Isomorphic Behavior of Random Copolymers: Thermodynamic Analysis of Cocrystallization of Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)

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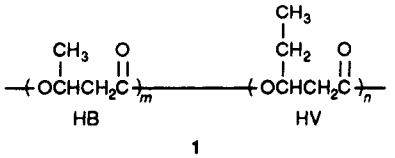
ABSTRACT: Isomorphism of random copolymers, namely, cocrystallization of comonomer units, is interpreted theoretically on thermodynamic grounds. A theory formulated here is applicable to cocrystallization phenomena observed over the whole composition range. A–B type random copolymers could form crystals in the lattices analogous to those of the parent homopolymers. In the A lattice, B units cost free energy relative to A units. In the B lattice, A units cost free energy. Thermodynamic equations are derived for the bulk free energy difference between a melt and the crystal containing both A and B comonomer units and for the comonomer composition and melting point of the crystal. Phase diagrams are proposed for A–B random copolymers showing isomorphism in a strict sense and isodimorphism. The experimental data on partitioning of comonomer units between crystalline and amorphous phases in copolymers of 3-hydroxybutyrate and 3-hydroxyvalerate (P(3HB–3HV)) are analyzed by using the equations formulated here. The melting point vs composition curve of the P(3HB–3HV) copolymers is consistent with the proposed diagram for an isodimorphic copolymer system. It is suggested that the less bulky minor component cocrystallizes thermodynamically easier than the more bulky one.

Introduction

There is some evidence to believe that the copolymer crystal includes different kinds of comonomer units in a crystalline lattice.[1,2] This is an isomorphic phenomenon.[3] The minor component of crystal should influence the whole properties of solid copolymers. Thus, it is of interest to study comonomer composition in the crystalline phase. However, only a few studies have been reported on copolymer isomorphism.[3-5]

A theory of copolymer isomorphism was proposed by Helfand et al.[4] They estimated comonomer compositions in the crystalline phases formed under the thermodynamic conditions. A more sophisticated theory was developed by Sanchez et al.[5] to estimate the bulk free energy of fusion, melting temperature, crystal thickness, and nucleation rate of copolymer crystals containing two kinds of monomer units. The analysis[1,2] of the partitioning of comonomer units in ethylene–1-butene copolymers containing less than 5% 1-butene showed that a small fraction of ethylene branches is found in the crystalline phases. The attention of those reports was, however, devoted only to the cases where the contents of the second component are relatively low. Isomorphism of copolymers over the whole composition range has not taken so much interest.

A wide variety of bacteria produce optically active copolymers of 3-hydroxybutyrate and 3-hydroxyvalerate (P(3HB–3HV); 1). These copolymers exhibit typical eutectic behavior in the melting of their crystals, which suggests the occurrence of isodimorphism in the crystalline phase of this copolymer.[6] The HV mole fraction within the P(3HB) crystalline lattice is, however, smaller than that of the whole copolymer.[7] In a previous paper,[8] we have reported the partitioning of comonomer units between the crystalline and amorphous phases in a series of P(3HB–3HV) copolymers containing from 0 to 93% HV using high-resolution solid-state ^{13}C NMR spectroscopy. In that study, the cocrystallization phenomenon, namely, the coexistence of both comonomer units in the crystals, was observed over a wide range of comonomer composition. It is thus expected that more extensive studies of a series of P(3HB–3HV) copolymers enable us to obtain the comprehensive picture of isomorphism in copolymer systems.



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In the present paper, we develop a theory of the thermodynamics of comonomer cocrystallization in copolymers. One of the most important features of this theory is that it takes into account the nearest-neighbor interaction between comonomer units. As a result, this theory is applicable to cocrystallization over a wide range of comonomer composition and thus provides the phase diagrams for copolymers showing isomorphism in a strict sense and isodimorphism. According to the formalism of this theory, we analyze the experimental data about the melting of the P(3HB–3HV) copolymers.

Thermodynamic Theory

We consider the crystallization of a homopolymer. When a monomer unit enters a crystal, the free energy of the system is lowered by an amount of ΔG_f. ΔG_f is called the free energy of fusion, which is given by

$$\Delta G_f = \Delta H_f - T\Delta S_f = \Delta H_f(T_m - T)/T_m \qquad (1)$$

where ΔH_f and ΔS_f are the enthalpy and entropy of fusion per monomer unit, respectively, and T_m is the melting point of the pure crystal. The larger ΔG_f the polymer has, the more stable the crystal is.

The stability of a copolymer crystal, consisting of two kinds of comonomer units, is governed by comonomer composition as well as ΔG_f. Each monomer unit has a different value of ΔG_f. The minor component acts as lattice defects in the crystalline lattice of the major component and has smaller ΔG_f. Thus, the total ΔG_f contribution of the crystal consisting of the major component alone is larger than that of the crystal consisting of both kinds of comonomer units. The crystal becomes less stable, in

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general, with increasing content of the minor component. However, the coexistence of two kinds of comonomer units in a crystal causes an increase in the configurational freedom of monomer units, i.e., the configurational entropy, ΔS_c. The value of ΔS_c becomes maximum when the comonomer composition in the crystalline phase is equal to that of the overall copolymer. The balance of these two factors determines the comonomer partitioning between the crystalline and melt phases.

A thermodynamic theory proposed by Helfand et al.[4] was formulated on the basis of the zeroth-order approximation, namely, the assumption that ΔG_f of each component is independent of the comonomer composition. This assumption may be insufficient to explain the melting behavior of the actual copolymer crystals, because ΔG_f should depend on the environment surrounding the monomer unit of interest as well as the structures of the monomer units and crystalline lattices. Thus, we modify the original theory by introducing the first-order approximation, namely, the incorporation of the nearest-neighbor interaction between the comonomer units.

Hereafter, we consider A–B copolymers crystallizing in the A crystalline lattice, which is a geometrical analogue of the crystalline lattice of the A homopolymer. In this lattice, B units form lattice defects. In the subsequent derivation, X_m and X_c are the mole fractions of B units in the melt and in the crystalline phase, respectively. $\Delta G_{AA}{}^A$ indicates the free energy of fusion per one A–A comonomer sequence in the A crystalline lattice. The value of $\Delta G_{AA}{}^A$ is assumed to be equal to that of ΔG_f of the A homopolymer. The superscript of ΔG refers to the type of the crystalline lattice. The sequence type of interest is designated by the subscript. Since the B units are lattice defects, the incorporation of A–B and B–B sequences into the crystal costs the free energy amounting to α and β, respectively. Thus, the relationship

$$\alpha, \beta \geq 0, \text{ and } 0 \leq X_c \leq X_m \tag{2}$$

is fulfilled. The parameters α and β are defined as the excess free energies of A–B and B–B sequences relative to a A–A sequence, respectively. Thus

$$\Delta G_{AB}{}^A = \Delta G_{AA}{}^A - \alpha$$

$$\Delta G_{BB}{}^A = \Delta G_{AA}{}^A - \beta \tag{3}$$

The probabilities of finding three types of diad sequences, A–A, A–B, and B–B, in the crystalline phase are $(1 - X_c)^2$, $2X_c(1 - X_c)$, and $(X_c)^2$, respectively.

The expression of the bulk free energy, ΔG^A, of the given copolymer is easily obtainable if the crystal is infinitely thick. ΔG^A is given by

$$\Delta G^A = \Delta G_{AA}{}^A - 2\alpha X_c(1 - X_c) - \beta X_c{}^2 - RT\left[(1 - X_c)\ln\frac{1 - X_c}{1 - X_m} + X_c \ln\frac{X_c}{X_m}\right] \tag{4}$$

When the ΔG^A value vanishes, eq 4 yields an expression for the melting points of the infinitely thick copolymer crystal. The resulting equation is

$$\frac{1}{T_m} - \frac{1}{T_{mA}} = \frac{R}{\Delta H_A}\left[\frac{2\alpha X_c(1 - X_c) + \beta X_c{}^2}{RT_m} + (1 - X_c)\ln\frac{1 - X_c}{1 - X_m} + X_c \ln\frac{X_c}{X_m}\right] \tag{5}$$

where ΔH_A is the enthalpy of fusion of the A homopolymer.

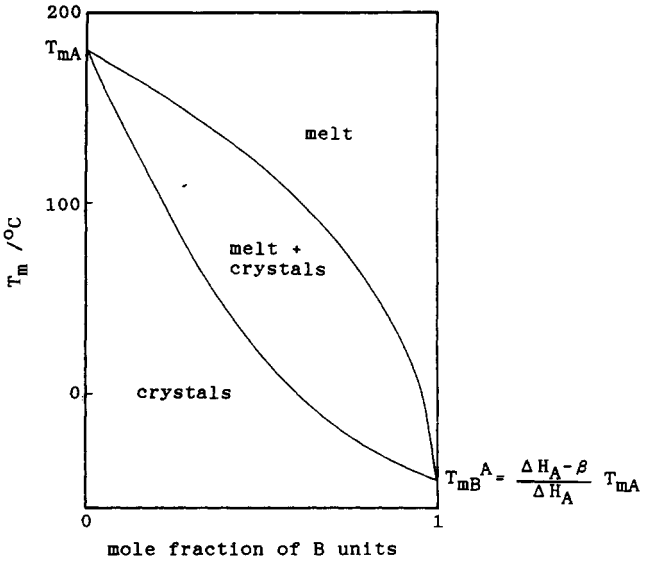

Figure 1. Phase diagram for an A–B random copolymer in the single-lattice system: T_{mA} = 180 °C, ΔH_A = 12 kJ·mol^{-1}, α = 2.5 kJ·mol^{-1}, and β = 6.0 kJ·mol^{-1} for the A lattice.

The contribution of the configurational entropy, $T\Delta S_c$, to the total free energy of fusion of the copolymer is given by the terms in the square brackets of eq 4 or the second and third terms in the square brackets of eq 5.

$$T\Delta S_c = -RT\left[(1 - X_c)\ln\frac{1 - X_c}{1 - X_m} + X_c \ln\frac{X_c}{X_m}\right] \tag{6}$$

The value of ΔS_c increases with incorporation of B units into the crystalline phase. The total contribution of the excess free energy, ΔG_{ex}, is given by the second and third terms of eq 4 or the first term in the square brackets of eq 5.

$$\Delta G_{ex} = 2\alpha X_c(1 - X_c) + \beta X_c{}^2 \tag{7}$$

ΔG_{ex} includes all enthalpy and entropy contributions except ΔS_c. The value of ΔG_{ex} decreases with incorporation of B units into the crystal.

The equilibrium state of the given system at temperature T is found by maximizing the value of ΔG^A in compositions X_c and X_m. Then, the composition X_{eq} of the crystal, which is in equilibrium with the melt of composition X_m, must satisfy the following equation:

$$X_{eq} = \frac{X_m p}{1 - X_m + X_m p} \qquad p = \exp\left\{\frac{-2}{RT}[(1 - 2X_{eq})\alpha + X_{eq}\beta]\right\} \tag{8}$$

Using this relationship, the melting point of the given crystal is expressed as follows:

$$\frac{1}{T_m} - \frac{1}{T_{mA}} = \frac{R}{\Delta H_A}\left[\frac{(2\alpha - \beta)X_{eq}{}^2}{RT_m} - \ln(1 - X_m + pX_m)\right] \tag{9}$$

The phase diagram can be deduced as shown in Figure 1.

The A–B copolymer could also crystallize in the B lattice. Thus, the A–B copolymer may show eutectic behavior in its melting. The corresponding phase diagram is shown in Figure 2 with a eutectic point appearing as (X_{eu}, T_{eu}). The behavior of this phase diagram is a little like the phase diagram of a Ag–Cu alloy. This is the general feature of isodimoprhic systems of copolymers. In the eutectic

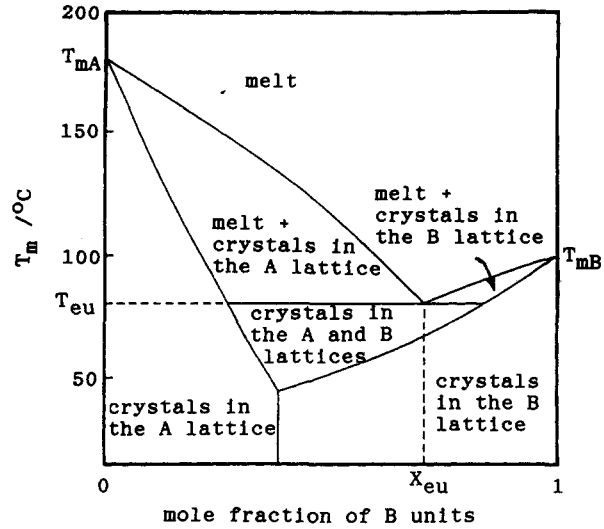

Figure 2. Phase diagram for an A–B random copolymer in the double-lattice system: T_{mA} = 180 °C, ΔH_A = 12 kJ·mol^{-1}, α = 2.5 kJ·mol^{-1}, and β = 6.0 kJ·mol^{-1} for the A lattice; T_{mB} = 100 °C, ΔH_B = 10 kJ·mol^{-1}, α = 1.2 kJ·mol^{-1}, and β = 2.0 kJ·mol^{-1} for the B lattice.

region, the two kinds of crystals are compatible on the scale of a crystallite but incompatible on the scale of a monomer unit. Eutectic behavior in crystallization has been observed in many copolymers.[9,10]

When $\Delta G_{BB}^A = \Delta G_{BB}^B$, the eutectic behavior mentioned above should not be observed because the relationship of $\Delta G^A > \Delta G^B$ is always fulfilled. In this case, the A and B comonomers must have much structural similarity, and thus only one type of crystalline lattice is formed. As a result, the phase diagram appears as shown in Figure 1. This is the case of isomorphism in a strict sense.[3] Such melting behavior has been reported for a few copolymers.[11,12]

Crystallization of Actual Copolymers

The physical state of copolymers should change according to the phase diagram shown in Figure 1 or Figure 2. Thus, the state is determined by specifying the composition X and temperature T. The crystallinity of copolymers increases with a lowering of the temperature, and the values of X_c and X_m change along the crystallizing and melting curves, respectively, in Figure 1 or Figure 2 while crystallization proceeds. Crystallization of actual polymers is stopped by the lowering of chain mobility at a certain temperature, T_s. In other words, T_s is the temperature at which the crystals start melting. The melting temperature of copolymers is, thus, not a single point but range from the starting melting temperature to the ending melting temperature. Each of the X_c and X_m values also has a range according to the range of the melting temperature.

Each of the observable X_c and X_m is, however, the single point that is an average value of a whole copolymer. Thus, we assume X_c and X_m are in equilibrium at T_m, which is measured at the peak of the DSC melting curve.

Since the value of X_c changes depending on crystallization temperature, the equilibrium melting temperature of copolymers that demonstrate comonomer cocrystallization cannot be estimated from a Hoffman–Weeks plot. The equilibrium melting temperature should be determined by plots of observed melting temperature against inverse lamellar thickness.

Table I
Composition[a] and Melting Points of P(3HB–3HV) Copolymers

	exptl[b]			calcd[c]		
X	X_m	X_c	T_m/°C	X_c	T_m/°C	param[d]
0.000	0.000	0.000	175.0	0.000	175.0	
0.183	0.478	0.000	109.0	0.059	121.8	α = 5.1 kJ·mol^{-1}
0.316	0.644	0.102	75.5	0.105	81.4	β = 7.7 kJ·mol^{-1}
0.407	0.486	0.142	64.2	0.138	53.7	κ = 2.4
0.407	0.486	0.586	64.2	0.585	66.4	α = 1.2 kJ·mol^{-1}
0.554	0.321	0.721	78.3	0.721	77.5	β = 2.0 kJ·mol^{-1}
0.931	0.808	1.000	104.5	0.966	103.6	κ = 1

[a] X, X_m, and X_c indicate an HV mole fraction of a whole P(3HB–3HV) sample, that in the amorphous phase (melt) and that in the crystalline phase, respectively. [b] Data of composition were obtained by high-resolution solid-state ^{13}C NMR and those of melting points by DSC, which were all cited from ref 7. [c] Calculated from eqs 8 and 9. [d] α and β are the excess free energies of HB–HV and HV–HV sequences relative to a HB–HB sequence. κ is an adjustable parameter.

Analysis of Experimental Data of P(3HB–3HV) Copolymers

In the previous paper,[8] we have concluded that the P(3HB–3HV) copolymers containing less than 40 mol % HV crystallize in the P(3HB) lattice. The HV mole fraction in this crystalline phase is smaller than that of the whole copolymer and also than that in the noncrystalline region. The P(3HB–3HV) copolymer containing 41 mol % HV (P(3HB–41% 3HV)) is the unique case where the coexistence of the P(3HB) and P(3HV) crystalline lattices has been confirmed from our solid-state ^{13}C NMR study.[8] This suggests that the value of X_{eu} of P(3HB–3HV) is near 0.40.

The values of X_m and X_c of P(3HB–3HV), which are determined by the solid-state ^{13}C NMR for the melt-quenched P(3HB–3HV) samples,[8] are listed in Table I. When a copolymer whose X is smaller than X_{eu} crystallizes according to Figure 2, X_m of the final state must be smaller than X_{eu}. On the contrary, X_m's in P(3HB–32% 3HV) and P(3HB–55% 3HV) are 0.64 and 0.32, respectively. Because of this contradiction, we use the experimental values of X instead of X_m for the following analysis. The use of X instead of X_m should cause the estimation of smaller excess free energies, α and β.

When eqs 8 and 9 are used, the thermodynamic parameters of the P(3HB–3HV) copolymers can be estimated. The thermodynamic parameters for the homopolymers have been chosen as follows:[8,13]

$$\Delta H_f \text{ for P(3HB)} = 11 \text{ kJ·mol}^{-1}$$

$$T_m \text{ for P(3HB)} = 175 \text{ °C}$$

$$\Delta H_f \text{ for P(3HV)} = 10 \text{ kJ·mol}^{-1}$$

$$T_m \text{ for P(3HV)} = 108 \text{ °C}$$

The values of the heat of fusion, ΔH_f, are for 100% crystalline materials. The value of ΔH_f for P(3HV) has been assumed to be equal to that of ΔH_f for P(3HB–93% 3HV).

For the crystal in the P(3HV) lattice, the super- and subscripts A and B in eqs 8 and 9 correspond to HV and HB units, respectively. Equation 8 can be solved in α and β after the parameters T_m, X_m, and X_{eq} are substituted by two sets of the corresponding observed data, namely, T_m, X, and X_c. Here the data for P(3HB–41% 3HV) and

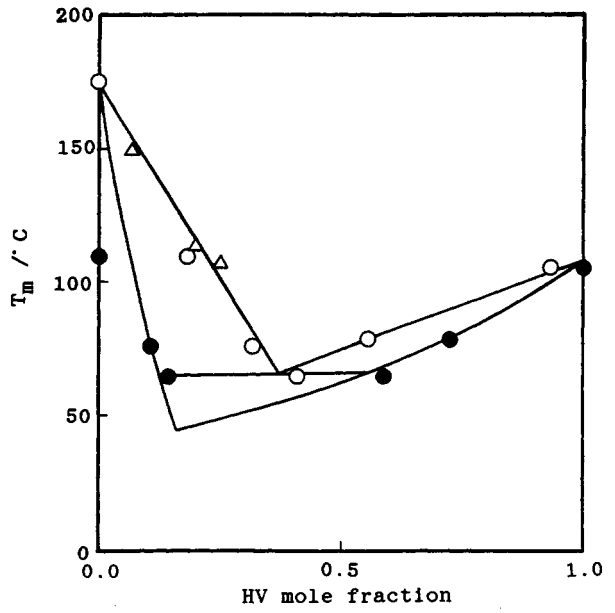

Figure 3. Phase diagram for P(3HB–3HV). Calculated data (—): T_{mA} = 175 °C, ΔH_A = 11 kJ·mol^{-1}, α = 5.1 kJ·mol^{-1}, β = 7.7 kJ·mol^{-1}, κ = 2.4 for the P(3HB) lattice; T_{mB} = 108 °C, ΔH_B = 10 kJ·mol^{-1}, α = 1.2 kJ·mol^{-1}, β = 2.0 kJ·mol^{-1}, and κ = 1 for the P(3HV) lattice. Experimental data: (○, △) X vs T_m; (●) X_c vs T_m: (○, ●) data of Kamiya et al. (*Macromolecules*, in press); (△) data of Kamiya et al. (*Macromolecules* 1989, *22*, 1676).

Table II
Contribution of Excess Free Energy and Configurational Entropy to the Free Energy of Fusion of P(3HB–3HV) Copolymers at Each Melting Temperature

lattice	X	ΔG_{ex}/kJ·mol^{-1}	$T_m\Delta S_c$/kJ·mol^{-1}
P(3HB)	0.316	1.0	0.37
	0.407	1.4	0.47
P(3HV)	0.407	0.84	0.18
	0.554	0.63	0.17

P(3HB–55% 3HV) were used. As a result, the values of α and β have been determined to be 1.2 and 2.0 kJ·mol^{-1}, respectively. The calculated values of X_c from eq 8 and T_m from eq 9 are listed in Table I. The calculated T_m vs X and T_m vs X_c curves are shown in Figure 3. These curves reproduce the melting points of the crystals in the P(3HV) lattice of P(3HB–3HV) samples.

For the crystals in the P(3HB) lattice, the super- and subscripts A and B in eqs 8 and 9 correspond to HB and HV units, respectively. In the same way as in the P(3HV) lattice, after the substitution of T_m, X, and X_{eq} in eq 8 by the corresponding experimental data for P(3HB–32% 3HV) and P(3HB–41% 3HV), the values of α and β were determined to be 2.1 and 3.2 kJ·mol^{-1}, respectively. When we use these values in eq 9, this equation, however, could not reproduce the melting point depression of the crystals in the P(3HB) lattice. The slope of this melting curve is too steep to be followed by eq 9. The calculated values of T_m were, thus, larger than the experimental ones. We introduce an adjustable parameter κ into eq 8. Then eq 8 is rewritten as follows:

$$X_c = \frac{X_m p'}{1 - X_m + X_m p'} \qquad p' = \exp\left\{\frac{-2}{RT\kappa}[(1 - 2X_c)\alpha + X_c\beta]\right\} \quad (10)$$

The larger the κ value is, the smaller the influence of the excess free energies α and β becomes. When the κ value is larger than unity, the relationship $X > X_c > X_{eq}$ is satisfied, and thereby the melting point is steeply decreased, which explains the melting behavior in the P(3HB) lattice. The melting point of a crystal whose composition is determined from eq 10 is given by

$$\frac{1}{T_m} - \frac{1}{T_{mA}} = \frac{R}{\Delta H_A}\left[\frac{2\alpha X_c(\kappa - 1) - (2\alpha - \beta)X_c^2(\kappa - 2)}{RT_m\kappa} - \ln(1 - X_m + p'X_m)\right] \quad (11)$$

For the crystals in the P(3HB) lattice, the values of α/κ and β/κ have been determined to be 2.1 and 3.2 kJ·mol^{-1}, respectively, by using eq 10. When these values are applied to eq 11, the κ values of P(3HB–32% 3HV) and P(3HB–41% 3HV) have been estimated to be 2.5 and 2.2, respectively. The difference in the κ values of these samples indicates that the excess free energies α and β might depend on composition and/or temperature. In fact, when the HV content is smaller than 40%, the lattice parameter a increases with composition in the P(3HB) lattice.[6,7] This lattice parameter change results in the changes in the excess free energies.

When κ is taken to be 2.4, α and β are determined to be 5.1 and 7.7 kJ·mol^{-1}, respectively. The calculated values of X_c from eq 10 and T_m from eq 11 are also listed in Table I. The calculated T_m vs X_m and T_m vs X_c curves are shown in Figure 3. The calculated data well reproduce the experimental data.

Incorporation of the minor components into the crystal generates the excess free energy ΔG_{ex} and the configurational entropy ΔS_c. These contributions can be calculated from eqs 6 and 7. As shown in Table II, ΔG_{ex} and $T_m\Delta S_c$ are 0.6–1.4 and 0.2–0.5 kJ·mol^{-1}, respectively. ΔG_{ex} is about 4 times larger than $T_m\Delta S_c$. It can be thus concluded that the cocrystallization of the P(3HB–3HV) copolymer is mainly governed by the excess free energy. The ΔH_f values of P(3HB) and P(3HV) are 11 and 10 kJ·mol^{-1}, respectively. Thus, the excess free energy has significant effect on the free energy of fusion of P(3HB–3HV). The configurational entropy does not have so much effect.

Discussion

P(3HB–3HV) shows an isodimorphic system. When eqs 8–11 are applied, the values of α, β, and κ have been estimated to be 5.1 kJ·mol^{-1}, 7.7 kJ·mol^{-1}, and 2.4 in the P(3HB) crystalline lattice and 1.2 kJ·mol^{-1}, 2.0 kJ·mol^{-1}, and 1.0 in the P(3HV) lattice, respectively. Since we have used observable melting temperature for analysis, the values of α, β, and κ have been roughly estimated. The lamellar thicknesses of the copolymers used may be different from one another. This may result in a little error in estimation of α, β, and κ.

The excess free energies in the (3HB) lattice are much larger than that in the P(3HV) lattice. The less bulky minor component is suggested to have smaller excess free energies than the more bulky one.

The steric hindrance of the minor component in the crystals becomes large with an increase in the excess free energies. The large excess free energies in the P(3HB) lattice should result in the increase of the lattice parameter a with an increase in the fraction of the HV unit. The change of the lattice parameter should result in the change of the excess free energies. The change of the κ values in the P(3HB) lattice indicates the change of the excess free energies.

Since κ = 1 in the P(3HV) lattice, the crystallization in this lattice should proceed under the thermodynamic conditions. The crystalline phase formed under the kinetic

conditions includes a greater number of minor components than those formed under the thermodynamic conditions.[4] The κ values of the P(3HB) lattice, which is larger than unity, suggests that the crystal in the P(3HB) lattice is formed under the kinetic conditions. Composition of the crystal whose crystallization is kinetically driven is not governed only by the excess free energy. In this crystal, crystallization rate and crystallization temperature also influence the comonomer partitioning between the crystalline and noncrystalline phases.

Concluding Remarks

In order to understand the properties of solid copolymers, it is necessary to obtain a variety of thermodynamic parameters determining the crystalline state. One of the most important parameters is the comonomer composition in the crystalline phase. Early theories of copolymer crystallization were based on the assumption that the minor component is excluded from the crystalline lattice formed by the major component.[14] However, recent high-resolution solid-state NMR studies have enabled us to determine the comonomer composition in both the crystalline and noncrystalline phases separately and revealed the inappropriateness of the above assumption. Thus, the crystallization of copolymers is expected to follow the thermodynamics in a more strict sense than predicted by Flory.[14] The present study attempts to confirm this point.

The P(3HB–3HV) copolymers are an appropriate example of the analysis of the cocrystallization of copolymers because the crystalline phase of those copolymers includes a considerable amount of the minor component, as can be seen in Table I. The theory formulated here, combined with the data of partitioning determined by the analysis of high-resolution solid-state NMR spectra, provides the parameters for semiquantitative estimation of the cocrystallization of P(3HB–3HV). Although the application of the theory includes some assumptions, the melting behavior of P(3HB–3HV) has been reproduced. The cocrystallization of the P(3HB–3HV) copolymers has been followed by the theory formulated here.

The analysis reveals a manner of crystallization of copolymers and provides the thermodynamic parameters required for the quantitative determination of cocrystallization. A small amount of the minor component in the crystalline phase has a large effect on the whole properties of copolymer solids. The analysis of composition in the crystalline phase should contribute to a better understanding of properties of solid copolymers.

In some cases, the fraction of the minor component in the crystalline phase should be within the range of experimental error or the so-called lattice defects. A more significant number of the minor components enter crystals in the other cases, which we call isomorphism. The borderline of comonomer composition between isomorphism and lattice defects is ambiguous.

Systems of copolymer cocrystallization are divided into three classes; isomorphism in a strict sense, isodimorphism, and isopolymorphism. Although the definition of the excess free energy admits of improvement, behavior of phase diagrams for copolymers should be expressed as in Figures 1 and 2, which indicate isomorphism in a strict sense and isodimorphism, respectively. The theory in the present paper can easily be extended to the case of isopolymorphism.

Glossary

ΔG_f	free energy of fusion per mole of monomer unit
ΔH_f	enthalpy of fusion per mole of monomer unit
ΔS_f	entropy of fusion per mole of monomer unit
ΔS_c	configurational entropy per mole of monomer unit
ΔG_{ex}	total excess free energy per mole of monomer unit
ΔG^K	free energy of fusion (per mole of monomer unit) of a copolymer crystallized in the K crystalline lattice
$\Delta G_{IJ}{}^K$	free energy of fusion per mole of IJ comonomer sequence in the K crystalline lattice
ΔH_I	enthalpy of fusion of the I homopolymer
α	excess free energy per mole of the A–B sequence relative to the A–A sequence
β	excess free energy per mole of the B–B sequence relative to the A–A sequence
κ	adjustable parameter
T_m	melting temperature of a pure crystal
T_{eu}	eutectic temperature
T_s	starting melting temperature of a copolymer
X	mole fraction of B units of a whole copolymer
X_m	mole fraction of B units in the melt (amorphous phase)
X_c	mole fractions of B units in the crystalline phase
X_{eq}	mole fraction of B units in the crystalline phase, which is in equilibrium with X_m
X_{eu}	eutectic composition (mole fraction of B units)

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