A New Model Describing the Cocrystallization Behavior of Random Copolymers

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ABSTRACT: We have developed a new model to describe the melting point depression of isomorphic copolymers. The model combines the common models applied for nonisomorphic and isomorphic copolymers and is capable of fitting the transition between both assuming the concentration dependence of the mean defect Gibbs energy. The model is tested with success on a set of melting temperatures of copolymers from ethylene terephthalate and ethylene 2,6-dicarboxynaphthanoate (PET and PEN), demonstrating the influence of defect aggregation during copolymer crystallization. The comparison of the model fits to the free energy values for comonomer inclusions from thermodynamic-integration simulations, making obvious the power of that computational method.

Introduction

The attempts to explain crystallization in random copolymers go back to the work of Flory in 1947.[1] His principal assumption was that the comonomer units, which are excluded from the crystals, change the configurational entropy of the system and therefore influence the melting temperature. Baur[2] further developed this model considering “hindered equilibrium”, a concept introduced by Kilian[3] to describe the quasi-eutectic behavior of mixtures, by including the average length of homopolymer sequences that are able to segregate and crystallize. It was found that the Baur model gives better predictions of the experimentally obtained copolymer melting temperatures than the original Flory model. These comonomer-exclusion models both require only intrinsic homopolymer thermodynamic parameters such as the equilibrium melting temperature and the equilibrium heat of fusion.

At least one additional parameter, the defect Gibbs energy of a comonomer inclusion, is required for models dealing with comonomer inclusions. Models that include the possibility of comonomer inclusions were first discussed by Helfland and Lauritzen[4] and by Sanchez and Eby.[5] 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 ϵ ($\epsilon \geq 0$). As these models are based on Flory's assumptions, they may hold for small values of ϵ; as ϵ increases, however, the assumption of independent defects becomes less satisfactory when comonomer inclusion becomes less and less probable. A comonomer inclusion model preferred by Windle et al.[6] suggests that the “crystals” are built up by matching of similar but random sequences on neighboring copolymer chains. In that case, the assumption of independent comonomer defects in the host crystal is completely abandoned.

In the preceding paper in this issue,[7] we report on a novel approach to the prediction of the defect Gibbs energy of single comonomer inclusions based on MD calculations. Here we develop a new model to predict copolymer melting temperatures that may hold for every value of defect Gibbs energy and compare the predictions of our MD calculations to experimental results.

Thermodynamics of Copolymer Crystallization

The kinetic and equilibrium aspects of copolymer crystallization have been addressed by a number of authors.[1−8] 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, 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. Starting with the general equation $\Delta G = \Delta G° + RT \ln \alpha$, where α is the activity of the crystallizing copolymer, Flory found the melting temperature equation

$$\frac{1}{T_{\rm m}°} - \frac{1}{T_{\rm m}(X_{\rm B})} = \frac{R}{H_{\rm m}°} \ln(1 - X_{\rm B}) \quad \text{(Flory)} \qquad (1)$$

$X_{\rm B}$ is the concentration of B units in the polymer and $\ln(1 - X_{\rm B})$ equals the collective activities of A sequences in the limit of the upper bound of the melting temperature. $T_{\rm m}°$ and $H_{\rm m}°$ denote the homopolymer equilibrium melting temperature and heat of fusion and R is the gas constant. The drawback of this model is Flory's assumption that these homopolymer sequence of infinite length build up unfolded crystals of the length of A runs, an assumption that is unrealistic for polymers.

Attempts to overcome this drawback treat copolymer crystals as a “pseudo-eutectic” system, where the homopolymer sequences of length ξ may only be included into crystals of lamellar thickness corresponding to that length.[2,3] The activity of a sequence of length ξ is then related to the mean sequence length $\langle\xi\rangle$ as follows:

$$\Delta G = \Delta G° + RT\frac{1}{\xi} \ln (X_{{\rm A}\xi}/f_{{\rm A}\xi}) \qquad (2)$$

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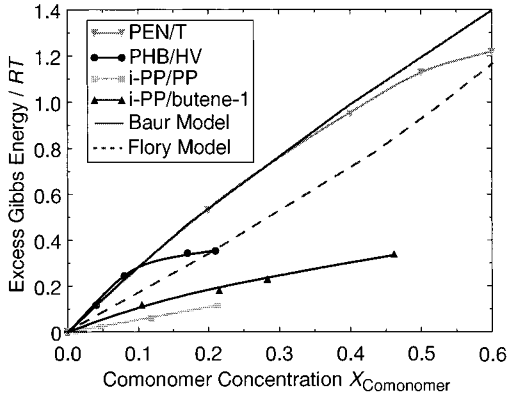

Figure 1. Excess Gibbs energy/RT as obtained from experiment for random copolymers of PEN/T, poly(ethylene 2,6-dicarboxy naphthanoate-*co*-terephthalate);[12] PHB/HV, poly(β-hydroxybutyrate-*co*-β-hydroxyvalerate);[11] i-PP/PP, stereoregularity defect in isotactic poly(propylene);[15] and i-PP/butene-1, isotactic poly(propylene-*co*-butene-1),[16] compared to the theoretical value given by copolymer exclusion theory.[2]

$X_{A\xi}$ is the concentration and $f_{A\xi}$ is the activity coefficient for crystallizing sequences of length ξ. Baur[2] used the activity coefficient

$$f_{A\xi} = \frac{\xi}{\langle\xi\rangle} e^{-((\xi/\langle\xi\rangle)-1)} \qquad (3)$$

The melting point of infinitely long homopolymer sequences is then given by

$$\frac{1}{T_m^\circ} - \frac{1}{T_m(X_B)} = \frac{R}{H_m^\circ}[\ln(1 - X_B) - \langle\xi\rangle^{-1}] \quad \text{(Baur)} \quad (4)$$

where $\langle\xi\rangle = [2X_B(1 - X_B)]^{-1}$ is the average length of homopolymer sequences in the melt. This model, while incorporating finite crystal thickness and concomitant depression in the melting point, still neglects the fact 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 ξ) is unrealistic. However, it was shown by several investigations[2,9] that the Baur model fits experimental data much better than the Flory equation.[1]

Inspection of experimental data shows readily that comonomer exclusion alone cannot account for the observed melting point depression in many cases. In Figure 1 we plot the experimental excess crystallization Gibbs energy (obtained as $H_m^\circ/(RT_m)(1 - T_m/T_m^\circ)$) together with the corresponding theoretical values (calculated as $\ln(1 - X_B) - \langle\xi\rangle^{-1}$ in the case of the Baur model and $\ln(1 - X_B)$ in the case of the Flory model), as a function of copolymer composition. In the cases of PEN/T and PHB/HV copolymers, the experiment and Baur model match 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 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 the melting point prediction.

The case of comonomers B that are included into the crystal of A where they act as defects was considered by Helfand and Lauritzen[4] and later in a more general way by Sanchez and Eby.[5] They write a partition function as

$$Q = \sum_{m=0}^{n} P(m) e^{-m\epsilon/RT} = \sum_{m=0}^{n} q(m) \qquad (5)$$

where $P(m)$ is the binomial distribution of m comonomers in a chain of length n, and ϵ denotes the excess free energy of a defect created by the incorporation of one B unit into the crystal. Neglecting interactions between these defects, Sanchez and Eby derived an expression for the Gibbs free energy difference ΔG between such a crystal and the melt for the crystal of defect concentration $X_{CB} = M_{CB}/n$ as:

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln M_{CB} \\ &= \Delta G - RT\left\{\frac{\epsilon X_{CB}}{RT} + (1 - X_{CB}) \ln \frac{1 - X_{CB}}{1 - X_B} + X_{CB} \ln \frac{X_{CB}}{X_B}\right\} \end{aligned} \qquad (6)$$

X_B is the overall concentration of B in the melt and X_{CB} the actual concentration of B in the cocrystal that is determined by the kinetic conditions of the crystal formation. With $\Delta G^\circ = H_m^\circ(1 - T_m/T_m^\circ)$, the melting temperature is then given by

$$\frac{1}{T_m(X_B)} - \frac{1}{T_m^\circ} = \frac{R}{H_m^\circ}\left\{\frac{\epsilon X_{CB}}{RT_m} + (1 - X_{CB}) \ln\frac{1 - X_{CB}}{1 - X_B} + X_{CB} \ln\frac{X_{CB}}{X_B}\right\} \quad \text{(Sanchez–Eby)} \quad (7)$$

This equation (eq 7) holds for any concentration X_{CB}, including two limits: when $X_{CB} = X_B$, uniform inclusion takes place and eq 7 reduces to

$$T_m(X_B) = T_m^\circ\left(1 - \frac{\epsilon X_B}{H_m^\circ}\right) \qquad (8)$$

For the equilibrium state, the concentration of B units in the cocrystal is given by

$$X_{CB}^{eq} = \frac{X_B e^{-\epsilon/RT}}{1 - X_B + X_B e^{-\epsilon/RT}} \qquad (9)$$

and the equilibrium melting point is derived from eq 7 as

$$\frac{1}{T_m^\circ} - \frac{1}{T_m(X_B)} = \frac{R}{H_m^\circ} \ln(1 - X_B + X_B e^{-\epsilon/RT}) \quad \text{(Sanchez–Eby, equilibrium)} \quad (10)$$

This equation is similar to the Flory equation (eq 1) but includes the equilibrium fraction $X_B e^{-\epsilon/RT}$ of repeat units B that are able to crystallize. It is obvious that eq 10 reduces to the Flory model for the case of high defect free energies, and one might not be surprised that it also overestimates the melting temperatures for $\epsilon \gg 0$ or, in the general application of this model, underestimates the defect free energy. The temperatures derived by eq 10 can be taken as an upper bound of the melting temperature. The behavior at $\epsilon \gg 0$ is the principal shortcoming of the Sanchez–Eby model: when

ϵ is too high to allow cocrystallization, eq 10 reduces to the Flory model, eq 1, but it should preferentially converge to the Baur model, eq 4. A new model would equal eq 4 and eq 10 in the limits of high and low defect free energies. This is achieved as follows.

Following the derivations of Flory,[1] Baur,[2] and Helfand and Lauritzen,[4] the more general melting temperature equation for copolymers in a frustrated thermodynamic equilibrium can be obtained. Starting with the general equation

$$\Delta G = \Delta G° + RT \ln \alpha \qquad (11)$$

where α is the activity of the crystallizing copolymer sequence, we include the quasi-eutectic behavior by replacing α with $q(M_{\mathrm{CB}})\, f_{\mathrm{A}\xi}$. $q(M_{\mathrm{CB}})$ is, as in eq 5, the term of the partition function that relates to the actual concentration X_{CB}, and $f_{\mathrm{A}\xi}$ is the activity coefficient for homopolymer sequences of length ξ. In the limit of infinite long sequences, $\xi \rightarrow \infty$, eq 11 becomes

$$\Delta G = \Delta G° + RT(\ln q(M_{\mathrm{CB}}) + \langle\tilde{\xi}\rangle^{-1}) \qquad (12)$$

The solution for $\ln q(M_{\mathrm{CB}})$ is similar to that in the Sanchez–Eby equation

$$\ln q(M_{\mathrm{CB}}) = -\left\{\frac{\epsilon X_{\mathrm{CB}}}{RT} + (1 - X_{\mathrm{CB}}) \ln\frac{1 - X_{\mathrm{CB}}}{1 - X_{\mathrm{B}}} + X_{\mathrm{CB}} \ln\frac{X_{\mathrm{CB}}}{X_{\mathrm{B}}}\right\} \qquad (13)$$

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

$$\langle\tilde{\xi}\rangle^{-1} = 2(X_{\mathrm{B}} - \tilde{X}_{\mathrm{CB}})(1 - X_{\mathrm{B}} + \tilde{X}_{\mathrm{CB}}) \quad \text{for } \tilde{X}_{\mathrm{CB}} \leq X_{\mathrm{CB}} \text{ and 0 otherwise} \qquad (14)$$

where $\tilde{X}_{\mathrm{CB}} = X_{\mathrm{CB}}(1 - X_{\mathrm{B}})/(1 - X_{\mathrm{CB}})$ is the concentration of B units (with respect to the entire copolymer) that are included into the crystal. Notice that the concentration X_{CB} is related to the crystal only. Then eq 12 becomes

$$\Delta G = \Delta G° - RT\left\{\frac{\epsilon X_{\mathrm{CB}}}{RT} + (1 - X_{\mathrm{CB}}) \ln\frac{1 - X_{\mathrm{CB}}}{1 - X_{\mathrm{B}}} + X_{\mathrm{CB}} \ln\frac{X_{\mathrm{CB}}}{X_{\mathrm{B}}} + \langle\tilde{\xi}\rangle^{-1}\right\} \qquad (15)$$

and the melting temperature is given by

$$\frac{1}{T_{\mathrm{m}}(X_{\mathrm{B}})} - \frac{1}{T_{\mathrm{m}}°} = \frac{R}{H_{\mathrm{m}}°}\left\{\frac{\epsilon X_{\mathrm{CB}}}{RT_{\mathrm{m}}} + (1 - X_{\mathrm{CB}}) \ln\frac{1 - X_{\mathrm{CB}}}{1 - X_{\mathrm{B}}} + X_{\mathrm{CB}} \ln\frac{X_{\mathrm{CB}}}{X_{\mathrm{B}}} + \langle\tilde{\xi}\rangle^{-1}\right\} \quad \text{(new model)} \qquad (16)$$

Assuming equilibrium comonomer inclusion, eq 9, eq 16 reduces to

$$\frac{1}{T_{\mathrm{m}}°} - \frac{1}{T_{\mathrm{m}}(X_{\mathrm{B}})} = \frac{R}{H_{\mathrm{m}}°}\{\ln(1 - X_{\mathrm{B}} + X_{\mathrm{B}}e^{-\epsilon/RT}) - \langle\tilde{\xi}\rangle^{-1}\} \quad \text{(new model, equilibrium)} \qquad (17)$$

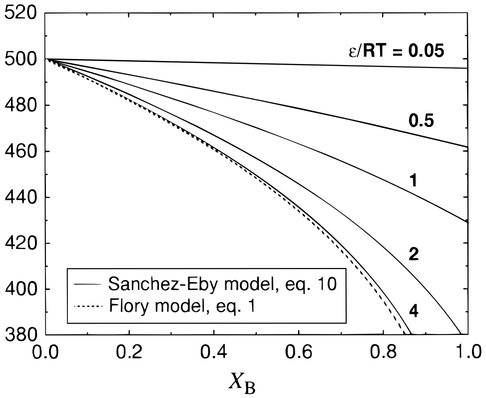

Figure 2. Copolymer melting temperatures as obtained by eqs 1 and 10 for different values of the defect Gibbs energy ϵ. The Sanchez–Eby model converges to the Flory model for high values of ϵ.

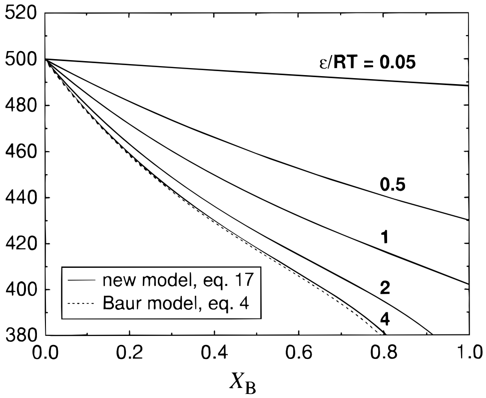

Figure 3. Copolymer melting temperatures for the frustrated equilibrium state as obtained by eqs 4 and 17 for different values of the defect Gibbs energy ϵ. Our new model converges to the Baur model, which is appropriate for the case of strict comonomer exclusion (for high values of ϵ).

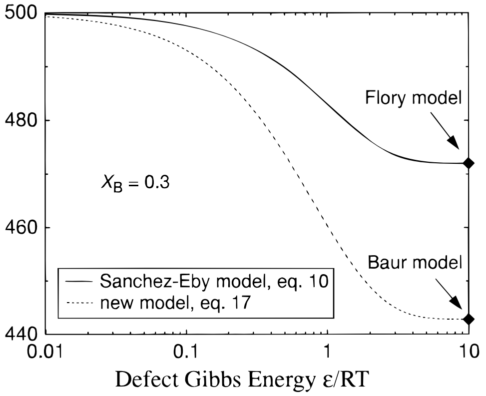

Figure 4. Copolymer melting temperatures for $X_{\mathrm{B}} = 0.3$, obtained by different models vs defect Gibbs energy ϵ/RT. The comonomer inclusion models converge to the corresponding comonomer exclusion models at high defect Gibbs energies ϵ.

where

$$\langle\tilde{\xi}\rangle^{-1} = 2(X_{\mathrm{B}} - X_{\mathrm{B}}e^{-\epsilon/RT})\cdot(1 - X_{\mathrm{B}} + X_{\mathrm{B}}e^{-\epsilon/RT}) \qquad (18)$$

In Figures 2–4 the melting temperatures obtained by these models are compared for an arbitrary copolymer with equilibrium inclusion into the crystal and a host–homopolymer melting temperature $T_{\mathrm{m}}°$ of 500 K and an equilibrium melting enthalpy $H_{\mathrm{m}}°$ of 25 kJ/mol. Notice that the Sanchez–Eby model always gives higher melting temperatures than our new equation (eq 17).

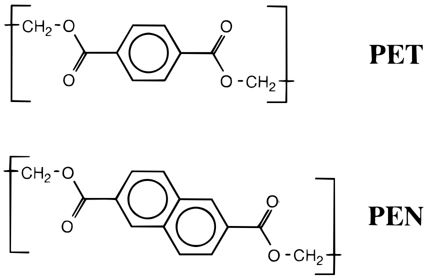

Figure 5. Chemical repeat units of poly(ethylene terephthalate) (PET) and poly(ethylene naphthalene-2,6-dicarboxylate) (PEN).

There are two further points that need to be discussed: First, it was shown on poly(β-hydroxybutyrate-*co*-β-hydroxyvalerate) copolymers (PHB/HV) that the mean defect Gibbs energy ϵ of HV comonomers included into the PHB crystal decreases significantly with increasing concentration of the HV comonomer.[11] Assuming that ϵ will approach zero if the comonomers are perfectly interchangeable in the lattice, the decreasing ϵ reveals that inclusion is favored with increasing HV composition.[11] This concentration dependence of the mean defect energy ϵ stands in contradiction to the assumption of independent (noninteracting) comonomer inclusions usually discussed with the cocrystallization models. We can easily include it into eq 16 by assuming a nonconstant mean defect energy $\epsilon(X_{\mathrm{CB}})$.

Second, the formation of crystals in general is influenced by the kinetic conditions of crystallization leading to smaller and less perfect crystals when the system is far away from its equilibrium state. If one assumes that the crystallization kinetics predominantly influence the lamellar thickness, whereas the lateral dimensions are preserved at comparatively high values, then one can include these conditions into the models by incorporating the expression for ΔG (e.g. eq 15 or the corresponding expressions for the other models) into $\Delta G - 2\sigma_e/l = 0$ (σ_e denotes the fold surface Gibbs energy and l is the lamellar thickness). This results in a further decrease of the copolymer melting temperature of $\Delta T_m^{(\mathrm{kinetic})} = T_m°/\Delta H_m°\cdot 2\sigma_e/l$. This expression is constant if one assumes a constant lamellar thickness l and can therefore be neglected if one uses the apparent homopolymer melting temperature T_m*, obtained at the same kinetic conditions as those for the copolymers, instead of $T_m°$. This approximation will also be used in our discussions.

The Model System

A well-investigated isobimorphic copolymer system is that of the random copolymers of poly(ethylene terephthalate) (PET) and poly(ethylene naphthalene-2,6-dicarboxylate) (PEN). The cocrystallization behavior of PET–PEN random copolymers was recently investigated by Lu and Windle.[12] Up to a naphthalenedicarboxylate content of 20% the copolymer crystallizes in a PET-like crystal structure, whereas for a composition of 30% naphthalenedicarboxylate or more the crystal structure is PEN-like, but with varying lattice parameters that indicate the cocrystallization behavior of PET–PEN copolymers. The chemical structures of PET and PEN repeat units are given in Figure 5.

We will compare our model to the melting temperatures reported by Lu and Windle[12] for annealed fiber samples. The equilibrium thermodynamic data of PET and PEN homopolymers are given in Table 1. We used the apparent homopolymer melting temperatures instead of the equilibrium values to fit the model equations to ensure that all data represent the same crystallization conditions.

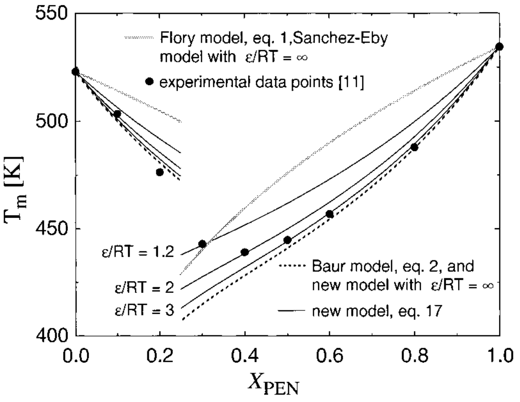

Figure 6. Theoretical melting temperatures of PET–PEN copolymers as obtained by eqs 1, 4, 10, and 17 compared to experimentally observed values.[12] The equilibrium homopolymer melting temperatures $T_m°$ were replaced by the experimental values T_m*.

Table 1. Thermodynamic Data of PET and PEN

	PET[13]	PEN[14]
$T_m°$ (K)	583.0	610.0
T_m* (K)	523.0	534.5
$H_m°$ (kJ/mol)	26.9	25.0

Defect Gibbs Energy of Comonomer Inclusions

First we will compare the equilibrium models to experimental data of PET–PEN random copolymers (Figure 6). The melting temperatures predicted by the Flory model, eq 1, are always higher than the experimentally obtained values reported by Lu and Windle.[12] As the cocrystallization model of Sanchez and Eby, eq 10, always predicts values of the melting temperature even above the Flory model, it is impossible to fit the experimental values (see Figure 6). This clearly demonstrates the weakness of the Sanchez–Eby equilibrium-inclusion model in the limit of high defect Gibbs energies.

In contrast, the melting temperatures predicted by the model of Baur, eq 4, which are the same as those predicted by our new model in the limit of high defect Gibbs energies, are always lower than the experimental data points (the exception at a naphthalene-2,6-dicarboxylate content of 0.2 may be due to a crystallization kinetics different from the other samples; we will not discuss this part of the phase diagram because of the sparse data available).

At a composition of approximately 30 mol % of naphthalene-2,6-dicarboxylate, the type of the crystal lattice changes from PET-like to PEN-like. In the higher range of compositions where the PEN-like crystal is observed, the experimental melting temperatures of the copolymers were always higher than the limiting values obtained with the Baur model. The melting temperatures obtained by our new model, eq 17, can explain these higher melting temperatures assuming a concentration dependent defect free energy $\epsilon(X_{\mathrm{CB}})$; solutions of eq 17 for $\epsilon/RT = 1.2$, 2, and 3 are shown in Figure 6. The average defect Gibbs energies obtained by fitting eq 17 to the experimental melting temperatures are given in Table 2 (for these fits, T in the

Table 2. Values of the Average Defect Gibbs Energy for the Terephthalate Inclusion into a PEN Crystal, Obtained by Fitting Eq 17 to Experimental Data[12]

PET content in the copolymer (X_B)	av equilibrium defect Gibbs energy ϵ (kJ/mol)	PET Content in the Crystal (X_{CB})	
		equilibrium	experimental
0.2	17	0.004	0.03
0.4	12	0.025	0.38
0.5	11	0.055	0.54
0.6	7	0.179	0.67
0.7	4	0.555	0.83

Table 3. Values of the Average Defect Gibbs Energy for Terephthalate Inclusion into a PEN Crystal, Obtained by Fitting the Nonequilibrium Models, Eqs 7 and 16, to Experimental Data[12]

PET content in the copolymer (X_B)	nonequilibrium defect free energy ϵ (kJ/mol)	
	Sanchez−Eby model	new model
0.2	58.9	101.8
0.4	9.7	10.4
0.5	7.8	7.8
0.6	6.6	6.6
0.7	5.0	5.0

Boltzmann function was chosen as the crystallization temperature). These energies decrease with increasing PET content in the copolymer, indicating that the PET inclusion is favored for copolymers of intermediate composition.

Using these defect free energies, we are able to calculate the equilibrium concentration of PET repeat units in the crystal (X_{CB}) applying eq 9. They are also given in Table 2. It is evident that a large amount of comonomer inclusions is predicted by the new model. However, these comonomer concentrations do not fit the experimental data obtained from the variations of the length of the crystal *c*-axis (direction of polymer extension), assuming a linear variation of this length with PET concentration.[12] The real concentrations are always higher as it is expected for a nonequilibrium inclusion concentration forced by the crystallization kinetics; in the intermediate range of composition, essentially uniform inclusion occurs.

To analyze the state of nonequilibrium, we fitted the nonequilibrium models, eqs 7 and 16 to the experimental melting temperatures and comonomer concentrations. Defect free energies obtained in this way are reported in Table 3.

No differences between both models occur at intermediate PET composition, because the crystal size effect dropped to zero. Compared to our equilibrium model one finds that the assumption of equilibrium crystallization fortuitously reveals similar defect free energies as the assumption of a hindered equilibrium (sequence length effect).

For a PET concentration of 0.2 the expectation for the equilibrium defect concentration is close to zero, but the experimental comonomer concentration in the crystal is substantial higher. As a result, the defect Gibbs energy at this composition is very high in our model, since it must compensate for the influence of the higher defect concentration on the entropy of mixing. The crystal-size effect leads to a further increase of the defect free energy.

At a higher PET concentration of 0.7, the transition from a PEN-based crystal structure to a PET-based crystal structure occurs.[12] Hence, our analysis, based on the assumption that the observed melting temperature is related to the PEN-like cocrystal (which strongly dominates the experimental X-ray patterns at this concentration), gives a lower limit of ϵ.

Table 4. Values of Defect Gibbs Energy, Calculated for the Inclusion of a Single Naphthanoate Defect in a PET Crystal and a Terephthalate Defect in a PEN Crystal[7]

type of defect	ϵ (kJ/mol)	ϵ/RT
naphthanoate in a PET crystal	86	34
terephthalate in a PEN crystal	85	34

The change of the defect Gibbs energy with defect concentration clearly demonstrates the role of defect aggregation. Assuming that only single inclusions occur at a PET-concentration of 0.2 and that the addition of a second terephthalate unit beside a first one costs no energy, one can expect that aggregates of at least 10 terephthalate units characterize the terephthalate concentration of 0.4, and 16 such units at $X_{PET} = 0.6$.

Comparison to Free Energy Calculations

In the preceding paper of this issue,[7] we introduced a method to calculate the defect Gibbs energy of comonomer inclusions via the thermodynamic-integration approach. The defect Gibbs energy values obtained there are compiled in Table 4. These values were very high so that no inclusion of single comonomer defects can be expected, according to eq 9.

The defect Gibbs energy of a single terephthalate inclusion in a PEN crystal, thus simulated, is in good agreement with the value obtained from the fit of the new nonequilibrium model discussed above (i.e., 101.8 kJ/mol). The agreement clearly demonstrates that the computational method employed for the estimation of free energy is well suited for the prediction of copolymer isomorphism. The results obtained from our new model and the available experimental data (see Table 3) demonstrate clearly, however, that an expansion to the whole range of compositions is necessary. Such an undertaking will be reported on at a later time.

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