SUPPORTING INFORMATION

High molecular weight unsaturated copolyesters derived from fully biobased *trans-β*-hydromuconic acid and fumaric acid with 1,4-butanediol: Synthesis and thermo-mechanical properties

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Calculation of the degree of randomness (*R*). The chemical structures were further investigated by ^{13}C NMR, the corresponding assignments and an enlarged ^{13}C NMR spectrum in the range of 64.8–64.0 ppm were shown in Figure 5. The methylene carbons of butylene (d, h) were split into four peaks which were assigned to fumarate butylene hydromuconoate (FBH) at 64.80, fumarate butylene fumarate (FBF) at 64.69 ppm, hydromuconoate butylene hydromuconoate (HBH) at 64.16 ppm, and hydromuconoate butylene fumarate (HBF) at 64.07 ppm, respectively. From the four peak areas (A_{FBH}, A_{FBF}, A_{HBH}, and A_{HBF}), molar ratios of butylene hydromuconoate (P_{BH}) and butylene fumarate (P_{BF}) groups were firstly calculated by the following equations:

$$P_{BH} = [(A_{FBH} + A_{HBF})/2 + (A_{HBH})] \qquad \text{Equation S1}$$

$$P_{BF} = [(A_{FBH} + A_{HBF})/2 + (A_{FBF})] \qquad \text{Equation S2}$$

Next, the following equations were used to calculate number average sequence length of butylene succinate (L_{nBH}) and *cis*-butene succinate (L_{nBF}) segments:

$$L_{nBH} = 2 P_{BH} / (A_{FBH} + A_{HBF}) \qquad \text{Equation S3}$$

$$L_{nBF} = 2 P_{BF} / (A_{FBH} + A_{HBF}) \qquad \text{Equation S4}$$

Then, the following equation was used to calculate the degree of randomness (*R*):
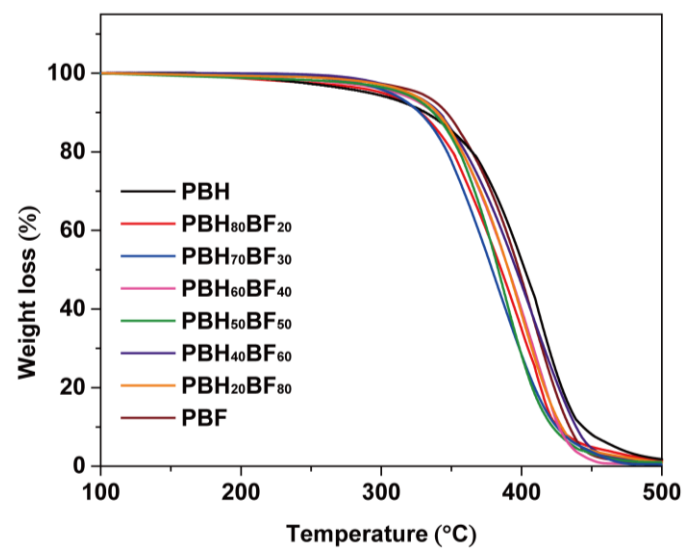
$$R = 1/L_{nBH} + 1/L_{nBF} \qquad \text{Equation S5}$$

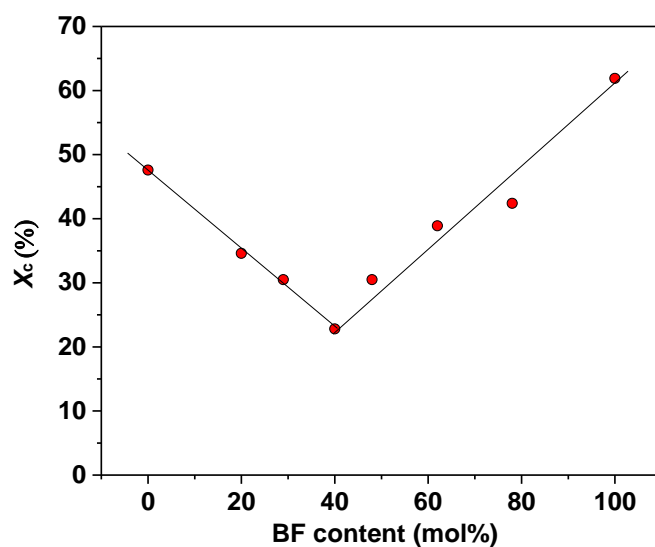**Figure S1.** TGA traces of PBH, PBF, and PBHBF copolyesters.

Figure S2. Composition dependences of degree of crystallinity.

Study of comonomer miscibility by thermodynamic analysis.

The study of comonomer miscibility between BH and BF units in crystal was carried out by thermodynamic analysis. All the samples were measured by the isothermal melt-crystallization experiment the samples were quenched to the desired crystallization temperature under a cooling rate of 60 ℃/min after being melted at 180 ℃ for 3 min. After the isothermal crystallization was fully completed, the samples were heated to the melt again at a rate

of 10 °C/min to study the subsequent melting behavior for the estimation of equilibrium melting point temperatures. Figure S3 shows DSC results of heat flow curves of the samples during heating scan after crystallized isothermally at various temperatures.
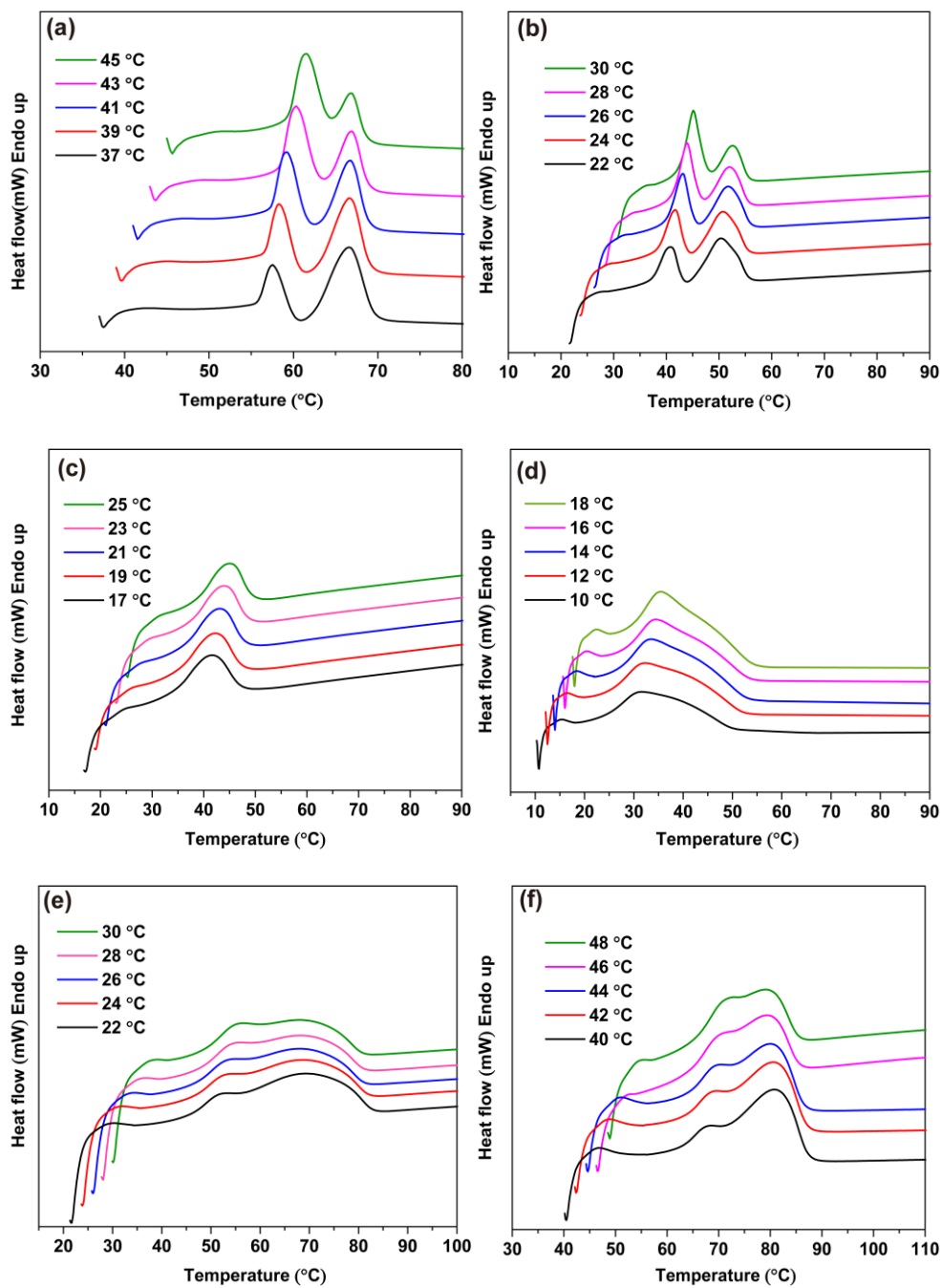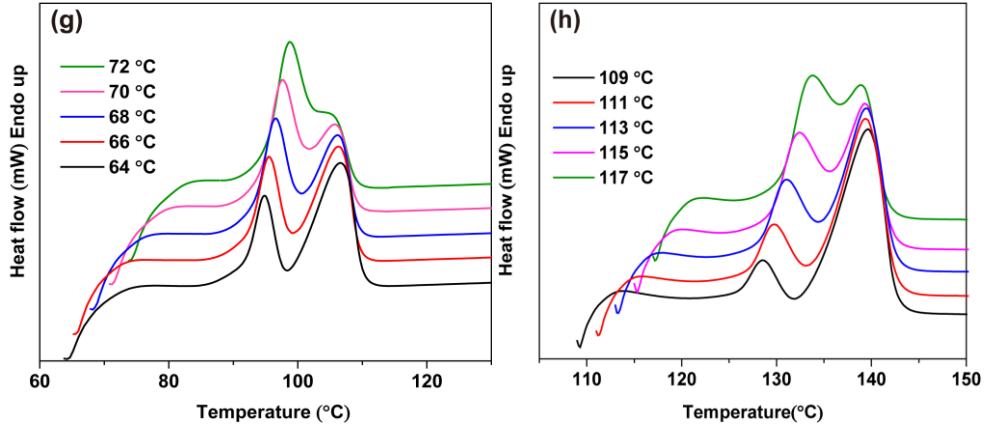
Figure S3. DSC heating scans after isothermal crystallization at the indicated temperatures: (a) PBH, (b) PBH$_{80}$BF$_{20}$, (c) PBH$_{70}$BF$_{30}$, (d) PBH$_{60}$BF$_{40}$, (e) PBH$_{50}$BF$_{50}$, (f) PBH$_{40}$BF$_{60}$, (g) PBH$_{20}$BF$_{80}$, and (h) PBF.

Hoffman-Weeks method has been commonly used and accepted to estimate the equilibrium melting temperature (T_m^0), particularly for the polyester systems.[1] The Hoffman-Weeks equation is given by:

$$T_m = T_m^o\left(1 - \frac{1}{r}\right) + \frac{T_c}{r} \qquad \text{Equation S6}$$

where r is the thickening coefficient, which depends on the lamellar thickness during the crystallization.

According to this equation, a linear extrapolation of observed T_m as a function of crystallization temperature T_c intersects the equilibrium line $T_m = T_c$ at an intersection point, and this point is T_m^0. The melting temperatures of the tested copolyesters and parent homopolyesters were well fitted by straight regression lines, as shown in Figure S4.
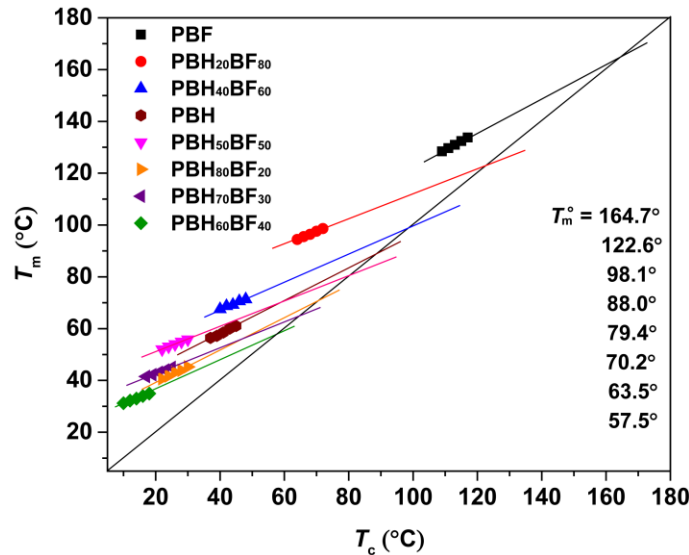

Figure S4. Hoffman-Weeks plots for the determination of the equilibrium melting points. Equilibrium melting temperatures are explicitly indicated at the intersection point with the $T_m = T_c$ line.

Several theories have been introduced for the copolymer crystallization. There is a distinction between those which

assume comonomer exclusion and those which assume comonomer inclusion in the crystal. Representatives of the class of theories for comonomer exclusion are those of Flory [2-3] and Baur [4-5].The most known theories of comonomer inclusion are those of Helfland and Lauritzen, [6] and by Sanchez and Eby[7]. Recently, Wendling and Suter have proposed a new general theory, who introduced a novel method to calculate the defect Gibbs energy of comonomer inclusions via the thermodynamic-integration approach.[8-10]. This theoretical approach has been checked with success on the crystallization behavior for many copolymer systems. .[1, 11-17]

The expression for the equilibrium melting temperature proposed by Flory was:

$$\frac{1}{T_m^o} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^o} \ln(1 - X_B) \qquad \text{Equation S7}$$

where T_m^0 and ΔH_m^o denote the homopolymer equilibrium melting temperature and heat of fusion, respectively, R is the universal gas constant. X_B is the concentration of the minor comonomer B in the copolymer, and $\ln(1 - X_B)$ equals the collective activities of A sequences in the limit of the upper bound of the melting temperature.

The theoretical method of Sanchez-Eby was given by

$$\frac{1}{T_m^o} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^o} \ln(1 - X_B + X_B e^{-\in/RT}) \qquad \text{Equation S8}$$

Where $X_B e^{-\in/RT}$ equals the equilibrium fraction of B repeat unit that is able to crystallize, and each B unit in the crystal creates an energy penalty $\in$.

The calculation method of melting point which was introduced by Baur was shown as follows:

$$\frac{1}{T_m^o} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^o} \left[\ln(1 - X_B) - \langle \xi \rangle^{-1} \right] \qquad \text{Equation S9}$$

Here, $\langle \xi \rangle = \left[2 X_B (1 - X_B) \right]^{-1}$ is the average sequence index of homopolymer sequences in the melt.

A new general theory proposed by Wendling and Suter was able to describe the comonomer inclusion as well as the comonomer exclusion. The model was given by:

$$\frac{1}{T_m^o} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^o} \left[\frac{\in X_{CB}}{RT} + (1 - X_{CB}) \ln \frac{1 - X_{CB}}{1 - X_B} + X_{CB} \ln \frac{X_{CB}}{X_B} + \langle \bar{\xi} \rangle^{-1} \right] \quad \text{Equation S10}$$

Where X_{CB} is the concentration of the B unit in the crystal.

In the equilibrium comonomer inclusion, the concentration of comonomer B unit in the crystal formed by A unit was given by:

$$X_{CB}^{eq} = \frac{X_B e^{-\in/RT}}{1 - X_B + X_B e^{-\in/RT}} \qquad \text{Equation S11}$$

When X_{CB} in Eq. S10 is substituted by Eq.S11, Eq.S10 turns out to be simplified and becomes:

$$\frac{1}{T_m^o} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^o}\left\{\ln\left(1 - X_B + X_B e^{-\epsilon/RT}\right) - \langle\bar{\xi}\rangle^{-1}\right\} \qquad \text{Equation S12}$$

where

$$\langle\bar{\xi}\rangle^{-1} = 2\left(X_B - X_B e^{-\epsilon/RT}\right)\left(1 - X_B + X_B e^{-\epsilon/RT}\right) \qquad \text{Equation S13}$$

When $X_{CB} = X_B$ and $X_{CB} = 0(\epsilon\to\infty)$, Eq. S12 reduces to the inclusion situation and the exclusion situation, respectively.

As shown in Figure S5, the Flory, Baur, Sanchez-Eby and Wendling-Suter equations were employed to determine the equilibrium melting temperatures of the polyesters in comparison to the experimental values acquired from the Hoffman-Weeks extrapolation. When cocrystallization behaviors of the copolymers are analyzed with various models, it shows that the Wendling-Suter theory predicts the experimental results better than the others. The equilibrium melting points of copolyesters were in general higher than the Baur prediction and lower than the Flory and Sanchez-Eby prediction. Hence, the second comonomer is neither complete exclusion nor uniform inclusion with the host crystal. The Wendling-Suter model is employed to calculate the defect Gibbs free (ϵ) by comparing melting temperatures predicted by the model with T_m^0 of PBHBF copolyesters determined experimentally. The ϵ was calculated from the function ϵ/RT which was determined as an adjustable parameter and was constant, irrespective of comonomer composition. Easier the inclusion behavior is, lower the defect Gibbs energy is.

Calculation of ϵ for PBH leads to an average defect free energy $\epsilon = 2.5$ kJ/mol in the case of incorporation of BF unit into PBH crystal. On the other hand, the defect Gibbs free energy is $\epsilon = 2.7$ kJ/mol in the case of incorporation of BH unit into PBF crystal. These values are relatively small, showing that comonomer units have fine miscibility in PBHBF. A part of BF could insert into the PBH crystal and vice versa. Hence, it is reasonable to conclude that the PBH type crystal structure developed up to 40 mol % BF content; i.e., the PBH lattice accommodated the BF units, whereas, samples containing > 40 mol % of BF units crystallized according to the PBF lattice.
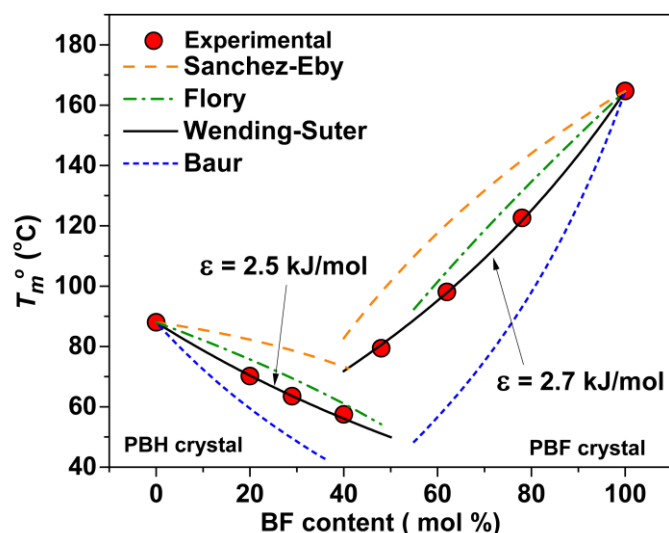
Figure S5. Comparison of the experimental equilibrium melting temperatures with the theoretical melting temperatures predicted by the Sanchez-Eby theory (orange curves), the Flory theory (green curves), Baur theory (blue curves) and the Wendling-Suter theory (black curves).

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