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Thermodynamics of statistical copolymer melting

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Abstract

The melting temperature of a crystal formed of sequences of a statistical A/B copolymer depends not only on crystal composition and lamellar thickness, but on the composition of the coexisting melt as well. Hence analytical expressions are derived for the *final* melting temperature, where the melt composition equals the known overall composition, generally expressed as mole fraction x_A of crystallizable monomer. Of the various treatments for final equilibrium melting of A crystals from which B units are excluded, only Flory's T_m^c is correct, but it is unobservable. The Sanchez–Eby theory extends Flory's treatment of final melting temperature to metastable folded sequence crystals of arbitrary thickness l_{max}, and also allows for incorporation of B units in the crystal. The Gibbs–Thomson method for extrapolating final melting temperatures when $l_{max} \rightarrow \infty$ leads to a limiting T_m^* that can be compared to theory for determining if B units are excluded from the crystals. Extrapolation to equilibrium melting by the Hoffman–Weeks method will yield $T_m^f < T_m^c$, confusing attempts to verify comonomer exclusion or inclusion.

Keywords: Equilibrium melting; Final melting temperature; Comonomer exclusion

1. Introduction

Comonomers have long been used to tailor the morphology and properties of semicrystalline polymers. In the vast majority of cases, dilute comonomer B units are excluded from crystals composed of majority A units. It is agreed that increased B concentration leads to lower crystalline fraction f_c, while the melting range becomes broader and shifts to lower temperatures. Additionally, crystallization rates are reduced tremendously by the presence of comonomer. While these phenomena have been fruitfully employed in the industrial sector for decades, our basic understanding of copolymer crystallization and melting is far from satisfactory. The present study is focused on the melting of statistical copolymers, with emphasis on systems in which comonomer is rejected from the crystal. Existing theories are described and evaluated, and appropriate techniques for relating experiment to theory are discussed.

2. General considerations

This presentation is restricted to compositionally uniform statistical copolymers of A and B, i.e. those in which the mole fraction x_A of A units is the same for all chains. This excludes heterogeneous systems such as ethylene/α-olefin copolymers from Ziegler–Natta catalysts, and further implies that the degree of polymerization is well in excess of 100. Also neglected are any explicit chain length effects such as end group exclusion. Dilute, excluded B units define the ends of consecutive A sequences that may crystallize. For a molten A/B copolymer that has been cooled to a particular crystallization temperature T_c, there are two important distinctions from the crystallization of homopolymer A. The first is that lamellar crystal thicknesses l_c in a copolymer are determined, at least in part, *thermodynamically* by the length distribution of A sequences, whereas lamellar thicknesses in high molecular weight homopolymers are controlled by *kinetic* nucleation barriers. Second, copolymer crystallization involves demixing pure A sequences from the melt that contains both A and B units, a step that is obviously absent in the homopolymer case.

Similar arguments apply to melting. For homopolymer A, the melting range is a function of the distribution of lamellar crystal thicknesses (absent melting and recrystallization). The melting range for a copolymer reflects to some extent the distribution of crystallizable A sequence lengths, and fusion additionally involves the mixing of initially crystalline A sequences with the liquid composed of A and

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B sequences. Melting is treated as a thermodynamically reversible process for which the free energy change $\Delta G = \Delta H - T_\mathrm{m}\Delta S$ is zero. It is instructive to write the melting temperature as

$$T_\mathrm{m} = \frac{\Delta H(l_\mathrm{c})}{\Delta S} \tag{1}$$

For a homopolymer crystal of thickness l_c, the enthalpy of fusion of a single stem consisting of $n = l_\mathrm{c}/l_\mathrm{u}$ A units (l_u is the length of a crystalline A unit) is

$$\Delta H(l_\mathrm{c}) = n\,\Delta H_\mathrm{u}^0 - 2\sigma \tag{2}$$

Here ΔH_u^0 is the enthalpy of fusion for A in a perfect crystal, while σ represents the basal surface energy (J/stem). The entropy of fusion

$$\Delta S = n\,\Delta S_\mathrm{u}^0 = n\frac{\Delta H_\mathrm{u}^0}{T_m^0} \tag{3}$$

is assumed to be independent of temperature; $n\,\Delta S_\mathrm{u}^0$ includes the disruption of crystalline order and relaxation of the stem to the random coil conformation in the liquid state. T_m^0 is the equilibrium melting temperature of homopolymer A, achieved in the limit of $n \to \infty$, where the basal surface energy term 2σ in Eq. (2) is negligible. Substitution of Eqs. (2) and (3) into Eq. (1) gives the well known Gibbs–Thomson relation for the melting of lamellar crystals

$$T_\mathrm{m} = T_\mathrm{m}^0\left(1 - \frac{2\sigma}{n\,\Delta H_\mathrm{u}^0}\right) \tag{4}$$

Be reminded that the melting temperature T_m is for equilibrium between molten A chains and metastable, lamellar (folded chain) homopolymer A crystals of thickness $l_\mathrm{c} = nl_\mathrm{u}$.

Crystals of statistical copolymers also melt according to Eq. (1). Assuming for simplicity that there is strict exclusion of B units, lamellar crystals of A stems will have thickness l_c and an enthalpy of fusion given by Eq. (2). For the moment we let ΔH_u^0 and σ be the same as for the homopolymer case. At this time we also allow l_c to be of unspecified origin; kinetics and chain folding may be involved for A sequences of length greater than l_c. When one stem of length l_c melts, the n units go from a pure A (crystalline) phase to a mixed A/B (melt) phase. This change from unmixed to mixed states leads to an additional positive contribution to the entropy of fusion, so the melting temperature becomes

$$T_\mathrm{m} = \frac{\Delta H(l_\mathrm{c})}{n\,\Delta S_\mathrm{u}^0 + \Delta S_\mathrm{mix}} \tag{5}$$

It must be emphasized that a lamellar crystal of A stems, formed with a statistical copolymer by rejecting B units, will melt at a lower temperature than a homopolymer A crystal of the same thickness l_c. The difference lies in the term ΔS_mix in Eq. (5), which in turn depends on the A/B composition of the liquid state, which is generally not known.

It may be that complete exclusion is not appropriate for some comonomers or isomeric defects. In the (unrealistic) limit of uniform inclusion of B units in both the crystalline and amorphous phases, there is no modification of the entropy term because $\Delta S_\mathrm{mix} = 0$. Letting the enthalpy penalty for incorporating a single B unit in the lamellar crystal be ϵ, and writing the mole fraction of B units as $x_\mathrm{B} = 1 - x_\mathrm{A}$, the melting temperature is

$$T_\mathrm{m} = T_\mathrm{m}^0\left(1 - \frac{2\sigma}{n\,\Delta H_\mathrm{u}^0} - \frac{x_\mathrm{B}\epsilon}{\Delta H_\mathrm{u}^0}\right) \tag{6}$$

In this case the comonomer modifies the numerator of Eq. (1), not the denominator. If there is partial inclusion of B, both numerator (enthalpy) and denominator (entropy) are changed.

In this paper we first review existing theories and models for the melting of statistical copolymers, with emphasis on the physical principles that differentiate the treatments. The order of presentation is approximately chronological. Subsequently, the various approaches are evaluated for relevance to experimental procedures and results.

3. Flory theory

The first treatment of copolymer melting was developed by Flory [1], who evaluated ΔS_mix for complete exclusion of B comonomer by considering equilibrium crystallization, i.e. the reverse of melting. While sequence folding is not permitted, each lamellar crystal of thickness l_c is constructed of A runs of *different* index $j \geq n = l_\mathrm{c}/l_\mathrm{u}$ as sketched in Fig. 1(a). In the melt that coexists with crystals of thickness index n, the probability that a single A unit is

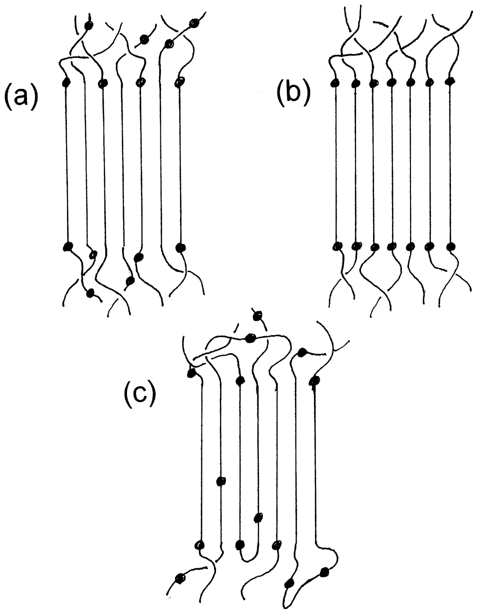

Fig. 1. Sketches of crystals indicating the location of B units (●). (a) corresponds to the Flory theory, (b) to the Baur theory, and (c) to one of many arrangements in the Sanchez–Eby treatment, illustrating in this case sequence folding and B inclusion.

part of a sequence having $j \geq n$ that may add to the crystal is designated P_n^{e}. In the crystal, the probability of an A unit being part of a sequence having $j \geq n$ is unity by definition. Using the Boltzmann expression for entropy, the mixing term for melting an A sequence in Eq. (5) becomes $\Delta S_{\mathrm{mix}} = -k \ln P_n^{\mathrm{e}}$, where k is Boltzmann's constant. Equilibrium between the melt and coexisting crystals of thickness indices n, $n+1$ and $n+2$ is used to define through P_n^{e} the *equilibrium* volume fraction w_n^{e} of $j = n$ sequences in the liquid state in terms of T, T_{m}^0, ΔH_{m}^0 and σ. The Flory theory ignores any enthalpy of mixing for A and B units.

It is important to realize that, when crystals are present, the equilibrium distribution of A sequences w_n^{e} in the coexisting melt differs from the global distribution w_n^{o} established during copolymerization; w_n^{o} applies only when the material is entirely molten (or virtually so). When crystals have been formed, w_n^{e} will be decreased for large n (long sequences crystallize preferentially) and enhanced for small n (to retain normalization). The global sequence distribution w_n^{o} is invariant for a particular statistical copolymer, and it can be specified completely in terms of p, the probability that an A unit in the chain is followed by another A unit. Recalling that w_n^{o} is the *volume* fraction of the polymer that is n sequences of A units, one writes [1]

$$w_n^{\mathrm{o}} = n\Phi_{\mathrm{A}}(1-p)^2\,p^{n-1}$$

Here Φ_A is the overall volume fraction of A units in the copolymer; if the volumes of A and B units are the same, volume fraction Φ_A equals mole fraction x_{A}. Flory used equality of equilibrium w_n^{e} and global w_n^{o} at a particular n to establish the smallest crystal thickness index n^* that can exist at any temperature T. The increase of n^* with T corresponds to equilibrium melting; the thinnest crystals melt first, and the remaining (thicker) crystals adjust their compositions to remain in equilibrium with the changed amorphous distribution w_n^{e}. For any statistical copolymer, the *last* equilibrium crystals to melt are very thick ($n^* \rightarrow \infty$); these are present in exceedingly small number because of the paucity of very long sequences ($n \rightarrow \infty$) provided by w_n^{o}. As this limiting crystalline fraction is infinitesimal, the coexisting melt has the global distribution described by $w_n^{\mathrm{e}} = w_n^{\mathrm{o}}$ for all $n < \infty$ that leads to the familiar expression for the equilibrium melting temperature $T_{\mathrm{m}}^{\mathrm{c}}$ [1]:

$$\frac{1}{T_{\mathrm{m}}^{\mathrm{c}}} = \frac{1}{T_{\mathrm{m}}^0} - \frac{k}{\Delta H_{\mathrm{u}}} \ln p \qquad (7)$$

For an ideal random copolymer, p is equal to x_{A}, although p exceeds x_{A} for statistical copolymers with alternating character, and p is less than x_{A} for blocky copolymers [2].

While the thermodynamic basis for Eq. (7) is clear, its implementation in the laboratory is impossible. For one thing, the growth of polymer crystals with extremely large n is fraught with kinetic impediments, and, furthermore, the melting such large structures is subject to superheating [3]. With statistical copolymers these problems are exacerbated by the minuscule fraction of sequences with $n \rightarrow \infty$ available to form very thick crystals. In the unlikely event that thick equilibrium crystals are formed in a copolymer, the melting of these very few structures at $T_{\mathrm{m}}^{\mathrm{c}}$ causes changes that are not observable, as demonstrated in Fig. 2, wherein the calculation is done for random copolymers of ethylene and butene-1 [4]. The *measurable* equilibrium melting range ends at $T_{\mathrm{m}}^{\mathrm{f}}$, which is sensibly below $T_{\mathrm{m}}^{\mathrm{c}}$ from Eq. (7). The interval between the measurable $T_{\mathrm{m}}^{\mathrm{f}}$ and the thermodynamic $T_{\mathrm{m}}^{\mathrm{c}}$ involves the melting of crystals that comprise less than 10^{-4} of the polymer, and the effects on macroscopic volume, heat capacity, etc. are too small to observe. Hoffman and Weeks [5] realized that kinetic barriers make the direct measurement of equilibrium T_{m}^0 for a homopolymer impossible, and therefore proposed a method for extrapolating observed melting temperatures to the $n \rightarrow \infty$ state. The situation with statistical copolymers is similar, but compounded by the rarity of long sequences available to form thick crystals. This concentration effect not only slows further the growth of thick crystals, but it restricts their number so that equilibrium melting at $T_{\mathrm{m}}^{\mathrm{c}}$ is not observable. Even if kinetic impediments were overcome in some manner, the final melting temperature recorded in such an ideal equilibrium experiment would be $T_{\mathrm{m}}^{\mathrm{f}}$, not the $T_{\mathrm{m}}^{\mathrm{c}}$ in Eq. (7).

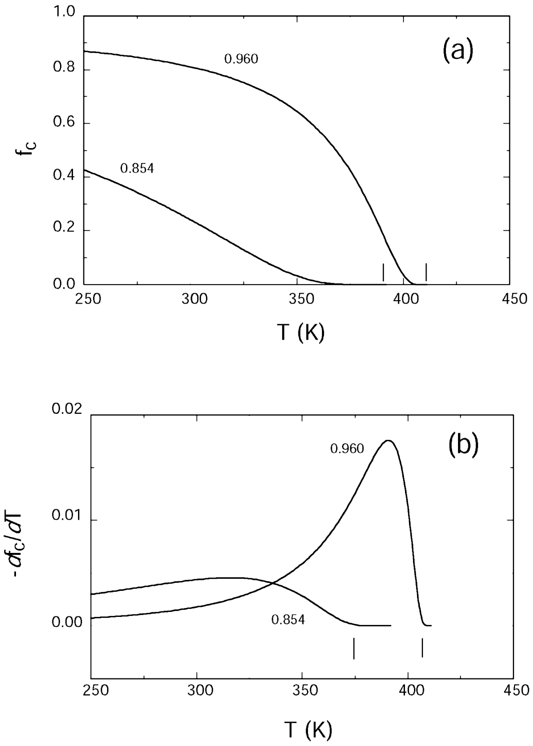

Fig. 2. Results of Flory theory with parameters for a copolymer of ethylene (A) and butene-1 (B) for two values of p; $T_{\mathrm{m}}^0 = 418.7$ K. Part (a) shows equilibrium crystallinity falling with increasing temperature; thermodynamic $T_{\mathrm{m}}^{\mathrm{c}} = 411.6$ K and $T_{\mathrm{m}}^{\mathrm{c}} = 392.5$ K from Eq. (7) are designated by vertical lines. The temperature derivative in part (b) is comparable to a DSC trace, and the final observable melting temperatures $T_{\mathrm{m}}^{\mathrm{f}} = 407.5$ K and $T_{\mathrm{m}}^{\mathrm{f}} = 377$ K are indicated by vertical lines.

4. Baur theory

While the Flory expression for T_m^c is rigorous and simple, it cannot be applied to experiment for the reasons mentioned above. A popular alternative is due to Baur [6], whose approach is based on the notion of Kilian [7] that the A sequences and B sequences in a copolymer may be treated as separate molecules, i.e. as oligomers. As with Flory, ΔS_{mix} is calculated for a stem of n A units going from the pure crystal to the mixed liquid state. There are two points of distinction, however. First, each crystal of thickness l_c is composed of sequences having *exactly* $n = l_c/l_u$ A units, as sketched in Fig. 1(b). Second, the entropy of mixing is calculated with Flory–Huggins theory (with $\chi_{AB} = 0$) in which each sequence of A units or B units is treated as a separate molecule. Equilibrium melting of infinitely thick crystals ($n \rightarrow \infty$) occurs at T_m^c given by [6]

$$\frac{1}{T_m^c} = \frac{1}{T_m^0} - \frac{k}{\Delta H_u^0}\left(\ln p - \frac{1}{\bar{n}_t}\right) \tag{8}$$

where $\bar{n}_t$ is the average sequence index for *both* A runs and B runs for the entire copolymer. For an ideally random statistical copolymer, $p = x_A$, and $1/\bar{n}_t = 2(1 - x_A)x_A$.

It should be emphasized that the Baur theory, Eq. (8), is for the melting of an unobservably small fraction of infinitely thick A crystals, just as with the Flory theory. Furthermore, crystals in the Baur theory are composed of perfectly segregated A sequences of length l_c, corresponding to a lower entropy state that is more difficult to achieve than the crystals of mixed sequence length in the Flory model. However, the major difference derives from Baur's treatment of sequences as *individual* molecules. The gas-like, center of mass configurational entropy calculated for a discrete molecule of n A units in a liquid of individual A sequence and B sequence molecules (the majority of the latter being monomers and dimers) is obviously greater than that for a sequence of n A units that is fixed in a molten copolymer chain. One can also appreciate that the gas-like entropy for a particular n in the Baur model would be larger in a solution of smaller 'solute molecules'. That is the physical basis of the $1/\bar{n}_t$ term in Eq. (8), which lowers T_m^c below the Flory result Eq. (7). Some have mistakenly identified $\bar{n}_t$ in Eq. (8) as the average length of crystallizable (A) sequences, with the implication that the Baur T_m^c is for melting of finite thickness crystals. That is not the case; be reminded that $\bar{n}_t$ applies to the *melt* that is in equilibrium with crystals of effectively infinite thickness.

5. Kilian model

Kislian has modified and extended the treatment of copolymer melting in which sequence free energies are calculated as if the sequences were individual molecules. The scheme is included here for completeness, although it has not been adopted by others and it is described by Kilian himself as an 'unconventional model'[8]. The basic idea, like Flory's, is that the A runs aggregate to form extended sequence crystals, the thicknesses of which reflect the overall sequence length distribution w_n^o. As in the Flory theory, mixed sequence crystals are permitted, but the index distribution width Δn for sequences comprising a crystal of thickness index n is an adjustable parameter. A related feature is that B units are considered to occupy part of the surface region of each crystal. Kilian is not concerned with the ultimate melting temperature analogous to T_m^c. He concentrates instead on the observed melting range. Various parameters, some phenomenological, are adjusted to match to DSC endotherms, for which the peak and final melting temperatures are characteristic. Kilian contends that the typical copolymer melting experiment is described by *equilibrium melting* of extended sequence crystals that continuously adjust their compositions as the thinner crystals are melted and the coexisting w_n^e is altered [8].

6. Sanchez–Eby theory

Sanchez and Eby [9] following the approach of Helfand and Lauritzen [10] for including B units within the A crystal, also extended the analysis of copolymer melting to lamellar crystals of finite thickness $l_{\max}$. The following relation may be used for the *final* melting temperature of an ideally random copolymer ($p = x_A$) containing arbitrary amounts of nonequilibrium chain folding, trapped comonomer, etc.; see Fig. 1(c). As in the Flory and Baur treatments, the coexisting melt is assumed to have the global sequence distribution w_n^o.

$$\begin{aligned}\frac{1}{T_m(l_{\max})} = {} & \frac{1}{T_m^0} + \frac{1}{\Delta H_u^0 T_m(l_{\max})}\left(\frac{2\sigma}{n_{\max}} + \epsilon x_B^c\right) \\ & + \frac{k}{\Delta H_u^0} \\ & \times\left((1 - x_B^c)\ln\left(\frac{1 - x_B^c}{1 - x_B}\right) + x_B^c \ln\left(\frac{x_B^c}{x_B}\right)\right)\end{aligned} \tag{9a}$$

The most stable (last to melt) lamellar crystals of thickness $l_{\max} = n_{\max}\, l_u$ contain mole fraction x_B^c of B units, and these crystals coexist at $T_m(l_{\max})$ with the melt having the global concentration $x_B = 1 - x_A$. Each B unit in the crystal creates an energy penalty ϵ. The second and third terms on the right side of Eq. (9a) reflect enthalpic costs from finite thickness and comonomer inclusion, respectively. The final two terms are for mixing crystalline stems, here characterized by B concentration x_B^c, with the melt having the global concentration x_B.

Some limiting cases are instructive. Of principal interest here is when B is totally excluded, or $x_B^c = 0$. Eq. (9a) reduces to

$$\frac{1}{T_m(l_{max})} = \frac{1}{T_m^0} + \frac{2\sigma}{n_{max}\Delta H_u^0 T_m(l_{max})} + \frac{k}{\Delta H_u^0} \ln\left(\frac{1}{1-x_B}\right) = \frac{1}{T_m^c} + \frac{2\sigma}{n_{max}\Delta H_u^0 T_m(l_{max})} \tag{9b}$$

The lower expression can be rearranged to the familiar Gibbs–Thomson relation for lamellar crystals, in which the equilibrium melting temperature is Flory's T_m^c for a copolymer (see Eq. (7); $1 - x_B = x_A = p$), rather than T_m^0 for the homopolymer. This result has been derived or asserted by others [11–13].

The opposite extreme of no partitioning of B units between crystalline and liquid phases ($x_B^c = x_B$) may be physically unrealistic, but it gives

$$\frac{1}{T_m(l_{max})} = \frac{1}{T_m^0} + \frac{1}{\Delta H_u^0 T_m(l_{max})}\left(\frac{2\sigma}{n_{max}} + \epsilon x_B\right) \tag{9c}$$

In this case $\Delta S_{mix} = 0$ because the compositions of the crystalline and amorphous phases are the same. Eq. (9c) is the same as Eq. (6); the melting point is lowered because of two enthalpic effects.

The final case is for the equilibrium concentration of B units in the crystal, which balances the enthalpic penalty ϵ with the increased entropy of the crystalline state[10]. The result is expressed in terms of the (global) B composition of the coexisting melt:

$$\frac{1}{T_m(l_{max})} = \frac{1}{T_m^0} + \frac{2\sigma}{n_{max}\,\Delta H_u^0 T_m(l_{max})} - \frac{k}{\Delta H_u^0}\ln(1 - x_B + x_B\,e^{-\epsilon/kT_m(l_{max})}) \tag{9d}$$

For large inclusion energy ϵ, Eq. (9d) reduces to the exclusion result (9b), and for small values of $\epsilon/kT_m(l_{max})$, the same expression recovers the uniform inclusion case, Eq. (9c).

The Sanchez–Eby (S–E) approach takes a copolymer result that is correct in the limit of very large $l_c(n \to \infty)$ and modifies it with the conventional term for finite l_{max}. The appropriateness of this step is considered below; for now, be reminded that only the *final* melting increment is described by $T_m(l_{max})$ in Eq. (9a) through Eq. (9d). Consider, for example, complete exclusion of B units for an ideal statistical copolymer in which all crystals have exactly the same $l_c = l_{max}$. Melting will start at a temperature below the value in Eq. (9b), because the melt is richer in B than the global $x_B = 1 - x_A$. With increasing transformation, the liquid concentration drops toward x_B, and the last crystals melt at $T_m(l_{max})$ given by Eq. (9b). In this illustration, the range of melting temperatures *does not* reflect the distribution of crystal thicknesses. The same arguments hold for partial exclusion (Eq. (9a) with $x_B^c < x_B$). Because l_{max} is not related to copolymer composition x_A, there is no restriction on the fraction of lamellar crystals with $l_c = l_{max}$, and Eqs. (9a)–(9d) correspond to the maximum *experimental* melting temperature T_m'.

One sees immediately that the S–E theory is more general than the equilibrium exclusion theories of Flory and Baur, but this attribute is coupled to additional parameters; ϵ and x_B^c to account for inclusion of B units, and l_{max} and σ for the Gibbs–Thomson term. Perhaps more importantly, Eq. (9a) and its variants apply directly to experimental final melting temperatures. There is no need to extrapolate to equilibrium conditions that correspond to Eq. (7) or (8).

Wendling and Suter [14] modified the Sanchez–Eby theory in two ways. First, they dropped the surface energy term, so the melting temperature T_m^c applies to infinitely thick crystals. Secondly, they incorporate an 'activity coefficient' modeled after Baur's $1/\bar{n}_t$ term (see Eq. (8)) that further reduces T_m^c. Their results are not reproduced here; for the case of complete exclusion of B units from A crystals, the expression is identical to Baur's Eq. (8). Yet another hybrid approach was taken by Goulet an Prud'homme [15], wherein Baur theory for infinite crystals is combined with inclusion with no energy penalty ($\epsilon = 0$). In this case inclusion simply elevates the *effective* concentration of crystallizable units above $p = x_A$, and T_m^c is larger than the value given by Eq. (8).

7. Goldbeck-Wood theory

Certain simulations of copolymer crystallization indicate that the average crystal thickness $\langle l_c \rangle$ does not increase without limit as the crystallization temperature is raised. Goldbeck-Wood and Sadler found that crystals of finite maximum thickness l_c are associated with the temperature at which the simulated copolymer crystallization rate goes to zero[16]. It was concluded that the zero rate temperature is the copolymer melting temperature. In a subsequent paper, Goldbeck-Wood derived an expression that purports to capture this feature. In that work, ΔS_{mix} is increased beyond the Flory treatment by an additional factor reflecting that n A units are contiguous in a crystal of thickness $l_c = nl_u$. This creates a severe entropy penalty for crystals of large index n, and leads to a final melting temperature [11]

$$\frac{1}{T_m(l_c)} = \frac{1}{T_m^0} - \frac{n-1}{2}\frac{k}{\Delta H_u^0}\ln p + \frac{2\sigma}{n\,\Delta H_u^0 T_m(l_c)} \tag{10a}$$

The distinguishing feature of this model is the factor $(n-1)/2$ in the second 'copolymer' term that reduces the melting temperature substantially below that in the analogous Sanchez–Eby Eq. (9b).

As with other treatments of copolymer melting, at $T_m(l_c)$ crystals of A units are in equilibrium with the melt of global composition x_A. In this case, however, the final crystals to melt are not infinitely thick (Flory, Baur) nor of arbitrary thickness (Sanchez–Eby), but the thickness l_c is determined by growth kinetics (with entropic barriers). For later comparison to Flory and Baur, the Goldbeck-Wood expression is rewritten without the surface energy term as:

$$\frac{1}{T_m^c} = \frac{1}{T_m^0} - \frac{n-1}{2}\frac{k}{\Delta H_u^0}\ln p \tag{10b}$$

8. Discussion

The four treatments described above are assessed first from the perspective of thermodynamic correctness, and then for relevance to laboratory practice.

Thermodynamics. The equilibrium approach of Flory [1] written as Eq. (7) is correct, but recall that T_m^c cannot be observed, even if very thick, equilibrium crystals are formed (see Fig. 2). Baur's treatment [6], like Flory's, gives T_m^c for infinitely thick crystals present in vanishingly small, hence unobservable, amounts. The larger entropy of mixing employed by Baur reduces the equilibrium melting temperature substantially, as shown in Fig. 3. It is acknowledged that Baur theory is closer to the usual experimental results as illustrated by final melting temperatures T'_m for random ethylene/butene-1 copolymers [4]. But such 'improvement' with respect to Flory theory is achieved by treating the A and B sequences as discrete molecules to enhance improperly the entropy of mixing, and the Baur result Eq. (8) should not be used. The same conclusion applies to the related approach of Wending and Suter [14] when partial or total exclusion of B units is invoked. The method of Goulet and Prud'homme [15] is also based on Baur theory, and it suffers further from a casual handling of inclusions. That analysis should be avoided as well.

In Fig. 3 is plotted also the modified Goldbeck-Wood [11] expression (Eq. (10b), no surface energy term) where n has the most probable value $1/(1-p)$. The increase of T_m^c with comonomer content is contrary to other models and to experimental results. That unique behavior derives from the $(n-1)/2$ factor, which is said to occur because there are n consecutive A units in a crystalline stem. However, the same n A units are consecutive in the molten copolymer, so the factor of $(n-1)/2$ is not justified, and Eq. (10a) is incorrect.

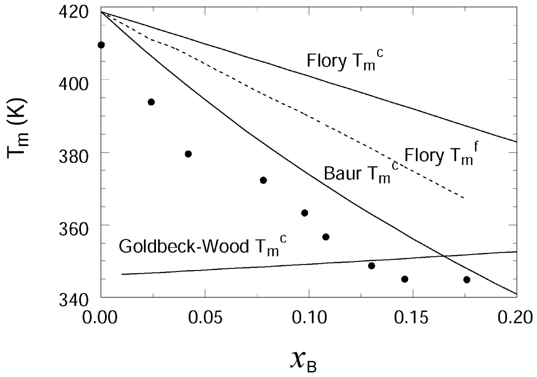

Fig. 3. Thermodynamic T_m^c versus $x_B = 1-p$ for calculated for ethylene/butene-1 copolymers with Flory theory Eq. (7), Baur theory Eq. (8), and Goldbeck-Wood theory Eq. (11). The dashed line is for maximum observable T_m^f (Flory theory) evaluated from melting curves like those in Fig. 2(b). Circles are conventionally measured final melting points T'_m for model ethylene/butene-1 random copolymers taken from Ref. [4].

While Kilian's approach of modeling the entire melting curve [7,8] has not gained acceptance, certain related terminology has. Kilian's thermodynamic treatment of sequences as oligomers leads to the consideration of a statistical copolymer as a multicomponent system described as 'eutectic', 'pseudoeutectic' or 'eutectiod,' terms that have been adopted by some others. 'Eutectiod' refers to equilibrium between one solid phase and two (or more) different solids [17] and it has nothing to do with melting and/or crystallization. In an N component system, 'eutectic' refers to equilibrium between one liquid phase of unique composition and N solid phases, a concept that Kilian never invokes. In fact, Kilian envisions (defective) crystals of decreasing thickness to form sequentially on cooling, and to melt in the reverse sequence on heating. As there is nothing eutectic (or pseudoeutectic) about these processes, it is recommended that those adjectives be reserved for more appropriate uses.

In summary, only the Flory treatment of equilibrium copolymer melting with complete exclusion of B units is correct. The approaches of Baur and Goldbeck-Wood employ unrealistically large ΔS_{mix} terms that lower T_m^c excessively, as indicated in Fig. 3.

The attractively versatile Sanchez–Eby theory relaxes the requirements for complete exclusion and infinite crystal thickness. Eq. (9a) is obtained by modifying the equilibrium melting temperature of infinitely thick crystals ($n \to \infty$) for the basal surface energy 2σ deriving from finite thickness. Since the assumptions of infinite and finite crystal thicknesses are mutually exclusive, one may wonder if the combined result is correct. That it is so may be demonstrated as follows. Flory theory is used to generate curves like those in Fig. 2(b) for copolymers of different p, for which the final observable melting temperature T_m^f corresponds to a crystalline fraction $f_c \approx 10^{-4}$, and the melt distribution is very close to the global w_n^o. The crystals that melt at T_m^f have thickness index n^f, which is equated to n_{max} in the S–E Eq. (9b) with no adjustable parameters to calculate $T_m(l_{max})$. The Flory and S–E results are compared in Fig. 4. Despite the format, this is not a Gibbs–Thomson plot, because each point is for a different copolymer having a different equilibrium T_m^c as well a different thickness $n^f l_u$. The important message is that the S–E Eq. (9b) gives an useful representation of the final observable melting temperature in terms of both l_{max} and melt composition x_A or p. The Flory T_m^f values are a bit below the S–E ones (by less than 3 K or 1%) because the seemingly insignificant residual crystallinity causes the melt to be fractionally richer in B than the global $x_B = 1-p$, lowering T_m^f below the value in Eq. (9b).

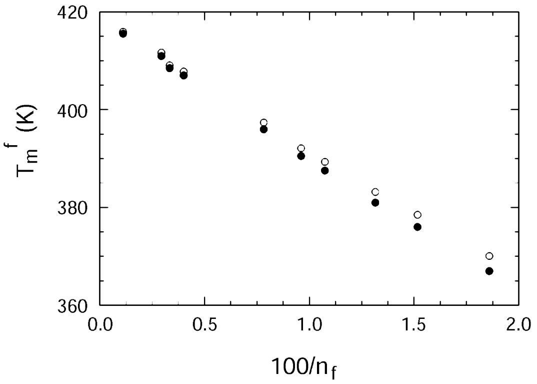

Fig. 4. Final observable melting temperature T_m^f as a function of reciprocal crystal thickness index n^f calculated for ethylene/butene-1 copolymers of different p. Solid points (●) are from Flory equilibrium melting theory, and open symbols (○) are calculated from S-E Eq. (9b) with $n_{max} = n^f$ taken from the Flory model.

This difference is largest for those copolymers with small p (smallest n^f) that have large concentration differences between melt and crystal. While this exercise is for complete exclusion, one has every expectation that the S–E approach is also valid when B units are included within the crystals.

Theory and experiment. The significance of the final melting temperature has been emphasized in the foregoing sections. Most melting experiments are conducted by conventional DSC, wherein determination of the final experimental melting temperature T'_m is usually straightforward, subject to normal concerns about irreversible morphology changes and thermal lag. Other techniques to evaluate the range and endpoint of polymer melting are optical microscopy, dilatometry and X-ray diffraction and/or scattering; the latter is considered below. Some clarifications of terminology are in order. The melting transition is by definition thermodynamically reversible because the free energy of the phase change $\Delta G = 0$. This statement applies to an equilibrium crystal that has the minimum free energy G_{cequil} and it may pertain to a small or defective crystal that has a larger free energy $G_c > G_{cequil}$ (and melts at a lower temperature). If the small or defective crystal melts without first rearranging to a lower free energy state, the transition is described as metastable equilibrium melting and it is thermodynamically reversible ($\Delta G = 0$). Crystals that rearrange by some means before or during melting experience an overall free energy change $\Delta G < 0$; this process has been termed 'irreversible melting' with reference to thermodynamic irreversibility of the composite mechanism (rearrangement plus melting) [3]. Irreversible melting may also occur if there are (kinetic) nucleation barriers to formation of the liquid phase, or if newly melted chains are temporarily prevented from adopting coiled conformations [3]. A signature of an irreversible process is dependence on rate or time, while reversible melting is insensitive to these variables.

The recent development of temperature modulated differential scanning calorimetry (TMDSC) has led to consideration of *reversing* and *non-reversing* melting in polymers. Reversing melting is that which absorbs and releases latent heat during positive and negative temperature excursions of amplitude 0.1–1 K. The implication is that reversing melting is associated with crystallization that occurs at very small undercoolings during the time of the temperature oscillation. The distinction between reversing and non-reversing melting thus lies in crystallization kinetics. Reversing melting can be from (thermodynamically) reversible or irreversible melting; in the latter case the reversing melting depends on time through scan rate or oscillation period. TMDSC has been reported for ethylene/octene-1 copolymers. Androsch [18] found that most of the melting in a copolymer with 7.3 mol% octene-1 was reversing; only over the final 25 K of the ca. 115 K melting range did melting become increasingly non-reversing. The final melting temperatures for overall melting (DSC) and reversing melting (TMDSC) appear to be the same. Equivalent results were reported by Wurm and Schick [19] for a similar copolymer, although T'_m may be as much as 5 K larger by conventional DSC. The reversing nature of melting and crystallization in ethylene/octene-1 copolymers, particularly at temperatures below that for primary crystallization, was established with conventional DSC by Alizadeh et al. [20]. Weak or nonexistent rate effects in the three studies above suggest that the reversing melting in these copolymers is reversible as well. This feature is reminiscent of the Flory equilibrium model for copolymer melting, but it is almost certain that metastable equilibrium, as opposed to true equilibrium, is present in real heating/cooling experiments.

Returning to theories for copolymer melting, the viable ones are those of Flory [1] and Sanchez–Eby [9]. Any utilization or test of Flory equilibrium theory must rely on extrapolation to T_m^c for effectively infinite extended sequence crystals. In Fig. 2 the largest observable melting temperature T_m^f, for which no analytical expression exists, is below T_m^c by about 4–16 K in this example, depending on p. The gap between T_m^c and T_m^f vanishes as p approaches unity (homopolymer), and it increases with the ratio $\sigma/\Delta H_u^0$. This distinction between T_m^f and T_m^c must be kept in mind when executing or interpreting experiments.

One method of extrapolation is the Hoffman–Weeks approach [5] in which the *final* experimental melting temperature T'_m is recorded as a function of crystallization temperature T_c and extrapolated to equilibrium T_m^f (not T_m^c) when $T'_m = T_c$. At T_m^f there is equilibrium between the melt and the thickest crystals, absent any kinetic restraints, that may be formed in observable quantity. For example, T_m^f for the two copolymers in Fig. 2 correspond to $n^f = 250$ and $n^f = 66$ ($l_c = 38.5$ nm and $l_c = 10.2$ nm). Recognizing that Hoffman–Weeks will give $T_m^f < T_m^c$, a plot of extrapolated 'equilibrium' melting temperatures as a function of comonomer content would correspond to the dashed line in Fig. 3, which falls below the solid line from Eq. (7). It would be mistaken to conclude that Flory theory is incorrect, however, because the discrepancy is due to the difference between T_m^f and T_m^c. If comonomer is allowed to crystallize ($x_B^c > 0$), the restriction on 'infinite' sequence lengths is mitigated (but not removed), and the final observable melting temperature will approach the thermodynamic value. In the limit of uniform inclusion Eq. (9c) there is no limitation of crystallizing sequence lengths, and the Hoffman–Weeks method will apply as if for a homopolymer.

All the studies cited below use linear extrapolation of observed T_m to the equilibrium melting temperature, even though Marand et al. have shown that this procedure is inadequate for homopolymers [21]. Thomann et al. [22], with linear Hoffman–Weeks based on final T'_m, achieved reasonable conformity to Flory theory for copolymers of syndiotactic polypropylene and octene-1 having $x_A > 0.9$. While those authors did not distinguish between T_m^f from extrapolation and the thermodynamic T_m^c, they did recognize that their analysis is approximate because of uncertainties associated with the large (ca. 40 K) extrapolations to 'equilibrium'. Others have reported well-behaved (linear) Hoffman–Weeks extrapolations of *peak* melting temperatures for copolymers of caprolactone [15], ethylene terephthalate [23] and butylene terephthalate [24], and for polypropylenes [25] and polylactides [26] of different stereochemical defect concentrations, although the results did not necessarily follow the Flory theory. Kim et al. [27] on the other hand, found Hoffman–Weeks to be unsatisfactory for ethylene/octene-1 copolymers. Plots with peak melting temperatures were curved, making extrapolated T_m^f uncertain. They also describe another difficulty; increasing T_c reduces undercooling as expected, but the concentration of suitably long sequences (large n) is reduced as well, meaning that very long times may be required to grow even a small amount (ca. 1%) of crystals for subsequent melting. Chiu et al. [28] also found that isothermally crystallized ethylene/hexene-1 copolymers did not conform to Hoffman–Weeks behavior, as did Liu et al. [29] with ethylene/octene-1 copolymers.

A method of extrapolating to T_m^c (not T_m^f) is the Gibbs–Thomson plot of experimental final melting temperature T'_m versus inverse lamellar crystal thickness $1/l_{max}$. Eqs. (9a)–(9d) cover all cases of inclusion or exclusion of B units, and these can each be written in the Gibbs–Thomson format as

$$T_m(l_{max}) = T_m^*\left(1 - \frac{2\sigma}{n_{max}\,\Delta H_u^0}\right) \tag{11}$$

Here T_m^* is the melting temperature of an infinitely thick crystal ($n_{max} \to \infty$) in equilibrium with molten copolymer of global composition x_A. For total exclusion, T_m^* equals T_m^c from Flory Eq. (7). For other cases, the appropriate T_m^* is readily assessed in terms of ϵ and x_B^c from Eqs. (9a), (9c) or (9d). Eq. (11) requires only that the last crystals to melt at $T'_m = T_m(l_{max})$ are lamellar. With no further assumptions, the slope of the Gibbs–Thomson plot gives the ratio $\sigma/\Delta H_u^0$. Unlike the Hoffman–Weeks method, the Gibbs–Thomson extrapolation is not limited by the lack of thick equilibrium crystals above T_m^f, because the relation between $T'_m = T_m(l_{max})$ is a unique, robust function of n_{max} that applies with or without equilibrium crystals.

The best sort of Gibbs–Thomson procedure uses small angle X-ray scattering (SAXS) during the heating of isothermally crystallized polymers. Here SAXS is used to infer the largest crystal thickness l_{max} that melts at the final melting temperature T'_m for one copolymer having thermal histories that give different pairs of T'_m and $1/l_{max}$. Strobl and coworkers have been the most active proponents of this approach, mostly for homopolymers [30]. In studies of the same polypropylene/octene-1 copolymers examined by Thomann [22], Hauser et al. [13] found T_m^f from this Gibbs–Thomson method that were within 4 K of the Hoffman–Weeks values T_m^f. In another study of two ethylene/octene-1 copolymers[31], Gibbs–Thomson behavior was observed for final melting that is consistent with complete exclusion of branch points from the crystal. It should be noted that this particular Gibbs–Thomson method works even for irreversible melting. If the crystals do rearrange during the heating/melting process, the crystal thickness l_{max} is measured for the (stabilized) crystal that melts reversibly at T'_m with $\Delta G = 0$.

In Gibbs–Thomson studies by others, the melting temperature T_m is measured by DSC, and the corresponding crystal thickness l_c is estimated from separate SAXS experiments. Kim et al. [27] followed such a procedure with SAXS done just below the peak T_m. The extrapolated melting temperature of ethylene-octene-1 copolymers, treated as equilibrium T_m^c, decreased more rapidly with x_B than Flory theory, a situation attributed to partial inclusion of comonomer. Liu et al. [29] did similar experiments, but used the crystal thickness l_c^* established during isothermal crystallization. With this procedure a common Gibbs–Thomson intercept $T_m^* \approx T_m^0$ was found for four different copolymers, an unexpected observation that likely results from the fact that crystal thickness l_{max} at the end of melting is larger than l_c^*. There are other examples of Gibbs–Thomson analyses with some average l_c determined at room temperature, a thickness that is certainly smaller than l_{max} corresponding to final melting. In such cases the significance of the extrapolated temperature at $1/l_c \to 0$ is not clear.

The final experimental method to be discussed involves no extrapolation. The basis is S-E theory with finite (maximum) crystal thickness. Sanchez and Eby [9] were appropriately the first to use this approach with data on polylactides reported by Fischer et al. [32]. From peak (not final) melting temperatures, l_c and x_B^c, reasonable values of σ and ϵ were inferred from Eq. (9a). Obi et al. [12] considered vinylidene chloride/methyl acrylate copolymers in the context of total exclusion Eq. (9b). From final melting temperature T'_m and (room temperature) l_c as a function of

$x_{\rm B}$, a composition dependent surface energy σ ($x_{\rm B}$) was evaluated.

The present author has advocated a somewhat different scheme based on total exclusion Eq. (9b) [4,33,34]. It rests on the notion that the first crystals to form or the last crystals to melt are composed of long A sequences that act like homopolymer A chains, hence $\Delta H_{\rm u}^0$ and σ correspond to homopolymer values. From the measured final $T'_{\rm m} = T_{\rm m}(l_{\rm max})$, Eq. (9b) is used to evaluate $n_{\rm max}$ and hence the thickness $l_{\rm max}$ of final crystals to melt. One notes that Eq. (9b) applies equally well to the *first* stages of crystallization, enabling the evaluation of the (smallest) stable $l_{\rm c}$ when $T'_{\rm m}$ is replaced by $T_{\rm c}$. Hence from just isothermal crystallization temperature $T_{\rm c}$ and final melting temperature $T'_{\rm m}$ are defined thermodynamically sound lower and upper bounds to the crystal thickness distribution. While this scheme has not been verified by independent measurements of $l_{\rm c}$ during initial crystallization or final melting, the calculated values are quite reasonable. For instance, the experimental final $T'_{\rm m}$ in Fig. 3 correspond to (maximum) $l_{\rm c}$ ranging from 12 to 5 nm [4].

We close this section with a comment on peak melting temperatures. While they have the advantage of being easily defined in experiments, they lack fundamental significance. In particular, it is readily demonstrated that the peak melting temperature *does not* correspond to melting of lamellar crystals having the most probable thickness, either for homopolymers [35] or copolymers [4,35]. As mentioned repeatedly above, copolymer melting cannot be interpreted unless the melt composition is known, which is not the case for the peak melting temperature. In a similar vein, any attempt to interpret a copolymer DSC curve in terms of a crystal thickness distribution will return incorrect results, although the apparent distribution for the largest $l_{\rm c}$ (smallest crystallinity $f_{\rm c}$) is the most reliable [35].

9. Conclusions

The analysis of copolymer melting contains some points that appear often not to be appreciated. Foremost is that, when comonomer units are totally or partially excluded from the crystals, the melting temperature is lowered by the entropy of mixing that accompanies the fusion process. The amount by which this mixing depresses $T_{\rm m}$ depends on the melt composition which is generally unknown. Hence analytical expressions have been derived for *final melting* when the liquid has the global composition expressed as mole fraction $x_{\rm A}$ or sequence perpetuation probability p. For this reason, only the *final* experimental melting temperature $T'_{\rm m}$ has a connection with theory. Peak melting temperatures have no fundamental significance.

The theory of Flory for equilibrium melting at $T_{\rm m}^{\rm c}$ of infinitely thick crystals in the limit of complete exclusion of comonomer B is correct, but inaccessible to direct experiment. A Gibbs–Thomson plot of final melting temperature $T'_{\rm m}$ versus reciprocal crystal thickness $1/l_{\rm c}$ gives an extrapolated equilibrium temperature that can be compared to theory. Flory theory also provides an observable final melting temperature $T_{\rm m}^{\rm f} < T_{\rm m}^{\rm c}$ that may be obtained by extrapolation of $T'_{\rm m}$ according to the Hoffman–Weeks procedure. There is, however, no analytical expression for $T_{\rm m}^{\rm f}$. A test of Flory theory with extrapolated $T_{\rm m}^{\rm f}$ for copolymers of different p (or $x_{\rm A}$) will fall below $T_{\rm m}^{\rm c}$ from the familiar Eq. (7), as shown by the dashed line in Fig. 3. This should not be taken as a failure of Flory theory.

Alternative theories for ‘equilibrium melting’ with complete rejection of comonomer proposed by Baur [6] and by Goldbeck-Wood [11] are incorrect not useful for interpreting copolymer melting. The same statement applies to other approaches based on Baur theory [14,15].

The pragmatic treatment of Sanchez and Eby Eqs. (9a)–(9d) has much to recommend it. The theory is correct for observed *final* melting temperatures $T'_{\rm m}$ of lamellar crystals with thickness $l_{\rm max}$, without any need for extrapolation to ‘equilibrium’. The required basal surface energy σ and heat of fusion ΔH^0 for lamellar crystals that melt at $T'_{\rm m} = T_{\rm m}(l_{\rm max})$ are in all probability the same as for homopolymer crystals. Furthermore, there is no need to assume complete exclusion of comonomer as with Flory theory. SAXS experiments during melting can establish both maximum crystal thickness and corresponding final melting temperature. If Eq. (9b) fails in this case, partial inclusion is indicated, although unique determination of energy ϵ and crystalline concentration $x_{\rm B}^{\rm c}$ is difficult. In this circumstance, other experiments to estimate $x_{\rm B}^{\rm c}$ [36,37] or calculations to establish a reasonable size for ϵ [38] are helpful for interpreting the copolymer melting temperature.

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