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Isothermal crystallization of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

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Abstract

Isothermal crystallization behavior of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) was investigated by means of differential scanning calorimetry and polarized optical microscopy (POM). The Avrami analysis can be used successfully to describe the isothermal crystallization kinetics of PHBV, which indicates that the Avrami exponent $n = 3$ is good for all the temperatures investigated. The spherulitic growth rate, G, was determined by POM. The result shows that the G has a maximum value at about 353 K. Using the equilibrium melting temperature (448 K) determined by the Flory equation for melting point depression together with $U^* = 1500\ \mathrm{cal\,mol^{-1}}$, $T_\infty = 30$ K and $T_g = 278$ K, the nucleation parameter K_g was determined, which was found to be $3.14 \pm 0.07 \times 10^5$ (K^2), lower than that for pure PHB. The surface-free energy $\sigma = 2.55 \times 10^{-2}\ \mathrm{J\,m^{-2}}$ and $\sigma_e = 2.70 \pm 0.06 \times 10^{-2}\ \mathrm{J\,m^{-2}}$ were estimated and the work of chain-folding ($q = 12.5 \pm 0.2\ \mathrm{kJ\,mol^{-1}}$) was derived from σ_e, and found to be lower than that for PHB. This implies that the chains of PHBV are more flexible than that of PHB.

Keywords: Isothermal crystallization; Poly(3-hydroxybutyrate-co-3-hydroxyvalerate); Kinetics

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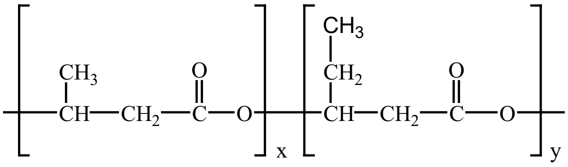
1. Introduction

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a biodegradable thermoplastic copolymer which can be produced from renewable resources [1]. PHBV was first manufactured by ICI in 1983 and was originally intended to be used as a biodegradable substitute for oil-based polyolefins in plastic containers, films and bottles [2]. Potential uses for it also include medical implants, such as sutures or drug delivery devices, which will gradually degrade in the body. Its formula is as follows:



$$\left[\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-O\right]_x\left[\overset{\displaystyle CH_3}{\overset{|}{\overset{\displaystyle CH_2}{\overset{|}{CH}}}}-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-O\right]_y$$

It possesses a wide range of properties depending on the HV content. However, PHBV is a semicrystalline polymer with high crystallinity at all compositions [3,4]. Its final properties, such as impact resistance and stress–strain property, depend on the crystallization procedure and on its crystallinity. Therefore investigation of the kinetics of crystallization is of importance. The crystallization behavior of PHBV in a solvent had been studied in detail by Barham, and the structure and morphology of PHBV has also been given [5]. Solid-state ^{13}C NMR results given by Kamiya show that PHBV crystallize in

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the same crystalline lattice as homopolymers of the main component and the main component is the HB unit for the copolymers containing up to 40 mol% HV [6]. If PHBV crystallizes in PHB lattice, then both nucleation and crystal growth for PHBV are lower than those for PHB. Similar result was obtained by Kunioka et al. [7] and Scandola et al. [8]. It has also been found that the crystallization conditions are as important as the HV content of sample. These affect both the crystallinity, which appears to increase with increasing crystallization temperature and HV content of the crystals which appears to decrease with increasing crystallization temperature [9,10]. The crystallization behavior of PHBV had been studied by means of FTIR [3], NMR [6], AFM [11], WAXD [4] and TEM [5]. However, the crystallization kinetics of PHBV has not been described in detail. In this work, the isothermal crystallization kinetics of PHBV was investigated by using differential scanning calorimetry (DSC) and hot-stage polarized optical microscopy (POM).

2. Experimental

2.1. Material

PHBV was produced by Biology Institute, CAS in Beijing. The product's HV content was 8 mol%. The weight-average molecular weight obtained by measuring its viscosity in chloroform at a temperature of 303 K was 5.8×10^5 according to the equation [12] $\eta = 1.18 \times 10^{-4} M_w^{0.78}$.

2.2. Polarized optical microscopy

Each specimen was sandwiched between two thin glass slides, kept at 463 K for 2 min on one hot stage. At the same time, the temperature on an OPTON hot-stage POM was set to the desired crystallization temperature. The specimen was transferred as quickly as possible onto the hot-stage microscopy to be crystallized isothermally at a given crystallization temperature (T_c). The growth of spherulites as a function of time was monitored. The slope of the spherulitic radius versus time was used for calculation of the radial growth rate of PHBV spherulites.

2.3. Differential scanning calorimetry

A Perkin Elmer DSC-7 was used to study the crystallization behavior of PHBV. The specimen weight used for the DSC measurement was about 6 mg. The temperature and energy readings were calibrated with indium and water. The procedure for isothermal crystallization kinetic experiments was as follows: all samples were heated to 463 K and annealed at that temperature for 2 min to cancel all crystals, then quenched to the desired crystallization temperature, T_c. The exothermic crystallization peak was recorded as a function of time at T_c. The relative degree of crystallinity, X_t, of the material, crystallized after time t, was determined by means of the following equation [13]:

$$X_t = \int_0^t (\mathrm{d}H/\mathrm{d}t)\mathrm{d}t \bigg/ \int_0^\infty (\mathrm{d}H/\mathrm{d}t)\mathrm{d}t \quad (1)$$

where the first integral is the heat generated after time t and the second integral is the total heat of crystallization for $t = \infty$.

3. Results and discussion

3.1. Isothermal crystallization kinetics from DSC analysis

The crystallization exotherms of PHBV at different crystallization temperatures are shown in Fig. 1. The crystallization process was completed in less than 20 min. From the figure, it can be seen that as the crystallization temperature was increased the peek of crystallization exotherm shifted to longer time and became flatter. According to Eq. (1), X_t at different crystallization times can be calculated. Plots of X_t versus time for PHBV are shown in Fig. 2 at different isothermal crystallization temperatures. The slopes of the curve at each point are a measure of the rate of crystallization [14]. From the figure it can be seen that in the range of 20–60% relative crystallinity the curves are straight. It indicates that the rate of crystallization keeps constant in this part. If we take V_c as the rate of crystallization corresponding to the straight section of the curve, then the activation energy associated with the overall process

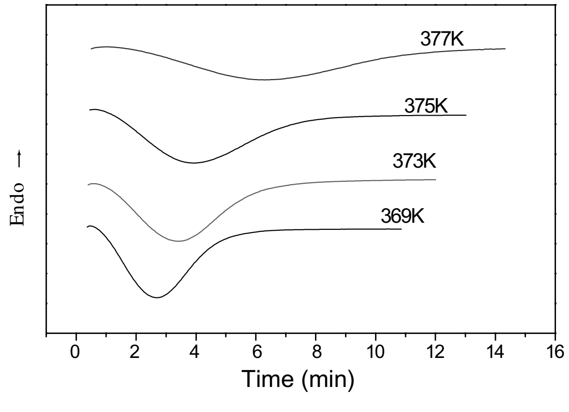

Fig. 1. Heat flow versus time during isothermal crystallization of PHBV at different crystallization temperatures by DSC.

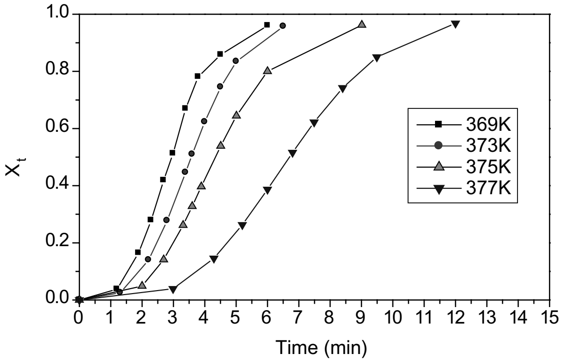

Fig. 2. Plots of relative crystallinity, X_t, versus time for PHBV at different crystallization temperatures.

of crystallization can be evaluated from the rates of crystallization by using the following equation [15]:

$$V_c = A\exp(-E/RT) \tag{2}$$

where A, E, R and T are the pre-exponential factor, the activation energy ($\mathrm{J\,mol^{-1}}$), the universal gas constant (8.314 $\mathrm{J\,mol^{-1}\,K^{-1}}$) and absolute crystallization temperature (K), respectively, that is, plotting $\ln V_c$ versus $(RT)^{-1}$, a line can be obtained and from the slope the activation energy E has been obtained. The value is 110 ± 14 $\mathrm{kJ\,mol^{-1}}$, bigger than that of PHB [16]. It indicates that the crystallization ability of PHBV is lower than that of PHB. This may be ascribed to the bigger size of the HV units.

The isothermal crystallization kinetics of PHBV was analyzed on the basis of the Avrami equation [17,18],

$$1 - X_t = \exp(-kt^n) \tag{3a}$$

$$\log[-\ln(1 - X_t)] = \log k + n\log t \tag{3b}$$

where X_t is the weight fraction of crystallinity, n is the Avrami exponent, k is the overall kinetic rate constant and t is the time of crystallization. Both k and n depend on the mechanism of the nucleation as well as the growth geometry. The double logarithmic plots of the Avrami analysis for PHBV at different crystallization temperatures are shown in Fig. 3. From the figure it can be seen that the experimental data fit well with the Avrami equation, plots of $\log[-\ln(1 - X_t)]$ versus $\log(t)$ at different T_c all result in linear relationship. From the slope and intercept of curves, the Avrami exponent n and rate constant k can be obtained. Meanwhile, the crystallization half-time $t_{1/2}$, which is defined as the time at which the extent of crystallization is 50%, can be determined from the measured kinetics parameters according to the following equation:

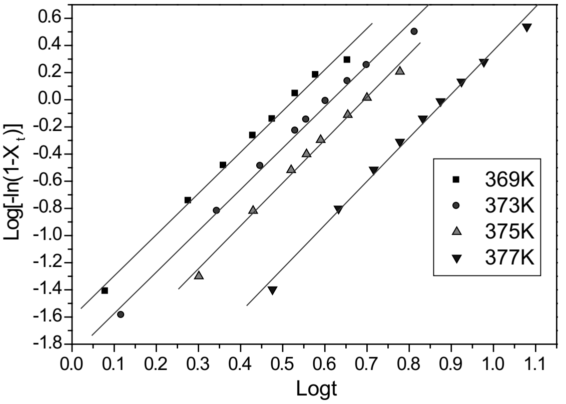

Fig. 3. Plots of $\log[-\ln(1 - X_t)]$ versus $\log t$ for isothermal crystallization at the indicated temperatures.

$$t_{1/2} = (\ln 2/k)^{1/n} \tag{4}$$

Usually, the rate of crystallization is also described as the reciprocal of $t_{1/2}$ ($g = (t_{1/2})^{-1}$). If the phase transition in crystallization is nucleation controlled, then the rate of crystallization g should increase with supercooling. This was observed for PHBV, as can be seen in Table 1. And this result is in good agreement with the result of POM.

The crystallization parameters k, n, g, and $t_{1/2}$ are all listed in Table 1. From the table it can be seen that the half-time of crystallization $t_{1/2}$ decreases with the decrease of crystallization temperature, indicating that the rate of crystallization is faster when the supercooling temperature was higher within the temperature range of our DSC experiment. The rate constant k, which is associated with both the nucleation and the growth processes, decreased with the increase in crystallization temperature. The Avrami exponent n is about 3 for all the temperatures investigated. This indicates that, in the temperature range of our DSC experiment, both the

Table 1
The values of k, n, $t_{1/2}$ and g as a function of T_c for PHBV

T_c (K)	k	n	$t_{1/2}$ (min)	g (min^{-1})
369	0.025 ± 0.002	3.0 ± 0.1	3.0 ± 0.2	0.33 ± 0.02
373	0.013 ± 0.001	3.1 ± 0.1	3.7 ± 0.2	0.28 ± 0.02
375	0.0064 ± 0.0008	3.2 ± 0.1	4.4 ± 0.3	0.23 ± 0.02
377	0.0014 ± 0.0002	3.2 ± 0.1	6.9 ± 0.8	0.14 ± 0.02

nucleation mechanism and geometry of crystal growth of PHBV are almost not affected by crystallization temperature. In general, $n = 3$ corresponds to two different kinds of possible crystallization mechanism. One is three-dimensional growth and instantaneous nucleation; the other is two-dimensional growth and homogeneous nucleation. So, it is difficult to elucidate the growth and type of nucleation only from the values of the exponent n. Additional information on nucleation, morphology, and possibly even mechanism is necessary to fully interpret the exponent n. The nucleation behavior of PHB and the effect of nucleating agents (talc and saccharin) on it had been studied by Barham [19]. He drew a conclusion that pure PHB melts may undergo homogeneous nucleation. According to Doi [6], PHBV crystallize in the same crystalline lattice as homopolymer of the main component when HV content is lower than 40%. From our POM experiment we also observed that the nucleation of PHBV is at random. We think that PHBV melts also undergo homogeneous nucleation. So in our experiment, $n = 3$ maybe corresponds to two-dimensional growth and homogeneous nucleation.

3.2. Spherulitic growth analysis

There are many works studying the crystallization kinetic by determination of spherulitic growth rate, G [20–23]. The method, established by Hoffman and coworkers [24,25], is often employed to deal with the experimental results. In this work, the spherulitic growth rates of PHBV at different crystallization temperatures were determined by observation with a POM. The dependence of G on T_c is shown in Fig. 4. The range of crystallization temperature is from 348 to 388 K. From the figure, it can be seen that G has a maximum value at about 353 K. When the crystallization temperature was higher than 353 K, the spherulitic growth rate of PHBV decreased with the increase in T_c. When the crystallization temperature was lower than 353 K, the spherulitic growth rate of PHBV increased with the increase in T_c.

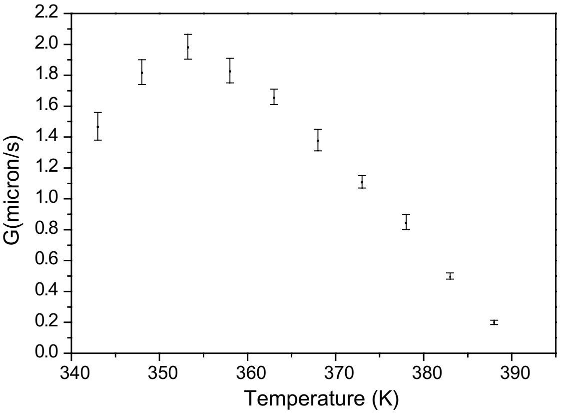

Fig. 4. Radial growth rate (G) as a function of T_c for PHBV.

The radial growth rate of spherulites may be described qualitatively by equation of the form proposed by Tumbull and Fisher [26]

$$G = G_0 \exp[-E/(RT)] \exp[-\Delta F/(RT)] \tag{5}$$

The first term, $\exp[-E/(RT)]$ is a molecular diffusion term describing the transport which takes place when molecular segments are added to the crystal surface. The second term, $\exp[-\Delta F/(RT)]$, describes the surface nucleation process in which ΔF is the free energy of formation of a surface nucleus. These two terms are in opposition in the sense that as the crystallization temperature is decreased the first term decreases and the second increases, explaining the presence of a maximum in the behavior of the growth rate.

On the basis of Tumbull equation, Lauitzen and Hoffman obtained the famous Lauritzen–Hoffmann equation, as follows:

$$G = G_0 + \exp[-U^*/[R(T - T_\infty)] \times \exp[-K_g/(fT\Delta T)] \tag{6a}$$

where G_0 is a constant which is temperature independent, U^* is the activation energy for transport of crystallizable segments through the melt to the site of crystallization, T_∞ is a hypothetical temperature where all molecular motion associated with viscous flow ceases and is related to T_g by $T_\infty = T_g - C$, where C is a constant; T is the crystallization temperature; $\Delta T = T_m - T$ is the degree of supercooling, and T_m is the equilibrium melting point; f is a factor which accounts for the variation in the bulk enthalpy of fusion per unit volume with temperature, and is given by $f = 2T/(T_m + T)$; K_g is the nucleation constant and can be expressed as [22,24,27]:

$$K_g = nb_0\sigma\sigma_e T_m/(\Delta H_f k) \tag{7}$$

where σ and σ_e are the lateral and surface free energies of the growing crystal, respectively, b_0 is the molecular thickness, k is the Boltzmann constant, its value is 1.38×10^{-23} J K^{-1}, and n is a constant, its value may have the value 2 or 4 depending on the growth mechanism [25]. Hoffman proposed that there are three distinct regimes of growth of polymer crystals, depending on the relative rates of formation of new secondary nuclei on the growth front and the rate at which the nuclei once formed spread along the growth front. At low supercoolings the rate of spreading is so large compared with the rate of nucleation that a nucleus once formed spreads rapidly across the growth front: Regime I. At higher supercoolings several nuclei form and spread across the growth front together, the separation between them decreasing as the supercooling increases: Regime II. At a sufficiently high supercooling the separation of nuclei is comparable with the molecular with so that no more spreading takes place: Regime III. The three regimes may be distinguished by the value of the constant n in Eq. (7); in Regime I and Regime III it takes the value 4 and in Regime II it takes the value 2. According to Barham et al. [28] and in our previous work [29,30], for PHB and its blends, the regime of crystallization was assigned to be Regime III in the investigated temperature range. So $n = 4$ was adopted.

The equilibrium melt point can be predicted by using the Flory equation for melting point depression [31].

$$1/T_m - 1/T_m^0 = -R\ln(X_b)/\Delta H_u \tag{8}$$

where ΔH_u is the enthalpy of fusion per mole of repeating units, R is the universal gas constant in appropriate units, T_m is the melting point of the copolymer, T_m^0 is the equilibrium melting point of the homopolymer (PHB) and X_b is the mole fraction of HB units in the copolymer. Here, $T_m^0 = 470$ K [28], $\Delta H_u = 1592$ cal mol^{-1} [4]. Hence, according to Eq. (8), $T_m = 448$ K.

It is most convenient to rearrange Eq. (6a) as:

$$\ln G + U^*/[R(T - T_\infty)] = \ln G_0 - K_g/(fT\Delta T) \tag{6b}$$

According to Eq. (6b) a plot of $\ln G + U^*/[R(T - T_\infty)]$ against $1/(fT\Delta T)$ should yield a straight line with an intercept $\ln G_0$ and a slope $-K_g$. To do this we need to know the values of U^* and T_∞. In general, the Williams–Landel–Ferry (WLF) [32] values $U^* = 4120$ cal mol^{-1} and $T_\infty = T_g - 51.6$ K were employed. But in our present work, using the WLF values cannot obtain a good fit of the experimental data. In the work of Suzuki and Kovacs [33], it was found that the "universal" values $U^* = 1500$ cal mol^{-1} and $T_\infty = T_g - 30$ K allowed the best fit of the rate of crystallization data. It happens to our experimental data that a very good fit is obtained with universal values (Fig. 5). From the figure it can be seen that a straight line is obtained. Here, $T_g = 278$ K was used in our analysis [34]. Thus, the K_g obtained with the above analysis from Fig. 5 is $3.14 \pm 0.07 \times 10^5$ (K^2) for PHBV, which is lower than that for pure PHB as reported in our previous work [29,30]. The derived K_g can be used to calculate the apparent lateral and end surface free energies for PHBV, σ and σ_e, using the empirical relation [35]

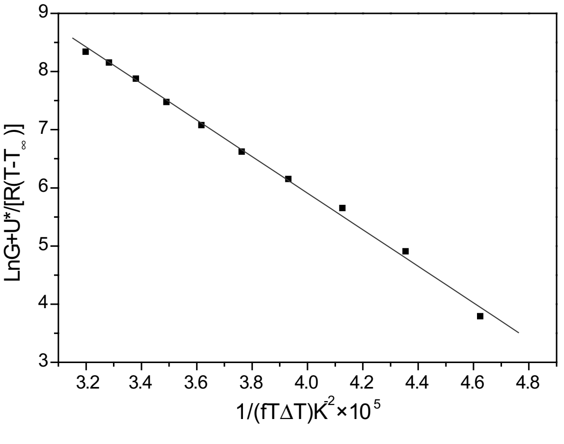

Fig. 5. Plot of $\ln G + U^*/[R(T - T_\infty)]$ versus $1/(fT\Delta T)$ for PHBV.

$$\sigma = \alpha(\Delta H_f)(a_0 b_0)^{1/2} \tag{9}$$

where $\alpha = 0.25$ appropriate for high-melting polyesters [36] (e.g., poly(pivalolactone) [20]. According to Doi and co-workers [37], when the HV content in PHBV is lower than 37 mol%, only the parameter a of the unit cell changes with increasing HV content in PHBV. So, for the PHBV (8 mol% HV content) investigated in our experiment, the unit cells can be considered orthorhombic [5] with $a = 5.8 \times 10^{-10}$ m, $b = 13.2 \times 10^{-10}$ m and $c = 5.96 \times 10^{-10}$ m. Therefore the values of a_0 and b_0 can be determined. a_0 is 6.6×10^{-10} m and b_0 is 5.8×10^{-10} m. The heat of fusion of this copolymer has not been measured directly. Here, for convenience of calculation, we adopted the data reported in the literature [38] for PHBV containing 7mol% HV, $H_f = 1.65 \times 10^8$ J m^{-3}. Hence according to Eq. (7), $\sigma\sigma_e = 6.88 \pm 0.05 \times 10^{-4}$ (J m^{-2})^2. The value of σ calculated from Eq. (9) is 2.55×10^{-2} J m^{-2}, thus σ_e obtained from them is $2.70 \pm 0.06 \times 10^{-2}$ J m^{-2}. The values are also lower than those for pure PHB [29,30,39]. Compared with PHB, the decrease of k_g, σ and σ_e indicates that the crystallization ability of PHBV is lower than that of PHB. This is an expected result since the ethyl side chains of the 3 HV units prevent the crystallization of P(3HB) lattice due to steric effects. This makes the crystallization of PHBV more difficult compared with that of PHB.

The work of chain folding per molecular fold can be obtained by the following equation [25,40]:

$$\sigma_e = \sigma_e^0 + q/2a_0b_0 \tag{10a}$$

where σ_e^0 is the value of σ_e by assuming that no work is required to form the fold, and q is the work required to blend a polymer chain back upon itself, taking into account the conformational constraints imposed on the fold by the crystal structure. As a first approximation, σ_e^0 may be taken as being roughly equal to the lateral surface energy, σ. It is expected, therefore, that σ_e^0 will be significantly less than $q/2\ a_0b_0$, and, consequently it may be set equal to zero as the second approximation. Accordingly, Eq. (10a) is usually written as follows:

$$q = 2a_0b_0\sigma_e \tag{10b}$$

The value of q obtained for PHBV (containing 8 mol% HV) from Eq. (10b) is $2.07 \pm 0.04 \times 10^{-20}$ J per molecular chain fold, that is 12.5 ± 0.2 kJ mol^{-1}. This value is lower than that for pure PHB [29] (18.4

$\mathrm{kJ\,mol^{-1}}$), which means that the chains of PHBV are more flexible than those of PHB. This was expected since the valerate units in the chains of PHBV have an ethyl side group, longer than methyl side group in the chains of PHB.

4. Conclusion

Isothermal crystallization kinetics of PHBV was investigated by means of DSC. The Avrami analysis shows that the Avrami exponent $n = 3$, is good for all the temperatures investigated. The activation energy associated with the overall process of crystallization has also been evaluated, and was found to be $110 \pm 14\ \mathrm{kJ\,mol^{-1}}$, bigger than that of PHB. The spherulitic nucleation and growth kinetics were discussed. The spherulitic growth rates, G, were determined by POM. The result shows that G has a maximum value at about 353 K. Using the equilibrium melting temperature (448 K) determined by Flory equation for melting point depression together with $U^* = 1500\ \mathrm{cal\,mol^{-1}}$, $T_\infty = 30$ K, and $T_g = 278$ K, the nucleation parameter K_g was determined. It was found to be $3.14 \pm 0.07 \times 10^5$ ($\mathrm{K^2}$), lower than that for pure PHB. The surface-free energy $\sigma = 2.55 \times 10^{-2}\ \mathrm{J\,m^{-2}}$ and $\sigma_e = 2.70 \pm 0.06 \times 10^{-2}\ \mathrm{J\,m^{-2}}$, obtained by estimation, were also lower than those of PHB. These indicate that the crystallization ability of PHBV was lower than that of PHB. The work of chain-folding ($q = 12.5 \pm 0.2\ \mathrm{kJ\,mol^{-1}}$) derived from σ_e, was lower than that for PHB. This implies that the chains of PHBV were more flexible than those of PHB.

Acknowledgement

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