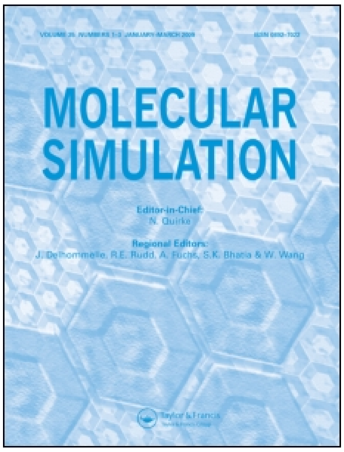

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SIMULATION OF STEADY STATE AND TRANSIENT POLYMER GROWTH KINETICS. APPLICATION TO PEEK

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A simple two-dimensional rate-theory model demonstrates the principal effects of the Sadler/Gilmer theory of isothermal polymer crystallization. In addition it can be used to describe specific polymers by setting its parameters accordingly. We report on recent results of modelling the aromatic thermoplastic poly(aryl-ether-ether-ketone) (PEEK), in particular its isothermal growth rates, lamellar thicknesses and melting point. An extension of this model has made possible for the first time the study of transient processes such as heating scans and annealing. We report on first results.

KEY WORDS: Polymer crystallization, polymer melting, rate theory model, rough surface growth, modelling PEEK crystallization, 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 has long been thought to arise from a nucleation controlled growth process [2–4]. It has now been shown [5–7] that this is not necessarily the case, since reentrant corners on the perimeter of the lamellae do not have the dramatic effect on crystallization rate that would be predicted.

An alternative explanation [8–10] of lamellar growth is based on a "frustration" mechanism: the molecules attaching to a growth face are thought to do so "blind", i.e. they do not necessarily choose conformations which are suitable for a later stage of growth. This leads to a) the existence of steps in the growth face ("roughness" [8]) and b) to many crystal surface sites being pinned by loops (Figure 1). These pinning sites result in growth being blocked to an increasing extent as the lamellar thickness increases with crystallization temperature (i.e. as the number of unsuitable rounded-edge configurations with pinned surface sites increases exponentially [11]). Net advance of growth faces is thought to occur by a constant on and off flux. This only gradually sorts out chain conformations suitable for incorporation into the body of the crystals. This process has been identified as an entropy barrier [8–10] which has to be overcome for growth to proceeed. Based on these characteristics of roughness and pinning a new theory of polymer crystallization has been proposed [8–10]. It has been demonstrated [8–10] that this model reproduces well the main characteristics of

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[†] Dr. D.M. Sadler died tragically in May 1988. The work presented here is based on his ideas and guidelines and it is to him that credit is due. After his death I have worked out the results as they are presented here. So all blame for any errors is mine. (G. Goldbeck-Wood)

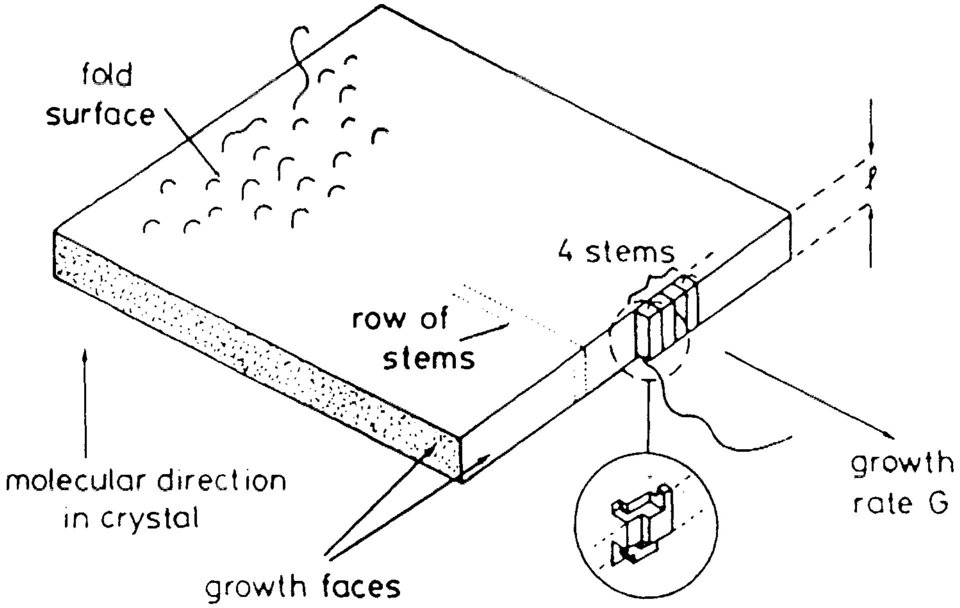

Figure 1 Schematic representation of a polymer crystal indicating the chain direction, fold and growth surfaces, and the nature of a growth face step as envisaged by nucleation theories [2]. The inset shows an alternative view of the region of the growth face involving a step in which case the stems at the growth face can be short.

polymer crystallization, namely the dependence of lamellar thickness l and growth rate G on the supercooling ΔT:

$$l \sim \Delta T^{-1}, \tag{1}$$

$$G \sim \exp(-C/T\Delta T). \tag{2}$$

In this paper we aim to show how this theory can be adapted for the modelling of the aromatic thermoplastic poly(aryl ether ether ketone) (PEEK) [12], and how it can be extended for the simulation of transient processes.

THE MODEL

The investigations presented in this paper are based on the two dimensional rate theory row model [9, 10]. A schematic representation is shown in Figure 2: a slice of "stems" (sequences of chains in the lamella) is cut out of the crystal perpendicular to the growth face (Figure 1), neglecting any lateral correlations. This is a good approximation if the surface is sufficiently "rough" [8, 9]. Growth proceeds by the addition and removal of "units" (small chain segments which are not much greater than the molecular repeat) according to rate constants for nearest neighbour interactions. The ratio of off to on rate constants is given by

$$k^-(m)/k^+ = \exp[2\varepsilon/kT_m^0 - m\varepsilon/kT], \tag{3}$$

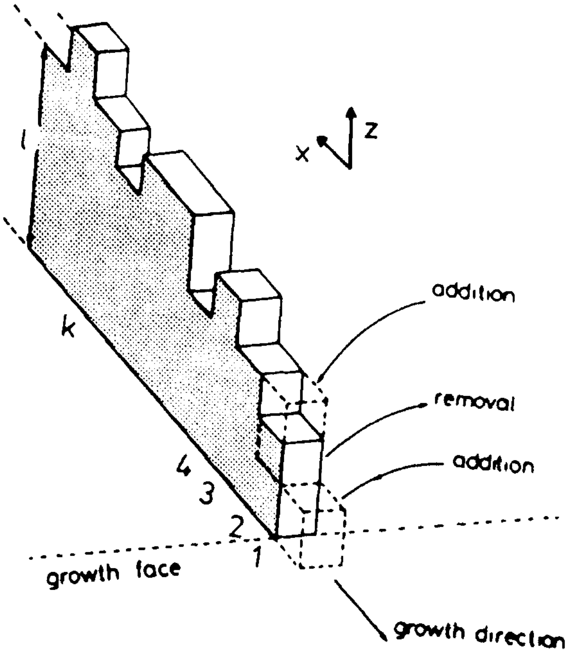

Figure 2 Representation of the row of stems model. Modifications to the lengths of stems are only permitted at the outermost end of the row (that is at k = 1): The length may be increased or decreased by one unit, stems of length unity can be removed, and a new stem of one unit can be created adjacent to the previous outermost stem.

where m is the number of nearest neighbours to the growth unit, ε is the interaction energy between these units, and T_m^0 is the equilibrium melting point. Due to the pinning effect these processes are restricted to the growth front, i.e. position k = 1, as indicated in Figure 2. These kinetics can be expressed as a strictly sequential process and written in the form of rate equations for the joint probabilities $P_1(i,j)$ [9], where i is the stem length in number of units at position $k = 1$ and j is the stem length of the second layer. Taking account of all possible events at the growing face of the crystal we get for $i > 1$,

$$dP_1(i,j)/dt = k^+P_1(i-1,j) + k^-(i+1,j)P_1(i+1,j) - k^+P_1(i,j) - k^-(i,j)P_1(i,j) + P_1(1,i)k^-(1,i)f_1(i,j) - k^+P_1(i,j), \quad (4)$$

and for $i = 1$,

$$dP_1(1,j)/dt = k^+C_1(j) + k^-(2,j)P_1(2,j) - k^+P_1(1,j) - k^-(1,j)P_1(1,j) + P_1(1,1)k^-(1,1)f_1(1,j) - k^+P_1(1,j). \quad (5)$$

where $C_k(i)$ is the concentration of stems of length i at position k behind the outermost stem and $f_k(i,j)$ is the conditional probability that the $k+1$th stem is of length j given that the k stem is of length i.

Numerical integration of these equations leads to a steady state where conditional probabilities are found to be independent of position. Therefore concentrations $C_k(i)$

and average lengths of stems can be calculated at any position k on the basis of the front configuration [9, 10]. If, however, we are interested in transient processes we need to consider rate equations for the joint probabilities at all k throughout the crystal down to some substrate where appropriate boundary conditions are applied. The additional rate equations for $k > 1$ are [13]:

$$\begin{aligned} dP_k(i,j)/dt &= k^+ P_{k-1}(i,j) - k^+ P_k(i,j) \\ &+ k_1^-(k-1,i) f_{k+1}(i,j) - k_1^-(k-2,i) f_k(i,j), \end{aligned} \qquad (6)$$

where
$k_1^-(k-1,i)$ is the sum over all lamellae with a length i at position $k-1$ times the rate of removal of the outermost stem. This is the extended version of the "rate model" which will allow the simulation of polymer growth kinetics, both steady state and transient, with high numerical accuracy.

MODELLING ISOTHERMAL CRYSTALLIZATION OF PEEK

PEEK crystallized from the melt or glassy state forms spherulites with curved lamellar branches. The roughness/pinning row model should therefore be suitable for the description of crystallization of this polymer. To this end we must adjust the model parameters to the specific values of PEEK:

a) The equilibrium melting temperature T_m^0: Isothermally crystallized PEEK analyzed by differential scanning calorimetry (dsc) shows two distinct melting peaks. There is at present a controversy concerning the origin of these peaks. D.J. Blundell [14, 15] interpretes the lower peak as being due to the initial morphology and the upper peak as the melting of the lamellar structure which has rearranged during the scan. The equilibrium melting point has therefore been determined by a Gibbs-Thomson extrapolation of the lower melting points which yields $T_m^0 = 395°C$. The error in this value must be regarded as non-negligible, however, as the extrapolation extends over more than 60 K with the additional assumption that the ratio of enthalpy and surface free energy is constant over this range. The interpretation of D.C. Basset *et al.* [16], on the other hand, is that the upper peak is related to the melting of the main structure and the lower peak represents a substructure which has formed at a later stage of crystallization. By a rough Gibbs-Thomson extrapolation of the upper peaks we have obtained a value for T_m^0 of about 350°C. A very recent investigation [17] of equilibrium melting of polymer crystals, claiming high precision, estimates the PEEK melting point to lie at 370°C. In view of this uncertainty as to the value of T_m^0 we will compare the simulation results with experimental data scaled by all three values, i.e. 350°C, 370°C, and 395°C.

b) The length of one "unit": l_u. The complete unit cell of PEEK consists of six aryl units in the c direction [12]. The effective subcell, however, is only two aryl units long [12]. We will regard this subcell as the growth unit of our model. Its length l_u is therefore approximately 10 Å.

c) The interaction energy ε. An estimate of the average unit-unit interaction energy can be based on the enthalpy of fusion h for one unit in a perfect crystal. In our nearest neighbour approximation this must be set equal to the sum of interactions of one unit with neighbouring cells. For a system with four nearest neighbours we have $h = 2\varepsilon$. With the value [14] $h = 130\,J/g$, the density $\varrho = 1.4\,g/cm^3$ and the unit cell par-

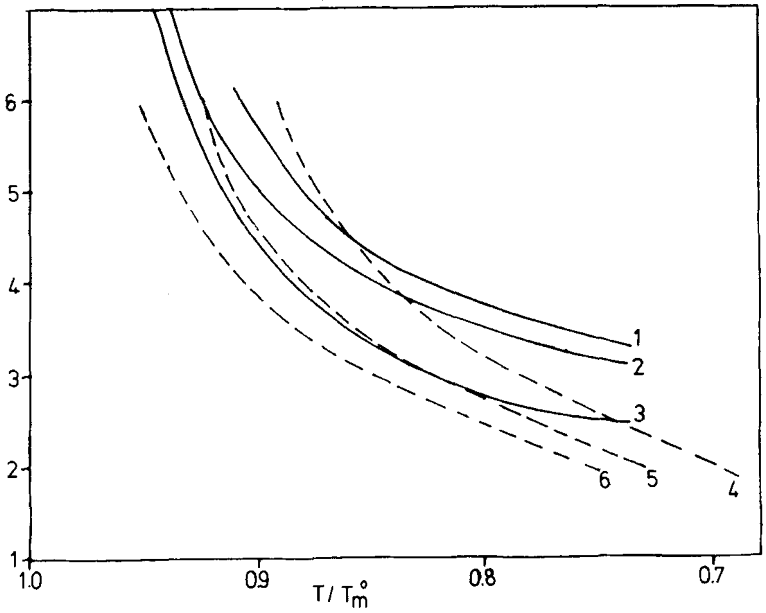

Figure 3 Lamellar thickness vs. temperature as obtained from simulation (solid lines) for $kT_m^0/\varepsilon = 0.35$ (1), 0.55 (2) and $kT_m^0/\varepsilon_{1,2} = 0.32, 0.5$ (3), and for PEEK scaled by $T_m^0 = 395°C$, 370°C, and 350°C (dashed lines 4, 5, and 6, respectively).

ameters [12] $a = 8Å$, $b/2 = 3Å$ (the next layer is at the 1/2 position), and $c = l_u = 10Å$, we get $\varepsilon = 2.2*10^{-20}$ J/unit, or $kT_m^0/\varepsilon = 0.43$ for $T_m^0 = 395°C$ and $kT_m^0/\varepsilon = 0.40$ for $T_m^0 = 350°C$.

Steady state growth rate and lamellar thicknesses have previously [10] been obtained using equations (3), (4), and (5) with the energy ratios $kT_m^0/\varepsilon = 0.2, 0.35$, and 0.55. Because of the "stiffness" of the PEEK molecule [18] we have introduced an anisotropy by setting $kT_m^0/\varepsilon_1 = 0.32$ and $kT_m^0/\varepsilon_2 = 0.5$, where ε_1 and ε_2 are the interaction energies in the x and z direction, respectively (see Figure 2). The curves thus obtained will be compared with PEEK data [14, 19] scaled by T_m^0.

Lamellar Thickness

The thicknesses of isothermally grown lamellae are shown in Figure 3. The solid lines (1, 2, 3) are simulation curves for the three cases of interaction energies considered. The dashed lines (4, 5, 6) represent the experimental data with the different temperature scalings. A good fit is achieved with the anisotropic energy parameters and a T_m^0 of 370°C except for supercoolings greater than $0.2\,T_m^0$. In this regime the simulation curve seems to reach a plateau whereas the experimental thicknesses are decreasing almost linearly. A likely explanation for this discrepancy is that the simulation does not adequately describe the growth process at stem lengths of only about two units because surface effects become more important than the typical fluctuations in stem length on which the model is based (see Figure 1).

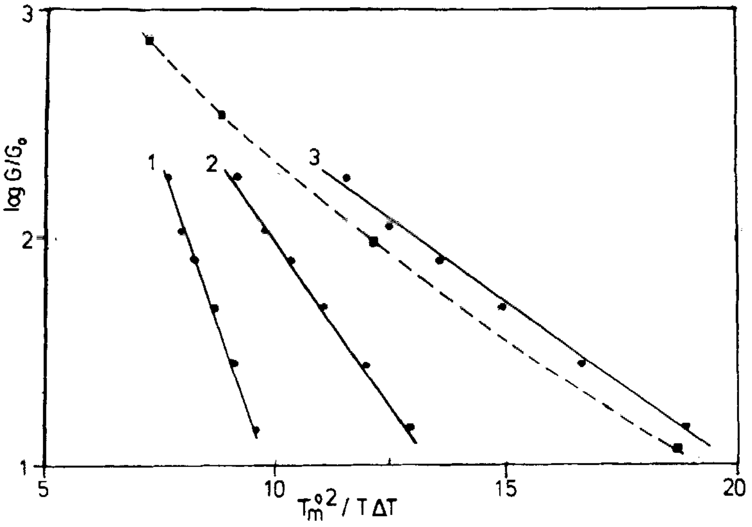

Figure 4 Logarithmic growth rate plot showing the simulation curve for $kT_m^0/\varepsilon_{1,2}$ = 0.32, 0.5 (dashed line) and PEEK data [19] scaled by T_m^0 = 395°C, 370°C, and 350°C (solid lines, 1, 2, and 3, respectively).

Growth Rates

The typical logarithmic growth rate plot is shown in Figure 4. The experimental data [19] are corrected by a transport factor [14]. The model growth rates are scaled linearly by the on-rate k^+ which has been chosen so that slopes can be compared easily. The change in slope with T_m^0 is very marked, giving a very good fit for T_m^0 = 350°C as against T_m^0 = 395°C, which is clearly too high.

We conclude that the rate equation row model is capable of simulating PEEK crystallization kinetics given the right choice of parameters. It gives further evidence for a melting point lower than 395°C. The steady state analysis is, however, not capable of telling us anything about lamellar rearrangement processes during heating and their influence on the melting point. This problem will be addressed in the following section.

SIMULATION OF TRANSIENT PROCESSES

As a starting point for any simulation of transients we have calculated a steady state configuration at a temperature T_0. This configuration is then subjected to some temperature changes, either in the form of a stepwise increase to simulate annealing processes or in the form of a slow linear heating for comparison with differential scanning calorimetry. This affects the rate constants (3) which enter into the rate equations (4), (5), and (6) for the $P_k(i, j)$. These are considered for twenty different positions k. At k = 20 the boundary conditions are a substrate of fixed length N in the case of melting (negative growth rates), or constant conditional probabilities $f_{21}(i, j) = f_{20}(i, j)$ (like in the steady state) in the case of positive growth rates. By means of numerical integration of this set of rate equations we can observe the development of the lamellar structure.

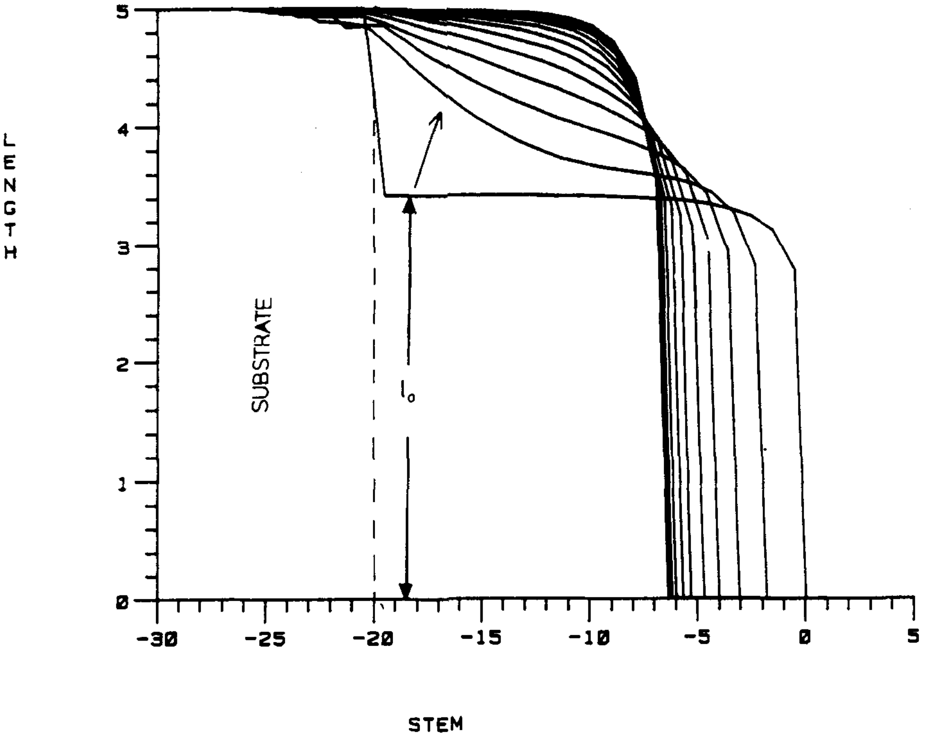

Figure 5 Stages of lamellar rearrangement during isothermal annealing. The arrow indicates the direction of time.

The process we will examine first is the annealing of a short chain polymer. The initial configuration was annealed at a temperature just below the melting point of the extended chain crystal. The time development of the average lamella is shown in Figure 5. Initially, at a temperature of $T_0 = 0.77\,T_m^0$, the average lamella has an average thickness of about 3.4 units, is tapered near the growth front and fixed to a substrate of length N = 5 units. This is also the maximum allowed stem length, i.e. the length of the extended chain. The temperature is then raised instantaneously to $0.9\,T_m^0$. The average lamella is 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. Therefore the thickening in the bulk of the average lamella must be due to fluctuations of some individual lamellae which take their growth fronts right back to the substrate, onto which they can grow again at a more stable thickness. The sequence in Figure 5 which is taken at equal time intervals shows how the melting slows down, and how it stops when the new steady state configuration is reached. The growth rate settles at a value just above zero (Figure 6) and the average thickness increases to 4.95, just below the limit of N = 5 (Figure 7).

A second transient process of particular interest is linear heating during crystallization. Although the simulation assumes the lamella to be surrounded by its melt (i.e.

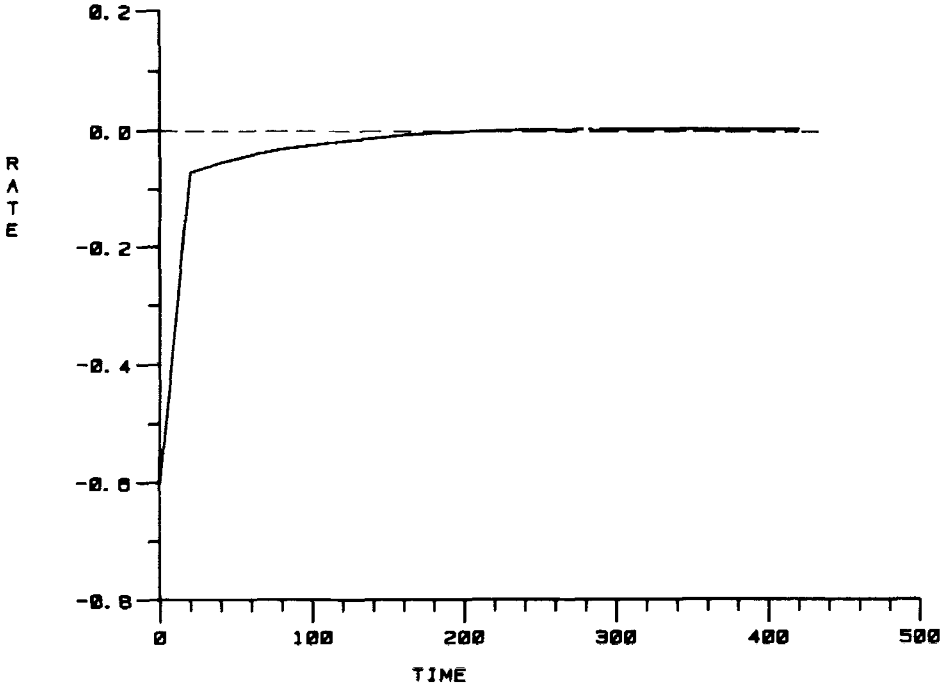

Figure 6 Growth rate development during isothermal annealing. Time is measured in arbitrary units.

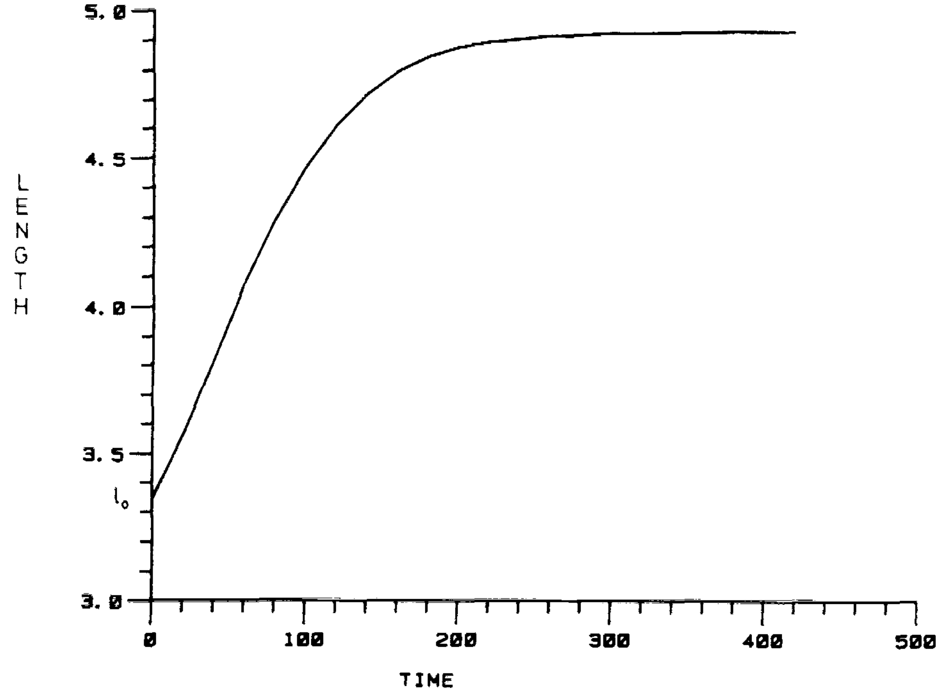

Figure 7 Lamellar thickness development during isothermal annealing.

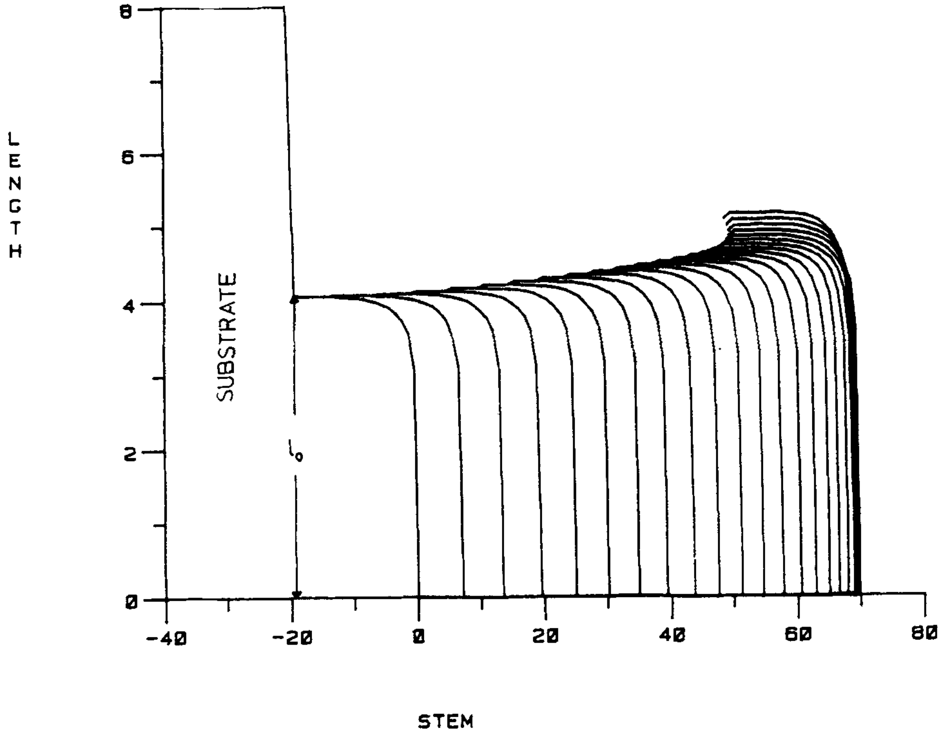

Figure 8 Lamellar growth during linear heating. At each stage only the first twenty stems behind the growth front are shown. The time sequence is taken at equal time intervals.

there is a flux k^+ of material onto the growth face), the lamellar rearrangement processes might be related to those in a dsc analysis. This time we do not put any constraint on the lamellar thickness (i.e. the number of units considered is taken to be sufficiently greater than the average thickness). The time sequence (Figure 8) shows a decreasing growth rate and a thickening near the edge region (see also Figures 9 and 10). Eventually the growth rate goes through zero. This should mark the onset of a final dsc melting peak. It is also possible to trace the "fate" of the initial structure by following the growth rate of the subset which has the initial thickness (Figure 11). Melting sets in at a considerably lower temperature than for the rearranged average lamella. This could be related to the typical lower dsc peak if that is considered to be due to the initial crystal morphology [16].

At this stage we cannot attempt any numerical comparisons, especially because the heating rate in the simulation shown above is unrealistically high – of the order of thousands of degrees per minute. A typical heating rate in a dsc experiment is 20°C/min. A simulated scan at this rate has taken several days of CPU time on the departmental Vax6200. Despite these limitations more detailed analyses are now under way.

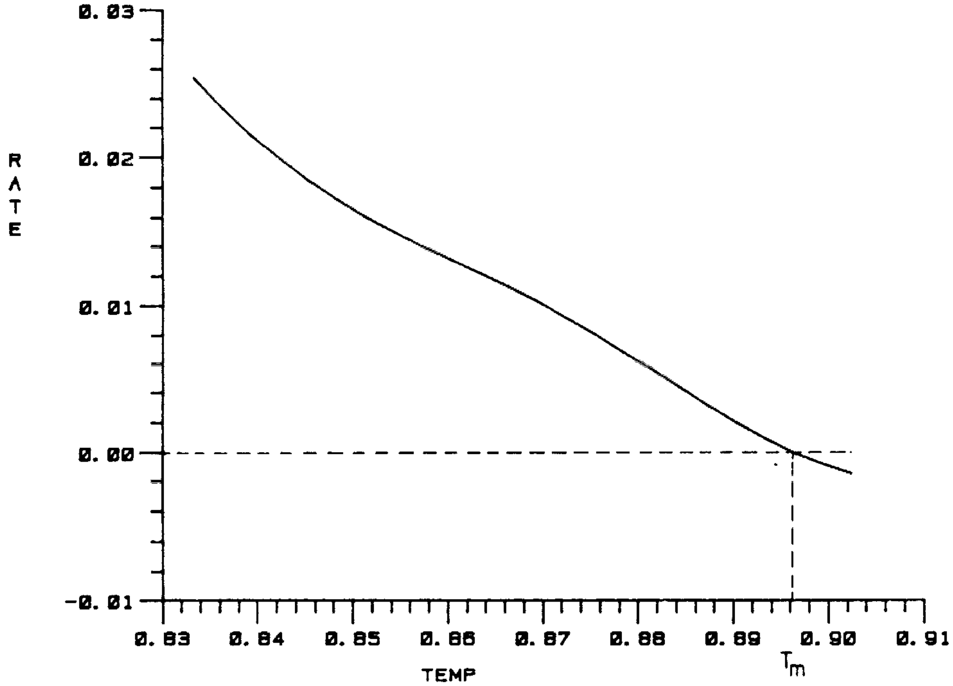

Figure 9 Growth rate of average lamella vs temperature during linear heating. Melting sets in at $T_m = 0.896T_m^0$.

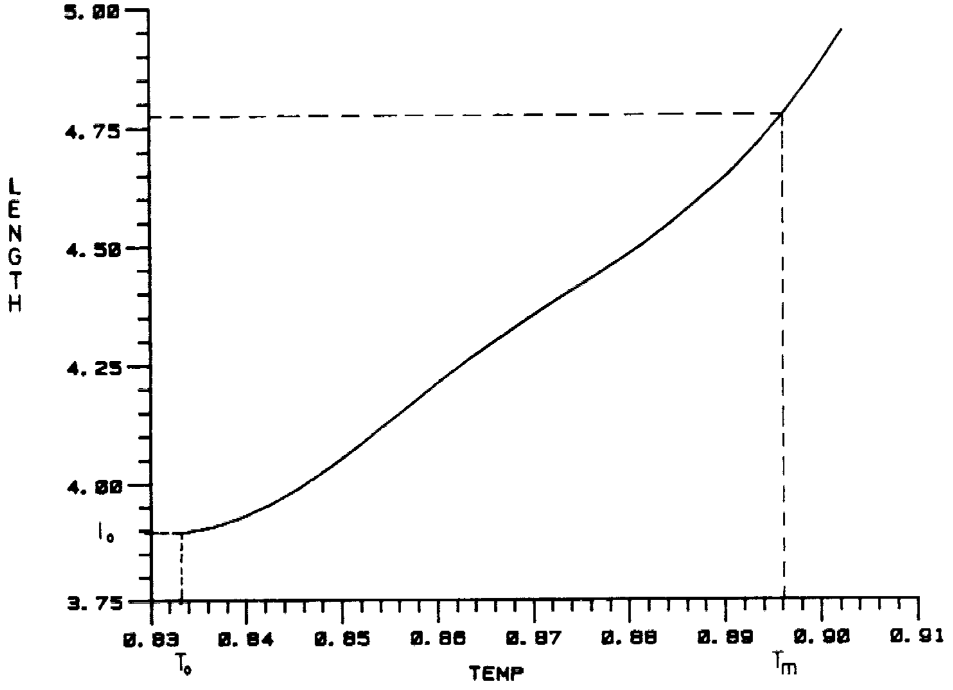

Figure 10 Lamellar thickness development during linear heating.

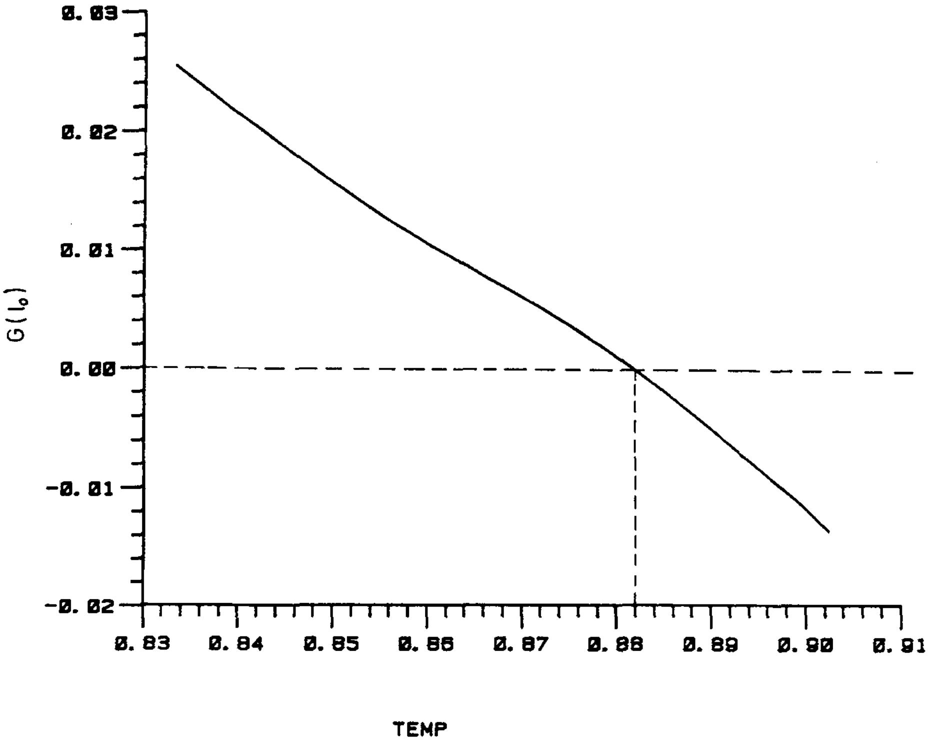

Figure 11 Growth rate of lamella of initial thickness l_0 vs temperature during linear heating. Melting starts at $T = 0.882T_m^0$.

CONCLUSION

We have demonstrated that the rate equation row model is capable of simulating PEEK crystallization kinetics. We have presented the first simulation of transient polymer growth and melting processes using an extended version of the rate equation row model. We believe that this will help us understand better the mechanisms involved.

Acknowledgement

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