

Kinetic Expression for the Isothermal Crystallization of Poly(3-hydroxybutyrate)–11%Poly(3-hydroxyvalerate)

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ABSTRACT: The use of polyhydroxyalkanoates as a biodegradable semicrystalline polymer is currently increasing. The prediction of crystallinity profiles produced in part with this polymer requires the knowledge of the kinetic expression. In the present article, a kinetic expression of the isothermal melt crystallization of poly(3-hydroxybutyrate)–11%poly(3-hydroxyvalerate) [P(HB-co-11%HV)] was studied in two temperature ranges, close to the melting point and close to the glass transition. Melting behavior and mo-

lecular mobility of the amorphous phase were analyzed as a function of crystallization temperatures by performing calorimetric experiments. The Avrami equation was used and the activation energy of the crystal nucleation and growth were obtained. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1657–1661, 2004

Key words: polyhydroxyalkanoates; crystallization; kinetics (polym.); induction time; glass transition

INTRODUCTION

The crystallization behavior of polyhydroxyalkanoates has been extensively studied. However, many experimental and theoretical questions are still unsolved because of the complexity of the nucleation and growth phenomena of macromolecular crystals of poly(3-hydroxybutyrate) (PHB). The melting history can modify the polymer structure as a result of the mechanical crosslinking or degradation phenomena, and the cooling rate can also modify the final structure because of a crystallinity profile.

The nucleation density of polyhydroxyalkanoates, compared to that of other thermoplastics, is relatively low, thus leading to low rates of crystallization. This low nucleation density means that it is possible to grow spherulites several millimeters in diameter on crystallization from the melted polymer. This has a consequence in the mechanical properties, in that this material will be more brittle because of the greater diameter of the spherulites. Also, the low nucleation density achievable through homogeneous nucleation leads to an excessively long cycle time in the fabrication processes, such as injection molding.^{1,2}

The study of the crystallization phenomena is of great importance in polymer processing, for several reasons. One is control of the temperature profile during cooling, in the final stage of a process, that determines the development of a specific morphology, which influences the final properties of the material. Modeling of isothermal crystallization gives information on kinetics and morphology developed at each crystallization temperature. Lamellar morphology depends strongly on the crystallization condition.^{1,2} It has been shown both experimentally and theoretically that it is the undercooling, more than the crystallization temperature, that indicates the lamellar thickness. The greater the degree of undercooling, the smaller becomes a critical lamellar thickness value, l_c . The melting temperature T_m depends on l_c . The thicker the lamellae, the higher the T_m value. Plotting the inverse of lamellar thickness against the observed melting point T_m allows extrapolation to infinite lamellar thickness and calculation of T_m^0 , the equilibrium melting point of the infinite crystal.

In the macrokinetic approach, the dependency of the degree of crystallization on time and temperature must be defined to model and optimize the final crystallinity structure of the polymer.

The aim of this work was to analyze the isothermal crystallization of poly(3-hydroxybutyrate)–11%poly(3-hydroxyvalerate) copolymer [P(HB-co-11%HV)] and to find a kinetic expression from such experiments. This expression is necessary for predicting the differences in crystallinity on the thickness of the specimen when it is under a temperature profile during fabrication.

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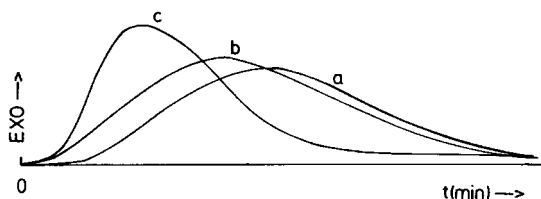


Figure 1 Crystallization peaks showing the induction time from DSC thermograms at isothermal mode for the following samples: (a) 40°C, (b) 43°C, and (c) 50°C.

EXPERIMENTAL

The P(HB-co-11%HV) was supplied by Aldrich Chemical Co. (Milwaukee, WI). The films were prepared by casting from chloroform solution (10% w/v) at room temperature on a plane Pyrex surface and then kept 15 days at room temperature to develop full crystallization.

A Dupont 990 thermal analyzer (Dupont, Boston, MA) was used for the calorimetric study. Sample masses were typically 5–10 mg. Isothermal crystallization was performed on the following schedule under nitrogen atmosphere: samples (5–10 mg) were fused from 25 to 180°C at 10°C/min, kept at this temperature for 10 min, and quenched with dry ice. As previously reported,³ some degradation could be obtained during the heating. After quenching, the samples were immediately placed into the DSC apparatus, preset to a crystallization temperature. Isothermal runs were performed until complete crystallization peak reached the base line. Crystallization temperatures used ranged from 37 to 100°C.

RESULTS AND DISCUSSION

Crystal nucleation

The DSC signal for the isothermal thermogram presents a delay, which represents an induction time (Fig. 1). Induction time is a relevant parameter, from the perspective of processing, that is associated with crystal nucleation. Nucleation is heterogeneous in nature and is a thermally activated phenomenon that can be characterized by measuring the induction time as a function of the test temperature in isothermal DSC. The induction time may be considered as the only detectable macroscopic parameter that represents the nucleation process. Following the general approach reported in the literature for nucleation and crystallization growth,⁴ the temperature dependency of the induction time is given by

$$t_i = K_0 \exp\left[\frac{E_{tg}}{R(T - T_g)}\right] \exp\left[\frac{E_{tm}}{R(T_m^\circ - T)}\right] \quad (1)$$

where K_0 is a preexponential factor. The two exponentials account for the driving force of nucleation above the glass-transition temperature T_g and below the theoretical melting point T_m° , where E_{tg} and E_{tm} are the activation energies of these two contributions.⁵

The transition temperature T_g was determined by means of dynamic mechanical analysis ($T_g = 0^\circ\text{C}$) and the T_m° value was taken as 169.9°C.⁶ By taking logarithms on both sides of eq. (1), the representation of $\ln t_i$ as a function of $1/(T - T_g)$ and $1/(T_m^\circ - T)$ has two zones related with the intervals close to T_g and T_m° , respectively. However, to fit all of the curves, the

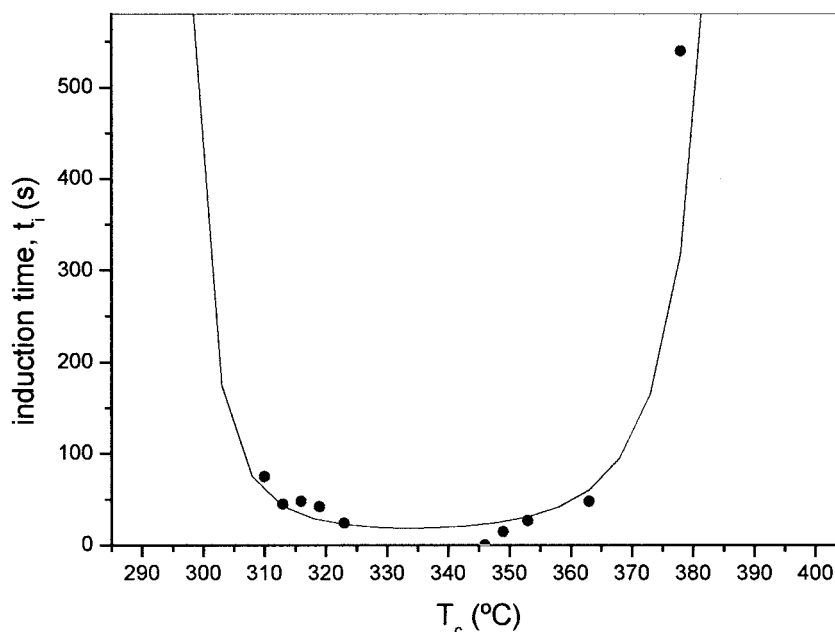


Figure 2 Induction time values fitted by the Hoffman equation: ●, experimental; —, model.

TABLE I
Parameters of the P(HB-co-11%HV) Kinetic Models with $T_g = 0^\circ\text{C}$ and $T_m^\circ = 169.9^\circ\text{C}$

Parameter	E_{tm} (kJ/mol)	E_{tg} (kJ/mol)	K_0 (s)
Induction time = t_i (s), eq. (1)	5.76	1.79	9.5×10^{-4}
	E_m (kJ/mol)	E_g (kJ/mol)	k_0 (min^{-n})
Avrami constant = k (min^{-n}), eq. (4)	4.95	2.29	1498
	$K_g \times 10^5$ (K^2)	U (kJ/mol)	$k_{0.5}$ (s)
Half-time = $t_{0.5}$ (s), eq. (5)	11.9	6.28	3.6×10^{17}
	3.3	6.28	7.1×10^5
Half-time = $t_{0.5}$ (s), eq. (6)	$E_{0.5m}$ (kJ/mol)	$E_{0.5g}$ (kJ/mol)	$k_{0.5}$ (s)
	4.28	1.79	4.5×10^{-2}

values obtained in this way were taken as first approximations. The final values were calculated by proof-and-error methods. Figure 2 shows the result of the fitted values and Table I shows the activation energy values.

Cold crystallization kinetic and crystal growth

Rozsa et al.⁶ studied macrokinetic models of isothermal crystallization using the Avrami equation:

$$x_r = 1 - \exp(-kt^n) \quad (2)$$

where

$$x_r = \frac{\Delta H(t)}{\Delta H_{\text{total}}} \quad (3)$$

where x_r is the relative volume fraction of crystallinity, referring to the final amount of crystallinity developed under the same thermal condition for a long time, ΔH_{total} . The values of k and n indicate the mechanism of crystallization⁷ and they are related to the half-time and to the type of nucleation together with the geometry for the crystal growth.

Table II shows the results of induction time, half-time, n , and the Avrami constant value. For the range of crystallization temperatures of 37 – 50°C , the exponent n is close to 2.14 and it is an indication that the growth of crystals is two-dimensional.⁶

If the overall crystallization was modeled considering heterogeneous nucleation and growth of crystals as a series process, the temperature dependency of the kinetic constant in the Avrami equation can be proportional to the crystal linear growth rate G . Taking into account the theory proposed by Hoffman et al.^{8–10}

$$k = k_0 \exp\left[\frac{-E_g}{R(T - T_g)}\right] \exp\left[\frac{-E_m}{R(T_m - T)}\right] \quad (4)$$

where k_0 is a preexponential factor. The first exponential accounts for the increase in the molecular mobility in the highly viscous region above the glass-transition temperature T_g that induces the cold crystallization process. The second exponential accounts for the driving force of crystallization, given primarily by the degree of undercooling ($T_m^\circ - T$) according to the theoretical melting point T_m° . Figure 3 shows the fitting values for eq. (4). The activation energies in this case are lower than those from the crystal nucleation process (Table I). However, the activation energy for the range close to T_m is higher than the activation energy for the range close to the T_g value.

Half-time was calculated at $x_r = 0.5$ for each run. The half-time is also a parameter related to the crystallization and the type of nucleation. The analysis of the half-time values (Table II) indicates that the time taken for half of crystallization to develop is a strong characteristic of the crystallization temperature. The half-time ($t_{0.5}$) for crystallization was obtained by the equation $t_{0.5} = (\ln 2/k)^{1/n}$.¹¹ These values are also

TABLE II
Parameters of Avrami's Equation at Different Crystallization Temperatures of the Copolymers P(HB-co-HV)

T_c ($^\circ\text{C}$)	n	t_i (s)	$-\ln(k)$ (min^{-n})	$t_{0.5}$ (exp) (min)	$t_{0.5}$ (calcd) (min)
37	2.13	75	4.48	7.23	6.89
40	2.14	45	4.29	6.57	6.28
43	2.08	48	4.16	6.20	6.21
46	2.08	42	3.98	5.69	5.69
50	2.12	24	3.62	4.52	4.64
73	1.56	0	2.39	3.19	3.67
76	1.5	15	2.43	2.83	3.05
80	1.77	27	2.53	3.28	3.4
90	1.70	48	3.16	5.00	5.17
100	1.44	540	4.46	9.21	21.95

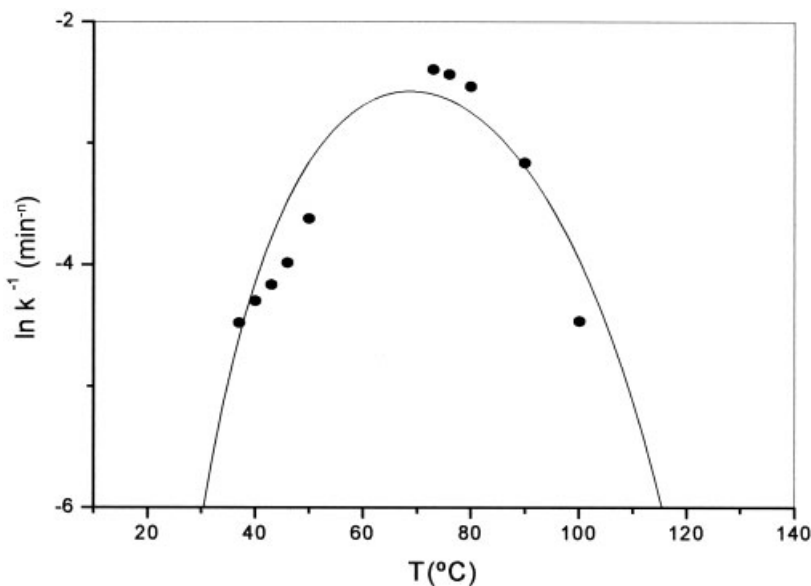


Figure 3 Arrhenius equation for the Avrami constant in function of crystallization temperature. Fitting of eq. (4) $\ln(1/k)$ versus T_c : ●, exp; —, model.

listed in Table II, and they agree with reported values of $t_{1/2}$ for $x_r = 0.5$.

By taking into account the Hoffman–Lauritzen theory,^{8–10} it can be shown that the linear growth rate G can be considered proportional to $1/t_{0.5}$. A very high rate appears at 80°C, which is in accordance with the literature.^{12,13} The half-time can be determined by the following equation:

$$\left(\frac{1}{t_{0.5}}\right) = k_{0.5} \exp\left[-\frac{U}{R(T_c - T_\infty)}\right] \exp\left[-\frac{K_g}{T_c \Delta T f}\right] \quad (5)$$

where factor f is defined as: $f = 2T_c/(T_c + T_m^\circ)$; U is the transport activation energy; R is the universal gas constant; T_∞ is chosen to be $T_\infty = T_g - 30^\circ\text{C}$ ¹⁸; T_m° is the infinite-crystal melting point; and ΔT is the degree of undercooling ($\Delta T = T_m^\circ - T_c$). The factor f in the second exponential is a correction term to account for changes in the fusion heat ΔH_f with higher degrees of undercooling.

The first exponential accounts for the increase in the molecular mobility in the highly viscous region above the T_g that induces the cold crystallization. The second exponential accounts for the driving force of crystallization, given primarily by the degree of undercooling ($T_m^\circ - T_c$). These constitutes the driving force of crystallization, which indicates a decrease of the overall rate when the temperature approaches the thermodynamic melting point.

Therefore, to investigate the overall kinetics for P(HB-co-11%HV) in Figure 4, $\ln(1/t_{0.5}) + U/R(T_c - T_\infty)$ versus $1/T(\Delta T)f$ were plotted. Taking the U value as 6.28 kJ/mol,¹¹ the figure shows two regions, indicating a break in the crystallization temperature. This

behavior agrees with the change in the Avrami exponent. Table I shows the K_g values. The nucleation constant $K_g(\text{II})$ in regime II is in agreement with the results reported in the literature.^{14,15} However, the value of $K_g(\text{II})$ is higher than the value predicted by the theory. As a consequence, the slope ratio of both zones is 3.6 instead to 2, in agreement with the result of Iannace and Nicolais,¹⁶ and perhaps is related with the approximated values of U and T_∞ .

Equation (5) can be expressed in a simple form as

$$\left(\frac{1}{t_{0.5}}\right) = \frac{1}{k_{0.5}} \exp\left[-\frac{E_{0.5g}}{R(T - T_g)}\right] \exp\left[-\frac{E_{0.5m}}{R(T_m^\circ - T)}\right] \quad (6)$$

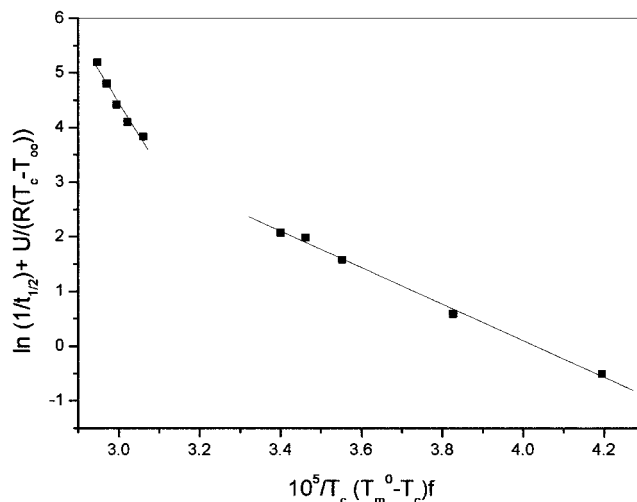


Figure 4 Half-time values fitted by the Arrhenius equation for the P(HB-co-HV) for eq. (5): ■, experimental; —, fitting.

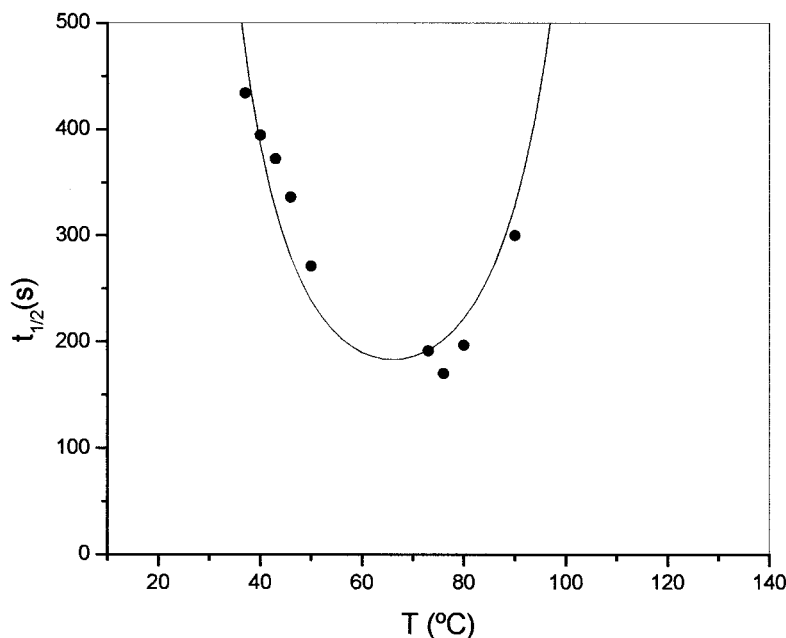


Figure 5 Half-time values fitted by the Arrhenius equation for the P(HB-co-HV) for eq. (7): ●, experimental; —, fitting.

Figure 5 shows the representation of eq. (6). Table II shows the $E_{0.5m}$ and $E_{0.5g}$ values. When the temperature of crystallization is close to the melting point, the activation energy is higher than the crystal-growth process ($E_{0.5m} > E_{0.5g}$). As a consequence, the crystallization process close to the melting point is more difficult than that when close to the glass-transition value.

When crystal formation is the control stage, the first crystal formed easily grows several millimeters in diameter. When hydroxybutyrate content increases, the spherulitic growth rates decreases.¹ As a consequence, the obtained activation energy for nucleation is higher ($E_{tm} = 5.76$ kJ/mol) than the activation energy of crystal growth ($E_{0.5m} = 4.28$ kJ/mol). The literature on this subject¹ reported that, compared to other semicrystalline thermoplastics, this kind of polymer has remarkably low nucleation density.

CONCLUSIONS

Isothermal crystallization of polyhydroxyalkanoates was performed. The Avrami equation was applied and the exponent was determined to be close to 2. The activation energy for the crystallization process was determined by fitting the experimental values of induction time and half-time. The activation energy of the nucleation ($E_{tm} = 5.76$ kJ/mol) is higher than the activation energy of the crystal growth ($E_{0.5m} = 4.28$ kJ/mol). The activation energy close to the melting point is higher than the activation energy close to the glass transition temperature. According to the changes observed of K_g values and the Avrami exponent. Taking into account the n values and the linearity of the

plot confirms the existence of heterogeneous nucleation and two-dimensional crystal growth model.

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