

Crystallization Kinetics of Bacterial Poly(3-hydroxybutyrate) Copolyesters with Cyanuric Acid as a Nucleating Agent

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ABSTRACT: Effects of cyanuric acid (CA) on nonisothermal and isothermal crystallization, melting behavior, and spherulitic morphology of bacterial copolyesters of poly(3-hydroxybutyrate), i.e., poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH), have been investigated. CA has excellent acceleration effectiveness on the melt crystallization of bacterial PHB, PHBV, and PHBH, better than the nucleating agents reported in the literatures, such as boron nitride, uracil, and orotic acid. PHBV and PHBH do not crystallize upon cooling from the melt at 10°C/min, while they are able to complete crystallization under the same conditions with an addition of 1% CA, with a presence of sharp crystallization exotherm at 75–95°C. Isothermal crystallization kinetics of neat and CA-containing PHBV and PHBH were analyzed by Avrami model. Crystallization half-times ($t_{1/2}$) of PHBV and PHBH decrease dramatically with an addition of CA. The melting behavior of isothermally melt-crystallized PHBV and PHBH is almost not influenced by CA. Spherulitic numbers of PHBV and PHBH increase and the spherulite sizes reduce with an incorporation of CA. Nucleation densities of PHBV and PHBH increase by 3–4 orders of magnitude with a presence of 1% CA. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1374–1382, 2013

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INTRODUCTION

Polyhydroxyalkanoates (PHAs), a family of bio-based polyesters with diverse structures, are the typical bio-plastics that can be completely synthesized by microorganisms. They have been attracting considerable attentions as potential substitutes for the oil-based plastics.^{1,2} Poly(3-hydroxybutyrate) (PHB) is the most well-studied bacterial polyesters in the family of PHAs. However, it has two major drawbacks. First, it is brittle and rigid due to the high crystallinity, large spherulitic size, and the occurrence of secondary crystallization under ambient conditions. Second, PHB has a low thermal decomposition temperature, resulting in a narrow temperature window in melt processing. Copolymerization is a typical approach to modify the physical performances of PHB.^{3–6} Compared with PHB homopolymer, its bacterial copolyesters such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) have the better physical properties. For instance, PHBH is tough and flexible, and PHBH containing 15 mol % hydroxyhexanoate (HH) can elongate to ca. 760% in tensile deformation.³ Besides, the melting temperature and melt viscosity decrease with introducing the

comonomer units into PHB, conferring PHB copolyesters the broader temperature window in melt processing.

Despite the better physical properties, bacterial copolyesters of PHB have a critical drawback in processing and molding. Crystallization of PHB copolyesters is too slow, which further deteriorates with increasing the comonomer unit content. Generally, crystallization does not proceed in the commercial PHBV and PHBH in a cooling condition similar as the practical injection-molding and extrusion, resulting in the long molding-cycle time, low productivity, and high energy consumption in industrial processing. Furthermore, the low crystallizability and degree of crystallization (X_c) can induce the low strength, modulus, and heat deformation temperature (HDT) of final products. The poor crystallizability and processability of PHB bacterial copolyesters have been the bottleneck for their large-scale commodity application.

In general, polymer crystallization consists of two stages, i.e., nucleation and crystal growth. Crystallization rate of semicrystalline polymers can be increased by accelerating the nucleation process, which consists of the homogenous and heterogeneous

nucleation. Nucleating agent (NA) is an efficient additive to accelerate the heterogeneous nucleation in industrial processing.⁷ NA can lead to the fast crystallization, high X_c , and small spherulitic size of semicrystalline polymers. Thus, NA can improve the processability, productivity in melt processing, HDT, mechanical strength, modulus, toughness, and optical transparency⁸ of the semicrystalline polymers. For example, a typical NA of PHB and its copolyesters, boron nitride (BN),^{9,10} can improve the mechanical properties of PHBV due to the increased X_c and decreased spherulitic size. With the help of BN, PHBV fibers with high strength and X_c have been successfully prepared.^{11,12} Therefore, the utilization of NA would be an economical and cost-effective approach to modify the physical performances of PHB bacterial copolyesters.

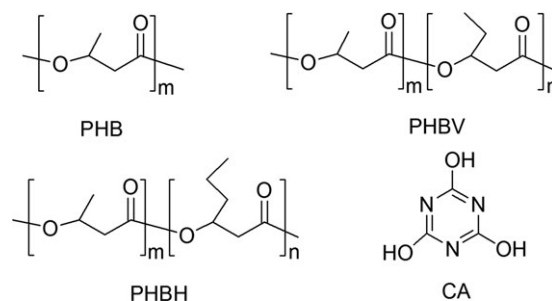
Up to now, some chemicals have been introduced as NAs for the bacterial PHB and its copolyesters, such as talc,¹³ α -cyclodextrin,¹⁴ PHB/ α -cyclodextrin inclusion complex,¹⁵ poly(vinyl alcohol) particle,¹⁶ terbium oxide,¹⁷ saccharin,¹⁸ metal phosphonate,¹⁹ thymine,²⁰ uracil,²¹ orotic acid (OA).^{22,23} For example, Qian et al. have reported that thymine increases the overall crystallization rate of PHBV and demonstrates a similar nucleation efficiency as BN.²⁰ We have found that uracil and its derivative (i.e., orotic acid) increase the crystallization rate of PHBH with a HH unit content ranging from 0 to 18 mol % and reveal a better nucleation efficiency than BN, especially for PHBH with a high content of HH unit.^{21–23} Although some of NAs reported in literatures are efficient for PHB homopolymer, their nucleation efficiency on melt crystallization of PHB copolyesters such as PHBV and PHBH are relatively limited. Therefore, it is significant to develop the high efficient NAs and investigate their influences on the crystallization kinetics of PHB bacterial copolyesters.

A recent study has reported that cyanuric acid (CA), a nontoxic compound,²⁴ can accelerate the crystallization of PHB and its copolyesters.²⁵ However, the effects of CA on crystallization kinetics of PHB and its copolyesters have not been explored. In this work, we introduced CA as a NA for PHB copolyesters, i.e., PHBV and PHBH. The effects of CA on crystallization kinetics of PHBV and PHBH were compared with other NAs of PHAs. CA was found to have the best nucleation efficiency to the melt crystallization of PHBV and PHBH. The effects of CA on nonisothermal/isothermal crystallization, melting behavior, and spherulitic morphology of PHBV and PHBH were investigated, and the isothermal crystallization kinetics was quantitatively analyzed.

EXPERIMENTAL

Materials

PHB ($M_w = 6.5 \times 10^5$ g/mol, $M_w/M_n = 2.24$) was provided by PHB Industrial S/A (Brazil). PHBV ($M_w = 3.6 \times 10^5$ g/mol, $M_w/M_n = 2.13$) with 12 mol % HV and PHBH ($M_w = 2.1 \times 10^5$ g/mol, $M_w/M_n = 2.29$) with 10 mol % HH were kindly supplied by Metabolix and Kaneka (Osaka, Japan), respectively. CA, uracil, and OA were purchased from Sinopharm Chemical Reagent (Shanghai, China) and milled before use. BN was purchased from Nacalai Tesque (Kyoto, Japan). Chemical structures of PHB, PHBV, PHBH, and CA are illustrated in Scheme 1.



Scheme 1. Chemical structure of PHB, PHBV, PHBH, and CA.

Sample Preparation

PHB, PHBV, or PHBH was mixed with NA through solution blending to avoid the possible thermal degradation of polymer in melt-mixing. Preweighted NA was added into chloroform and ultrasonically treated for 20 min. All NAs used here are insoluble in chloroform and dispersed as particles with the sizes less than 20 μm . PHB or its copolyester was then added into the suspension and stirred rigorously. The mixture was cast onto a polytetrafluoroethylene dish and the solvent was allowed to evaporate under ambient conditions. The film obtained was dried at 60°C under vacuum for 24 h. The concentration of NA in polymer was kept to be 1 wt %.

Measurements: Differential Scanning Calorimetry (DSC)

Nonisothermal and isothermal crystallizations of PHB and its copolyesters were measured by a TA Q200 differential scanning calorimeter (TA Instruments, USA) under a nitrogen atmosphere. The sample (6–8 mg) was encapsulated in an aluminum pan and first melted at 190°C for 2 min to erase the thermal history. In the nonisothermal crystallization, the sample was cooled to -50°C from the melt at a cooling rate of 10°C/min. In the isothermal crystallization, the sample was cooled to the desired crystallization temperature ($T_c = 40$ – 100°C) with a controlled rate of 100°C/min. There was no overshoot of either program or sample temperature in the fast cooling process. After the nonisothermal or isothermal crystallization, the sample was heated to 190°C at a rate of 10°C/min to detect its melting behavior.

Polarized Optical Microscopy

Spherulitic morphology was examined on a polarized optical microscopy (Eclipse E600 POL, Nikon, Tokyo, Japan). The sample was sandwiched by two glass slides and melted at 190°C for 2 min in a Linkam THMS600 hot stage (Linkam Scientific Instrument, Surrey, UK). It was then quickly cooled to the desired temperature by liquid nitrogen for isothermal crystallization. Spherulitic morphology was recorded after the crystallization completed. To measure the spherulitic growth rate (G), the sizes of growing spherulites were monitored at an appropriate time interval before spherulites impinged. G was evaluated from the slope of spherulitic radius (R) vs. growth time (t), that is, $G = dR/dt$.

RESULTS AND DISCUSSION

Nonisothermal Crystallization Kinetics

Effects of CA on the nonisothermal melt crystallization of PHB, PHBV, and PHBH were studied via DSC. Figure 1 shows DSC

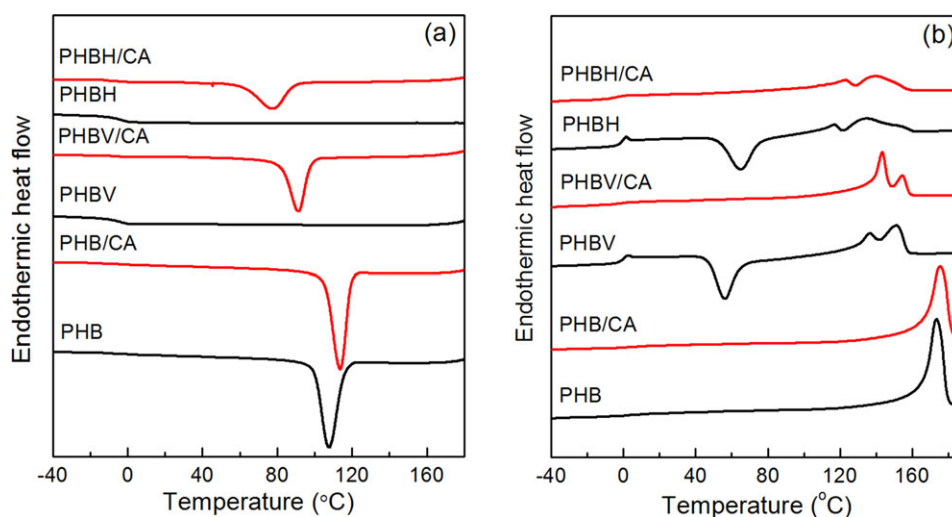


Figure 1. DSC curves recorded in (a) nonisothermal melt crystallization and (b) subsequent heating scan for neat PHB, PHBV, PHBH, and those containing 1% CA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thermograms of the nonisothermal melt crystallization and subsequent heating scans for neat polymers and those containing 1% CA. On basis of the DSC curves, the thermal parameters including melt-crystallization temperature (T_{mc}), enthalpy (ΔH_{mc}) during cooling, cold-crystallization temperature (T_{cc}), enthalpy (ΔH_{cc}) during following heating, melting temperature (T_m), melting enthalpy (ΔH_m), and X_c were evaluated. These thermal parameters are tabulated in Table I. Enthalpies were normalized by the weight of polymer matrix. X_c was estimated by comparing ΔH_m with the value of an infinitely large crystal (ΔH_m^0), taken as $\Delta H_m^0 = 146 \text{ J/g}^{26}$ ($X_c = \Delta H_m / \Delta H_m^0 \times 100\%$).

Neat PHB can complete crystallization in cooling scan, without showing the cold crystallization peak in subsequent heating scan. Because the minor comonomer units of HH and HV retard the crystallization of HB units, crystallizations of neat PHBV and PHBH become very slow and no crystallization peak is shown in a cooling scan at $10^\circ\text{C}/\text{min}$ [Figure 1(a)]. In the subsequent heating scan, a cold crystallization peak appears in the temperature range $40\text{--}80^\circ\text{C}$ for neat PHBV and PHBH

[Figure 1(b)]. Due to the introduction of minor comonomer unit, PHBV and PHBH show lower X_c values than neat PHB (Table I). Generally, crystallization rate and X_c of bacterial copolyesters of PHB decrease with increasing the content of minor comonomer unit.^{3,21} As shown in Table I, PHBV with 12 mol % HV content has a smaller T_{cc} and higher X_c than PHBH with 10 mol % HH unit. This indicates the faster crystallization and better crystallizability of PHBV than PHBH, even though the former has a higher content of minor comonomer unit. The better crystallizability of PHBV than PHBH is attributed to the smaller volume/size of BV unit and the inclusion of minor BV unit into PHB crystalline phase, i.e., isomorphous crystallization of PHBV.^{27,28}

Generally, a high T_{mc} is taken as an indicator of fast crystallization in nonisothermal melt crystallization. Interestingly, CA accelerates the crystallization of PHB, PHBV, and PHBH dramatically. T_{mc} value of neat PHB is increased by $\sim 6^\circ\text{C}$ with an incorporation of 1% CA. Acceleration effect is more predominant for the bacterial copolyesters of PHB that has slow crystallization rate. After an addition of 1% CA, PHBV and

Table I. Thermal Parameters of Neat and NA-Containing PHB, PHBV, and PHBH Attained in Nonisothermal Melt Crystallization and Subsequent Heating Scan

Sample	T_{mc} ($^\circ\text{C}$)	ΔH_{mc} (J g^{-1})	T_{cc} ($^\circ\text{C}$)	ΔH_{cc} (J g^{-1})	T_m ($^\circ\text{C}$)	ΔH_m (J g^{-1})	X_c (%)
PHB	107.7	74.6	NP	0	173.4	86.5	59.2
PHB/CA	113.6	76.1	NP	0	175.4	87.3	59.8
PHBH	NP ^a	0	64.8	34.8	111.6	33.8	23.2
PHBH/CA	77.0	37.8	NP	0	123.4, 140.1	40.8	27.9
PHBV	NP	0	48.4	50.1	136.6, 151.2	52.3	35.8
PHBV/CA	91.4	50.4	NP	0	143.6, 154.4	56.5	38.7
PHBV/BN	84.2	49.5	NP	0	141.7, 153.4	54.6	37.4
PHBV/uracil	82.5	48.5	NP	0	141.9, 153.5	53.9	36.9
PHBV/OA	86.4	49.4	NP	0	143.1, 154.1	55.0	37.7

^aNP: no peak is shown.

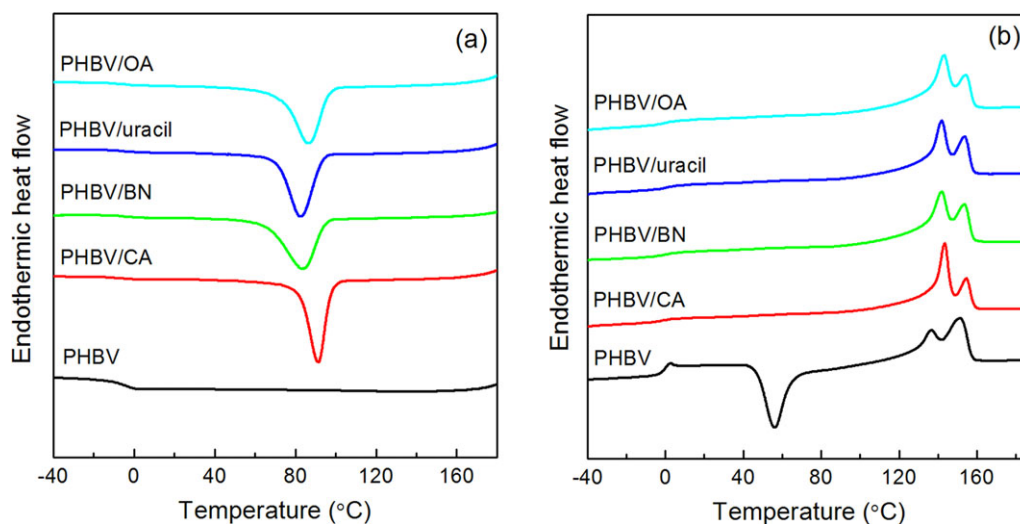


Figure 2. Comparison of different NAs on nonisothermal melt crystallization and melting behavior of PHBV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PHBH can completely crystallize in cooling scan, with an appearance of sharp exotherm. This indicates that CA is an efficient NA for the bacterial copolyesters of PHB.

Effects of CA on the crystallization kinetics of PHB copolyesters were compared with those of BN,^{20,21} uracil,²¹ and OA,^{22,23} all of which were good NAs of PHB and its copolyesters. PHBV was taken as an example to compare the nucleation efficiency of different NAs. DSC curves recorded in nonisothermal melt crystallization and melting process of PHBV containing different NAs are compared in Figure 2. The corresponding thermal parameters derived from these DSC results are summarized in Table I. As shown in Figure 2 and Table I, T_{mc} value of PHBV containing 1% CA is 5–10°C higher than that containing the equal amount of BN, uracil, or OA. Similar results are recognized for PHBH through comparing with our previous results of BN, uracil, or OA-nucleated PHBHs.^{21–23} As shown in panel b of Figures 1 and 2, NA does not influence the melting behavior of PHB, PHBV, and PHBH. In contrast to the single melting peak of PHB, PHBV and PHBH show two melting peaks upon heating, ascribing to the melt-recrystallization mechanism.²⁹

Isothermal Crystallization

Isothermal crystallization kinetics of neat and CA-containing PHBV and PHBH were investigated by means of DSC. Parts a and b of Figure 3 show the DSC curves of isothermal melt crystallization at $T_c = 40$ – 100°C for the neat and CA-containing PHBVs, respectively. Parts c and d of Figure 3 depict the corresponding DSC curves of PHBH. As shown in this figure, the crystallization peaks of neat PHBV and PHBH are broad. They become sharp and shift to the short time side with an incorporation of CA, indicating the increase of crystallization rate. As seen in part b and d of Figure 3, CA-containing PHBV and PHBH show the incomplete DSC traces at $T_c < 80^\circ\text{C}$, indicating the occurrence of crystallization in cooling process. This is because of the fast crystallization of CA-containing polymers and the too low T_c .³⁰

To evaluate the isothermal crystallization kinetics, the heat flow in isothermal DSC curve was integrated to attain the relative degree of crystallinity (X_t) at different crystallization time (t). X_t was calculated from the integrated area of DSC curve from $t = 0$ to $t = t$ divided by the integrated area of whole heat flow curve. A horizontal line from a point after the crystallization exotherm was used as the baseline for integration. Half time of crystallization ($t_{1/2}$) was evaluated from the time with $X_t = 50\%$. Figure 4 shows the typical $X_t \sim t$ plots of neat polymers crystallized at 80°C and CA-containing polymers crystallized at 100°C . Isothermal crystallization kinetics were analyzed by Avrami equation.^{31,32} Considering the presence of crystallization induction time t_0 , Avrami equation can be written as³⁰

$$1 - X_{t-t_0} = \exp[-k(t - t_0)^n] \quad (1)$$

where n is the Avrami index and k is the overall rate constant. Linear form of eq. (1) can be written as

$$\log[-\ln(1 - X_{t-t_0})] = \log k + n \log(t - t_0) \quad (2)$$

k and n can be estimated from the linear fitting of $\log[-\ln(1 - X_{t-t_0})]$ vs. $\log(t - t_0)$. Because the incomplete DSC traces usually induce severe errors in Avrami analysis,³⁰ the kinetic modeling of CA-containing polymers crystallized at high temperature (100°C) and neat polymers was only performed. To ensure the accuracy of Avrami analysis, the data in a limited conversion range of 3–30% was employed for linear fitting.³⁰ Figure 5 shows the typical Avrami plots of neat and CA-containing polymers. Excellent fits were attained with the correlation coefficients above 0.999.

Kinetic parameters $t_{1/2}$, n , and k of neat and CA-containing PHBV and PHBH are tabulated in Table II. Predicted data by Avrami equation are compared with the experimental values in Figure 4. As seen in this figure, predicted values of neat polymers agree well with the experimental data within whole conversion

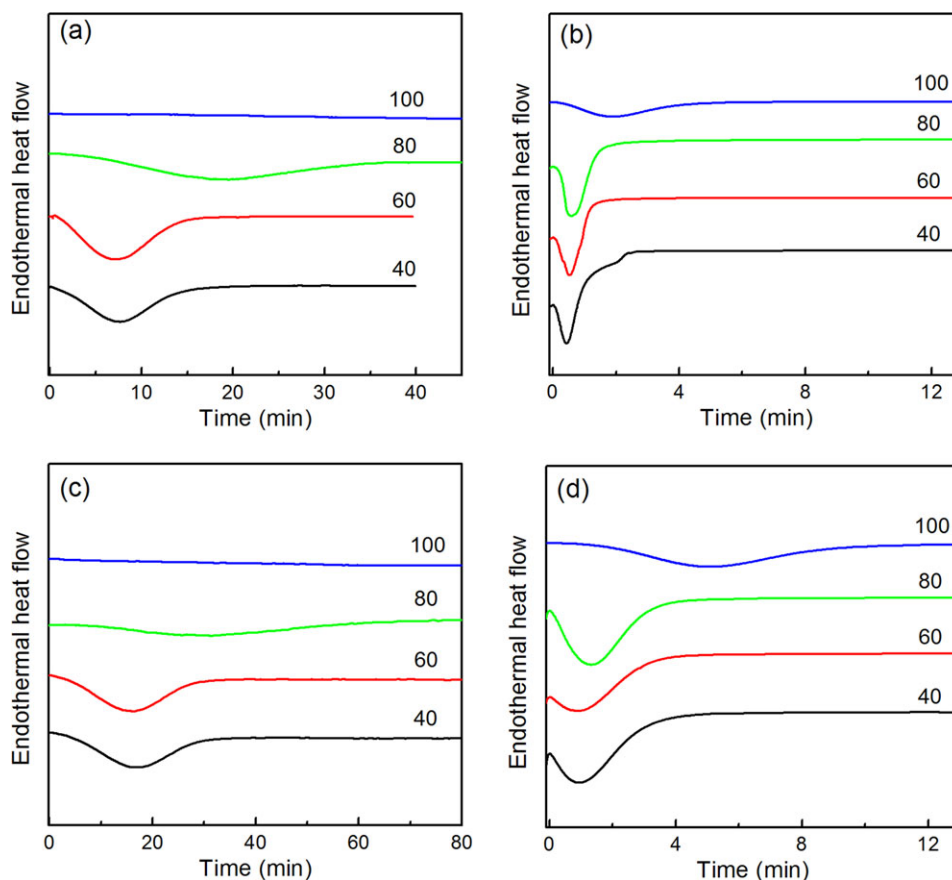


Figure 3. DSC curves recorded in isothermal melt crystallization of neat, CA-containing PHBV and PHBH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

range. However, predicted data of CA-containing polymers deviate from the experimental values at high conversion. This may be ascribed to the impingement of spherulites and secondary crystal-

lization in the latter stage, which produces nonlinearity in Avrami plot.³⁰ n is between 2 and 3 and insensitive to CA. It should be noted that the n values evaluated from Avrami analysis are lower

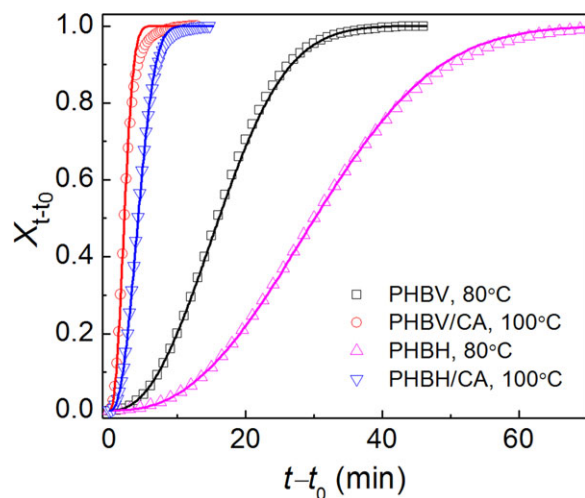


Figure 4. Variation of relative degree of crystallinity with crystallization time for neat, CA-containing PHBV and PHBH. Isothermal crystallization temperatures are 80 and 100°C for neat and CA-containing polymers, respectively. Solid lines represent the predicted data from Avrami equation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

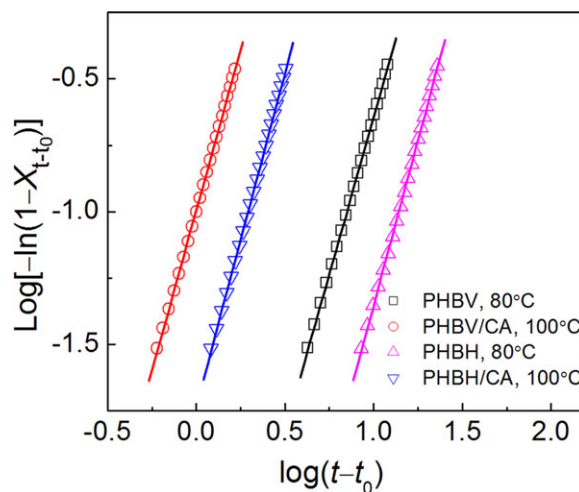


Figure 5. Avrami plots of neat and CA-containing PHBV and PHBH within conversion range of 3–30%. Isothermal crystallization temperatures are 80 and 100°C for neat and CA-containing polymers, respectively. Solid lines represent the linear fitting. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Kinetic Parameters of Neat, CA-Containing PHBV, and PHBH Crystallized at 80 and 100°C^a

sample	$T_c = 80^\circ\text{C}$			$T_c = 100^\circ\text{C}$			N (/mm ³)
	$t_{1/2}$ (min)	n	k (min ⁻ⁿ)	$t_{1/2}$ (min)	n	k (min ⁻ⁿ)	
PHBV	19.6	2.36	9.88×10^{-4}	83.2	2.23	4.05×10^{-5}	63
PHBV/CA	0.72	-	-	2.22	2.42	0.10	1.6×10^5
PHBH	38.0	2.49	1.43×10^{-4}	95.7	2.41	1.17×10^{-5}	37
PHBH/CA	1.50	-	-	5.42	2.52	0.018	5.7×10^4

^aAvrami analysis was not performed for CA-containing polymers crystallized at 80°C due to their incomplete DSC traces.

than the predicted values of polymers crystallized in the 3D spherulitic morphology, that is, 4 for neat polymer nucleated sporadically and 3 for NA-modified polymers nucleated instantaneously.^{30,33} As reported in the literatures, some neat and NA-containing polymers crystallized in spherulitic morphology also show the n values between 2 and 3, for example the neat hydrogenated polybutadiene,³⁰ neat, NA-containing poly(lactic acid),^{34,35} and poly(butylene succinate).^{36,37} Neat polymer usually contains some impurities that can induce the heterogeneous nucleation to some extent, which can surpass the ideal sporadic and homogenous nucleation in crystallization. This may induce the decrease of n values of neat polymer.

As shown in Table II, $t_{1/2}$ values of PHBV and PHBH decrease dramatically with an incorporation of CA. At $T_c = 80^\circ\text{C}$, $t_{1/2}$ values decrease to 0.72 and 1.50 min from 19.6 and 38.0 min of neat PHBV and PHBH, respectively, with an addition of 1% CA. This implies the high nucleation efficiency of CA to PHBV and PHBH, consistent with the DSC results of nonisothermal melt crystallization.

Melting behavior of PHBV and PHBH was studied after the isothermal melt crystallization. Panels a and b of Figure 6 show the DSC heating curves of neat and CA-containing PHBVs after isothermal melt crystallization at $T_c = 40$ – 100°C , respectively. Parts c and d of Figure 6 show the corresponding DSC curves

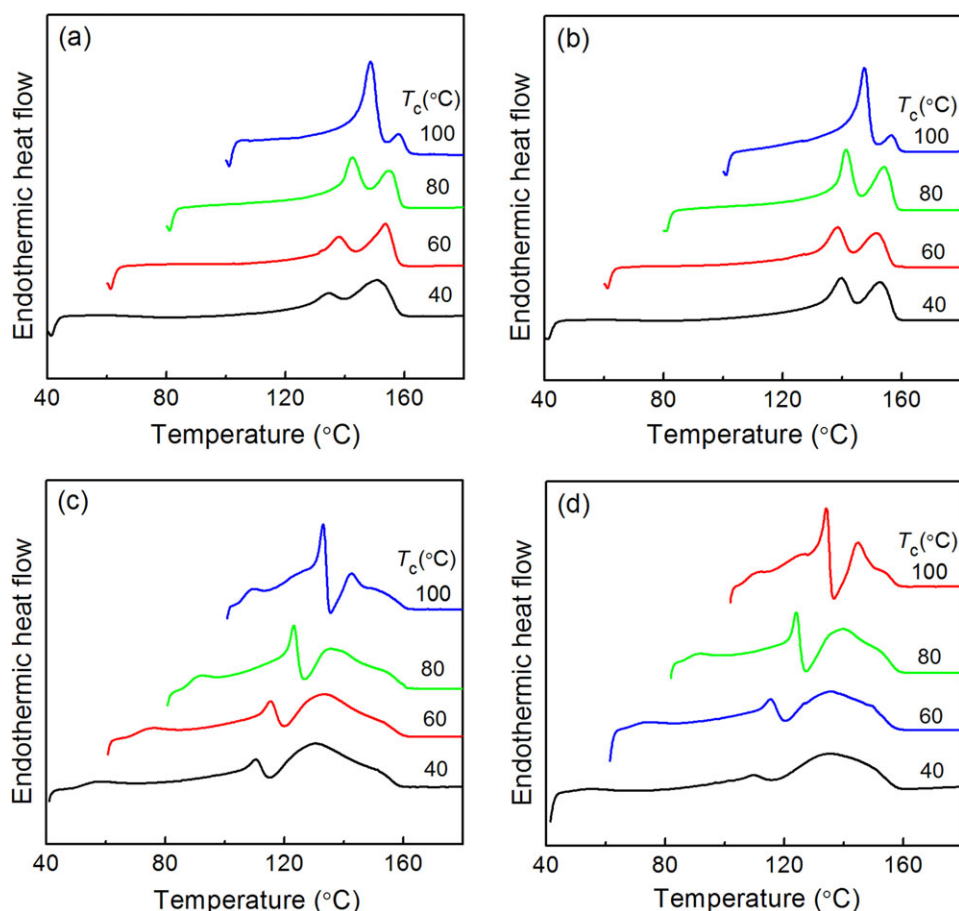


Figure 6. DSC heating curves of (a) neat PHBV, (b) CA-containing PHBV, (c) neat PHBH, and (d) CA-containing PHBH crystallized at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

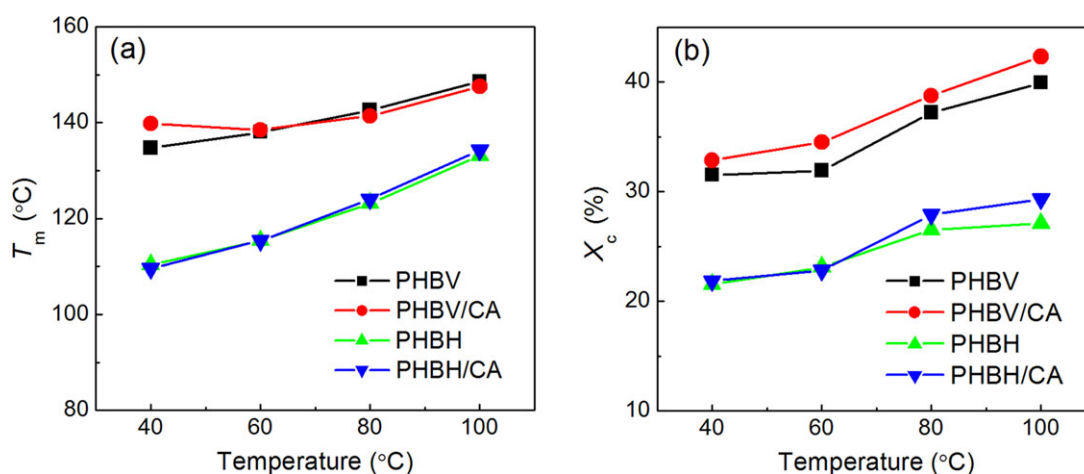


Figure 7. Dependences of (a) melting temperature and (b) degree of crystallinity on crystallization temperature for neat, CA-containing PHBV, and PHBH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of PHBH. As shown in this figure, CA has no discernible effect on melting behavior of PHBV and PHBH. Neat and CA-containing polymers melt-crystallized at the same T_c show the similar DSC melting curves. Melting behavior of PHBH is more complex than PHBV, indicating the larger effects of HH units on the crystallization of HB units than HV. Different from the DSC curves of PHBV, an annealing peak, usually ascribed to the secondary crystallization during long time annealing,^{38,39} is present at 10–20 $^{\circ}\text{C}$ above T_c in the DSC heating curves of PHBH. This suggests that secondary crystallization of PHBH is more distinct than that of PHBV, due to the larger retardant effects of minor HH unit on the crystallization of HB unit.

On basis of the DSC melting curves, T_m and X_c of neat and CA-containing PHBV and PHBH crystallized at different T_c were evaluated. T_m was taken as the temperature of peak located at lower temperature in melting region, which corresponded to the melt of crystals formed in isothermal crystallization. T_m and X_c are plotted

as a function of T_c in Figure 7. As seen in this figure, CA does not affect T_m and the CA-containing PHBV and PHBH have similar T_m as neat polymers. X_c values of PHBV and PHBH increase slightly with an addition of CA. Because more perfect crystals with larger lamellar thickness are formed at high T_c , T_m and X_c of both neat and CA-containing PHBV and PHBH increase with T_c .

Spherulitic Morphology

Spherulitic morphology of neat and CA-containing PHBV and PHBH was investigated by POM. Figure 8 shows the photomicrographs of spherulites of neat and CA-containing PHBV and PHBH after isothermal melt crystallization at 60 and 80 $^{\circ}\text{C}$. Neat PHBV and PHBH show huge spherulites with a diameter of several micrometers, which are much larger than those of other aliphatic polyesters such as poly(lactic acid) and poly(butylene succinate). The difficulty of nucleation may account for the slow crystallization and large spherulites of PHB bacterial copolyesters. PHBV and PHBH containing 1% CA exhibit

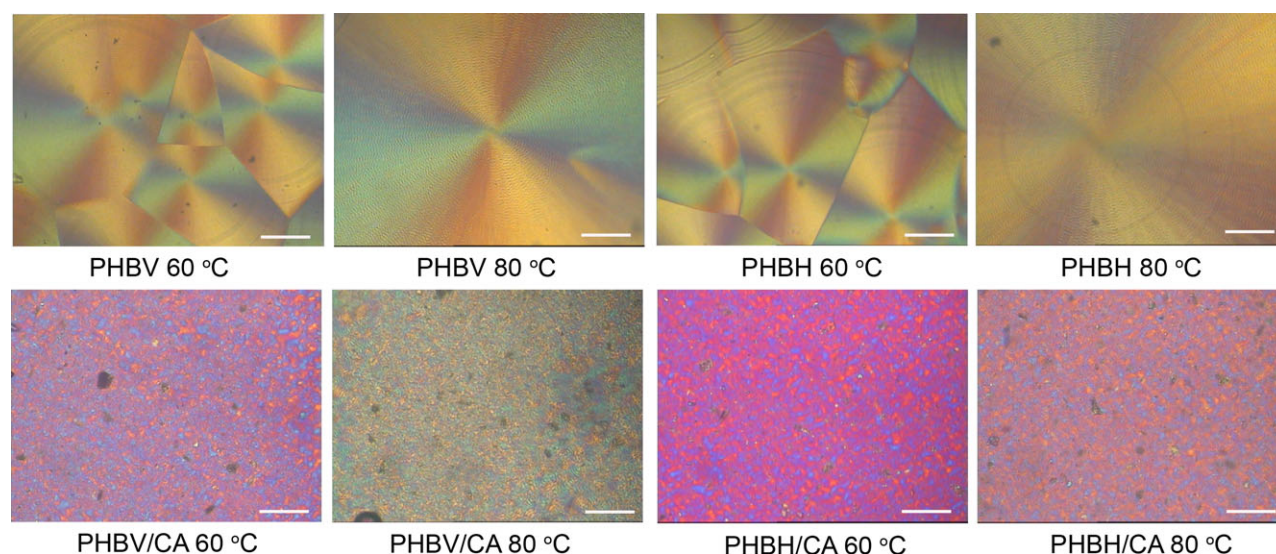


Figure 8. POM photographs of neat and CA-containing PHBV and PHBH crystallized at 60 and 80 $^{\circ}\text{C}$. The scale bar represents 50 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

much smaller size and larger density of spherulites than their neat counterparts. Because of the difficulty of nucleation at high temperature, spherulitic sizes of neat PHBV and PHBH increase and their spherulitic densities decrease with increasing T_c . On the other hand, the crystalline structure of CA-containing PHBV and PHBH were examined via wide-angle X-ray diffraction (data not shown). It is found that CA does not affect crystalline structures of PHBV and PHBH. CA-containing PHBV and PHBH form the typical α -form PHB-type crystals in melt crystallization, analogous to neat polymer.

Effects of CA on nucleation densities of PHBV and PHBH were quantitatively analyzed. Nucleation density (N) in isothermal crystallization was estimated according to a model of three-dimensional spherulitic growth simultaneously initiated from the active nuclei ($n \approx 3$)⁴⁰

$$N = \frac{3k}{4\pi G^3} \quad (3)$$

where k is the Avrami rate constant; G is the linear radius growth rate of spherulite, which can be determined from POM measurements. G values of PHBV and PHBH melt-crystallizing at 100°C were measured to be 5.4 and 4.2 $\mu\text{m}/\text{min}$, respectively. NA does not change the spherulite growth rate of polymers because it only affects the primary nucleation but not secondary nucleation.¹⁴ N values of neat and CA-modified PHBV and PHBH crystallized at 100°C were estimated from eq. (3), as shown in Table II. It can be seen that N values of PHBV and PHBH increase by 3–4 orders of magnitude with a presence of CA, indicating the good nucleation effectiveness of CA. The unit of k is min^{-n} and n values of neat and CA-containing polymers are not the same. This may result in errors in the estimation of nucleation density from eq. (3).

CONCLUSIONS

Effects of CA on nonisothermal and isothermal melt crystallization of PHB, PHBV, and PHBH have been investigated. CA accelerates the melt crystallization of PHB bacterial copolyesters remarkably and its acceleration effect is more significant than the typical NAs of PHAs reported previously. With an incorporation of 1% CA, PHBV and PHBH finish crystallization upon cooling at 10°C/min. Isothermal crystallization kinetics was analyzed by Avrami model. Crystallization half-time of PHBV and PHBH decreases remarkably with an addition of CA. Spherulitic numbers of PHBV and PHBH increase and their spherulitic sizes decrease significantly with a presence of CA. Nucleation densities of PHBV and PHBH were evaluated. They increase by 3–4 orders of magnitude with an addition of 1% CA. NA reported in this work may widen the applications of bacterial PHAs in the commodity applications, especially in the cases where the physical properties such as high strength, modulus, and HDT are desired.

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