Simulation of polymer crystallization kinetics with the Sadler/Gilmer model*

Gerhard Goldbeck-Wood
H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK
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We present the entropy barrier model which was proposed by Sadler and Gilmer as a model for polymer crystallization with chain folding in the roughening régime. We demonstrate how this model can be adapted and extended to deal with a wide range of crystallization phenomena. In particular it has been brought into agreement with growth rates and lamellar thicknesses of a specific polymer (PEEK); it offers a new approach to copolymer crystallization and melting and proves able to simulate crystallization under transient conditions.

(Keywords: polymer crystallization; entropy barrier; copolymer crystallization; copolymer melting; transient kinetics)

INTRODUCTION

Polymer crystals typically grow in the form of thin lamellae with chain-folding[1] back and forth across the thin dimension of the crystal (*Figure 1*). This morphology is understood to be a consequence of a free energy barrier[2–5] which kinetically limits the growth of thicker crystals. The so-called nucleation models[2–4] are based on the assumption that a secondary nucleation process forms a barrier to the crystallization of each layer of stems onto the growth face (*Figures 1* and *3a*). This is a reasonable model if the growth conditions are such that the interface is smooth. A typical example of this type of growth is the polyethylene lozenge shown in *Figure 2a*.

There is, however, strong evidence[5] of crystallization with rounded edges at low supercooling (*Figure 2b*). Despite recent attempts to explain these curved faces within a nucleation theory concept[6,7] the criticism[5,8–10] still holds that these models miss out one important contribution to the growth process. If the density of steps on the growth face is high (*Figure 1*, inset) small chain segments can attach anywhere without creating any extra surface. There is no or only a very small enthapy barrier. The multitude of possible chain configurations (*Figure 3*) which are allowed as intermediate stages of the growth process leads to an entropic growth barrier. It has been shown[8–10] that this mechanism alone suffices to explain the basic phenomenological laws of polymer crystallization, namely that the growth rate behaves like

$$G \sim \exp(-K_g/T\,\Delta T) \qquad (1)$$

and the lamellar thickness like

$$l = a/\Delta T + \delta l \qquad (2)$$

where T is the crystallization temperature, ΔT the supercooling, K_g a constant, and δl a small constant.

In the following section the basic ideas of the entropy barrier model will be presented. We aim to show how this model can be applied to a wide range of crystallization processes of homo- and copolymers.

SUMMARY OF THE SADLER/GILMER MODEL

The main concepts of the Sadler/Gilmer model are those of 'blind-attachment' and 'pinning'[8,9]. As a chain molecule attaches to a rough growth face it does not necessarily choose a conformation which is suitable for later stages of growth, i.e. the stem length lies below the limit required for thermodynamic stability (*Figures 3b* and *c*). It forms chain folds and loops which constitute 'pinned' surface sites; i.e. further attachment onto these sites is impossible. Therefore, growth tends to get frustrated, i.e. blocked by non-viable chain configurations. Net advance of the growth face can only occur by a constant on and off flux of segments which gradually sorts out chain conformations suitable for incorporation into the body of the crystal.

These concepts have been built into a model[8] which regards the polymer molecule as a sequence of so-called units (chain segments of a few monomers) which can attach and detach according to rate constants as if they were independent entities. The only effect of the chain connectivity is considered to be the pinning of certain surface sites as discussed above. This is taken into account by a set of rules which effectively limit the number of sites available for attachment and detachment.

The work presented in this paper is based on a simple two-dimensional version of the Sadler/Gilmer model[10]. A schematic representation of this 'row model' is shown in *Figure 4*. A row of stems is cut out of the crystal perpendicular to the growth face, neglecting all lateral correlations. This is a good representation of the lamella if the surface is sufficiently rough and lateral correlations are therefore small.

The rate constants are calculated from a set of nearest neighbour interaction energies on a square lattice assuming detailed balance to hold between neighbouring states. The ratio of 'off' to 'on' rate constants is fixed by the interaction energy ε and the number of occupied nearest neighbour sites m, the equilibrium melting point T_m° and the crystallization temperature T_c:

$$k^-/k^+ = \exp(2\varepsilon/kT_m^\circ - m\varepsilon/kT_c) \qquad (3)$$

The pinning rules are particularly simple. Attachments

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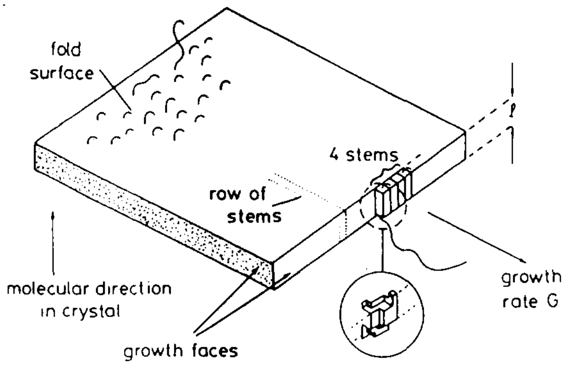

Figure 1 Schematic representation of a polymer crystal indicating the spreading of a layer of stems on the growth face as envisaged by nucleation theories. The inset shows the Sadler/Gilmer view of the rough growth face

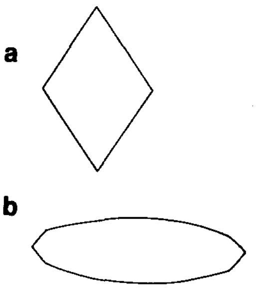

Figure 2 Outlines of shapes of polyethylene single crystals grown from solution (courtesy of S. Organ). (a) At high supercooling, xylene, $T_c = 70$°C. (b) At low supercooling, hexatriacontane, $T_c = 115$°C

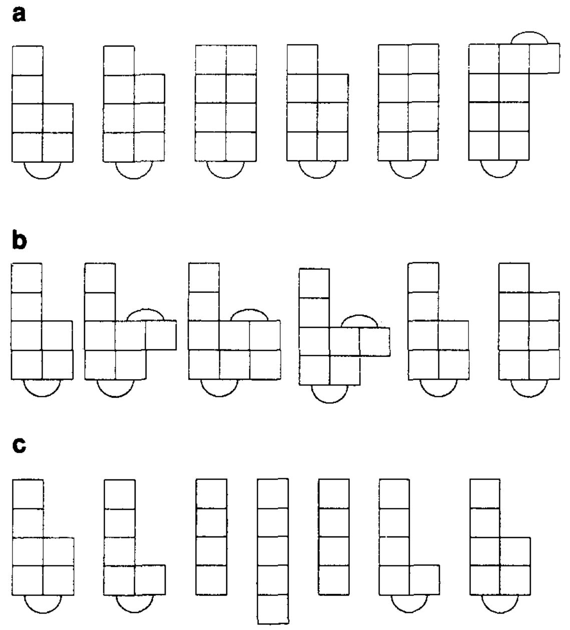

Figure 3 'Fine grained' model of chain folding crystallization as the 'zippering down' of monomer segments (represented by squares). (a) Chain folds only on reaching the specified lamellar thickness. This process is equivalent to the deposition of complete stems[3]. (b), (c) Chain folding allowed at any stage. Fluctuations in stem length involving folding and unfolding become important. Nucleation models which incorporate such processes to a limited extent have been investigated by Point[11], Di Marzio and Guttman[12] and Dupire[13]

and detachments are only allowed at the outermost position (see *Figure 4*).

On this basis the crystallization kinetics can either be simulated using Monte Carlo (MC) techniques[8] or formulated as a set of rate equations which can be solved numerically[10]. The former is more intuitive because on and off events of units are simulated directly and the lamellar growth can be observed in real time on the screen. The statistical uncertainties are considerable however, and the determination of growth rates and lamellar thicknesses requires averaging over many simulation runs. The latter, on the other hand, is an ensemble method and yields a distribution of stem lengths $c_k(i)$, i.e. the fraction of stems at position k which have a length of i units. The statistical error is negligible but the direct information about rearrangements of individual lamellae is lost.

In the following sections we aim to show how both methods have been applied to handle various growth processes.

ISOTHERMAL HOMOPOLYMER CRYSTALLIZATION

Rate equation as well as MC methods have been used by Sadler and Gilmer to determine steady state growth rate and lamellar thickness curves for model homopolymers[8,10]. They could show that the typical phenomenological growth equations (1) and (2) are reproduced.

Recently, we have adapted the model parameters to values specific to poly(aryl-ether-ether-ketone), PEEK, and found[14], considering the simplicity of the model, surprisingly good agreement with experimental growth rate and lamellar thickness data.

ISOTHERMAL COPOLYMER CRYSTALLIZATION

The concepts of 'blind-attachment' and 'pinning' lend themselves to an application to copolymer crystallization. In the simplest case of comonomer exclusion from the crystalline phase the presence of non-crystallizable units simply increases the degree of pinning. Consider e.g. a random distribution of crystallizable units (called 'A') along the chain with a sequence perpetuation

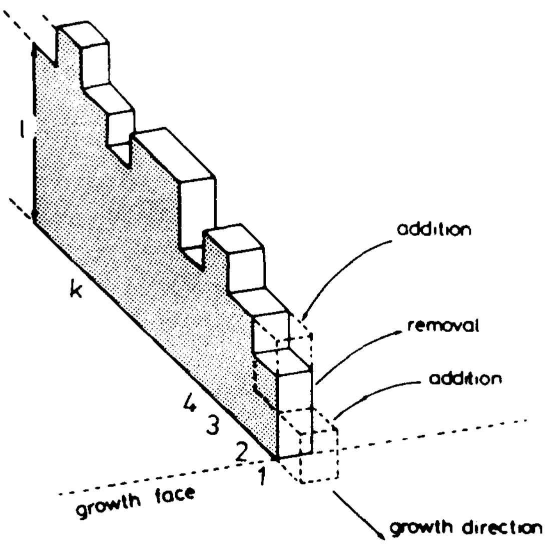

Figure 4 Representation of the row model. Modification to the length of the stems is only permitted at the outermost end of the row (that is at $k = 1$). The length may be increased or decreased by one unit, stems of length unity can be removed, and a new stem of one unit can be created adjacent to the previous outermost stem

probability p. The on-rate constant at position i up the stem is then reduced from its homopolymer value k_0^+ by the probability of finding a sequence of i consecutive A units:

$$k^+(i) = k_0^+ p^{(i-1)} \tag{4}$$

With these on rates and the off rates unchanged we have solved the copolymer rate equations and obtained the relevant steady-state variables as in the homopolymer case[15].

The most important results are as follows.

Growth rates and apparent melting points. The growth rates at a given crystallization temperature decrease with increasing comonomer content $x = 1 - p$ (*Figure 5a*). As the temperature is increased the copolymer rates diverge more and more from the homopolymer curve until they eventually go through zero. This defines an apparent copolymer melting point $T_m^{cop}(x)$. $T_m^{cop}(x)$ (*Figure 6*) decreases with increasing comonomer concentration x much more steeply than the Flory equilibrium melting point depression[16], but compares well with melting points of zero-entropy production experiments[17]. We have argued[15] that this method is closely related to our model.

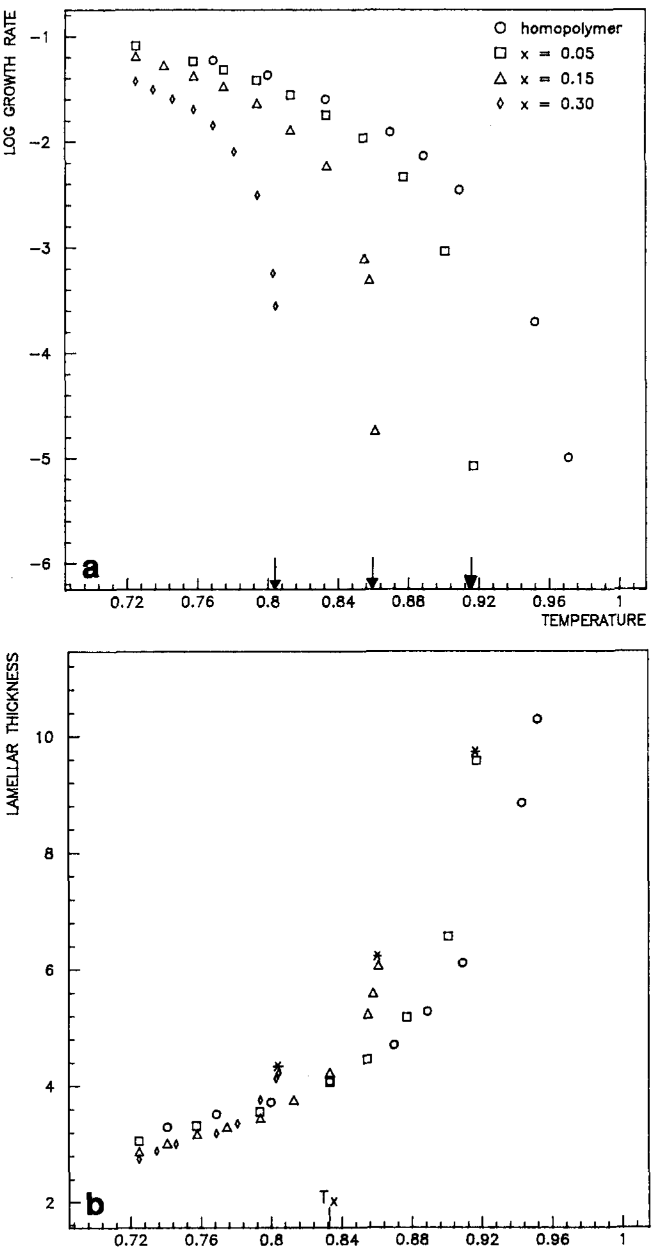

Figure 5 Growth rate and lamellar thickness dependence on temperature (scaled by the homopolymer melting point T_m°) of the model homopolymer and random copolymers. (a) Growth rates, scaled by the on rate constant k_0^+. The arrows indicate the apparent melting points $T_m^{cop}(x)$. (b) Lamellar thicknesses in number of basic growth units. The stars mark the maximum copolymer thicknesses $l_{max}(x)$ at $T_m^{cop}(x)$. T_x is the crossover temperature where (for $x \leqslant 0.15$) l is independent of x. The uncertainty in the data points is small compared with the size of the symbols

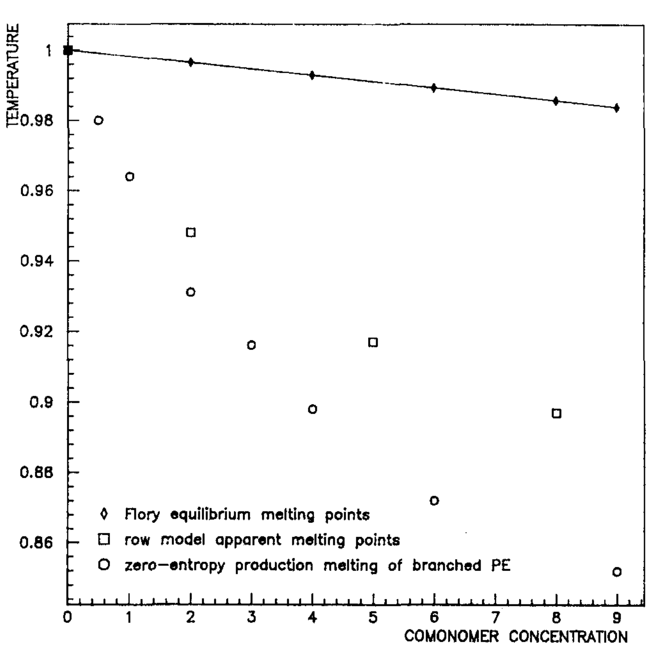

Figure 6 Copolymer melting point depression. Shown are the equilibrium Flory result (calculated with the same heat of fusion as in our model), apparent melting points from our model and maximum melting temperatures of branched polyethylene. The temperatures are scaled by T_m° and the comonomer concentration is given in mole percent

Lamellar thickness. The steady-state average lamellar thicknesses (*Figure 5b*) show a crossover from a low temperature regime where the lamellar thickness decreases on increasing the proportion of non-crystallizable material to a high temperature regime where the reverse is the case. Up to a comonomer concentration of at least 15% we observe a crossover temperature T_x at which the lamellar thickness is independent of comonomer content and equal to the homopolymer thickness. At the apparent melting point $T_m^{cop}(x)$ the lamellar thickness reaches a finite maximum value $l_{max}(x)$ which decreases with increasing comonomer content.

These results have been confirmed by MC simulation[18]. This method, furthermore, allows the treatment of the case of inclusion of comonomer units (called 'B') as defects into the crystal. The free energy gain of crystallization, Δf, is then reduced, or indeed outweighed, by a free energy penalty $f_d(\varepsilon_{AB}, \varepsilon_{BB})$ for AB and BB nearest neighbour interactions in the crystal lattice. (A similar approach to copolymer crystallization but within the framework of a mean field nucleation theory was taken by Helfand and Lauritzen[19].) The ratio of off to on rate constants, equation (3), becomes:

$$k^-(m)/k_0^+ = \exp\{2\varepsilon/kT_m^\circ - [m\varepsilon - f_d(\varepsilon_{AB}, \varepsilon_{BB})]/kT\} \tag{5}$$

In its most general form this model allows the simulation of copolymer growth kinetics for any choice of AA, AB and BB interaction energies. As a simple example we

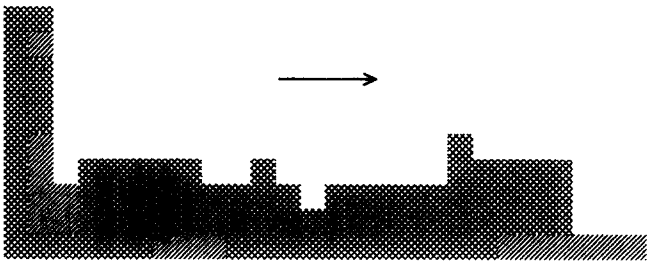

Figure 7 Example of an AB copolymer generated by MC simulation. (The arrow indicates the growth direction.) The cross-hatched area represents A units. The B units (diagonal lines) attract each other and have formed a few clusters in the crystal. The long projection of B's at the growth front is likely to come off again if growth continues

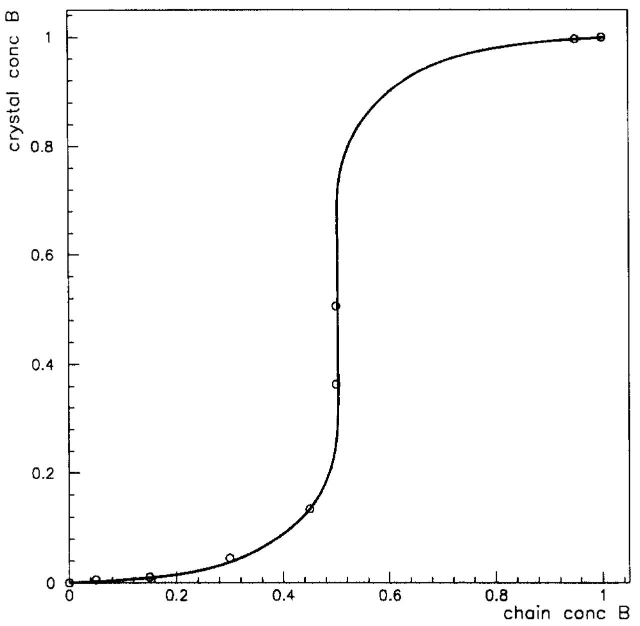

Figure 8 Concentration of B's in the crystal against their concentration along the chain. The S-shaped curve shows that the respective minority component is strongly suppressed from entering the crystalline phase

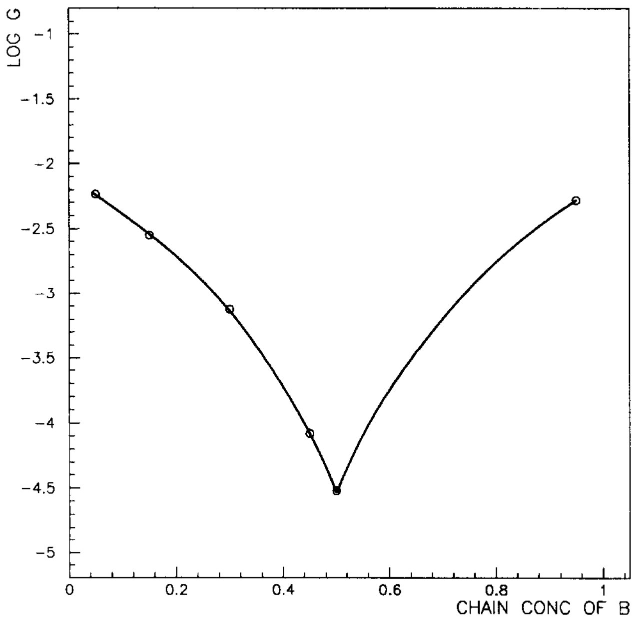

Figure 9 The copolymer growth rate at a fixed crystallization temperature decreases with increasing comonomer content and has a singular minimum at equal proportions of A and B

present here the case of isodimorphism, where both A's and B's can crystallize into an A or B homopolymer crystal but are defects in the respective cocrystals. For simplicity we have chosen the AA and BB interactions to be equal and ascribed to the AB interaction a free energy penalty ε_{AB}. A typical lamella as grown by MC simulation is shown in *Figure 7*. It can be seen that the B's form small clusters in the crystal.

If we fix the crystallization temperature and vary the concentration of B's along the chain from $x=0$ to 1 we notice how the respective minority component is preferentially excluded from the crystal because of the energy penalty (*Figure 8*). At exactly equal amounts of A and B, the concentration curve has a singularity. Random fluctuations decide which population gains the majority and these clusters will then grow. Therefore, the distribution of A's and B's varies strongly from case to case. It is not surprising that the growth rate has a minimum at this point (*Figure 9*). The concentration of defects which enters the crystal, C_B, is strongly dependent on supercooling (*Figure 10a*). At high supercoolings the free energy driving force is so strong that the defects are incorporated into the crystal at almost the same concentration as they occur along the chain. At lower supercoolings growth is slower so that there is time to sort out energetically more favourable configurations. This is in qualitative agreement with the result of Helfand and Lauritzen[19]. Similarly, we find agreement concerning the thickness of the copolymer lamellae in comparison to the pure ones grown at the same temperature (*Figure 10b*). The copolymer needs extra thickness to compensate for the free energy loss due to the defects. The supercooling dependence of defect concentration and lamellar thickness is such that their product, i.e. the actual number of defects per stem (however long) is independent of supercooling (*Figure 10c*).

This example should just serve to demonstrate the capabilities of this new approach to copolymer crystallization and further investigations are presently under way.

TRANSIENT CRYSTALLIZATION KINETICS

Crystallization experiments often involve non-isothermal conditions. Under such circumstances the kinetics cannot settle into a steady state but rather develop through transient states which are beyond the reach of nucleation type models. The rate theory row model in its most comprehensive form[14] however, is capable of treating this problem. In each time step we simply calculate a new set of rate constants according to the temperature prevailing at that instant and update the lamellar configuration by numerical integration. With this extended model we have studied the cases of crystallization during heating at a constant rate and crystallization under stepwise changes in temperature. A lamella which had reached its steady state thickness l_0 at temperature T_0 was used as an initial configuration. First, we consider the case of constant heating. *Figure 11* shows the position and thickness of the lamella in a sequence of equal time steps. It can clearly be seen how the lamellar thickness increases trying to keep above the limit required for thermodynamic stability. But even at extremely slow heating rates thickening is not fast enough and the growth rate decreases and eventually goes through zero. This simulation is computationally very expensive, however.

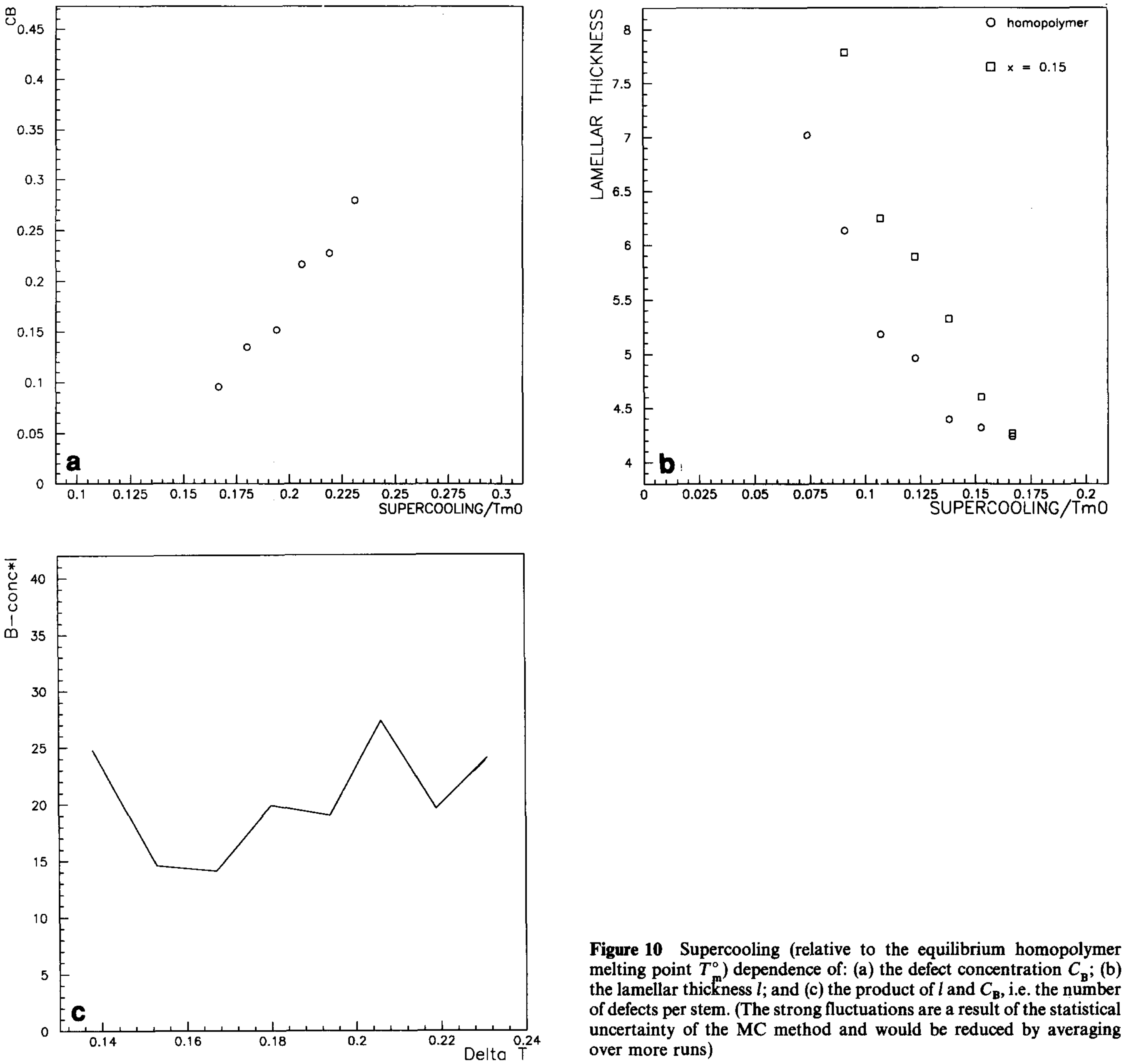

Figure 10 Supercooling (relative to the equilibrium homopolymer melting point T_m°) dependence of: (a) the defect concentration C_B; (b) the lamellar thickness l; and (c) the product of l and C_B, i.e. the number of defects per stem. (The strong fluctuations are a result of the statistical uncertainty of the MC method and would be reduced by averaging over more runs)

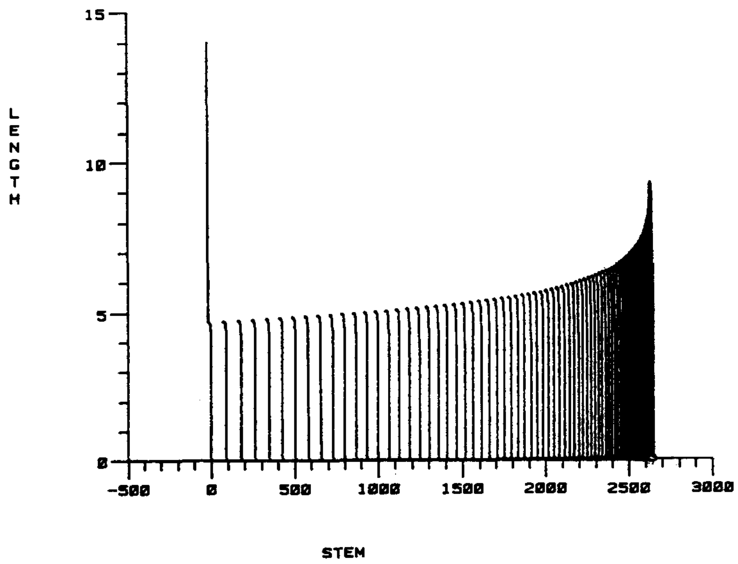

Figure 11 Lamellar growth during heating at a constant rate simulated by the rate equation row model. Positions and thicknesses of the lamella are shown in a sequence of equal time steps

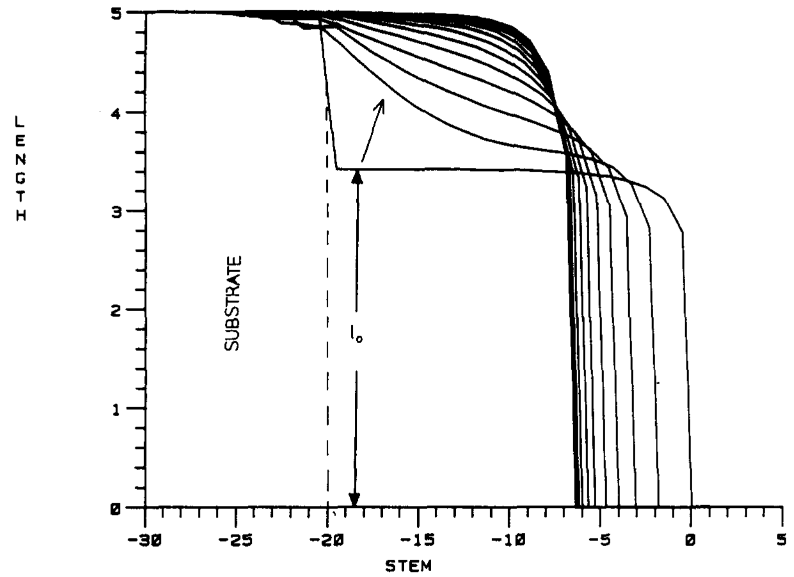

Figure 12 Lamellar rearrangement to a new steady state following a large temperature rise

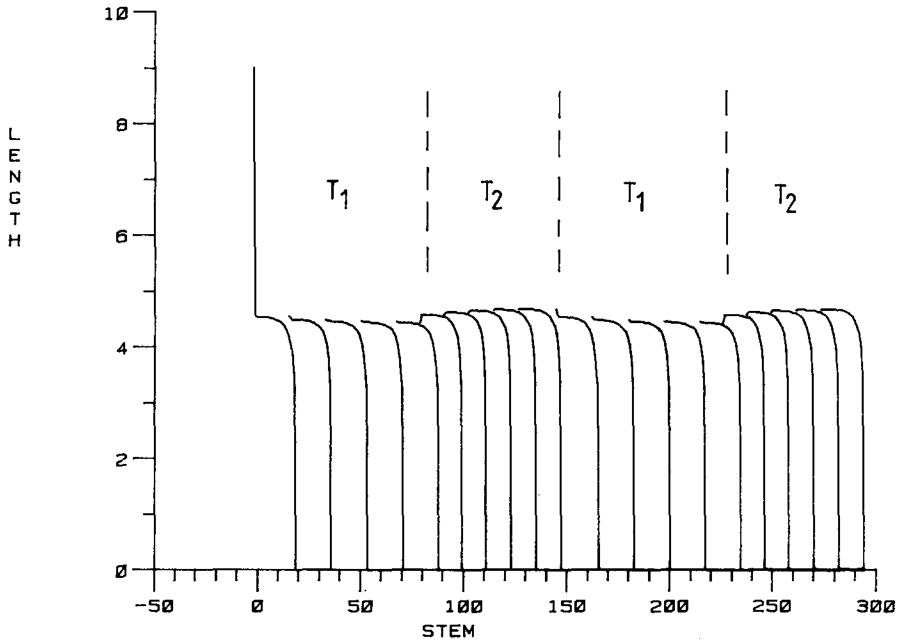

Figure 13 Simulation of isochronous decoration. Small up and down steps in temperature ($T_1 < T_2$) leave steps on the surface

The case shown in *Figure 11*, for example, has taken about 150 h of CPU time on an AMT-DAP 510 array processor. Second, we have submitted a lamella grown onto a substrate to an instantaneous rise in temperature. The step was taken to be so large that the lamellar thickness l_0 lay below the minimum stable thickness at the new temperature. As we observe in *Figure 12* the crystal starts melting back while thickening at the same time. The thickening is fastest near the substrate. At this point it is important to remember that on and off events are restricted to the growth front by the pinning rules. The thickening in the bulk must therefore be due to fluctuations of individual lamellae in the ensemble which take their hypothetical growth fronts right back to the substrate onto which they can grow again at a more stable thickness. A third interesting case is a series of small increases and decreases in temperature rather like those used by Dosière *et al.*[20] in their isochronous decoration technique. The growth sequence (*Figure 13*) shows the steps this leaves on the surface.

These examples should only serve to illustrate the model and its possible applications. Further and more detailed results will be published elsewhere[21].

CONCLUSIONS

We have presented a very simple version of the Sadler/Gilmer model of polymer crystallization which is based on the assumption that an entropy barrier is the rate determining factor under rough surface conditions.

We have demonstrated how this model, using either rate theory or MC techniques, can be applied to a wide range of crystallization processes and offers new insight into areas like copolymer crystallization and transient kinetics.

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