Primary and Secondary Crystallization Kinetic Analysis of Poly(Hexamethylene Succinate)

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Abstract: Isothermal crystallization kinetics of poly(hexamethylene succinate) (PHS) were investigated by using differential scanning calorimetry (DSC). Primary and secondary crystallization behaviors were described satisfactorily by a modified Avrami model. The obtained results suggest that primary crystallization under isothermal conditions involves three-dimensional spherulite growth with athermal nucleation, and secondary crystallization displays approximate one-dimensional crystal growth.

Keyword: Primary crystallization, secondary crystallization, poly(hexamethylene succinate), Avrami model.

1. INTRODUCTION

Biodegradable polymers have received great attention during the last few decades because of their potential applications in biomedical industries and as environmentally friendly materials. Nowadays, aliphatic polyesters derived from diols and dicarboxylic acids constitute a main group of biodegradable materials with applications as both commodity and speciality [1]. An understanding of the relationship between structure, morphology, and properties is a basic goal in order to be able to design new materials with enhanced physical and chemical properties. Like other semicrystalline polymers, the crystallization plays an important role in determining the properties of the final products dependent the morphology formed and the crystallinity. Therefore, the investigation of its crystallization kinetics is of significant importance both from theoretical and practical points of view.

Crystallization of polymers is usually divided into two processes, namely primary and secondary crystallization. During primary crystallization there arise and grow spherulitic crystalline formations which are characterized by a definite degree of organization, approaching more or less the ideal crystal structure. Secondary crystallization represents a further increase in crystallinity consisting in additional crystallization of uncrystallized material and/or in further development of the already formed crystalline structure [2]. In comparison with primary crystallization, however, the extent of secondary crystallization is usually relatively small, and in most cases it is quite difficult to determine the onset of secondary crystallization.

Poly(hexamethylene succinate) (PHS), one of aliphatic polyesters from the polycondenzation of succinic acid with 1,6-hexanediol, has received increasing attention because of its many interesting properties, including biodegradability, melt processability and compostability [3]. Although Puiggali *et al.,* [4] have studied the primary crystallization of PHS by means of DSC under isothermal and nonisothermal crystallization processes. However, it has not been investigated in all aspects of its crystallization behavior, especially secondary crystallization. Since secondary crystallization plays an important role in the later stage of the crystallization process, this present study aims to investigate the primary and secondary crystallization kinetics of PHS under isothermal and nonisothermal conditions. The mechanism of primary and secondary crystallization was also discussed in terms of the parameters.

2. EXPERIMENTAL

2.1. Sample and Characterization

Poly(hexamethylene succinate) (PHS) was synthesized from succinic acid using an excess of 1,6-hexanediol (molar ratio 1.05/1) by thermal polycondensation at 180 °C in a nitrogen atmosphere for 3~4 h and then in vacuum at 210 °C for 2~3 h. Stannous octoate was used as catalyst. The polymer was dissolved in chloroform and precipitated with ethanol several times, then dried at 25^{o}C in vacuum for 24 h [5].

^{1}H-NMR spectrum of PHS was recorded by a Bruker Avance 400MHz spectrometer. ^{1}H-NMR ($CDCl_3$): δ = 4.11 (t, $OC\boldsymbol{H}_2$, 4H), 2.64 (s, $COC\boldsymbol{H}_2$, 4H), 1.66 (m, $OCH_2C\boldsymbol{H}_2$, 4H) and 1.40 (m, $OCH_2CH_2C\boldsymbol{H}_2$, 4H).

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E-ISSN: 2409-5826/15

The molecular weight and its distribution of PHS were measured by gel permeation chromatography (GPC) on a Waters 1515 HPLC system using tetrahydrofuran as eluent at a flow rate of 1.0mL/ min at 25°C. Number and weight average molecular weights of 18700 and 32800 g/mol, respectively, were calculated using polystyrene standards.

Isothermal crystallization processes of PHS from the melt state were performed on a differential scanning calorimeter (Mettler Toledo DSC1) under a nitrogen purge. Samples (ca. 5 mg) were heated rapidly to 100 °C for 5 min to eliminate any thermal or mechanical history, and then cooled rapidly to the designated crystallization temperatures for isothermal crystallization. The exothermal curves of the heat flow as a function of time during the isothermal crystallization were recorded for later analysis.

3. THEORY AND METHOD

The Avrami equation is usually used for the description of crystallization kinetics in polymers on the basis of the isotherm of DSC [6]:

$$X_t = \frac{\int_0^t \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t}{\int_0^\infty \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t} = 1 - \exp\left(-kt^n\right) \qquad (1)$$

Where $\mathrm{d}H/\mathrm{d}t$ is the heat flow rate of a DSC exotherm, X_t is the crystallinity at the time t, k is the crystallization rate constant, and n is the Avrami exponent which contains information on nucleation and growth geometry.

As discussed previously, the crystallization process in polymers is not only based on the geometric growth of spherulites (primary crystallization), but also on a perfection process inside of them (secondary crystallization), which accounts for the deviation of linearity based on Avrami equation. Accordingly, several authors have proposed to modify the original Avrami theory to describe the secondary crystallization processes of PE, PEO, PEEK, PEA, PET, PBT, PTT, PA1212 [7-17].

Hillier [7] has proposed a model to calculate the overall crystallinity as a sum of two Avrami functions. The first one is a normal Avrami function while the second part is a first-order process with an Avrami form. That is, this model described the secondary crystallization on basis of the assumption of Avrami exponent is a constant and always equals 1. The mechanism of this secondary crystallization is usually interpreted in terms of an increase in lamellar thickness, perfection of the crystals, or formation of the secondary lamellar stacks, which obey a first-order low. Despite this model shows a better fit than the Avrami equation to some crystallization isotherms, the imposed invariable Avrami exponent seems quite arbitrary, since the actually fitted Avrami exponent in many cases is not integral but fractional.

Velisaris and Seferis [9] proposed a series-parallel Avrami model to consider secondary crystallization by describing the time dependence of crystallization degree as a linear combination of two Avrami expressions:

$$X_t = \omega_\mathrm{p}\left(1 - \exp\left(-k_\mathrm{p} t^{n_\mathrm{p}}\right)\right) + \omega_\mathrm{s}\left(1 - \exp\left(-k_\mathrm{s} t^{n_\mathrm{s}}\right)\right) \qquad (2)$$

Where the subscript p indicates the primary crystallization and the subscript s indicates the secondary crystallization; n_p and n_s are the Avrami exponents, k_p and k_s are the rate constants, and ω_p and ω_s are the mass fractions, in all cases for the primary and secondary crystallization, respectively. It is apparent that $\omega_\mathrm{p} + \omega_\mathrm{s} = 1$. This model can describe the whole crystallization process including secondary crystallization. However, the main limitation of this model is on the assumption that primary crystallization and the secondary one occur simultaneously.

Verhoyen *et al*. [13] took into account the defect of this model and extended it to be a new one:

$$X_t = \omega_\mathrm{p}\left(1 - \exp\left(-k_\mathrm{p}(t - t_{0,\mathrm{p}})^{n_\mathrm{p}}\right)\right) + \omega_\mathrm{s}\left(1 - \exp\left(-k_\mathrm{s}(t - t_{0,\mathrm{s}})^{n_\mathrm{s}}\right)\right) \qquad (3)$$

Because the secondary crystallization is certainly occurring well after the primary one, the induction time of the secondary crystallization, $t_{0,\mathrm{s}}$, is longer than that of the primary one, $t_{0,\mathrm{p}}$. But it is still difficult to obtain the kinetics parameters by fitting the experimental data with this model unless the values of $t_{0,\mathrm{p}}$ and $t_{0,\mathrm{s}}$ can be predetermined.

Generally, spherulites grow outward in the primary crystallization process. In most cased the secondary process starts when the specimen is completely filled with spherulites, thus it can be treated as a separated analogue from the primary process [15]. In the present study, it is assumed that the secondary crystallization process occurs once the primary process is completed and the secondary crystallization also can be described by Avrami model. As in the studies by Velisaris [9], Verhoyen [13], and Ye [15], the time dependences of crystallinity in the primary and secondary processes are given as:

$$X_{\mathrm{p},t} = \frac{\int_0^t \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t}{\int_0^{t_{\mathrm{p,end}}} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t} = 1-\exp\left(-k_{\mathrm{p}} t^{n_{\mathrm{p}}}\right) \qquad (4)$$

$$X_{\mathrm{s},t} = \frac{\int_{t_{\mathrm{p,end}}}^{t-t_{\mathrm{p,end}}} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t}{\int_{t_{\mathrm{p,end}}}^{\infty} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t} = 1-\exp\left(-k_{\mathrm{s}}\left(t-t_{\mathrm{p,end}}\right)^{n_{\mathrm{s}}}\right) \qquad (5)$$

Where $t_{\mathrm{p,end}}$ is the time at which the primary process finishes and the secondary one starts.

Furthermore, $X_{\mathrm{p,end}}$, the crystallinity at the end of the primary process, and X_{s}, the total crystallinity developed in the secondary one can be expressed as

$$X_{\mathrm{p,end}} = \frac{\int_0^{t_{\mathrm{p,end}}} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t}{\int_0^{\infty} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t} \qquad (6)$$

$$X_{\mathrm{s}} = \frac{\int_{t_{\mathrm{p,end}}}^{\infty} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t}{\int_0^{\infty} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t} \qquad (7)$$

Where $X_{\mathrm{p,end}} + X_{\mathrm{s}} = 1$. Then, combination with Equations 1, 6 and 7, Equations 4 and 5 are reduced to

$$X_{\mathrm{p},t} = X_{\mathrm{p,end}}\left(1-\exp\left(-k_{\mathrm{p}} t^{n_{\mathrm{p}}}\right)\right) \qquad (8)$$

$$X_{\mathrm{s},t} = X_{\mathrm{p,end}} + X_{\mathrm{s}}\left(1-\exp\left(-k_{\mathrm{s}}\left(t-t_{\mathrm{p,end}}\right)^{n_{\mathrm{s}}}\right)\right) \qquad (9)$$

This model can obtain the Avrami kinetic parameters of the primary and secondary crystallization processes of polymers from the crystallinity data. The model also gives the crystallinity X_{t} at actual crystallization time t developed from the two consecutive crystallization processes. However, the time at which the primary process finishes and the secondary one starts, $t_{\mathrm{p,end}}$ is needed to be predetermined. It is very important to identify the primary and the secondary processes. In the present paper, we define the critical time of $t_{\mathrm{p,end}}$ as the time at which the inflection point in the Avrami plot is located.

4. RESULTS AND DISCUSSION

Isothermal crystallization kinetics of PHS was investigated by differential scanning calorimetry (DSC) at different temperature intervals. Figure **1** shows the isothermal crystallization exotherms of PHS at 30, 35 and 40°C. As the isothermal crystallization temperature (T_{c}) increases, the exothermic peak becomes broader and shifts to a longer crystallization time. The development of the relative crystallinity X_{t} as a function of time is also shown in Figure **2**. It shows that with increasing crystallization temperature, the crystallization rate of PHS decreases and it requires a longer time to achieve the completion of crystallization. The conventional Avrami plot of $\ln[-\ln(1 - X_{\mathrm{t}})]$ versus $\ln t$ (from Equation 1) did not yield a single straight line, as shown in Figure **3**. Evidently, each curve has an inflection and this was attributed to the occurrence of secondary crystallization, which can

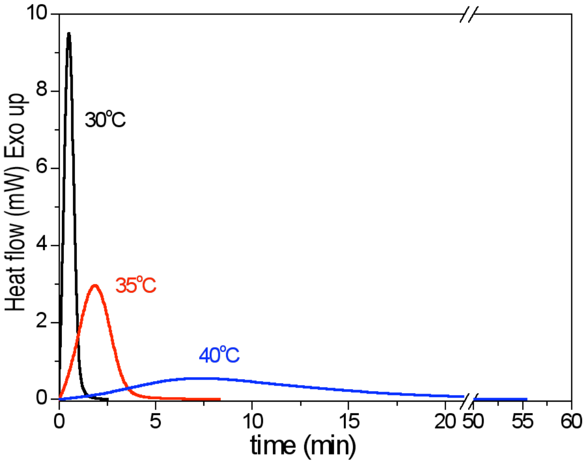

Figure 1: DSC exotherms of isothermal crystallization of PHS at indicated temperatures.

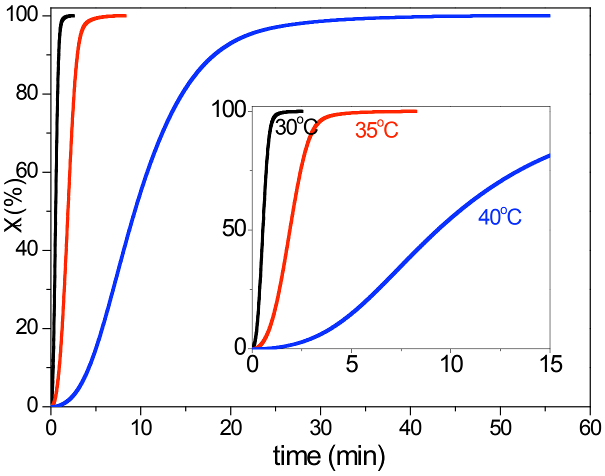

Figure 2: Relative degree of crystallinity with time of PHS for isothermal crystallization at different temperatures.

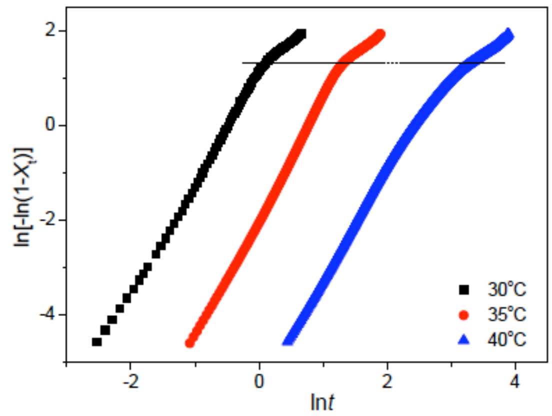

Figure 3: Avrami plots of ln[-ln(1-X_t)] versus ln*t* of PHS for isothermal crystallization at different temperatures.

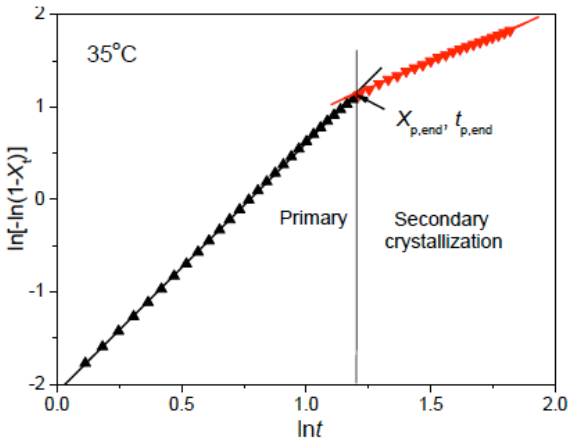

Figure 4: Determination of the critical point between primary and secondary crystallization at 35°C.

usually be identified by deviation of an Avrami plot at the later stage [18]. As shown in a representative Figure **4**, the primary and secondary crystallization processes occurred consecutively and were separated at a critical time of $t_{p,end}$, when a sudden change in the Avrami exponent from ca. 2.7 to 0.8 appeared. Accordingly, the critical crystallinity, $X_{p,end}$, which is also indicative for the completion of the primary crystallization, was directly obtained from the crystallinity curve at the corresponding critical time of $t_{p,end}$. The resulting values of $t_{p,end}$ and $X_{p,end}$ at different crystallization temperatures are listed in Table **1**. The results indicated that the onset time of PHS secondary crystallization increased with crystallization temperature, and the secondary processes started after the crystallization almost was completed (the total crystallinity was up to 95%).

Furthermore, the Avrami kinetics analyses of the primary crystallization by Equation 8 and the secondary crystallization by Equation 9 are shown in Figure **5** and Figure **6**, respectively. The Avrami parameters for

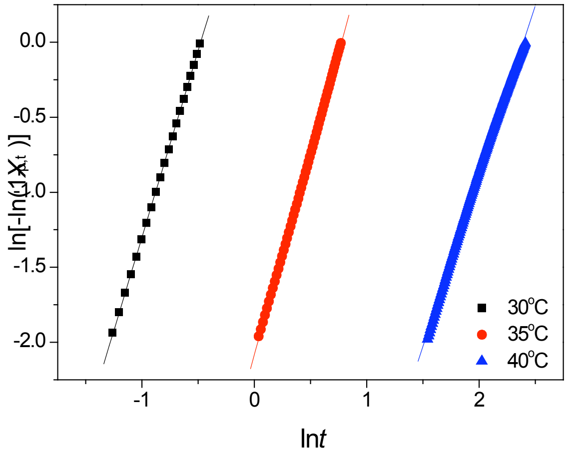

Figure 5: Avrami analysis for primary crystallization of PHS at different temperatures.

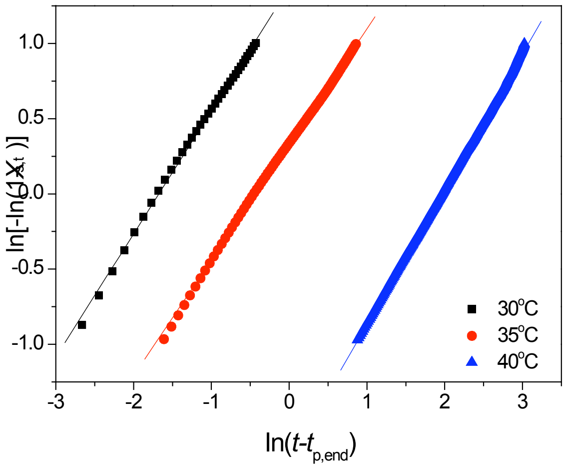

Figure 6: Avrami analysis for secondary crystallization of PHS at different temperatures.

Table 1: Avrami Parameters for Primary and Secondary Crystallization During Isothermal Crystallization of PHS

T_c(°C)	$t_{p,\ end}$(min)	$X_{p,\ end}$(%)	n_p	k_p	$t_{p,1/2}$(min)	n_s	k_s	$t_{s,1/2}$(min)
30	0.98	95	2.5	3.267	0.54	0.8	3.935	0.10
35	3.32	95	2.7	0.124	1.89	0.8	1.387	0.43
40	21.13	95	2.3	0.004	9.30	0.9	0.172	4.70

primary and secondary crystallization processes are listed in Table **1**. The values of the linear correlation coefficients R are larger than 0.998, which indicate that the experimental data fits the model very well. Good linear dependences were obtained with each curve in both processes. As shown in Table **1**, the crystallization rate constant *k* in the primary crystallization and the secondary crystallization decreases as the crystallization temperature increases. And more, the value of k_s in the secondary crystallization is higher than that of k_p in the primary crystallization at the identical crystallization temperature. More importantly, the Avrami exponent n_p values of the primary process were in the range between 2.3 and 2.7 with the average value being 2.5, which suggests a three-dimensional spherulite growth with predetermined (heterogeneous) nucleation since the n_p value is close to 3. The results are consistent with other studies on PHS crystallization [4, 5]. From Table **1** it can be seen that the n_s values of the secondary process were limited in a narrow range from 0.8 to 0.9, being close to 1.0. This is the typical characteristic of Avrami exponent of the secondary crystallization, which obeys a first-order law [7]. It could be interpreted in terms of the nature of the secondary crystallization including the thickening of lamellae, perfection of the crystals, or growth of defective crystallites [18]. This may be an interesting topic for the further study of the nature of the secondary crystallization in polymer crystallization. According to the Avrami theory, the changing of Avrami exponent from about 3 to about 1 indicates that the crystallization mechanism shifts from three-dimensional spherulite growth to one-dimensional crystal growth, which grows in a lower dimension between the fibrillar structure during secondary crystallization because of impingement and confinement of spherulite [15].

CONCLUSIONS

Isothermal melt-crystallization kinetics of PHS was investigated by DSC. The primary and secondary crystallization were successfully described by a modified Avrami model. The critical crystallinity of the onset secondary crystallization of PHS is determined almost at 95%. The primary crystallization is found to be three-dimensional spherulite growth with athermal nucleation, and the secondary crystallization is close one-dimensional crystal growth.

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Received on 25-07-2015 Accepted on 30-09-2015 Published on 31-12-2015

DOI: http://dx.doi.org/10.15377/2409-5826.2015.02.02.4