defining the zero-growth temperature  $T_0^S$ , and the under-cooling  $\Delta T = T_0^S - T$ .

### 2.2. Two state model for longer chains

For the long species, a new situation occurs since an once folded state F has to be considered in addition to the fully stretched state S. Here, we restrict ourselves to the case of long chains which are twice as long as the short ones, i.e.  $N_L = 2N_S$ . The basic assumption is that a new chain enters the crystal always in the folded state. This is in accordance to the original idea of Sadler and Gilmer (SG) [11] but simplified to the case that only one intermediate state F is considered. Note that in the original SG-model, the segments of a chain are treated completely independent; chain connectivity is only reflected by a pinning effect. By contrast, in the situation at hand, this picture must be modified in order to distinguish properly between long and short chains. A long chain in the folded state fills two places at the growth front. In order to stick to the simplest one-dimensional growth model, we apply the view of a virtual lateral neighbor at the growth front. In the folded conformation, this corresponds to the second stem while in a stretched conformation it represents an independent chain. Hence, in the folded conformation, we split our long chain into two stems and treat them formally independent. To stretch out a long chain one of the stems must leave the original state at the growth front and put itself on top of the other part. The introduction of a virtual lateral neighbor is important to obtain a realistic fluctuation dynamics: if we would have treated the folded chain as one unit, adding and removing it means to change two units of the growth front at once per step. Now, we regularly check the virtual neighbor place, as it would be an ordinary part of the simulation lattice. If a chain is in the folded state, the action of the virtual neighbor may cause stretching, while for stretched chains, the event at this site does not change the state of the crystal row.

In analogy to the short chains, an entropic barrier for each stem must be surmounted when a chain changes from the liquid to the crystalline state. To keep the model as simple as possible, here also we use the rate  $p_{\text{entr}}$  as for the short, half as long chains. (This makes sense if stretching of the chain

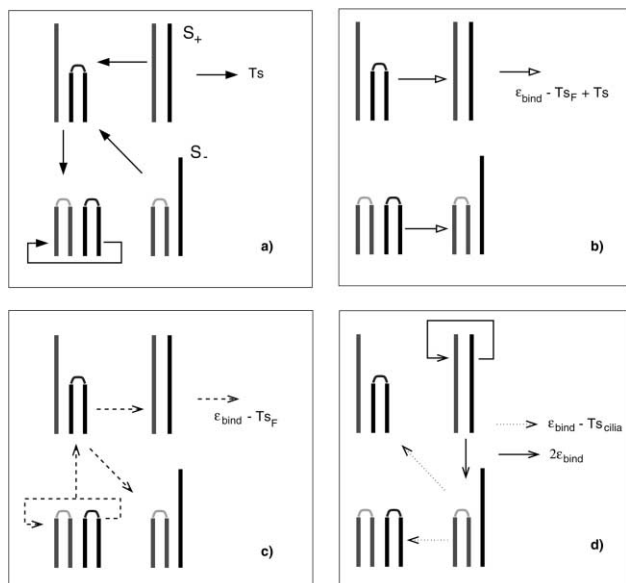


Fig. 1. Diagram of transitions between states formed by pairs of long chains at the growth front. (a) Growth events: only folded configurations are created in the growth step. The Metropolis weight  $Ts$  is independent of the state before the transition. (b) Stretching events: stretching can only occur out of folded states. The weight includes removal of a folded stem  $\epsilon_{\text{bind}} - Ts_F$  as well as additional stretching  $Ts$ . (c) Removal of folded chains: the weight is given by  $\epsilon_{\text{bind}} - Ts_F$ . (d) Removal of a stretched chain: here the weight depends on the state of the chain next to the front. For a pair of stretched chains, the weight is  $2\epsilon$ . Otherwise a cilia is removed with a weight of  $\epsilon_{\text{bind}} - Ts_{\text{cilia}}$ .

part is rate determining since both the short chain and a single stem of the folded chain have the same stretching length.) Now three possibilities emerge for the next step in the process. For simplicity, we consider only long chains.

First, the stem can be removed again. This occurs with a probability of

$$p_{\text{out}}^F = e^{-\epsilon_{\text{bind}}/T + s_F}, \quad (4)$$

where an effort for folding  $Ts_F$  has to be introduced which reduces the effective binding of the single stem compared to the unfolded short chain.

Second, a stem of a new chain from the liquid can enter. This freezes in the folded conformation behind the front. (It can only be released again by backward moves of the front.)

Third, the chain can stretch by moving over the other stem from the virtual lateral neighbor. The corresponding probability is given by

$$p^{\text{FS}} = p_{\text{out}}^F p_{\text{entr}}. \quad (5)$$

Here, we assume that the second stem has to be removed ( $p_{\text{out}}^F$ ) and, additionally, it has to be put on top of the crystal surmounting again the entropic barrier  $p_{\text{entr}}$ . A critical discussion of other possibilities are given in Section 4.

As a result of the stretching process, one obtains either a dangling end (cilia), which we call  $S_-$ -state, or, if also the chain directly behind the front is a long chain in the

stretched state, a locally fully extended chain crystal, which we call  $S_+$ -state. This is illustrated in Fig. 1a). For removing a long chain out of an  $S$ -state, two cases have to be distinguished: if we deal with a cilia ( $S_-$ -state) the unbinding probability is given by

$$p_{\text{out}}^{S-} = p_{\text{out}} e^{s_{\text{cilia}}}, \quad (6)$$

where  $s_{\text{cilia}}$  is the entropy effort of confinement for a cilia being grafted to the hard impenetrable crystal surface. It is easier to remove a chain with a cilia part compared to a small chain. A fully stretched crystallized chain ( $S_+$ -state) is removed with a probability

$$p_{\text{out}}^{S+} = (p_{\text{out}})^2, \quad (7)$$

indicating that now both half-chains are bounded, i.e. the doubled energy of binding is acting per site.

In case of a mixture, a new incoming chain is identified as a long chain with a probability of  $p$ . Otherwise, a short chain is assumed. Within the algorithm described earlier, only the stretching event does not exist for short chains. Hence, a transition to  $S_-$  or  $S_+$ -states is then impossible for a crystal site occupied by a short chain. Memory effects can be included into the probability  $p$ : The long chain displays some kind of memory of the crystalline conformation when being desorbed. This effectively increases the probability  $p$  to re-crystallize this chain again. We always consider  $p$  as the effective concentration of long chains directly at the growth front which can also incorporate selection effects due to adsorption.

Now, if the long chain is in an  $S$ -state, the rates for the outgoing events depend on state of the nearest stem behind it. If this stem is also in the  $S$ -state, Eq. (7) is applied, if it is a stem of an  $F$ -state or is a short chain, Eq. (6) must be applied. Therefore, for every step in the growth algorithm, the state of the first pair of chains at the growth front is of relevance. This is illustrated in Fig. 1 for long chains only. In order to simplify the picture for the  $F$ -state, the whole chain is sketched. In Fig. 1, the possible pathways between pairs of chains at the growth front are indicated. One might think of an analytic solution for the steady-state transition rates for all the four states. Unfortunately, such an endeavor is facing the difficulty as for some steps, more than one possibility exists depending on the actual distribution of states behind the front. Fluctuations of the front position can be considered. Hence, a possible self-consistent mean-field-like assumption about the distribution of  $S$ - and  $F$ -states hardly matches the actual problem. Therefore, we apply a Monte Carlo method.

To implement the algorithm a ‘three point model’ is used as illustrated in Fig. 2. This means that for each Monte Carlo step (MCS), one of the three possibilities is chosen by chance: (1) a new stem from the liquid phase tries to attach; (2) the front stem tries to remove; (3) a stem from a lateral neighbor moves over which results are stretching events if the stem belongs to long chain. It is important to note that

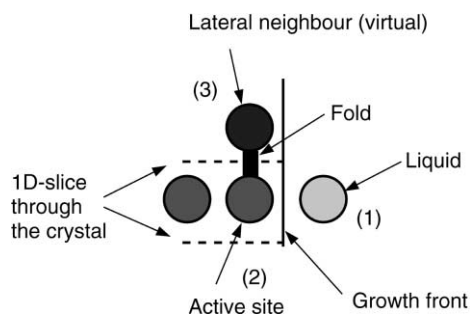


Fig. 2. Schematic view from the top onto the growing crystal illustrating the 'three-point' model. The SG-model corresponds to a 1D-slice through the crystal resulting in a 1D-growth process. Since a folded chain can stretch, we use a virtual lateral neighbor site which can supply the other part of the chain.

the third possibility is tried without checking first whether the front chain is folded. If this is not the case, the trial is rejected and no change of states occurs in this MCS. In each MCS, one of the three possibilities is chosen at random which mimics a fluctuation/diffusion-controlled dynamics. It has to be emphasized that though the placement of a fold in the lateral direction might be the preferred point of view, this model only serves as an illustration for the equal distribution of the events within an MCS. One might as well think of the other fold to be on in front of the stem under consideration.

### 2.3. Choice of model parameters

In addition to the concentration of long chains  $p$  (which is equal to the probability to find a long chain before the growth front), four parameters have to be considered. We use the freedom to fix the absolute scale of energy by setting the zero-growth temperature of the short chains to some arbitrary but experimentally reasonable value of  $T_0^S = 350$ . The entropy restriction for a cilia ( $S_-$ -state),  $s_{\text{cilia}}$ , Eq. (6) corresponds to the confinement of the cilia in one half-space (top or bottom of the lamella) and is of the order of unity (note  $k = 1$ ). In fact it is less, since at the growth front, the cilia has the freedom to fluctuate also into the region before the front ( $3/4$  space is available). We set this value to  $s_{\text{cilia}} = 1/2$ . Note that  $s_{\text{cilia}}$  only affects the events of desorption of  $S_-$ -states, see Fig. 1. On the other hand, the pathway to obtain  $S_-$  proceed via desorption of a folded chain part from the growth front. The penalty for this event is much higher for every physically reasonable situation (i.e.  $\epsilon_{\text{bind}} \gg T_0^S$ ), so that the effect of entropy gain by freeing a cilia chain is comparatively small. The predictions made with our model are also valid for  $s_{\text{cilia}} = 0$ .

Two parameters effectively control the dynamical behavior: the binding energy  $\epsilon_{\text{bind}}$  per stem and the folding effort  $s_F$ . We choose,  $\epsilon_{\text{bind}}/T_0^S = 3.0$ , for practical reasons in view of the computational time. A value of  $3kT$  per stem in the region around  $T_0^S$  is still certainly rather low but should not be too far away from the experimental situation. The

Table 1  
Fixed parameters in the simulations

Parameter	Value
$T_0^S$	350
$\epsilon_{\text{bind}}/T_0^S$	3.0
$s_F$	0.1
$s_{\text{cilia}}$	0.5

folding effort  $s_F$  is constrained to ensure that the zero-growth temperature  $T_0^L$  of long chains only must be higher than  $T_0^S$ : the long chains can grow in temperatures where short chains are not able to crystallize anymore. This implies also a higher melting point for the long chains, as observed experimentally. From this requirement, our model yields the condition  $s_F < 0.64$  (for the already discussed parameters  $\epsilon_{\text{bind}}$  and  $T_0^S$ ; again  $s_{\text{cilia}}$  only plays a minor role). We have first chosen  $s_F = 0.1$  and discuss other possibilities later. In Table 1, we display all the fixed values of the parameters for most of the results presented.

With these assumptions, the variables of the simulation model are the temperature  $T$  and the concentration of long chains  $p$ .

## 3. Results

The dependence of the growth rate  $G$  from the concentration of long chains  $p$  is displayed in Fig. 3 for different values of the temperature. We observe a non-monotonous behavior. Adding a small amount of long chains into short chains decreases the growth rate. The same is observed for the inverted situation. This agrees with experimental results obtained by Hosier et al. [13] for  $n$ -alkanes, although the ratio of the chain lengths used in these experiments is not 2:1.

When the temperature increases, but still below  $T_0^S$ , growth stops completely above a threshold value of  $p_1(T)$  but restarts again for a higher value  $p_2(T)$ . Hence, we observe a *growth-gap* as a function of concentration of long chains. Above  $T_0^S$ , the growth is not possible for

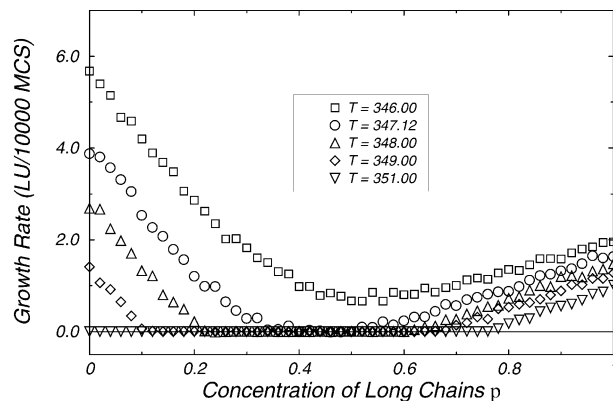


Fig. 3. The growth rate  $G$  is plotted vs. concentration of long chains  $p$  for different values of the temperature.

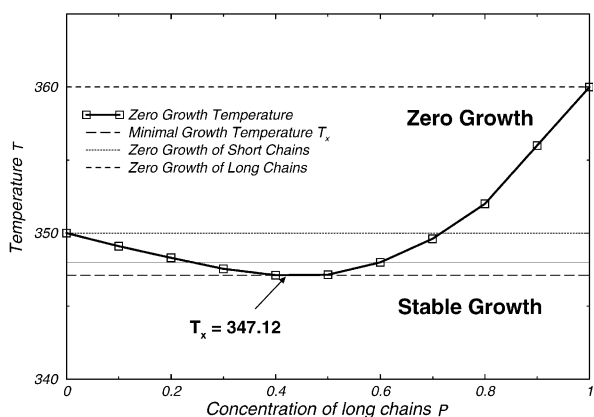


Fig. 4. Kinetic phase diagram in the  $p, T$ -parameter space. Two kinetic phases are distinguished: stable growth and zero-growth. These phases are separated by the zero-growth temperature  $T_0(p)$  thus representing a phase boundary. Close to the boundary, the fluctuations of the front position vs. time are extremely large, see Fig. 5.

short chains only ( $p = 0$ ). However, growth starts at higher concentrations for long chains. The zero-growth temperature for long chains  $T_0^L = T_0(p = 1)$  is located at  $T_0^L = 360$ . This value strongly depends on  $s_F$ . As noted, for  $s_F = 0.64$ , we obtain the limiting case of  $T_0^L = T_0^S$ .

From these data, we can construct a *growth phase diagram* as presented in Fig. 4. We distinguish two *kinetic phases* namely *stable growth* and *zero-growth*. In the zero-growth phase, the front always retreats back to the origin. Nevertheless, long excursions of the front can occur, but will never end up in a stable growth. In Fig. 5, we give an example of the evolution of the front position close to the phase boundary at  $p = 0.5$ . The zero-growth temperature here is  $T_0 = 347.15$ . As can be seen in Fig. 5, stable growth is found at  $T = 347$ , while zero-growth is obtained for  $T = 347.3$ . Note that a resolution of about 0.0003 in relative temperature units has been obtained.

The growth phase diagram in Fig. 4 shows a curved phase boundary. Most noticeable is the minimum at about  $p = 0.4$  which corresponds to a temperature

$$T_x = 347.12 < T_0^S. \tag{8}$$

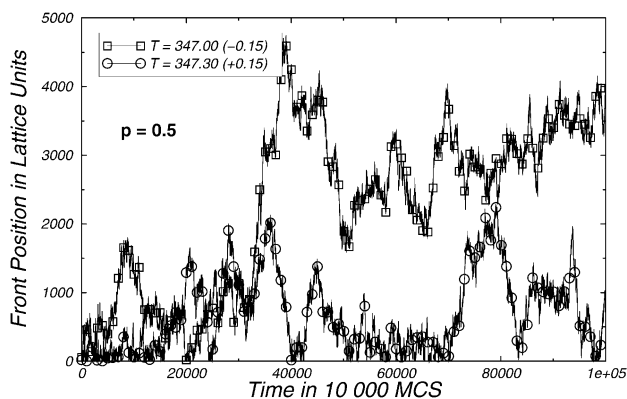


Fig. 5. Front position vs. time for two temperatures close to the phase boundary at  $p = 0.5$ .

Hence, a growth-gap as a function of concentration  $p$  is found in the temperature range

$$T_x < T < T_0^S. \tag{9}$$

Does such a behavior depend *qualitatively* on the value of  $s_F$  relative to  $\epsilon_{\text{bind}}/T_0^S$ ? To answer this question, we have plotted the zero-growth line as a function of  $s_F$  for different values of  $p$  in Fig. 6. As expected, increasing the folding penalty  $s_F$  decreases the zero-growth temperature  $T_0^L$  for a liquid of long chains only ( $p = 1$ ). For  $s_F = 0.64$ , the limiting value  $T_0^L = T_0(p = 1) = T_0^S = 350$  is reached. Increasing  $s_F$  gives a remarkable lowering of  $T_0$  at intermediate values of the composition, such as for  $p = 0.4$ . As a result, the growth-gap is enforced. On the other hand, for small values of  $s_F$ , the minimum shifts towards  $p = 0$ . Eventually, for  $s_F = 0$ , the minimum vanishes. This is because here the folded chains do not have a disadvantage along their kinetic pathway compared to the short chains.

We conclude that the existence of a growth gap does not depend on the parameters chosen but it is a rather general feature of the kinetic pathway proposed for long chains.

#### 4. Discussion

The simulations have shown that a mixture of short and long chains, treated here in the simplest way (long chains twice as long as short ones, short chains do not fold) yield a non-monotonous behavior for the growth rate as a function of composition  $p$ . The growth rate can even become zero at intermediate values of  $p$  — a growth-gap is predicted. Now, the reason for such a behavior can be understood on the basis of the kinetic pathways assumed for the long chains.

As a general, preliminary remark we note that lowering the concentration of the polymer liquid at the growth front results in the drop of the zero-growth temperature for the crystallization/growth process. This can be easily understood using a kinetic argument: the rate of successful

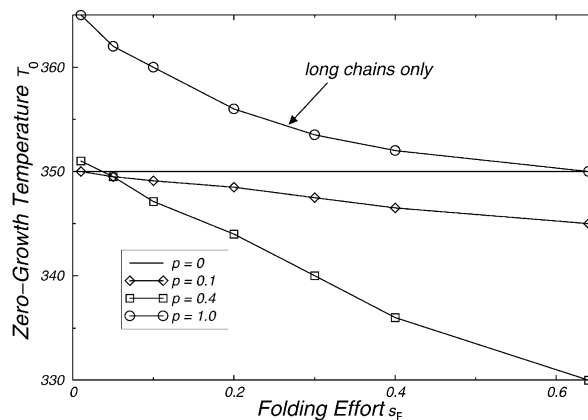


Fig. 6. Zero-growth temperature  $T_0$  as a function of  $s_F$  for different values of  $p$ .

attempts to remove a chain at the front compared to an incoming event is enhanced since the probability of incoming events is reduced.

Let us consider first the limiting cases, where  $p$  is either close to zero or close to unity, i.e. one species clearly dominates. The minority species is then not able to form an own growth phase. This has striking consequences if long chains form the minority ( $p \ll 1$ ). Now, the stretching step is practically useless since the probability for long chains to form pairs in the stretched state (see Fig. 1 upper right side) is negligible. Therefore, long chains act as defects, either in the folded state, where they are more easily removed, or in the stretched state, where they are almost always isolated, thus forming cilia which also have a higher rate of removal. As a consequence, the growth rate decreases. Since the long chains effectively dilute the short chain liquid for  $p \ll 1$ , according to our argument above the zero-growth temperature is reduced too.

$$T_0(p \ll 1) < T_0^S. \quad (10)$$

Consider now the opposite situation, where short chains form the minority ( $1 - p \ll 1$ ). Since  $T_0^L = T_0(p = 1) > T_0^S$ , the short chains are a priori in an unstable situation if attached to the crystal. Again, they act as defects and effectively dilute the long chain liquid. In turn, the zero-growth temperature of long chains is reduced

$$T_0(p - 1 \ll 1) < T_0^L. \quad (11)$$

As a consequence of the opposing trends in the slope of the zero-growth line  $T_0(p)$ , the latter must display a minimum  $T_x$ , see Fig. 4. Experimental evidence for the limiting relations (10) and (11) can be found in the paper of Hosier et al. [13] (see in particular Fig. 2c therein).

From Eq. (10), we obtain that a small amount of long chains added to short chains stops growth if we are close

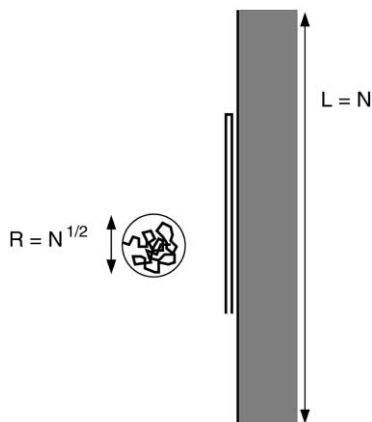


Fig. 7. Sketch of the relation between the characteristic length scales involved in the polymer crystallization process. In the liquid melt state, the extension of a chain is characterized by the average end-to-end distance  $R = N^{1/2}$  in statistical monomer units. In the crystal phase, depending on the state of folding, it is given by  $L = N$  and  $L/2$ , respectively. Here we set  $l = 1$  for the statistical segment length.

to  $T_0^S$ . However, increasing the concentration of long chains stable growth must set in again. We immediately see this for  $p \rightarrow 1$ . This is because for higher concentrations of long chains, the extension step is becoming successful in creating pairs of stretched chains at the growth front. To conclude we obtain a growth gap at intermediate concentrations as a consequence of the kinetic folding pathway for the physically reasonable assumptions  $s_F > 0$  and  $T_0^L > T_0^S$ .

Now, let us discuss critically which other possibilities may be considered for the kinetic pathway of the long chains. Sticking with the assumption that only two crystalline states exist, we might assume that long chains can enter the crystal directly with a cilia instead of being folded. Even then, slowing down of the growth rate for  $p \rightarrow 0$  is still expected because of  $s_{\text{cilia}}$ . The entropic effort for the cilia which enhances the rejection rate of an unpaired cilia-state  $S_-$  would now be responsible for this effect. However, there is a geometric argument against this scenario. In Fig. 7, we have sketched the characteristic ratio between the chain coil in the melt represented by the end-to-end distance  $R$  and the thickness  $L$  of an extended chain crystal. Here we assume a short chain only made of 50 Kuhn's segments of length  $l$ . For the melt chain, we have

$$R = l\sqrt{N}. \quad (12)$$

Therefore, we get for the ratio  $L/R$

$$\frac{L}{R} = \sqrt{N}. \quad (13)$$

From this, we see that even in our example, the ratio  $L/R$  is large. Therefore, the probability for a free long chain to join the growth front in the already stretched conformation is extremely low. On the contrary, one should think that the melt chain enters the crystal via a more complex pathway incorporating an adsorbed state and several steps towards a more extended conformation.

At this point, we can formulate an essential property responsible for the growth gap in bimodal mixtures of oligomers: The long chains have to pass through a kinetic pathway where the first step(s) must represent a weaker state compared to the crystalline state of the short species. An indication for this behavior would be the fact that the effective melting temperature of the folded crystal of long chains is below that of the short chain crystal.

Note that it is not necessary to have the ratio 2:1 between both chain lengths. The latter has been taken only for convenience in the simulations.

Let us finally discuss some general features of the SG-model. First, the model is essentially one-dimensional (representing a cut through the lamellae) assuming that lateral correlations are not important. As an extreme case, it should be contrasted to the Lauritzen–Hoffmann (LH) model [14] which is based on the effect of lateral correlations at the growth front. Moreover, the structure of the crystal is controlled only through the growth front (which is also true for the LH-model). Reorganization of chains

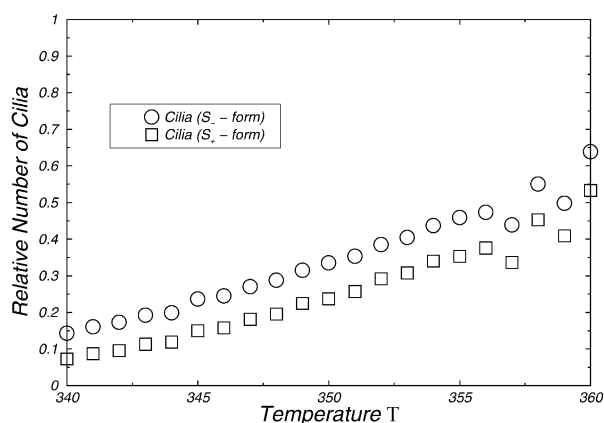


Fig. 8. The number of stretched conformations as a function of temperature for long chains only ( $p = 1$ ). Even at the zero-growth temperature,  $T_0^L \approx 360$ , half of the chains are still in the folded conformation, though the ratio of unbounded cilia ( $S_-$ ) to bounded cilia ( $S_+$ ) decreases to about 20%.

behind the front can only take place if the front retreats which becomes more and more unlikely with time for a given chain since the growth front moves ahead with an average velocity, see Fig. 5. Hence, reorganization is practically suppressed within the crystal. The correlation length for front controlled reorganization processes (it is better to call them reformation processes) is given by the fluctuations of the front position around its mean as a function of time. Therefore, interactions can only propagate a finite distance. This is best illustrated in Fig. 8, where the number of cilia and bonds between cilia, i.e. locally stretched chain crystals, are plotted for a large temperature interval in the case  $p = 1$ . As can be seen, there is no sharp step from the F to the S form. The number of cilia and bounded pairs gradually increases and in particular, the value of unity, i.e. a pure S state is never reached. This is clearly a consequence of the one-dimensional system and the missing reorganization within the crystal. Note also that correlation effects (as long as the correlations have a finite range) as discussed earlier cannot, by statistical reasons, change this observation in a qualitative manner. To obtain a rather sharp transition between F and S states of the crystal, internal reorganization processes behind the growth front together with the real two-dimensional character of the crystal are necessarily to be considered [8].

The SG-model cannot explain melting behavior, but only growth. Increasing the temperature causes just a step in the

thickness of the lamella. This is due to the fact that the liquid phase is not simulated. As a purely kinetic model, it can show only growth or zero-growth but no equilibrium or meta-stable equilibrium between crystal and liquid. Note that the zero-growth temperature discussed in this work is nevertheless an excellent experimental feature and differ from the melting temperature. In particular, there exists *only one* zero-growth temperature for a given chain length. However, most interesting is the result of the front-controlled growth model that *growth stops before the extended form of the crystal is reached*. Hence, one is inclined to conclude that the zero-growth temperature can become independent of chain length for long chains.

In view of the physical interpretations from our model analysis, it would be extremely interesting to test the growth-gap hypothesis in experiments with  $n$ -alkanes. Such experiments could be decisive with respect to the question which folding pathway is taken by long chains and whether a front controlled growth model can reflect this feature properly.

### Acknowledgements

The work has started out of a discussion with Ian Hosier who convinced the author to set up a computer simulation for this problem. The author would like to thank Ian Hosier and Günter Reiter for fruitful discussions.

### References

- [1] Keller A. *Phil Mag* 1957;2:1171.
- [2] Paynter O, Simmonds O, Whiting M. *J Chem Soc Chem Commun* 1982;1982:1165.
- [3] Bidd I, Whiting M. *J Chem Soc Chem Commun* 1985;1985:543.
- [4] Ungar G, Stejny J, Keller A, Whiting M. *Science* 1985;229:386.
- [5] Ungar G, Mandal P, Higgs P, Silva D, Boda E, Chen C. *Phys Rev Lett* 2000;85(20):4397.
- [6] Reiter G, Sommer J-U. *Phys Rev Lett* 1998;80(17):3771.
- [7] Reiter G, Sommer J-U. *J Chem Phys* 2000;112(9):4376.
- [8] Sommer J-U, Reiter G. *J Chem Phys* 2000;112(9):4384.
- [9] Sadler DM, Gilmer GH. *Polymer* 1984;25:1446.
- [10] Sadler DM, Gilmer GH. *Phys Rev Lett* 1986;56(25):2708.
- [11] Sadler DM. *Polymer* 1987;28:1440.
- [12] Doye JPK, Frenkel D. *J Chem Phys* 1999;110(14):7073.
- [13] Hosier I, Bassett D, Vaughan A. *Macromolecules* 2000;33:8781.
- [14] Hoffmann JD, Davis GT, Lauritzen JI. *The rate of crystallization of linear polymers with chain folding*, vol. 3. New York: Plenum Press, 1976. *Treatise in Solid State Chemistry* ed.