On the melting-point depression of copolymer crystals

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(Received 20 August 1990; accepted 23 November 1990)

The melting-point depression of a random copolymer with comonomer exclusion from the crystalline phase is investigated. The analysis is based on simulation results obtained with an extended Sadler–Gilmer crystallization model. Apparent copolymer melting points $T_m^{cop}(l)$ of lamellae of finite thickness l are observed. Further thickening is entropically suppressed. It is shown that the average lamellar thickness and the minimum thermodynamically stable thickness converge at T_m^{cop}. The fine-grained nature of the model reveals an entropic contribution to the melting-point depression, which is due to the so-called blind attachment of chain segments to the growth face. Our new 'kinetic' melting-point equation is compared with the 'equilibrium' result by Flory and shows a considerably stronger melting-point depression.

(Keywords: copolymer; melting point; mixing entropy; driving force; modelling; Sadler–Gilmer model)

INTRODUCTION

The calculation and interpretation of melting points is an issue of primary importance. It is central to the very practical problem of handling experimental data. Our understanding of the melting-point depression of copolymer crystals is based mainly on the equilibrium theory by Flory[1] and some extended versions thereof[2,3]. The assumption in the interpretation of experimental data has tended to be that an adjustment of the supercooling ΔT by the difference between the equilibrium copolymer melting point $T_m^{0,cop}$ and the equilibrium homopolymer melting point T_m^0 enables the usual equations for homopolymers to be employed. The lamellar thickness, for example, is predicted[2] to be inversely proportional to the copolymer supercooling, therefore going to infinity as $T_m^{0,cop}$ is approached. This is a drastic *ad hoc* assumption, which is most certainly not valid, at least in the light of simulation results presented in a previous paper[4]. As described there, the model copolymer shows a 'natural' or 'in-built' limit to the lamellar thickness as a result of non-crystallizable chain segments.

The following analysis of the forces at work in the kinetics of copolymer crystallization aims to explain the origin of this phenomenon and the associated melting-point depression.

MODEL AND SUMMARY OF SIMULATION RESULTS

The model employed (*Figure 1*) is an extension[4] of the Sadler–Gilmer model[5], which envisages polymer crystallization as a process of 'blind' attachment and detachment of small chain segments at the outermost position. At any stage of building up a straight sequence traversing the lamella (a so-called 'stem'), a new stem can start forming adjacently, thereby blocking further growth of the previously outermost stem.

This process can be interpreted as describing either regular adjacent chain folding along the growth face, therefore providing a model of a layer on a flat growth face, or 'rough surface growth' with the stems representing the laterally uncorrelated growth layers, in which case we have a simplified model of the whole lamellar crystal.

During crystallization many configurations $\{l_k\}$ (*Figure 1*) are explored before material gets finally incorporated into the 'bulk' of the crystal. This leads to a limitation in the fold length, which is entropic in nature[5,6], rather than enthalpic like in secondary nucleation models[7,8].

This fine-grained approach lends itself to the simulation of an A–B copolymer. The model which was put forward in a previous paper[4] is based on the conjecture that the presence of non-crystallizable (B) chain segments leads to a progressively reduced rate constant for attachment with increasing thickness. The simulation demonstrated that with increasing crystallization temperature the average lamellar thickness does not increase beyond a certain maximum value. This point, at which steady-state growth ceases, defines an apparent copolymer melting point T_m^{cop}. In the present paper we are going to derive an analytical expression for T_m^{cop} based on the Sadler–Gilmer model.

ANALYSIS OF GROWTH KINETICS

Introduction

In any kinetic theory of polymer crystallization[6–9] the average growth rate G of an ensemble of lamellae of average thickness l can be separated into a product of a barrier term $a_0(l)$ and a driving force term $d(\delta l)$ (*Figure 2*), where $\delta l = l - l_m$, and l_m is the minimum

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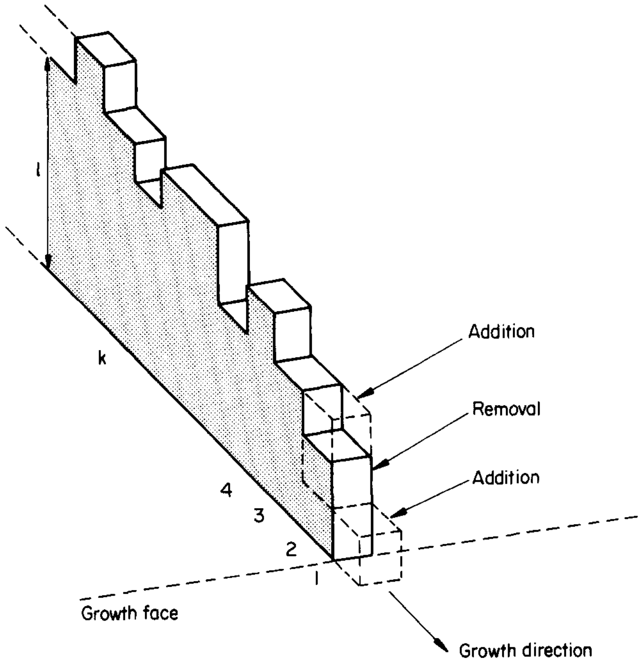

Figure 1 Schematic representation of the Sadler–Gilmer row model. Attachments and detachments are only allowed at the outermost end of the row (that is at $k=1$) because other surface sites are 'pinned' by folds and loops. The length may be increased or decreased by one unit, stems of length unity can be removed, and a new stem of one unit can be created adjacent to the previous outermost stem at any stage

thermodynamically stable thickness:

$$G = ka_0(l)d(\delta l) \tag{1}$$

The barrier term is responsible for limiting the lamellar thickness as observed by experiment. Its precise origin, however, is a matter of great dispute. There are essentially two opposing models:

(i) The so-called nucleation models[7,8] envisage some kind of high-energy barrier due to the need for secondary nucleation of stems.
(ii) 'Entropy barrier' models[5,6,9], to which group the present model belongs, emphasize the importance of the configurational path degeneracy of the long-chain molecule. In the attachment process this leads to an entropic contribution to the surface free energy, as described briefly in the previous section.

Both models predict a similar exponential dependence of the growth barrier on lamellar thickness.

The driving force, on the other hand, is generally thought to be related to the thermodynamically derived Gibbs free energy. In the presence of non-crystallizable chain segments, however, the envisaged mode of chain attachment—complete stems or small units—does affect the driving force term as well as the barrier. It will be shown that this has a strong influence on the expected copolymer melting behaviour.

An analytical expression for the driving force can be given in a first approximation by the Wilson–Frenkel law, which describes the growth at a kink site (German: *Halbkristallage*), i.e. a site at which addition or subtraction of a solid cell does not change the number of solid–fluid neighbours:

$$d(\delta l) = 1 - \exp(-\delta f/kT) \tag{2}$$

where δf is the net free-energy difference between the phases:

$$\delta f = \Delta f - (\sigma_e + \sigma_e')/l \tag{3}$$

Here σ_e and σ_e' are the free energies of the top and bottom end surfaces of a lamella of thickness l and infinite lateral extent. The bulk free-energy difference Δf can be approximated by:

$$\Delta f = h\Delta T/T_m^0 \tag{4}$$

where h is the heat of fusion at the equilibrium melting point T_m^0. With the condition that $\delta f = 0$ at $l = l_m$ we get the Gibbs–Thomson relation:

$$h\Delta T/T_m^0 = (\sigma_e + \sigma_e')/l_m \tag{5}$$

so that

$$\delta f = h\frac{\Delta T}{T_m^0}\frac{\delta l}{l} \tag{6}$$

Eventually, with equation (2) this leads to the following approximation of the driving force at low supercoolings:

$$d(\delta l) = \frac{h}{kT}\frac{\Delta T}{T_m^0}\frac{\delta l}{l} \tag{7}$$

In the homopolymer case[6] δl is approximately constant, and the driving force goes to zero only as ΔT goes to zero while l goes to infinity.

Copolymer simulation: minimum thickness and driving force

In the following the minimum thermodynamically stable thickness in the copolymer simulation model will be investigated.

In order to proceed we need to recall briefly some of the terminology of the Sadler–Gilmer rate theory model[5,6]. The state variable is the probability distribution $P(i,j)$ of lengths i and j of adjacent stems at the

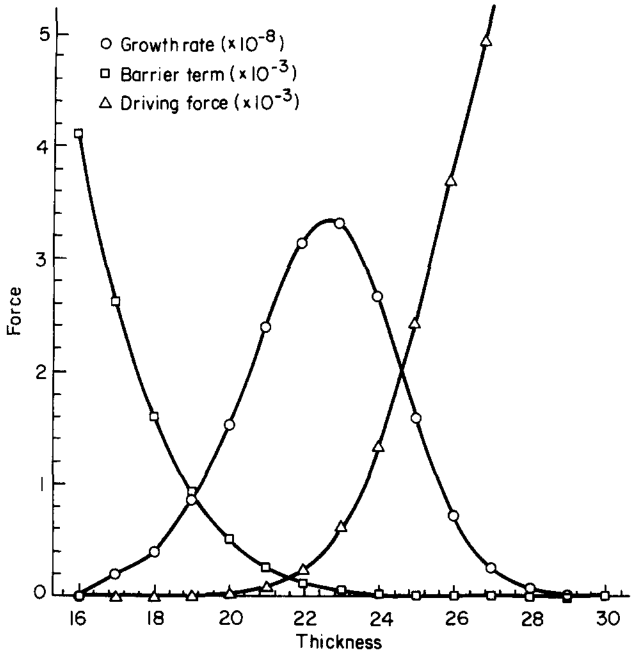

Figure 2 Growth rate G at a fixed supercooling as a product of barrier term a_0 and driving force term d. The lamellar thickness gets selected such that G is maximized. The 'force' is given in arbitrary units, the thickness is scaled by the length of a growth unit. (Numerical example calculated with the Sadler–Gilmer model[6])

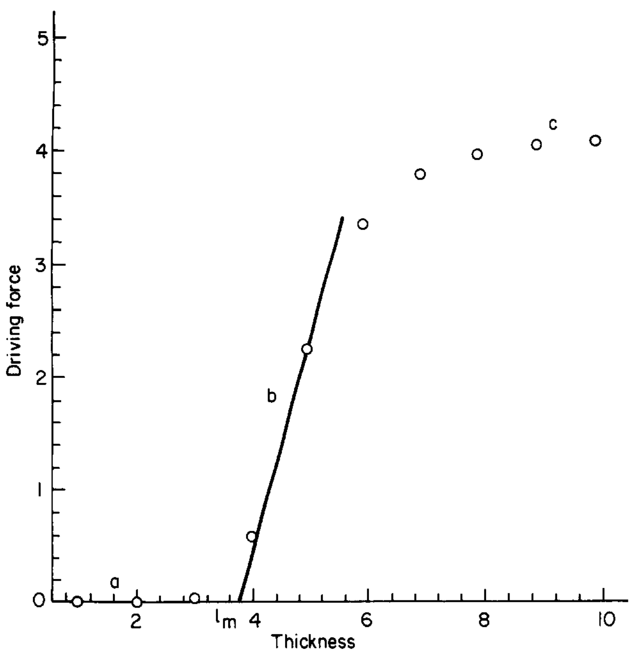

Figure 3 Driving force contribution for different thicknesses at a given supercooling. Extrapolation of the linear regime (b) to zero driving force yields the minimum thickness l_m

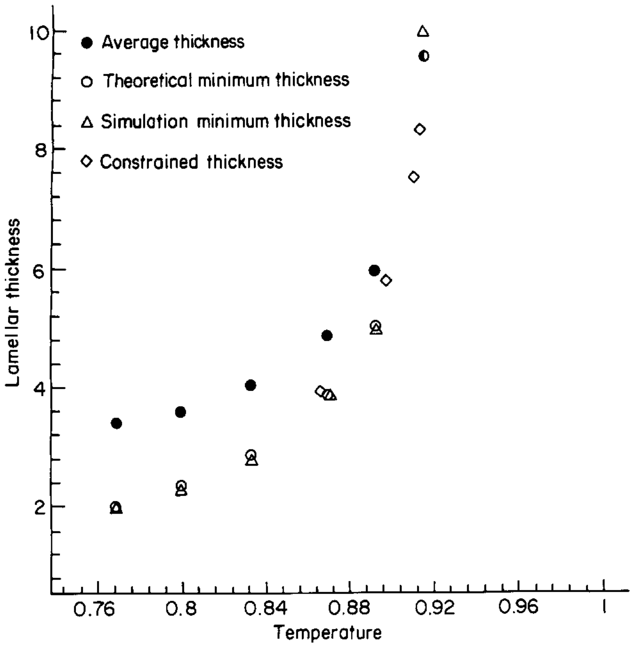

Figure 4 Average and minimum lamellar thickness of the model copolymer. The various methods by which the minimum thicknesses have been calculated are explained in the text. The concentration p of non-crystallizable segments in this example is $p=0.95$. The temperatures are scaled by T_m^0

growth front (see *Figure 1*). This steady-state distribution at a given supercooling ΔT is the basis for the calculation of average thickness and growth rate. Likewise, the driving force $d(i)$ for different thicknesses $i=1,2,\ldots,N$ (where N is so large that $P(N,j)$ is small) can be evaluated. Typically, three regimes can be distinguished (*Figure 3*): (a) for small i the driving force is almost zero; (b) around the average thickness l, $d(i)$ increases almost linearly; and (c) for large i the driving force reaches a plateau. This behaviour is consistent with the analytical expression (2) given above. Assuming a linear dependence for small ΔT like in equation (7), an estimate of l_m is obtained by linear extrapolation of regime (b) to zero driving force. This provides a minimum thickness curve $l_m(\Delta T)$, which in combination with the average thickness $l(\Delta T)$ yields $\delta l(\Delta T)$, and therefore a measure of the driving force dependence on supercooling.

In the homopolymer case Sadler and Gilmer[6] have found that δl is approximately constant. The driving force decreases with decreasing supercooling only through an increasing lamellar thickness (see equation (7)). This is in agreement with other crystallization models and interpretations of experimental results[7].

The model copolymer shows a very different behaviour, however (*Figure 4*). The minimum thickness l_m and the average thickness l converge as the crystallization temperature approaches T_m^{cop}. The driving force decreases and eventually vanishes at the copolymer melting point as the lamellar thickness cannot increase because of the decreasing concentration of crystallizable chain segments.

This result was confirmed by values of l_m obtained directly by simulation. Lowering the maximum stem length N until this constraint brings the growth rate to zero yielded upper limits for l_m, shown as diamonds in *Figure 4*. This method was described in more detail in ref. 6.

Analysis of copolymer free energy and melting-point depression

In this section we are going to approach the evaluation of the copolymer driving force analytically on the basis of equations (3) and (4). This will eventually lead us to a copolymer melting-point depression equation.

In the homopolymer case equations (3) and (4) combine to give the Gibbs–Thomson equation (5). Using an equilibrium expression of the surface free energy of a two-dimensional 'solid-on-solid' model $l_m(\Delta T)$ has been derived[6].

Application of this method to copolymers requires some modifications. As Richardson, Flory and Jackson[10] pointed out, the free-energy expression (3) must be amended, because the 'temperature at which a crystallite melts depends not only on its dimensions but also on the chemical potential of A sequences of the required length in the adjoining melt phase'. Under ideal solution conditions this leads to the following equilibrium free energy for a random copolymer of A-sequence perpetuation probability p:

$$\Delta f_{\text{cop}}^0 = h\Delta T/T_m^0 + kT\ln p \tag{8}$$

and to the well known Flory[1] equilibrium melting-point depression formula:

$$T_m^{0,\text{cop}} = T_m^0\left(1 - \frac{kT_m^0}{h}\ln p\right)^{-1} \tag{9}$$

which gives the melting point of crystallites in the limit of infinite thickness. Although this is the correct thermodynamic melting point, it sets conditions that cannot normally be reached experimentally[11]. In particular, the preferential ordering of copolymer chains into A sequences of matching sequence lengths is required. In contrast, the picture emerging from our simulation results is that the crystallization kinetics, in particular the mechanism of 'blind attachment' of small chain segments from A sequences of various lengths, actually prevents

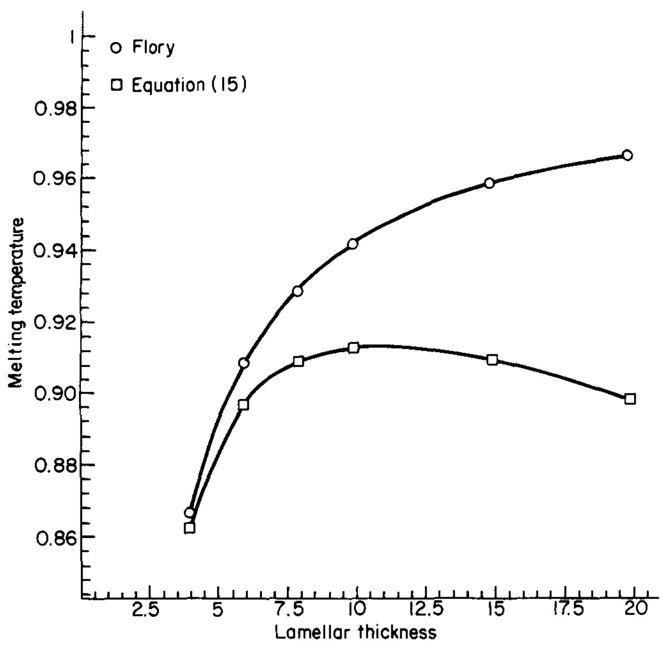

Figure 5 Melting-point depression with respect to T_m^0 for lamellae of finite thickness according to Flory, equation (16), and our own result, equation (15). The following parameters were implemented in this example: $p=0.95$, $\varepsilon=kT_m^0/0.35$, $h=2\varepsilon$, $\sigma_e=\sigma_e'=\varepsilon/2$

this ordering and therefore the formation of very thick crystallites. (Further thickening at a later stage is also unlikely because of the accumulation of non-crystallizable material on the surfaces. In fact, isothermal thickening is not observed in ethylene copolymers[2].) As we shall see, this is reflected in an additional entropic contribution to the free energy, which is revealed by our fine-grained model.

Consider the crystallization of a random copolymer, as schematically depicted in *Figure 1*, building up each stem segment by segment. The first segment in a stem is assumed to be an A unit with probability 1. It contributes an enthalpy $h\Delta T/T_m^0$. The second unit is an A unit with probability p and in addition to its enthalpy contributes a mixing entropy $S_2=-k\ln p$. In the same way the ith unit contributes an entropy:

$$S_i=-k\ln p^{(i-1)} \tag{10}$$

The free energy of the rate model copolymer lamella of average thickness l can now be obtained by summing over the normalized thickness distribution $C(i)$:

$$l\Delta f_{\mathrm{cop}}=\frac{h\Delta T}{T_m^0}\left(\sum_{i=1}^{N} iC(i)\right)+kT\left(\sum_{i=1}^{N} C(i)\sum_{j=1}^{i}(j-1)\ln p\right) \tag{11}$$

hence

$$\Delta f_{\mathrm{cop}}=\frac{h\Delta T}{T_m^0}+\frac{kT}{2l}\left(\sum_{i=1}^{N} i^2C(i)-l\right)\ln p \tag{12}$$

This expression can be simplified if we assume the distribution $C(i)$ to be Gaussian, so that $\sum_{i=1}^{N} i^2C(i)=l_m^2$:

$$\Delta f_{\mathrm{cop}}=\frac{h\Delta T}{T_m^0}+kT\frac{l-1}{2}\ln p \tag{13}$$

When the lamella is in equilibrium with the surrounding melt we get the following free-energy equation:

$$\frac{h\Delta T}{T_m^0}+kT_m\frac{l_m-1}{2}\ln p=\frac{(\sigma_e+\sigma_e')^{\mathrm{cop}}}{l_m} \tag{14}$$

Solving for T_m we finally obtain a new melting-point depression equation for copolymer lamellae of finite thickness:

$$T_m(l_m)=T_m^0\left(1-\frac{(\sigma_e+\sigma_e')^{\mathrm{cop}}}{hl_m}\right)\left(1-\frac{l_m-1}{2}\frac{kT_m^0}{h}\ln p\right)^{-1} \tag{15}$$

Note that here the thickness must be given in terms of numbers of growth units.

The corresponding 'thin-crystal' expression within the framework of Flory theory[2] can be obtained by simply substituting the Flory copolymer free-energy expression (8) into (3) so as to account for the surface free-energy contribution. This yields:

$$T_m^{Flory}(l_m)=T_m^0\left(1-\frac{(\sigma_e+\sigma_e')^{\mathrm{cop}}}{hl_m}\right)\left(1-\frac{kT_m^0}{h}\ln p\right)^{-1} \tag{16}$$

We are now in a position to make a direct comparison between our new formula (15) and the 'Flory–Sanchez–Eby' result (16): (i) Both expressions take account of the surface free-energy contribution via a Gibbs–Thomson term (first term in (15) and (16)). (ii) The depression caused by the non-crystallizable sequences is described by the second term. In the equilibrium theory this is independent of thickness, relating to the final melting of crystallites made of infinitely long sequences. In contrast, in our 'kinetic' theory the copolymer depression term is inherently thickness-dependent via the additional factor $(l_m-1)/2$. It has its origin in the counting argument of our derivation of the mixing entropy. Its effect is a stronger melting-point depression. As pointed out in a previous paper[4] this is indeed consistent with some experimental evidence[11]. A numerical example comparing both formulae is shown in *Figure 5*. The difference is almost negligible for very thin lamellae but becomes significant as the thickness increases towards the entropically feasible maximum. The new melting-point formula (15) has a maximum there, indicating that thicker crystals have in fact a lower melting point because of the 'entropic factor' $(l_m-1)/2$. The equilibrium formula (16), on the other hand, approaches the Flory melting point given by equation (9) as l goes to infinity.

In order to demonstrate that our new free-energy equation (14) is consistent with the simulation results we will in the following use this formula to calculate a minimum-thickness curve. As an expression for the equilibrium surface free energy of the copolymer system is not known, we are going to derive a semi-theoretical expression based on the simulation results. The simulation yields the average difference in length of adjacent stems (*Figure 6*):

$$s(T)=\textstyle\sum_{i,j}|i-j|P_{i,j}(T) \tag{17}$$

This is a measure of the entropic contribution to the surface free energy. As the enthalpy is simply the bond energy $\varepsilon/2$, we can write for the copolymer surface free energy:

$$\sigma_e^{\mathrm{cop}}(T)=\varepsilon/2-Cs(T) \tag{18}$$

for the top surface, and

$$\sigma_e^{\mathrm{cop}'}(T)=\varepsilon/2 \tag{19}$$

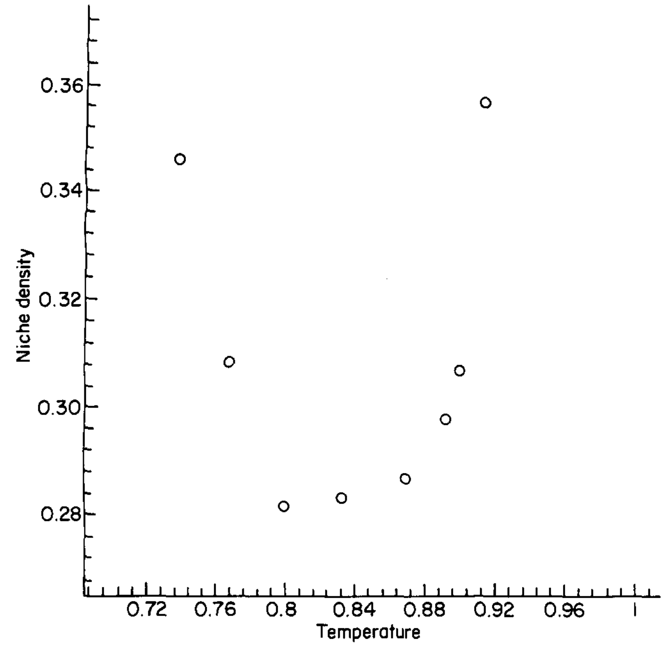

Figure 6 Average difference in length of adjacent stems, the so-called 'niche density', which is proportional to the surface entropy

for the straight bottom surface. The unknown proportionality constant C is evaluated by inserting (18) and (19) into (14) and enforcing that $l_m = l$ at the copolymer melting point T_m^{cop} as determined by simulation. This finally allows the calculation of the $l_m(\Delta T)$ values (circles in *Figure 4*), which agree very well with the values determined by the other methods described above. This consistency is a further corroboration of the new 'kinetic' copolymer melting-point depression equation (15).

CONCLUDING REMARKS

An analysis of the driving force in the Sadler–Gilmer rate theory model of copolymer crystallization[4] has helped us understand better the melting at finite thickness occurring in the simulation. Furthermore, it has led to a new free-energy expression and a melting-point depression relation for a random copolymer crystal of finite thickness, which involve an additional mixing entropy. The latter is due to the mechanism of 'blind attachment' inherent in the model. We believe this to be a more realistic picture of the crystallization kinetics than the ideal equilibrium demixing of matching A sequence lengths envisaged by Flory[1]. If such a fractionation process occurred to some extent during crystallization, it would obviously influence the A sequence statistics and raise the melting point.

The formulae derived can in principle be applied directly to experimental melting-point data of lamellar copolymer crystals. They should contribute to the interpretation of experiments wherever non-equilibrium effects are significant. In those cases the observed melting-point lowering is generally much bigger than given by the Flory equation[11]. In practice, however, the end-surface free energy is often not known, and the determination of the thickness of the actual crystalline layer, e.g. via the X-ray long spacing and the 'two-phase' model, can only provide a rough estimate.

Furthermore, the model discussed here requires the total exclusion of comonomer units, which is generally not the case in real copolymer crystals[13]. However, the trend will remain the same even if comonomers are partially incorporated as defects because the mechanism of 'blind attachment' is still at work. This has been demonstrated by simulation of such systems[14]. Further work investigating the effects of defects in polymer crystals is under way.

In conclusion, the melting-point depression of copolymers studied in this paper has proven to be a further example of the significance of a 'fine-grained' approach in the modelling of polymer crystallization and melting behaviour.

ACKNOWLEDGEMENT

I am pleased to acknowledge the support of the ICI Materials Research Centre, Wilton, and the SERC during the course of this research.

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