The Melting Point of Crystalline Copolymers – Applying Materials Simulation

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Abstract. The defect Gibbs energy of hydroxyvalerate comonomer inclusions into the crystals made up by random copolymers of poly(β-hydroxybutyrate-co-β-hydroxyvalerate) (PHB/HV) is calculated by means of the thermodynamic integration approach. The result obtained for a single inclusion is in excellent agreement with those obtained by fitting experimental melting temperature and cocrystal composition data. On decomposing the Gibbs energy, it is found that the crystallization entropy contributes the dominant part of the defect Gibbs energy. Our calculations on multi-inclusion crystals show that the Gibbs energy strongly decreases when the comonomers aggregate in a preferred pattern. Further information to the design of isomorphic copolymers is obtained from these calculations.

Introduction

Random copolymers are widely used in materials development to tune their properties, such as the melting temperature or the convenient processing temperature. Introducing, e.g., some ethylene or methylene units randomly into isotactic poly(propylene) (i-PP) promotes the formation of shorter, stereoregular blocks (of length $l$) and results in a linear depression of the melting point by almost 5 K per wt.-\% of the comonomer [1]. Higher amounts of random comonomer inclusions reduce the probability of homopolymer sequences long enough to crystallize sufficiently that the material is obtained completely amorphous (Fig. 1).

The thermodynamic theory of crystallization of this type of copolymers, where the guest comonomers are excluded from the crystallization of the host polymer, was first discussed by Flory [2] and later augmented by Baur by a more phenomenologic theory [3][4] that fits the experimental data better than the Flory model.

A different type of crystallization is observed for some copolymers where the comonomers can be included into the crystal of the host polymer. Depending on the amount of comonomer included, the melting temperature is also reduced (albeit less than for the exclusion case), and crystallization may occur for the whole range of copolymer composition. The limit of uniform inclusion, where the concentration of the comonomer in the crystal is the same as in the entire copolymer, is displayed in Fig. 2.

Up to now, the crystallization of random copolymers of this type is not well understood. Theoretical models dealing with cocrystallization of random copolymers usually assume a random distribution of the comonomers in the crystal [5-7]. However, this assumption holds only for the idealized case where the defect is small enough as not to affect the arrangement of neighboring chains. In general, every defect (inclusion of a ‘wrong’ monomeric unit) creates available volume in the neighboring part of the crystal, making additional inclusions at these positions more likely than elsewhere. The deformation of the neighboring chains may be small and compensated by small rearrangements of the polymer chains in the surrounding of the defect without affecting the long-range order of the crystal when the two comonomers consist of constitutionally identical units with different configuration (e.g., i/a-PP) or of units different only in the length of a flexible side chain (e.g., i-PP/but-l-ene or poly(β-hydroxybutyrate-co-β-hydroxyvalerate) (PHB/HV)).

The misfit created in chains of nonflexible units of rigid main-chain polymers by units of different length much stronger affects the crystal conformation and crystallization Gibbs energy, because it can not be compensated for within a small and localized region of the crystal. A popular example for rigid main-chain random copolymers is poly(hydroxybenzoic acid-co-hydroxynaphthoic acid) [8]. This

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The copolymer does not crystallize, but exists in the nematic liquid-crystalline state. However, crystallization of these copolymers is conceivable when the chains arrange by selection of similar and matching, yet random segments of the chain [9]. The probability of finding those matches is not too small, but it is uncertain whether these aggregates can reach the minimum size of thermodynamically stable crystal nuclei. The high molecular rigidity also might be limiting the chain mobility required for the constitutional matching of sequences.

In the first part of this paper, we discuss the theoretical background of copolymer crystallization and apply the crystallization model to experimental data. Here, the crystallization will be discussed in terms of the defect Gibbs energy, which is the energy required to replace one repeat unit in the crystal by a comonomer unit. The second part presents atomistic force-field simulations that gain more information on the thermodynamics and conformation of the cocrystallization of random copolymers.

Thermodynamics of Copolymer Crystallization

The kinetic and equilibrium aspects of copolymer crystallization have been addressed by a number of authors [2–7]. The idea behind using equilibrium thermodynamics is based on the assumption that, considering a copolymer of two comonomers A and B crystallizing in the crystal lattice of A, the comonomers B may either be excluded from the crystals or act as defects in the crystal. In both cases, the Gibbs energy of the crystal will increase and the melting temperature decrease. In the following, we address exclusively random copolymers, i.e., copolymers with a Bernoullian distribution of monomer sequences.

The case of comonomer exclusion in thermodynamic equilibrium was first described by Flory [2], who calculated the upper bound of the copolymer melting temperature, i.e., the melting temperature of crystals built up from ‘infinitely long’ homopolymer sequences of units A in the copolymer. Flory found the melting temperature equation:

$$\frac{1}{T_m} - \frac{1}{T_m(1-X_B)} = \frac{R}{H_m} \cdot \ln (1-X_B) \quad (1)$$

where $X_B$ is the concentration of B units in the polymer and $\ln (1-X_B)$ equals the collective activities of A sequences in the limit of the upper bound of the melting temperature. $T_m$ and $H_m$ denote the homopolymer equilibrium melting temperature and heat of fusion, respectively, and $R$ is the gas constant.

The probability of finding those crystals is very low, leading Kilian [3] and Baur [4] to develop a phenomenologic theory of copolymer crystallization based on the behavior of eutectic mixtures. The basic idea is that the homopolymer sequences of length $\xi$ may only be included into crystals of lamellar thickness corresponding to that length. The melting temperature is then given by

$$\frac{1}{T_m} - \frac{1}{T_m(1-X_B)} = \frac{R}{H_m} \cdot \left[\ln (1-X_B) - \xi^{-1}\right] \quad (2)$$

where $\left(\xi = [2 \cdot X_B (1-X_B)]^{-1}\right)$ is the average length of homopolymer sequences in the melt [4]. This model, while incorporating finite crystal thickness and the concomitant depression in the melting point, still neglects that the homopolymer sequences are invariably fixed in chains due to bond connectivity; the eutectic equilibrium, which requires total separation into the ‘components’ (the homopolymer sequences of same length $\xi$), is unrealistic. However, it was shown by several investigations [4][10] that the Baur model (Eqn. 2) fits experimental data much better than the Flory equation (Eqn. 1) [2].

Inspection of experimental data shows readily that comonomer exclusion alone cannot account for the observed melting-point depression in many cases. In Fig. 3, we plot the experimental excess crystallization Gibbs energy (obtained as $H_m^C / R T_m$ · $(1 - T_m/T_m^C)$) together with the corresponding theoretical values (calculated as $\ln (1-X_B) - \xi^{-1}$ in case of the Baur model) as a function of copolymer composition. In case of PEN/T and PHB/HV copolymers, the experiment and Baur model match the data at low comonomer composition, indicating that the comonomer exclusion model may hold in this range of composition. However, beyond a certain composition, the experimental excess Gibbs energy is lower for these copolymers, and for copolymers of i-PP, experimental values are always lower than those obtained by the model. Exclusion theories do not account for these observations.
hence, comonomer inclusion is to be considered in melting-point prediction.

At least, one additional parameter, the defect Gibbs energy of a comonomer inclusion, is required for models dealing with comonomer inclusions. Models that consider the possibility of comonomer inclusions were first discussed by Helfand and Lauritzen [5] and by Sanchez and Eby [6]. They assumed that the defects are randomly distributed in the crystal and do not interact with each other, so that they could be described by a mean defect Gibbs energy $\varepsilon (\varepsilon \geq 0)$.

Sanchez and Eby found that the melting temperature can be described by:

$$\frac{1}{T_m(X_B)} - \frac{1}{T_m^o} = \frac{R}{H_m^o} \cdot \left[ \varepsilon \cdot X_{CB} \frac{RT_m}{RT_m} + (1 - X_{CB}) \cdot \ln \frac{1 - X_{CB}}{1 - X_B} + X_{CB} \cdot \ln \frac{X_{CB}}{X_B} \right] \tag{3}$$

$$\xi^{-1} = 2 \left( X_B - X_{CB} \cdot e^{-\varepsilon RT} \right) \left( 1 - X_B + X_{CB} \cdot e^{-\varepsilon RT} \right) \tag{7}$$

Assuming equilibrium comonomer inclusion, where $X_{CB}$ is given by the Boltzmann weight of $\varepsilon$, Eqn. 4 reduces to

$$\frac{1}{T_m^o} - \frac{1}{T_m(X_B)} = \frac{R}{H_m^o} \cdot \left[ \varepsilon \cdot \frac{X_{CB}}{RT_m} + (1 - X_{CB}) \cdot \ln \frac{1 - X_{CB}}{1 - X_B} + X_{CB} \cdot \ln \frac{X_{CB}}{X_B} \right] \tag{6}$$

with

where $\xi^{-1}$ is found in analogy to Baur's approximation, treating the fraction $X_{CB}$ of B units that are cocryostallizing as if they were units of A, as

$$\xi^{-1} = 2 \cdot (X_B - X_{CB}) \cdot (1 - X_B + X_{CB}) \quad \text{for} \quad \frac{X_{CB}}{X_B} \leq \chi_{CN} \leq 1$$

Minden's approach to the same problem can be expressed as

$$\frac{1}{T_m^o} = \frac{1}{T_m(X_B)} + \frac{\varepsilon \cdot X_{CB}}{H_m^o} \cdot \frac{RT_m}{RT_m} + (1 - X_{CB}) \cdot \ln \frac{1 - X_{CB}}{1 - X_B} + X_{CB} \cdot \ln \frac{X_{CB}}{X_B} \tag{4}$$

Comparison to Experimental Data

We tested our model on several copolymers, but we will focus here on the random copolymer of poly(β-hydroxybutyrate-co-β-hydroxyvalerate), PHB/HV (Fig. 4).

A set of experimental data for the equilibrium melting temperature of PHB/HV copolymers was recently published by Orts, Marchessault, and Bluhm [11]. The authors crystallized copolymers at different melting temperatures and extrapolated their data for $T_m$ with inverse lamellar thickness to infinite lamellar (crystal) size. The so-obtained equilibrium melting temperatures $T_m^o$ are plotted in Fig. 5. The crystal HV concentration $X_{CV}$ was determined by VanderHart, Orts, Marchessault, and Bluhm by means of solid-state $^1$H-NMR spectroscopy [12] and small-angle X-ray scattering [13]. Both investigations revealed that the amount of HV units that are included into the HB crystal increases with increasing HV concentration in the copolymer.

These melting temperatures and crystal composition data are used to calculate an experimental estimate of the defect Gibbs energy based on the different models described above. An illustration of
these models for the PHB/HV copolymer is already given in Fig. 5. The dashed line corresponds to the complete exclusion of comonomers due to a sufficiently high defect Gibbs energy (which is equal to the Baur model, Eqn. 2), whereas the thin lines correspond to the equilibrium inclusion model, Eqn. 6, using different estimates for the defect Gibbs energy. As the melting temperatures at HV concentrations of 0.17 and 0.21 exceed the prediction of the exclusion model, some crystallization must occur at these concentrations.

Table 1 gives the defect Gibbs energies obtained by the different models; the differences make clear that knowledge of the real crystal composition is of great importance. An estimate for \( x_{v} \approx 0 \) is obtained by linear extrapolation of the experimental data for \( x_{CB} \) towards zero concentration which yields \( \epsilon \approx 17.8 \text{ kJ/mol} \).

These models, however, give no insight on the detailed crystal morphology. To gain more information, force-field computer simulations were performed to calculate the defect Gibbs energy for single- and multi-inclusion copolymer crystals.

**Simulation of Comonomer Inclusion Gibbs Energies**

For the assessment of the inclusion of a single comonomer unit into a homopolymer crystal, the problem to be treated computationally is the transformation from a system at state \( \lambda = 0 \) (a homopolymer single crystal of the host polymer plus one individual chain with a comonomer unit, somewhere outside) into a system at state \( \lambda = 1 \) (a copolymer crystal that includes one ‘defective’ chain plus one homopolymer chain unit outside). This ‘reaction’ (Fig. 6, a) would be governed by the excess Gibbs energy, usually called the single inclusion defect Gibbs energy. The approach that is more convenient to molecular dynamics (MD) calculations is the thermodynamic integration approach that estimates only the energy difference of the two states by slowly transforming the system from state \( \lambda = 0 \) to \( \lambda = 1 \) (Fig. 6, b). Crystal and single co-unit are transformed independently, but the sum of both calculations gives the Gibbs energy difference corresponding to the exchange reaction. During the transformation that is described in detail in [14], the derivative of the systems Hamiltonian with respect to the state of transformation described by \( \lambda \) must be calculated and the transformation Helmholtz energy (in an NVT ensemble) is then obtained by integration as [15]:

\[
\Delta G_{0 \rightarrow 1} = \int \left[ \frac{\partial H(\lambda)}{\partial \lambda} \right] d\lambda
\]

For further analysis, the Helmholtz energy was divided into an enthalpic and an entropic contribution as follows: the internal energy of defect inclusion was calculated as the total energy difference between the defective and the defect-free microstructure, i.e.,

\[
\Delta E_{0 \rightarrow 1} = [H(\lambda = 1) - H(\lambda = 0)]
\]

The values were taken from 50 ps NVT-MD calculations of the microstructures before and after the thermodynamic integration calculations were performed. The entropy change on defect inclusion is then given by

\[
\Delta S_{0 \rightarrow 1} = \frac{(\Delta G_{0 \rightarrow 1} - \Delta G_{\text{single}})T}{\Delta G_{0 \rightarrow 1}}
\]

As experimental results usually are obtained at constant pressure conditions, the calculated Helmholtz energy needs to be transformed into Gibbs energy for comparison. We approximate the Gibbs energy difference \( \Delta G_{0 \rightarrow 1} \) by adding the mechanical work (approximated by the mean pressure-energy change \( pAV \)) to \( \Delta G_{0 \rightarrow 1} \) from the thermodynamic integration results.

For all discussions in this paper on the HB \( \rightarrow \) HV transformation, a value of the coupling parameter \( \lambda = 0 \) corresponds to the HB structure of the repeat unit under transformation, whereas a value of \( \lambda = 1 \) corresponds to the HV structure. We consider the configuration at \( \lambda = 0 \) as the starting point of the thermodynamic integration and the configuration at \( \lambda = 1 \) as the finishing point.

**Gibbs Energy of Single Comonomer Inclusion**

A PHB/HV microstructure is shown in Fig. 7. One HB repeat unit is already replaced by a HV unit and labelled with...
'1'. We transformed this unit to HV by thermodynamic integration. The integration utilizing the trapezoidal integration scheme is illustrated in Fig. 8, and the integration results are listed in the first line of Table 2. After correcting for the mean mechanical work, the Gibbs energy difference between the defect creation in the PHB crystal and the PHB chain is found to be 16.5 kJ/mol, which is quite close to the estimate from experiments given in the previous section of this paper and within the range of uncertainty of these estimates. The further analysis of our data makes clear that this Gibbs energy difference is dominated by the conformational entropy; investigating cocrystallization by calculating the defect energy $\Delta E$ only would suggest, if available as the only piece of information, the misleading interpretation that cocrystallization is thermodynamically favored as soon as the assumption of independent defects is given up. The data for $\Delta E$ given in Table 2 demonstrate that indeed the crystallization entropy dominates the Gibbs energy of cocrystal inclusion and that its influence may not be neglected.

**Defect Aggregation**

In order to evaluate possible interactions between defects, the Gibbs energy calculations were now extended analogously to several defects in a microstructure. In particular, we focused on the question in how far the aggregation of HV units could lower the mean defect Gibbs energy.

A second HV defect was incorporated close to the first one (defect concentration of 1.5%); since there are two crystallographically distinct monomeric units in the unit cell, both of these positions were tested with the next unit cell in each of the principal cell directions.

The selected positions for this additional HV units are labelled in Fig. 7. The defects 'a1', 'a2', 'b1', 'b2' are located in the $(h k 0)$ plane of the microstructure (taking the position of '1' as $(0 0 0)$, see Table 2 for exact positions), whereas defects 'c1' and 'c2' are the next and the following possible positions in the same chain as defect '1'. Gibbs energies for these defects are listed in Table 2. All features of the simulation of single defects, described above, apply also to the structures with two defects. It is obvious that the HV units at positions 'a1', 'b1', and 'c1' produce a defect Gibbs energy similar to the energy of the first HV inclusion, whereas the units at positions 'a2', 'b2', and 'c2' give an average defect Gibbs energy that is on average 13% lower.

This is in contrast to investigations of Kamiya et al. [16] who surmised decreasing average defect Gibbs energies when diads HV-HV are included into the crystal. Based on our calculations, triads of type HV-HV-HV would have to be responsible for the decrease of $\varepsilon$. This behavior may be explained by a simple argument: a defect included at one position deforms the surrounding crystal lattice. A second defect far away from the first has its own deformation domain and gives rise to a defect Gibbs energy similar to that of the first defect. A second defect very close to the first one (inside its deformation domain) faces a defective lattice to deform that contains the additional CH$_3$ group in its deformation domain and hence gives rise to a similar defect Gibbs energy than the first defect.

That is the case for the defects at positions 'a1', 'b1', and 'c1' (see Fig. 7). However, if the second defect is located outside the deformation domain of the first one, but these domains overlap and cause displacements in the same direction, then the second defect benefits from the work of deformation done by the first one, leading to synergistic effects that lower the average defect Gibbs energy of this pair. This may explain the lower defect Gibbs energy at positions 'a2', 'b2', and 'c2'. These defects are oriented similarly as '1' revealing similar orientations of the anisotropic deformations domains, whereas the other defects ('a1', 'b1', and 'c1') produce deformation domains with different displacements.

**Extension to Higher Cocronomer Concentrations**

Based on our Gibbs energy calculations, a stronger decrease of the average defect Gibbs energy seems possible when the number of aggregated HV units increases, enabling higher degrees of cocrystallization. Unfortunately, the large variety of possible aggregates makes Gibbs energy calculations based on the thermodynamic integration approach impossible. However, lattice calculations based on nearest-neighbor interactions might give a good estimate on the possible behavior.

We chose a finite cubic lattice with von...
Table 2. Values (per Defect) of the Helmholtz and Gibbs Energy Change Calculated for the Inclusion of One or Two $\beta$-Hydroxy-valerate Defects into a PHB Crystal at $T = 300 K$. Defect Gibbs energy $\Delta G$ is obtained from Helmholtz energy $\Delta A$ after correcting for the mean mechanical work. The internal energy change $\Delta E$ is taken from NVT calculations before and after defect inclusion. The average numbers are calculated for the double inclusion results only. The statistical errors in the calculations of $\Delta A$ and $\Delta G$ are in the range of 1.6 $kJ/mol$.

![Fig. 8. The thermodynamic integration result for a single HV inclusion in a PHB microstructure. See also Table 2.](image)

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<table>
<thead>
<tr>
<th>Created Defect</th>
<th>Position of 2nd</th>
<th>$\Delta A$</th>
<th>$\Delta G$</th>
<th>$\Delta E$</th>
<th>$TAS$</th>
<th>$\Delta S$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fractional coord.</td>
<td>[kJ/mol]</td>
<td>[kJ/mol]</td>
<td>[kJ/mol]</td>
<td>[kJ/mol]</td>
<td>[J/mol/K]</td>
</tr>
<tr>
<td>1</td>
<td>0 0 0</td>
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<td>16.5</td>
<td>2.1</td>
<td>-15.2</td>
<td>-6.1 R</td>
</tr>
<tr>
<td>(1+$a_1$)</td>
<td>0.33 0.3 0.52</td>
<td>16.9</td>
<td>16.3</td>
<td>7.1</td>
<td>-9.8</td>
<td>-3.9 R</td>
</tr>
<tr>
<td>(1+$b_1$)</td>
<td>0 0 1</td>
<td>15.1</td>
<td>14.6</td>
<td>1.7</td>
<td>-13.3</td>
<td>-5.3 R</td>
</tr>
<tr>
<td>(1+$b_2$)</td>
<td>-0.49 -0.2 -0.22</td>
<td>17.7</td>
<td>16.9</td>
<td>-5.8</td>
<td>-23.5</td>
<td>-9.4 R</td>
</tr>
<tr>
<td>(1+$b_3$)</td>
<td>0.16 -0.5 0.28</td>
<td>14.8</td>
<td>14.1</td>
<td>-8.2</td>
<td>-23.0</td>
<td>-9.2 R</td>
</tr>
<tr>
<td>(1+$c_1$)</td>
<td>-0.66 0.30 0.5</td>
<td>17.4</td>
<td>16.9</td>
<td>3.9</td>
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<tr>
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<td>14.6</td>
<td>3.6</td>
<td>-11.5</td>
<td>-4.6 R</td>
</tr>
</tbody>
</table>

![Fig. 9. Simulation microstructure of a PEN/T crystal where the middle layer perpendicular to the image plane has already been transformed to ethylene terephthalate](image)

Neumann interactions. Hence, each lattice site has six interacting neighbors, two in each principal direction. Following the results of the thermodynamic integration approach for two defects, in our model, we only consider the interactions of a test lattice site with units on positions in the direction of the positive axes, i.e., '$a_1$', '$b_1$', and '$c_1$'. Interactions to units in the other positions ('$a_2$', '$b_2$', and '$c_2$') are ignored because the changes of rare small-

This procedure leads to an energy of 4.1 $kJ/mol$ when all possible test sites around a comonomer are allocated by a comonomer; this corresponds to a 100% HV inclusion. This is already in the range of thermal energy and enables such aggregates to participate in crystallization.

The strength of these interaction effects can be illuminated more clearly on polymers crystallizing in an extended-chain conformation. One example are the copolymers of poly(ethylene 2,6-dicarboxynaphthanoate-co-ethylene terephthalate) PEN/T. Using our Gibbs energy calculation scheme, we found an inclusion Gibbs energy of 84 $kJ/mol$ for a single inclusion [17], which reduces to 22 $kJ/mol$ per comonomer when including an infinitely large layer in the a-b plane of the crystal (Fig. 9, the chains are extended in the c-direction). This results supports the non-periodic layer model that is preferred for the crystallization of non-flexible copolymers [18].

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