



# Significant accelerated crystallization of long chain branched poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with high nucleation temperature under fast cooling rate



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## ABSTRACT

The long chain branched poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (LCB-PHBV) with rapid crystallization rate and high nucleation temperature was fabricated by only adding small amounts of dicumyl peroxide (DCP). NMR and FTIR spectra confirmed that long chain branched structures of LCB-PHBV were formed in the melting reaction process. The results from non-isothermal crystallization indicated that crystallization rate and crystallinity of LCB-PHBV presented an obvious increase while half crystallization time decreased obviously. Interestingly, during melting crystallization, the crystallization rate of LCB-PHBV increased with the increase of cooling rate and curves of crystallization peaks shifted obviously to higher temperatures. Based on polarized optical microscopy observation, it was found that the nucleation abilities of LCB-PHBV under a higher temperature had been improved, whereas the diffusion of molecular chains inhibited the radial growth of spherulites. However, such contribution of nucleation promoting effect on crystallization of polymers was larger than dispersion inhibition effect of segments, resulting in an inducement and acceleration on crystallization process of LCB-PHBV.

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## 1. Introduction

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), as a kind of bio-based polyester synthesized completely by microbial fermentation, was expected to partially replace petroleum-based polymer materials as its good biodegradability and biocompatibility [1]. Also, PHBV with hemicrystalline structure which was similar to Polypropylene (PP) could be thermoplastically processed. However, during melting processing, PHBV fibers were prone to surface adhesion under the influences of small nucleation density, slow growth rate of spherulites and large size of spherulites which caused subsequent processing difficulties. Hence, methods to improve the crystallization performances of PHBV became key points to breakthrough practical applications of PHBV. Up to now, effective methods, such as blending modification [2,3] and chemical modification technology [4], have been developed in recent years to regulate and investigate the crystallization performances of PHBV. Normally, the crystallization kinetics and crystallinity of

polymer composites can be enhanced by simply introducing inorganic particles which play the role of nucleating agents [5], then tungsten disulfide nanotubes (INT-WS<sub>2</sub>) [6] and carbon nanotubes (CNTs) [7] were introduced into PHBV respectively and all found that the heterogeneous nucleation density and the initial crystallization temperature of PHBV increased obviously while their scope for applications has been limited under the influences of sizes and colors of INT-WS<sub>2</sub> and CNTs. On the other hand, the crystallization behaviors of polymer can be modified directly and effectively via chemical structure design, and the study of polymer crystallization under structural confinement is of great importance for understanding and improving the structure and properties of nanomaterials or chemically modified polymers [8]. Dong L.S. et al. prepared P3HB-co-4HB branched/crosslinked copolymers [9] and PLA/P3HB-co-4HB composites with high compatibilities [10] where dicumyl peroxide (DCP) acts as an initiator and triallyl isocyanurate (TAIC) acts as crosslinking agent. It was found from research that molecular chain branching could enhance the cold crystallization properties of copolymer and the crystal defects caused by crosslinking decreased the melt temperature.

Therefore, the feasibility to adapt branched structure in improving the crystallization performance of PHBV during melt

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crystallization required to be considered. Several researchers have reported that the long chain branched structure could not only improve the lower polymer melt strength but could also enhance the crystallization rate of polymers [11,12]. Zheng A.N. et al. grafted chain extender containing amine oligomers (PHGH) and glycidyl methacrylate (GMA) on the main-chain of polypropylene molecular and found that the melt crystallization temperature of long chain branched polypropylene (LCBPP) increased with the increase of branching degree [13]. Compared with linear PP, the branched chain of LCBPP played a role of heterogeneous nucleation, resulting in an obvious decrease in the spherulite size and the crystallization time with the increase of branched chain contents [14]. Therefore, it was speculated that the long chain branched structure could also adjust the crystallization performances of bio-polyester PHBV.

Herein, long chain branched PHBV (LCB-PHBV) was prepared via melting reaction where dicumyl peroxide (DCP) acted as an initiator, crosslinking agent and second monomer were not included.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and FTIR spectra were adapted to characterize the chemical structure of LCB-PHBV. The crystallization performances of LCB-PHBV under different cooling rates were investigated by non-isothermal DSC and then the crystallization kinetics of LCB-PHBV were analyzed by Mo's equation and eventually spherulitic morphology of LCB-PHBV during isothermal crystallization process was observed via polarized optical microscopy.

## 2. Experimental section

### 2.1. Materials

PHBV with 1.05 mol-% 3-hydroxyvalerate (3HV) ( $M_n = 1.16 \times 10^4 \text{ g mol}^{-1}$ ,  $PDI = 2.30$ ) was supplied by Tianan Biologic Material Co., Ltd. (Ningbo, China). Dicumyl peroxide (DCP, 98%) was purchased from Sigma-Aldrich Company. Chloroform, acetone and ethyl alcohol, were purchased from Sinopharm Chemical Reagent Co., Ltd.

### 2.2. Preparation of long chain branched PHBV (LCB-PHBV)

In order not to destroy the characteristics of originally bio-based PHBV materials, LCB-PHBV was prepared where low molecular weight PHBV (LMW-PHBV) containing free radicals was produced as side chain and no other monomers were introduced. The specific preparation process was described as follows: PHBV powders were dried in a vacuum environment of  $80^\circ\text{C}$  for 24 h before usage. The measured PHBV was added into Haake torque rheometer (Thermo-Hakker Company, EUROLAB 16) with a reaction temperature of  $170^\circ\text{C}$  and then quantitative DCP (0 wt%, 0.05 wt%, 0.1 wt%, 0.2 wt%, 0.5 wt%, 1 wt%, 2 wt%, 4 wt%) was added into this premixed stage for 3 min under a rotor speed of 60 rpm following with an adjustment to 90 rpm for 10 min.

After the full dissolution of prepared samples in chloroform at  $80^\circ\text{C}$ , the filtration through a  $0.22 \mu\text{m}$  tetrafluoroethylene membrane and the precipitation with addition of filtrate into cold ether, LCB-PHBV could be obtained. Different LCB-PHBV samples could be expressed as PHBV- $x$ , where  $x$  was the mass percentage of DCP usages.

### 2.3. Characterizations

The chemical structure of LCB-PHBV was determined by Swiss Bruker Avance 400 NMR spectrometer and US Thermo Nicolet 8700 Fourier Transform Infrared spectroscopy (FTIR). The structural characterization methods of LCB-PHBV samples were supplied in the [Supplementary information](#).

The non-isothermal crystallization kinetics of LCB-PHBV

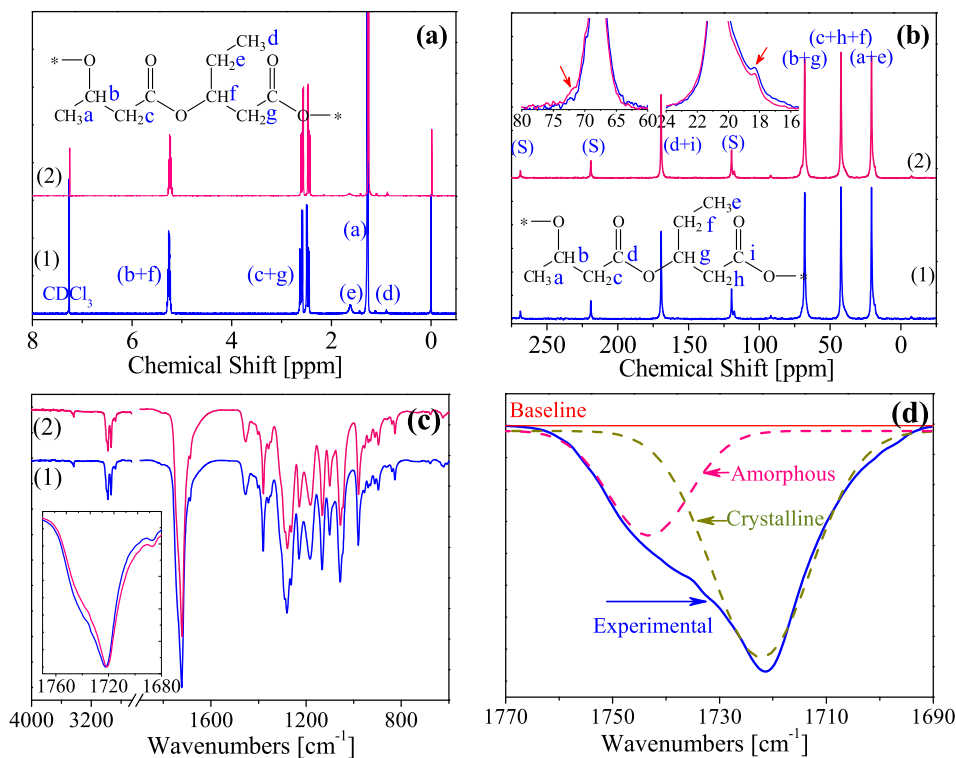
samples were measured by Q20 differential scanning calorimeter (DSC, TA, US). Firstly, about 10 mg of samples were heated from room temperature to  $195^\circ\text{C}$  in a nitrogen atmosphere at a rate of  $40^\circ\text{C}/\text{min}$ . After isothermality for 2 min to eliminate the thermal history, cooling rates of  $20^\circ\text{C}/\text{min}$ ,  $15^\circ\text{C}/\text{min}$ ,  $10^\circ\text{C}/\text{min}$ ,  $5^\circ\text{C}/\text{min}$  were successively adapted to reduce temperature to  $0^\circ\text{C}$ . Then non-isothermal crystallization kinetics of PHBV before and after modification were calculated according to changes of heat flux on time during cooling process. In order to describe influences of long chain branched structure on crystal growth of LCB-PHBV more intuitively, Leica DM2500P polarized optical microscopy (POM) equipped with LINKAM LTSE350 heat stage was adapted to observe changes in crystal morphology of LCB-PHBV during its isothermal crystallization process. Firstly, samples were heated to  $195^\circ\text{C}$  at a rate of  $30^\circ\text{C}/\text{min}$  and maintained isothermal for 2 min, and then were cooled to isothermal crystallization temperature at a rate of  $30^\circ\text{C}/\text{min}$  to observe and record the change process of crystal morphology.

## 3. Results and discussion

### 3.1. Chemical structure of long chain branched PHBV (LCB-PHBV)

During preparation of long chain branched polymers, poly-functional monomers, such as pentaerythritol (PETA) [15], furfuryl sulfide (FS) [16], triglycidyl isocyanurate (TGIC) [17] and triallyl isocyanurate (TAIC) [10], were usually used with initiator to obtain a higher branching inducement efficiency. However, this method could also cause partial crosslinking in molecular chains and at the same time gel phenomenon was formed which would therefore influence the melt flow and the crystallization behavior of polymer melt. In order not to change the specific and excellent characteristics of PHBV biomaterials, it was concluded from the experiments that the molecular branching structure of PHBV could be effectively achieved by only using DCP as an initiator. Even so the polymer gel was also induced by excess initiator contents. As shown in [Fig. S1](#), when DCP content was less than 0.5 wt%, the obtained gel content was less than 2 wt%, indicating that long chain branched structure was the main structure from melting reaction. When DCP content was higher than 0.5 wt%, the obtained gel content increased rapidly with the increase of DCP content and the gel content reached to 30 wt% when DCP content was 4 wt%. It was then concluded that the usage content of initiator DCP determined the branched structure and branching degree of long chain branched PHBV. The excessive content of initiator DCP would cause the crosslinking structure among PHBV molecular chains and form the gel phenomenon which influenced characteristics of melt processed from polymer.

To characterize chemical structure of LCB-PHBV, NMR and FTIR spectra were shown in [Fig. 1](#). It could be concluded from [Fig. 1\(a\)](#) that the chemical shift peaks of methylene group in the main-chain of PHBV were at  $\delta = 2.48 \text{ ppm}$  and  $\delta = 2.60 \text{ ppm}$ , the shift peak of tertiary carbon atom was at  $\delta = 5.25 \text{ ppm}$ , the shift peak of methyl hydrogen atom at the end of molecular chain appeared at  $\delta = 1.27 \text{ ppm}$ . Compared with NMR spectra, no new chemical shift peaks were found in generated LCB-PHBV. After uniformizing the shift peaks of methylene groups in the main-chain of PHBV and LCB-PHBV and defining the integral area as 1, it could be obtained from the integral vibration peaks of tertiary hydrogen atoms that its area was decreased from 0.5 of PHBV to 0.49 of LCB-PHBV and its intensity of the vibrational peaks was relatively weakened, indicating that the number of tertiary hydrogen atoms was reduced. In addition, the carbon atom was the basic skeleton of polymer which could better reflect the structural information of molecular chain. NMR spectra of materials before and after branched modification



**Fig. 1.** (a) <sup>1</sup>H NMR spectra, (b) Solid-state <sup>13</sup>C NMR spectra, (c) FTIR spectra of (1) PHBV and (2) PHBV-0.5 (S represents a side band), (d) experimental and fitted spectra for the PHBV-0.5 in the carbonyl-vibration region.

were presented in Fig. 1(b). According to <sup>13</sup>C NMR spectra, it could be found that the chemical shifts of primary carbon atoms, methylene secondary carbon atoms and tertiary carbon atoms in molecular chains were at  $\delta = 20.8$  ppm,  $\delta = 42.3$  ppm and  $\delta = 67.9$  ppm respectively, and the shift peak of carbonyl carbon atoms was appeared at  $\delta = 169.54$  ppm. In comparison with shift peaks of carbon atoms between PHBV and PHBV-0.5, there was no obvious change in the shift peak while a minor shoulder peak was appeared around 72.5 ppm and the strength of shoulder peaks at low frequency of methyl and methylene carbon atoms that were respectively around  $\delta = 39.0$  ppm and  $\delta = 18.3$  ppm was weakened to some certain degree. This was because that the shift peak appeared at 72.5 ppm was the vibration of quaternary carbon atom formed via long chain branched reaction [18], while peaks at  $\delta = 39.0$  ppm and  $\delta = 18.3$  ppm were amorphous vibration peaks, and the crystallization of LCB-PHBV increased due to the long chain branched structure with modification, leading to a relative weakness in area of shift peak in amorphous region [19] which could also be verified in FTIR spectra of LCB-PHBV [20,21] as shown in Fig. 1(c,d). At the same time, the effect of long chain branched structure on the complex viscosity and storage modulus was studied, and the variation of crystallinity of LCB-PHBV could be checked by the results of rheological behavior (Fig. S2) and WXRd spectrum for PHBV and LCB-PHBV, respectively (Fig. S3 and Table S1). Therefore, all above results indicated that LCB-PHBV copolymer with branched structure could be successfully prepared with the formation of free radicals after terthydride was induced by DCP.

As was shown in Fig. 2, chemical mechanism for the preparation of LCB-PHBV was speculated on the basis of chemical structure information such as gel content curves, NMR spectra and FTIR spectra, etc. It was indicated from Fig. 2 that, firstly, free radicals were generated by DCP under the effect of heating and tertiary carbon atoms in main-chain of PHBV molecular were attacked,

forming a short and medium PHBV chain with active free radicals. Secondly, PHBV molecular chains containing free radicals were very unstable where  $\beta$  bond was prone to broken to form large amounts of PHBV with low molecular weights (LMW-PHBV). At the same time,  $\beta$ -elimination reaction was prone to take place for PHBV as inducement function with heating, accelerating the formation of LMW-PHBV molecular chains [22]. Finally, LCB-PHBV was prepared by coupling reaction between free radicals in LMW-PHBV molecular chains and PHBV main-chains. When usage of DCP was excessive or partially uniform, bonding reaction between branched molecular chains was caused and PHBV molecular chain with network structure was formed, resulting in a gel phenomenon. In this paper, the preparation of LCB-PHBV was realized with free radical-induced method, and temperature, rotor speed, reaction time, content of initiator DCP during processing were especially important as long chain branched structure parameters.

### 3.2. Non-isothermal crystallization kinetics of LCB-PHBV

The research on non-isothermal crystallization kinetics of polymers helped to establish the relationship between macroscopic crystallization parameters of polymers with time in the temperature field which could provide theoretical guidance for processing of polymer materials and provide reference for optimizing performances of products. The non-isothermal crystallization curves of PHBV raw materials and series of LCB-PHBV were shown in Fig. 3 and peak temperature of crystallization peak ( $T_p$ ), total crystallization time ( $t_s$ ), half crystallization time ( $t_{1/2}$ ), melt crystallization enthalpy ( $\Delta H_c$ ) of samples were given in Table 1. According to Fig. 3 and Table 1, with the increase of cooling rate, the crystallization enthalpy of neat PHBV decreased from 74 J/g at 5 °C/min to 53 J/g at 20 °C/min, and the crystallization peak shifted to a lower temperature that decreased from 98 °C to 81 °C, and the  $t_{1/2}$  decreased

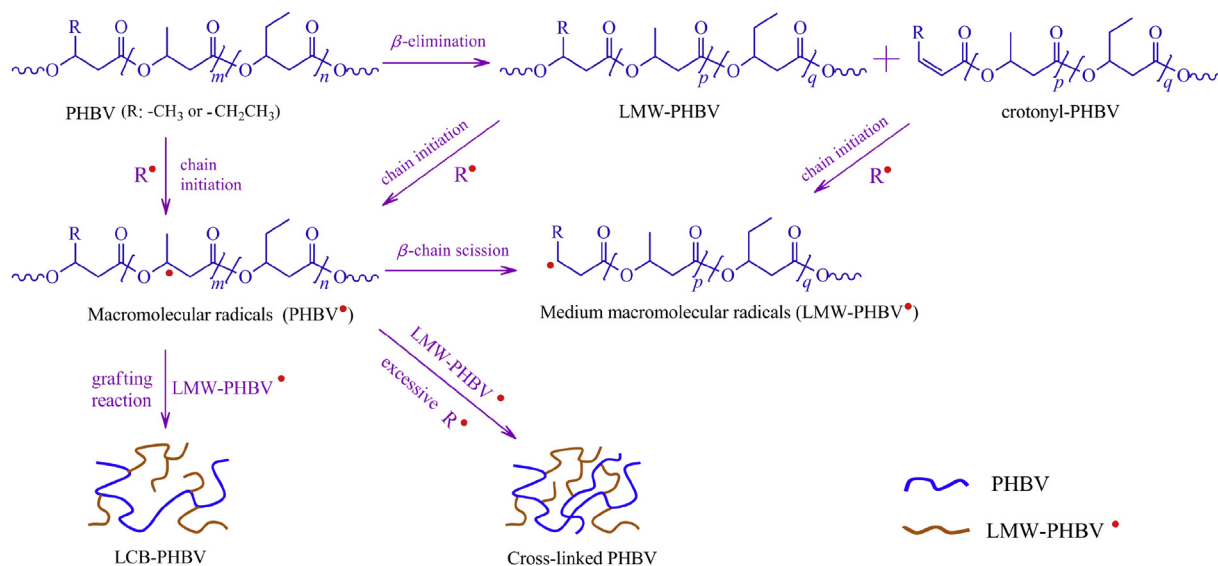


Fig. 2. Reaction schematic diagram of LCB-PHBV.

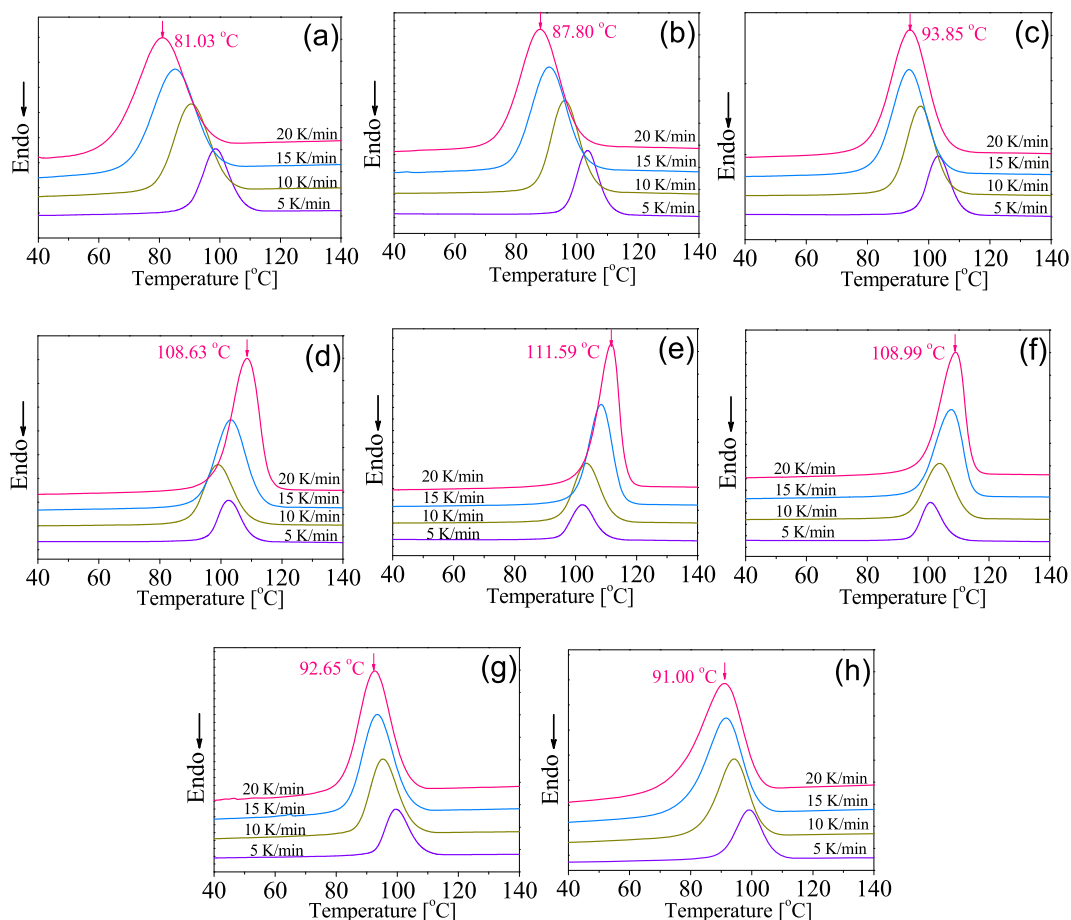


Fig. 3. DSC thermograms of nonisothermal cold crystallization for (a) PHBV, and series of LCB-PHBV copolymers: (b) PHBV-0.05, (c) PHBV-0.1, (d) PHBV-0.2, (e) PHBV-0.5, (f) PHBV-1.0, (g) PHBV-2.0, (h) PHBV-4.0.

from 169s to 69s. In general, the crystallization of polymers mainly consisted two stages of nucleation growth and crystal growth that mainly occurred between melting point and glass transition temperature. With the increase of cooling rate, the supercooling degree

increased and the crystallization rate presented an increase followed by a decrease. Although decreased temperature promoted the nucleation process, the activities of molecular chains decreased and molecular chains were diffused into crystal structures at a



**Table 1**  
Values of the  $t_s$ ,  $T_p$  and  $\Delta H_c$  at various cooling rates for PHBV and series of LCB-PHBV.

	$\varnothing$ [K/min]	$t_s$ [s]	$t_{1/2}$ [s]	$T_0$ [K]	$T_p$ [K]	$\Delta H_c$ [J/g]
Neat PHBV	-5	330.40	169.04	112.65	98.37	73.97
	-10	217.80	107.40	108.37	90.47	65.68
	-15	173.30	83.30	105.43	85.07	60.05
	-20	149.00	68.90	103.03	81.03	53.18
PHBV-0.05	-5	285.40	163.80	116.12	103.45	76.44
	-10	206.10	105.70	112.65	95.98	69.34
	-15	159.50	84.20	111.58	90.88	65.34
	-20	123.60	64.70	108.91	87.81	63.46
PHBV-0.10	-5	286.00	163.40	116.66	103.08	82.55
	-10	199.00	105.30	114.52	97.36	75.49
	-15	156.70	83.40	113.98	93.62	70.65
	-20	121.80	57.60	112.38	93.86	70.14
PHBV-0.20	-5	268.90	161.40	116.79	102.48	82.82
	-10	193.80	101.60	117.60	99.11	75.97
	-15	141.10	67.40	119.49	103.28	77.19
	-20	96.50	42.60	121.10	108.63	78.06
PHBV-0.50	-5	267.20	155.20	115.17	102.14	77.92
	-10	183.00	99.50	120.02	103.55	77.28
	-15	120.00	56.00	121.37	108.37	78.04
	-20	84.60	35.80	121.64	111.59	78.02
PHBV-1.00	-5	268.60	153.50	113.83	100.72	72.94
	-10	184.80	90.60	118.41	103.80	71.37
	-15	128.80	53.66	119.49	107.65	71.56
	-20	96.50	38.80	119.76	108.99	71.15
PHBV-2.00	-5	272.00	157.40	112.21	99.32	67.76
	-10	188.60	98.70	110.86	95.25	59.39
	-15	138.82	67.60	110.32	93.35	57.01
	-20	96.30	50.10	108.97	92.65	56.31
PHBV-4.00	-5	288.16	159.60	111.13	98.85	62.70
	-10	192.42	96.30	108.16	94.11	58.85
	-15	142.00	82.20	106.55	91.53	56.94
	-20	114.84	58.80	106.55	91.00	55.72

lower temperature, resulting in a whole decrease in crystallization rate where microscopic appearance was a shift of melt crystallization peak to a lower temperature. From Fig. 3, an interesting phenomenon was found that the  $t_{1/2}$  of LCB-PHBV decreased with the increase of cooling rate and the crystallization peak shifted to a higher temperature after modification. This phenomenon was significantly different from the tendency in LCBPP where melt crystallization curve shifted to a lower temperature with the increase of cooling rate [23]. Taking cooling rate of 20 °C/min as an example, the  $t_{1/2}$  of PHBV-0.5 with an addition of 0.5 wt% DCP decreased from 69s of neat PHBV to 36s. In addition, the  $T_p$  of LCB-PHBV with an addition of 0.05–1.0 wt% DCP shifted to a higher temperature with the increase of DCP content and the effect of cooling rate on crystallization peak was more obvious when 0.2–1.0 wt% DCP was adapted. It then could be concluded that the long chain branched structure effectively improve the crystallization abilities of LCB-PHBV. The main reasons for this could be summarized as on the one hand, the branch point induced the crystallization nucleation of polymers, and on the other hand the branch point increased the motion space of molecular chain segments [9]. PHBV-0.5 could be rapidly nucleated in a supercooling region that was 30 °C higher than that of neat PHBV under the cooling rate of 20 °C/min, and also diffusion migration and crystal growth of molecular chains were completed at a higher temperature range. This result was beneficial for inhibiting adhesion during the formation process of PHBV fibers.

Mo Z.S. et al. provided a useful method to analyze non-isothermal crystallization kinetics as followed [24]:

$$\lg \varnothing = \lg F(T) - a * \lg t \quad (1)$$

where  $\varnothing$  was cooling rate, the function  $F(T) = [K(T)/k]^{1/m}$  was

related to cooling rate which could be explained as the required cooling rate to achieve a certain degree of crystallization in unit time.  $F(T)$  was used as a parameter to characterize the crystallization speed of polymers. The parameter 'a' was 'n/m' where 'n' was apparent Avrami index and 'm' was Ozawa index in non-isothermal crystallization. Parameter  $t = |T_0 - T|/\varnothing$ , where  $T$  was the temperature at time  $t$  and  $T_0$  was the temperature at when crystallization started ( $t = 0$ ).

The relation curves between  $\lg \varnothing$  and  $\lg t$  of PHBV and LCB-PHBV copolymers calculated by Mo's equation were shown in Fig. 4. The parameters, such as  $F(T)$ ,  $\alpha$ , obtained from the curves were listed in Table S2. A well-fitted linear relationship in Fig. 4 showed that Mo's equation was suitable for the research on non-isothermal crystallization behaviors of LCB-PHBV. The value of  $F(T)$  reflected the required cooling rate for samples to achieve a certain degree of crystallinity per unit time. Based on  $F(T)$  values in Table S2, it could be indicated that the value of  $F(T)$  increased with the increase of crystallinity of samples, and the  $F(T)$  value of LCB-PHBV presented a decrease first and then followed by an increase with the increase of DCP content. It was therefore concluded that the activation energy for nucleation and the crystallization rate of LCB-PHBV molecular chains could be enhanced by controlling the branched points to a certain amount. And when the branched points were excessive or gel structure of molecular chain was formed, the activities of molecular chains would be limited and also the  $F(T)$  value was increased.

The nucleation rate of polymers and the growth abilities of crystals were closely related to the structures of molecular chains. In general, simple chemical structure, good symmetry and regularity, small steric hindrance, etc. were all conducive to the crystallization of polymers. In order to directly observe the changes in spherulite morphology and calculate radial growth rate in spherulite radius of PHBV and LCB-PHBV during isothermal crystallization process, POM equipped with hot stage was adapted to record experimental phenomenon. The isothermal crystallization morphology of PHBV and series of LCB-PHBV copolymers at 110 °C and their corresponding radial growth rates of spherulites were presented in Fig. 5. It could be observed that the spherulitic patterns of all samples exhibited typical black Maltese cross pattern of extinction. With the increase of DCP content, the nucleation number of LCB-PHBV increased rapidly which was probably due to the branched structure that promoted formation of molecular chains with partially sequential structures induced by thermal motion, resulting in the formation of thermodynamically stable nuclei with a certain volume which increased the nucleation number to a large degree. These findings from the experiment agreed well with the results obtained in DSC results.

Fig. 5 also presented the growth curves of spherulite radius with time during isothermal crystallization process, indicating a linear growth relationship that spherulite radius increased with the increase of time, while the growth rate  $G$  of spherulites was the fitting slope of the straight line. It was observed that  $G$  value of neat PHBV was 1.86  $\mu\text{m/s}$  and  $G$  value of LCB-PHBV decreased to 1.83  $\mu\text{m/s}$ , 1.72  $\mu\text{m/s}$ , 0.82  $\mu\text{m/s}$ , 0.80  $\mu\text{m/s}$  and 0.63  $\mu\text{m/s}$  gradually with the increase of DCP content. Therefore it was concluded from experimental results that the radial growth rate of linear PHBV spherulites at 110 °C during isothermal crystallization process was the highest and growth rate of spherulites decreased with the increase of branched degree. Liu et al. also found that growth rate of LCB-PLA spherulites was lower than that of linear PLA in studying isothermal crystallization process of LCB-PLA [25]. To conclude, long chain branched structure enhanced the nucleation abilities of crystal nucleus, while decreased the crystal growth rate due to the diffusion limitation of molecular chain segments. In combination with non-isothermal crystallization data in Fig. 3, it was indicated

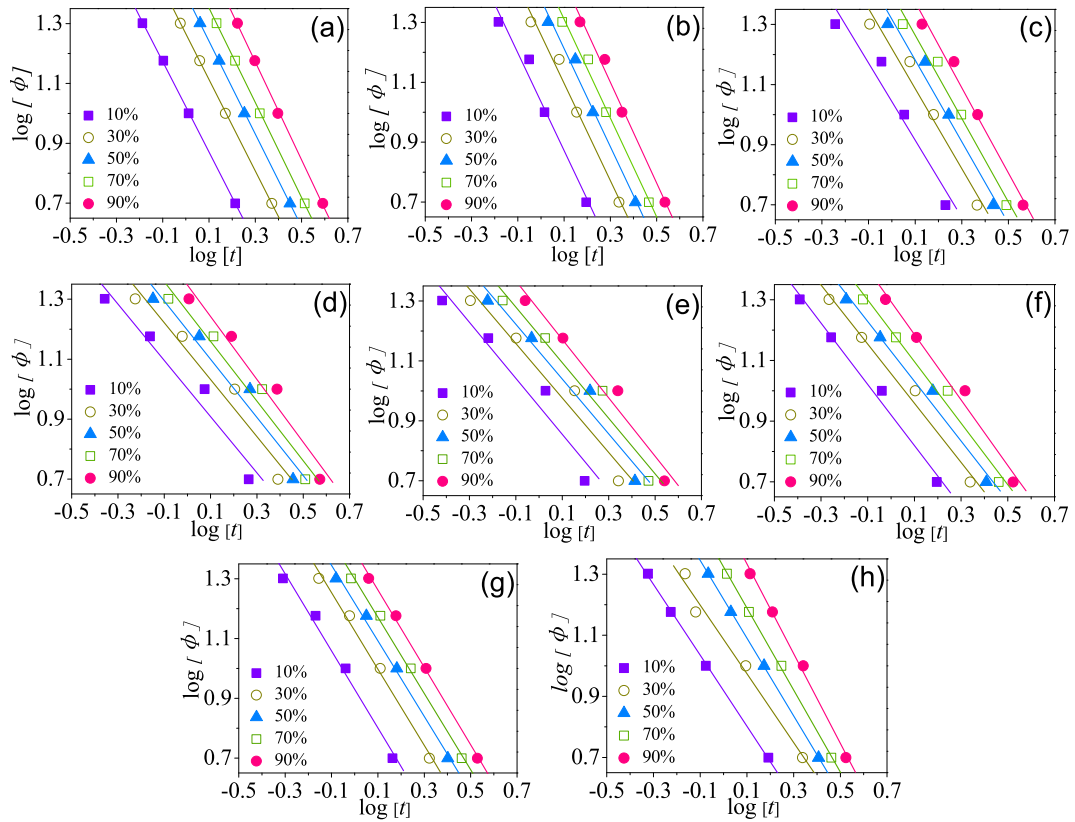


Fig. 4. Plots of  $\lg \phi$  vs  $\lg t$  for (a) PHBV, (b) PHBV-0.05, (c) PHBV-0.1, (d) PHBV-0.2, (e) PHBV-0.5, (f) PHBV-1.0, (g) PHBV-2.0, (h) PHBV-4.0.

that rate of induced nucleation crystallization was higher than limitation rate of molecular chain diffusion due to the long chain branched structure, and therefore the overall crystallization rate and crystallinity of LCB-PHBV were improved.

#### 4. Conclusions

A long chain branched PHBV (LCB-PHBV) copolymer has been successfully prepared via melting reaction. The main mechanism for preparation of LCB-PHBV was an inducement of perhydroxyl

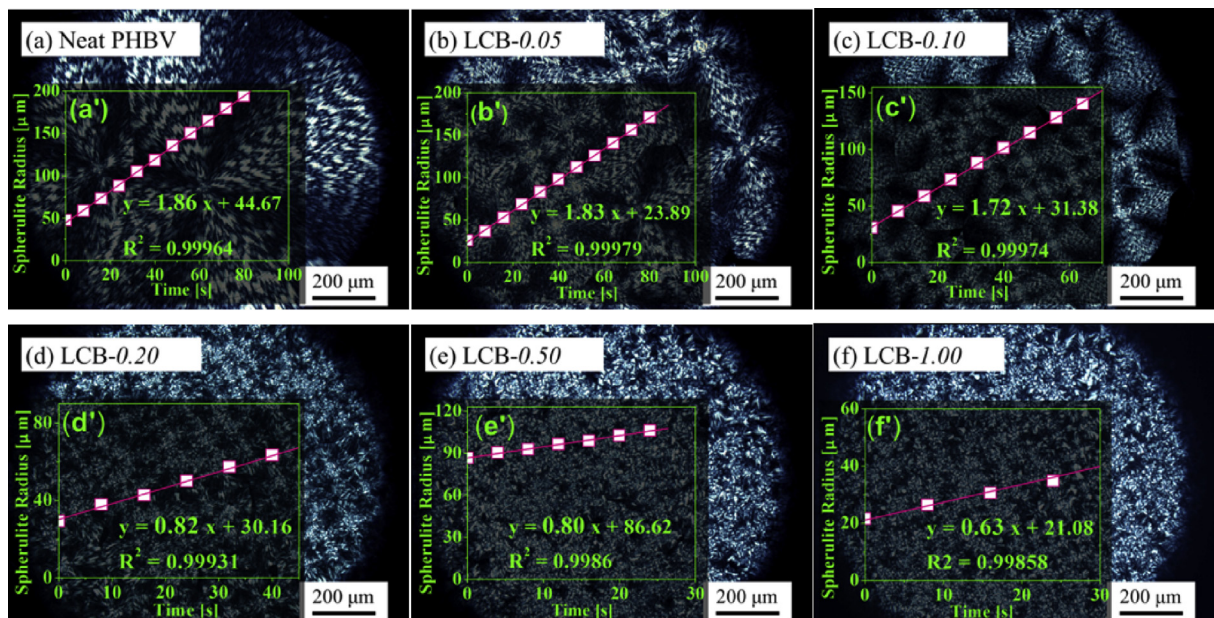


Fig. 5. POM of (a) PHBV, (b) PHBV-0.05, (c) PHBV-0.1, (d) PHBV-0.2, (e) PHBV-0.5, (f) PHBV-1.0 at 110 °C, insert is their corresponding radial growth rates of spherulites.

radicals on tertiary carbon hydrogen atoms of PHBV molecular main-chain to form a short and medium PHBV chain containing active free radicals and a coupling reaction with PHBV chains containing active free radicals. When DCP content was less than 0.5 wt%, LCB-PHBV mainly presented a long chain branched structure. This structure enhanced the nucleation abilities of LCB-PHBV crystal nucleus on the one hand, but restrained the crystal growth rate by limiting the diffusion of molecular chain segments, while this nucleation promotion effect was greater than diffusion and limitation effect of chain segments, resulting in an inducement and acceleration in crystallization rate of LCB-PHBV. The Mo's equation described the non-isothermal crystallization kinetics of LCB-PHBV very well. After modification with minor DCP content on PHBV, its  $t_{1/2}$  decreased. The  $t_{1/2}$  of PHBV-0.5 decreased from 71s of linear PHBV to 33s when the cooling rate was about 20 °C/min. It is noteworthy that the initial crystallization peak temperature of LCB-PHBV with addition of 0.2–0.5 wt%DCP was independent to cooling rate and whereas, melt crystallization curves shifted to a higher temperature with the increase of cooling rate. The resultant LCB-PHBV in this research had advantages of high nucleation temperature and rapid crystallization rate which could effectively inhibit problems during processing of bio-polyester PHBV such as slow crystallization rate and fiber adhesion.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.compscitech.2017.02.016>.

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