

Isothermal Crystallization Kinetics of Poly(butylene terephthalate-co-sebacate) Copolymer

Zuoxiang Zeng,¹ Hailing Zhang,¹ Weilan Xue,¹ Wanyu Zhu,² Xiaoling Xiao,¹ Yu Sun,¹ Zhelong Li²

¹Department of Chemical Engineering, Institute of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

²Shanghai Tianyang Hotmelt Adhesives Co., Ltd, 201802 Shanghai, People's Republic of China

Received 3 August 2010; accepted 22 November 2010

DOI 10.1002/app.33814

Published online 23 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Poly(butylene terephthalate) (PBT) and poly(butylene terephthalate-co-sebacate) (PBTS) copolymers containing 5 mol % and 10 mol % sebacate components ($M_n = 12,700$ – $14,600$) were synthesized by polycondensation. The isothermal crystallization kinetics and melting behaviors after isothermal crystallization of the polymers were investigated by differential scanning calorimetry (DSC). The equilibrium melting temperatures of the polymers were determined by Hoffman-Weeks equation. Analysis of the crystallization kinetic data using the Avrami equation showed that the introduction

of sebacate enhanced the crystallization of PBT in PBTS. And the Avrami exponent n varies in the range of 2.16–3.68, indicating that the isothermal crystallization follows two- and three-dimensional growth mechanism. The isothermal crystallization activation energies of the polymers were also calculated by the Arrhenius equation. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 735–742, 2011

Key words: copolymerization; crystallization; DSC; Avrami equation; activation energy

INTRODUCTION

Poly(butylene terephthalate) (PBT) has been highly researched for many years both in theoretical and actual field, which is a thermoplastic polyester widely used for its good mechanical and thermal properties. Many articles provided a thorough analysis of the crystallization process of PBT.^{1–5}

The physicochemical and mechanical properties of polyesters depend strongly on their morphologies and crystallization structures established during the solidification process. Therefore, it is very important to investigate the crystallization kinetics. Lee et al.⁶ studied the nonisothermal behaviors of poly(ethylene-co-trimethylene terephthalate) (PETT) copolymers. Wu and Lin⁷ reported the isothermal crystallization behaviors and morphologies of PETT copolymers. Chang et al.⁸ revealed that the introduction of 2 mol % isophthalate into PET caused a change of the crystal growth process from a two-dimensional to a three-dimensional spherulitic growth. The addition of more isophthalate up to 12 mol % induced a change from a three-dimensional to a two-dimensional crystal growth.

The low-molecular-weight ($M_n = 1200$ – 3700) poly(butylene terephthalate-co-sebacate) (PBTS) was synthesized by Ueberreiter et al. and its melting behavior was characterized.⁹ Marrs et al.^{10–13} reported the melting and crystallization behaviors of PBTS with the molecular weight (M_n) of 25,350–36,310. It is needed to point out that Marrs et al. found the crystallization rate of PBTS decreased as sebacate content increased. On the other hand, the chain of poly(butylene sebacate) (PBS) is more flexible than that of PBT, and the crystallization rate of PBS is larger than that of PBT.^{11,14–16} Generally, the addition of the minor segment with high crystallization rate into a polymer backbones with low crystallization rate results in an enhanced crystallization of the polymer segment in the copolymer.^{17,18} Moreover, it is well-known that the introduction of the longer chain, i.e., more flexible structure, enhances crystallization.¹⁹ Therefore, it is worth further discussing how the isothermal crystallization kinetics of PBTS is affected by the addition of sebacate into PBT.

In this article, the pure PBT and PBTS containing 5 mol % and 10 mol % sebacate components ($M_n = 12,700$ – $14,600$) were synthesized by direct esterification and subsequent polycondensation. The effects of the copolymers composition on their isothermal crystallization kinetics and the melting behaviors were investigated by differential scanning calorimetry (DSC). The Avrami equation was employed to investigate the isothermal crystallization

Correspondence to: ZX Zeng (zengzx@ecust.edu.cn).

process. The equilibrium melting temperature after isothermal crystallization of the productions was also calculated according to the Hoffman-Weeks theory.

EXPERIMENTAL

Materials

Terephthalic acid (TPA) was purchased from Sinopec Yangzi Petrochemical Company. Chemically pure-grade 1, 4-butanediol (BDO) was purchased from Shanghai Chemistry Reagent Company (China). Sebacic acid (SA) was purchased from Yatai Chemical Co., Ltd (Wuxi, China). The mass fraction purity of these three materials were all better than 99% and used without further purification. Tetrabutoxytitanium ($\text{Ti}(\text{OBU})_4$) used as the catalyst in the whole process, was also purchased from Shanghai Chemistry Reagent Company (China).

Preparation of copolymers

PBTS used in this study was synthesized by a two-step process including esterification and subsequent polycondensation reaction from TPA, SA and BDO in the presence of $\text{Ti}(\text{OBU})_4$ as a catalyst. The feed molar ratio of TPA to SA was 100 : 0, 95 : 5, 90 : 10, assigned as S0, S5, and S10, respectively. The amount of BDO was twice the total acid. The detailed preparation of these polymers was described similarly in elsewhere.²⁰ Before any measurements, these samples were dried under vacuum at 80°C for 24 h.

Characterization

Gel permeation chromatography

The average molecular weights (M_n , M_w) of the samples were determined by GPC (Waters 1515, USA) with refractometer 2414 as a detector. The measurements were performed at 40°C on polymeric solutions in *m*-cresol. Calibration was performed using polystyrene standards with narrow molecular weight distribution. The average molecular weights of these polymers, shown in Table I.

Differential scanning calorimetry

Isothermal crystallization kinetics and the glass transition temperature (T_g) were measured on a Perkin-Elmer Pyris-1 DSC (America) equipped with a liquid nitrogen cooling accessory. Calibration for temperature scale was carried out using a pure indium standard, with accuracy of temperature control being $\pm 0.01^\circ\text{C}$. The sample weights in the DSC were in the range of 3–5 mg.

TABLE I
The Molecular Weight and Molecular Weight Distribution for S0, S5, and S10

Polymer	TPA (mol%)	SA (mol%)	BDO (mol/ (TPA+SA)mol)	M_n	M_w/M_n
S0	100	0	2	13,200	1.60
S5	95	5	2	14,600	1.74
S10	90	10	2	12,700	1.64

Isothermal crystallization and melting process

The samples were first heated from room temperature to 250°C, which was higher 20–30°C than melting temperature at a rate of 80°C/min, and kept at this temperature for 10 min in order to erase the prior thermal history. Then they were cooled to the designated crystallization temperatures (T_c s) at $-100^\circ\text{C}/\text{min}$, which were four different temperatures in the range of 170–200°C for each sample, and held at this temperature for 30 min until crystallization was complete. Finally, the samples were heated to 250°C from T_c at 20°C/min for determining the equilibrium melting temperature.

RESULTS AND DISCUSSION

Melting behaviors and equilibrium melting temperature

Figure 1 shows the DSC heating scans for S0, S5, and S10 after isothermal crystallization at various T_c s and then heating directly from T_c to 250°C at a heating rate of 20°C/min, respectively. From Figure 1, it can be seen that there are two melting endotherms for all samples. The first melting peak [referred as T_m (I)] shifts to a higher temperature with increasing T_c , while the second melting peak [referred as T_m (II)] is independent on the T_c . And the profile of the first peak becomes smaller but the second peak enlarges with increasing T_c . The double melting behavior of these polymers can be attributed to recrystallization phenomena during the heating process.^{2,21} Thus, the first peak is due to the melting of crystals grown at T_c , and the T_m (I) is defined as melting point (T_m) and used for the determination of equilibrium melting temperature T_m^0 . With an increase of T_c , the crystals become thickened and more perfect, so T_m (I) is enhanced. The second melting peak originates from the melting of crystallite formed by melting and recrystallization during the DSC heating scans. Table II summarizes the endothermic peak temperatures and enthalpies of all endotherms for these polymers crystallized at various T_c s.

T_m^0 is an important parameter characteristic of the crystal of the linear polymer. It can be determined by the plot of the experimental $T_m - T_c$ data using the Hoffman-Weeks equation²²:

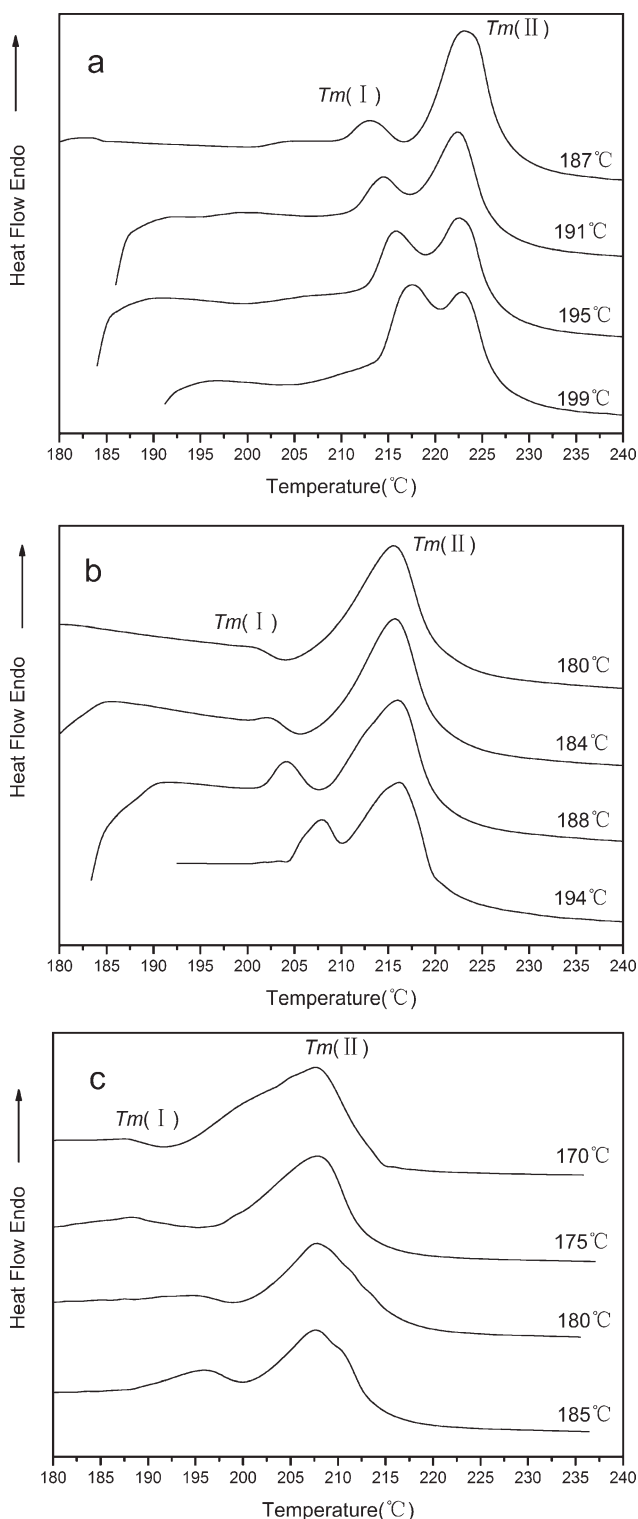


Figure 1 The DSC heating curves of samples after the isothermal crystallization at a heating rate of 10°C/min: (a) S0, (b) S5, and (c) S10.

$$T_m = \frac{T_c}{\gamma} + T_m^0 \left[1 - \frac{1}{\gamma} \right] \quad (1)$$

where γ is a factor depending on the final lamellar thickness, which indicates the ratio of the thickness

of the mature crystal L_c to that of the initial one L_c^* , i.e., $\gamma = L_c/L_c^*$. γ is supposed to be close to 0.5.

Based on eq. (1), T_m^0 for S0, S5, and S10 can be determined by T_m as a function of the T_c and extrapolating the plot to the $T_m = T_c$ line, shown in Figure 2. As predicted by the equation, the T_m values exhibit a good linear relationship with the T_c s within the range of 170–200°C. The correlation coefficients r^2 for S0, S5, and S10 are 0.997, 0.997, and 0.980, respectively.

The T_m^0 s are 229.2, 223.1 and 213.8°C for S0, S5, and S10, respectively. The results are listed in Table II. A T_m^0 of 229.2°C for PBT is a little lower than the values obtained by Marrs and coworkers (236°C) ($M_n = 25,000$ – $36,000$),¹¹ Runt et al. (236°C) ($M_n = 43,000$)²³ and Chisholm et al. (238°C) ($M_n = 32,000$ – $36,000$).³ From Table II, it can be seen that the values of T_m^0 decrease with increasing content of sebacate, which is attributed to the change of molecular structure of samples by introduction of sebacate.

Isothermal crystallization kinetics analysis based on Avrami equation

Figure 3 shows the DSC curves of S0, S5, and S10 crystallized isothermally at various crystallization temperatures. From Figure 3, it can be seen that longer time is taken for the samples crystallized at a higher T_c , i.e., the crystallization rate decreases with increasing T_c . Meanwhile, the crystallization peaks shift to higher temperatures with the addition of sebacate, which means that the crystallization ability of copolymers increases with increasing sebacate content.

The relative crystallinity, $X(t)$, is defined as the ratio of crystallinity developed at time t to crystallinity developed at time $t \rightarrow \infty$. And $t = t_i - t_0$, where t_i is the time elapsed from obtaining temperature control at T_c , and t_0 , the time required for the onset of crystallization to be observed. $X(t)$ can be determined by the following equation:

$$X(t) = \Delta H_t / \Delta H_0 \quad (2)$$

where ΔH_t is the total heat evolved at time t , and ΔH_0 is the total heat evolved as time approaches infinity. Figure 4 shows the development of relative crystallinity with time for S0, S5, and S10 at four different T_c s. All four curves tend to be similar S-shape, which indicates that crystallization procedure is similar at each crystallization temperature.

The isothermal crystallization process is described by Avrami equation as follows:

$$X(t) = 1 - \exp(-Kt^n) \quad (3)$$

$$\log\{-\ln[1 - X(t)]\} = n \log t + \log K \quad (4)$$

where n is the Avrami exponent which is associated with nucleation mechanisms and the dimensions of

TABLE II
Melting Temperatures and Enthalpies of All Endotherms for S0, S5 and S10
Crystallized at Various T_c 's

Polymer	T_c (°C)	T_m (I)(or T_m) (°C)	T_m (II)(°C)	ΔH (I)(J/g)	ΔH (II)(J/g)	T_m^0 (°C)
S0	187	212.5	223.4	2.67	27.48	229.2
	191	214.4	222.1	3.03	8.24	
	195	215.7	223.0	3.37	5.27	
	199	217.3	223.2	5.60	2.49	
S5	180	200.7	215.7	0.55	37.64	223.1
	184	202.2	216.0	1.07	32.52	
	188	204.7	216.3	3.02	14.28	
	194	207.9	216.5	5.44	2.79	
S10	170	187.4	207.8	0.21	27.17	213.8
	175	188.7	208.0	2.35	21.39	
	180	193.7	207.5	3.31	11.64	
	185	196.0	207.4	7.40	5.79	

the growth during the crystallization; K is the isothermal crystallization rate parameter.

Figure 5 shows the plots of $\log\{-\ln[1-X(t)]\}$ versus $\log t$ for S0, S5, and S10. From Figure 5, a linear relationship is observed in each plot of $\log\{-\ln[1-X(t)]\}$ versus $\log t$. Linearity was obtained up to about $X(t) = 0.8, 0.9, 0.9$ for S0, S5, and S10 at each four different T_c 's, respectively, indicating that the Avrami equation can properly describe the isothermal crystallization behaviors of these samples. The Avrami exponent n and K were obtained from the slope and intercept, respectively. Each curve shows an initial linear portion, and then tends to level off. This is mainly attributed to the secondary crystallization, which is caused by the spherulite impingement. The values of n and K are listed in Table III. The Avrami exponent n varies from 2.16 to 3.68, indicating that there is an average contribution of simultaneous occurrence of various types of nucleation and growth of crystallization. The crystallization mode of these polymers may follow two- and three-dimensional and nucleation-controlled crystal growth with thermal nucleation mechanism. Table III also shows the crystallization rate parameter K decreases with increasing T_c for each sample, indicating the higher the crystallization temperature, the slower the homogeneous nucleation become. In addition, it is worth noticing that K increases with increasing sebacate content under the same supercooling degree. For example, at the same cooling rate of 43°C , the values of K for S0, S5, and S10 are 2.91, 6.22, and 13.48, respectively. That means the more flexible ability of PBS segment which could act as a plasticizer may increase the crystallization rate of PBT in PBTS. In the similar study, when a long aliphatic chain is introduced into a polymer, enhanced crystallization rates of the copolymer have been observed.^{17,18} The results are contrary to what Marrs et al. found.¹¹ Generally, sebacate plays two roles in the crystallization of the matrix: (1) it acts as a longer chain or

more flexible structure to facilitate crystallization, and (2) as a third component which disturbs the regularity of the copolymer molecular chain to retard crystallization. Which role of sebacate is dominant depends on both the sebacate content and the crystallization behavior of the matrix itself. Here, it may be concluded that sebacate can enhance crystallinity of PBT when the sebacate content is small and molecular weight of PBTS is lower ($M_n = 10,000\text{--}15,000$).

Except for the crystallization rate parameter K to characterize the crystallization rate, the crystallization half-time $t_{1/2}$ (min) is another important parameter. The $t_{1/2}$ is defined as the time at which the crystallinity degree is 50% of the maximum achievable crystallinity. It can be calculated from the following equation:

$$t_{1/2} = \left(\frac{\ln 2}{K}\right)^{1/n} \quad (5)$$

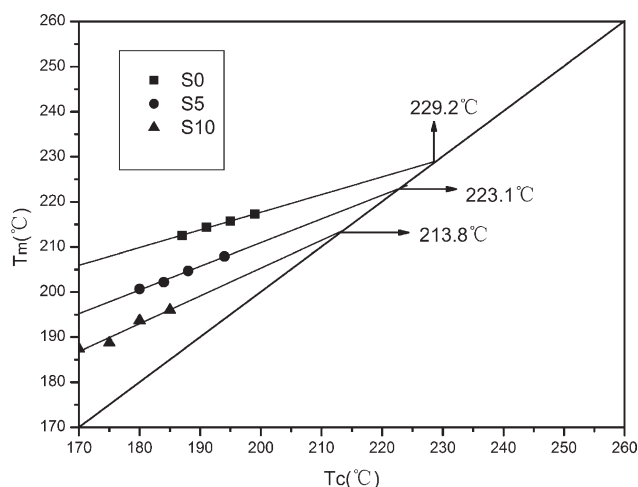


Figure 2 The change of the melting temperature taken as a function of the crystallization temperature for S0, S5, and S10.

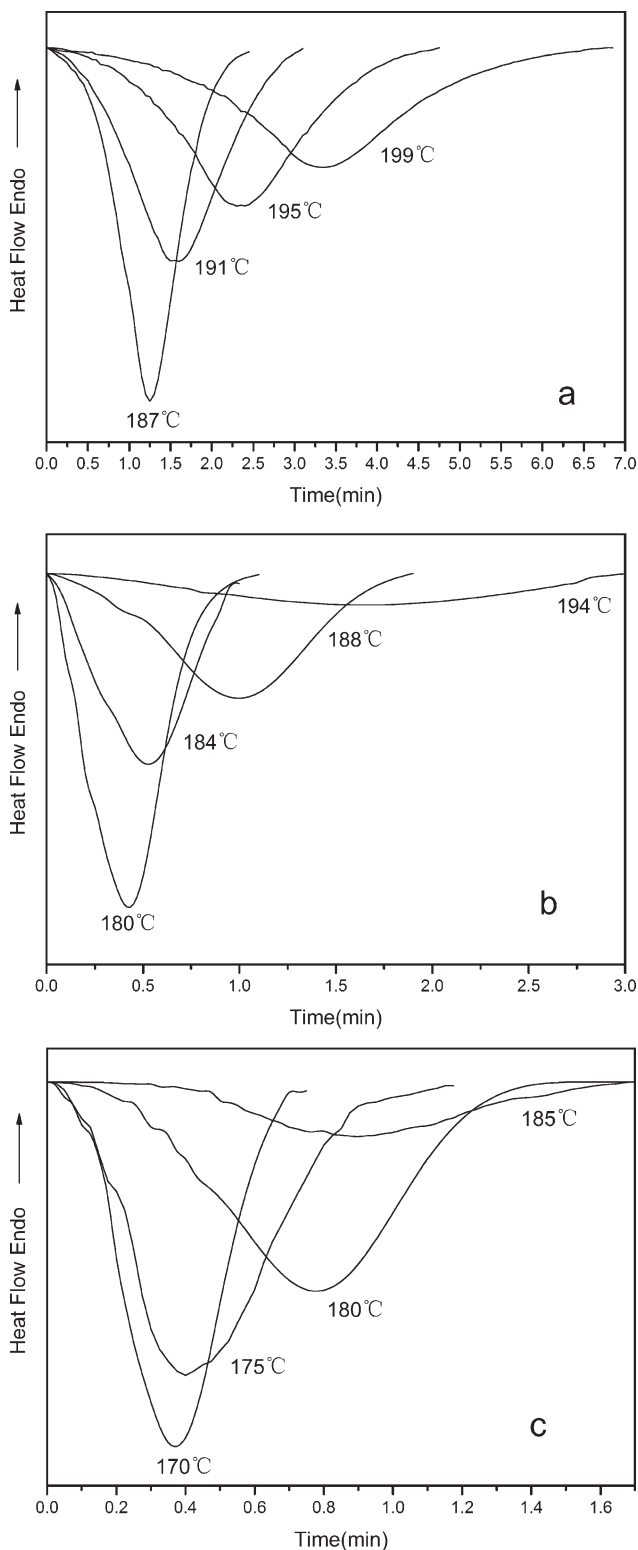


Figure 3 The DSC curves of samples versus time during the isothermal crystallization at various crystallization temperatures: (a) S0, (b) S5, and (c) S10.

The calculated values of $t_{1/2}$ for S0, S5, and S10 are listed in Table III. From Table III, $t_{1/2}$ decreases with increasing T_c for each sample

and decreases with an increase of sebacate content at the same cooling rate for these three samples.

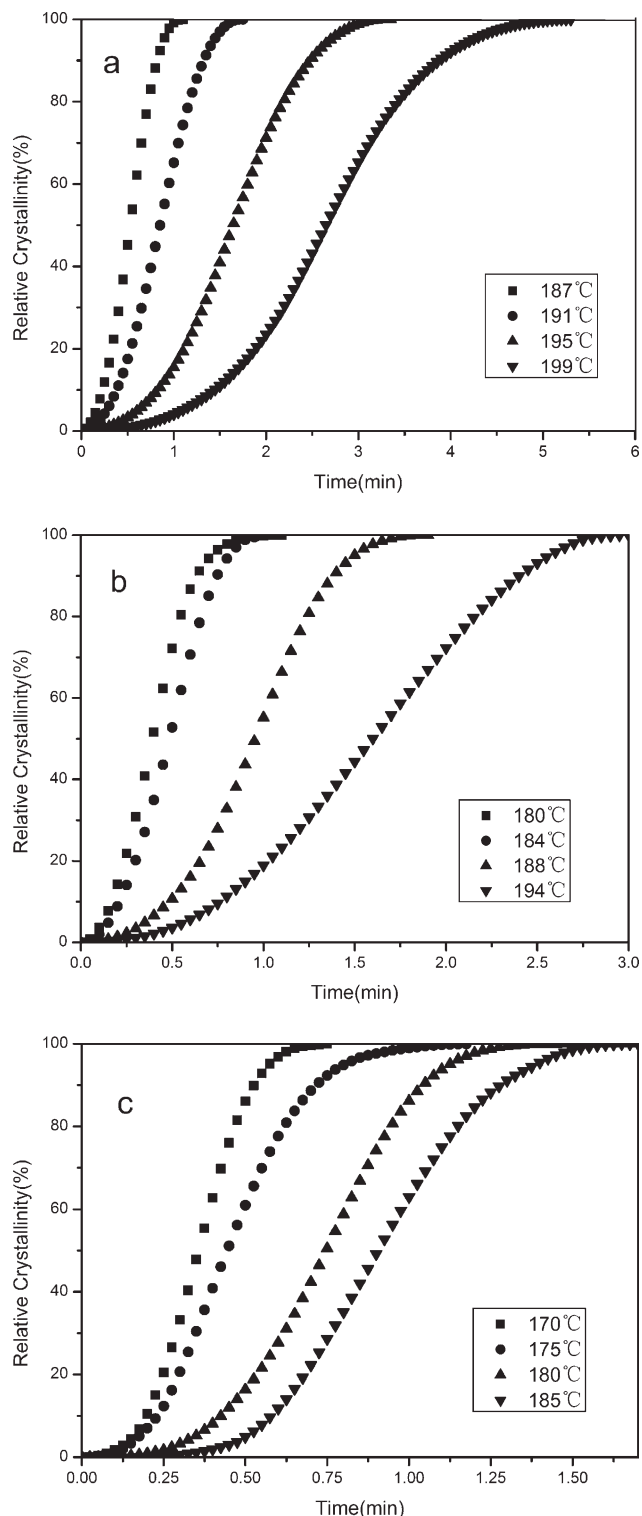


Figure 4 The development of relative crystallinity with time at four different crystallization temperatures: (a) S0, (b) S5, and (c) S10.

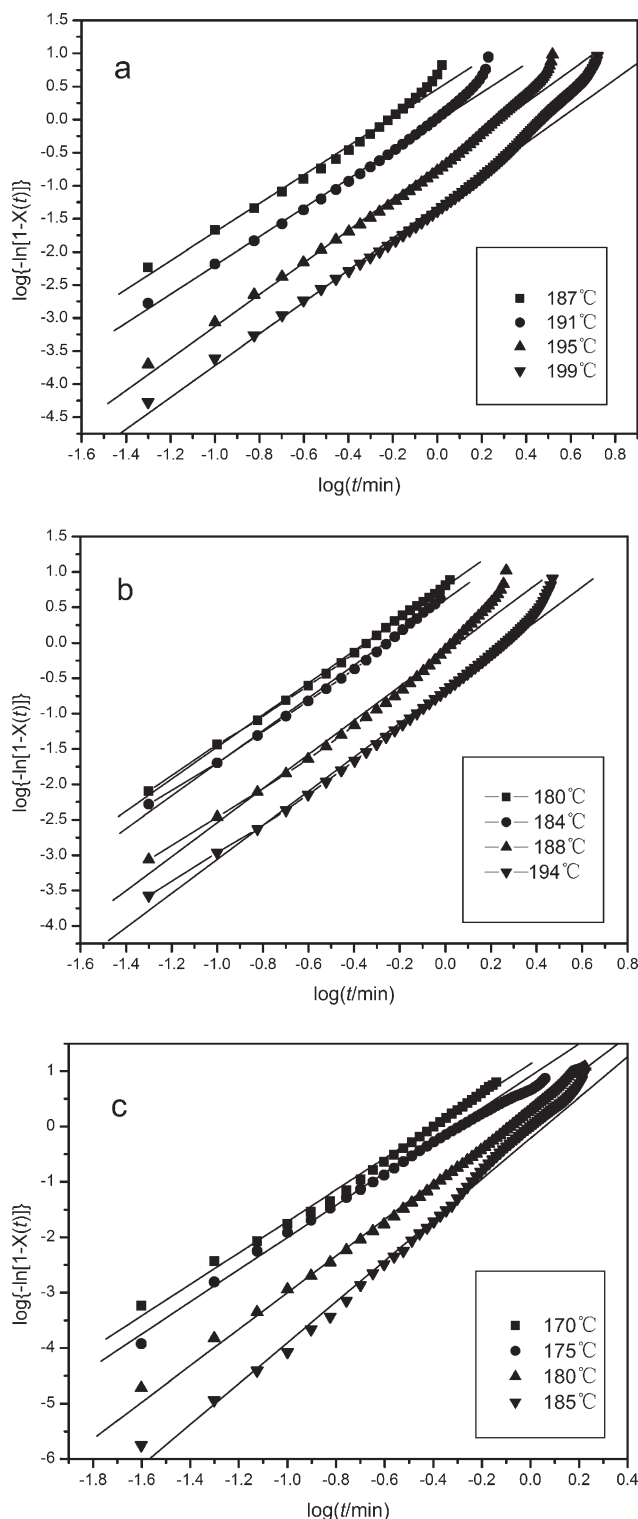


Figure 5 Avrami plots of $\log\{-\ln[1-X(t)]\}$ versus $\log t$ at four different crystallization temperatures: (a) S0, (b) S5, and (c) S10.

Crystallization activation energy (ΔE)

On the assumption that the crystallization process of polymers is thermally activated, the following Arrhenius equation can describe the crystallization rate parameter K :²⁴

TABLE III
Collection of Kinetic Parameters of S0, S5, and S10 for Isothermal Crystallization

Polymer	T_c (°C)	ΔT (°C)	n	K (min^{-n})	$t_{1/2}$ (min)	G (min^{-1})
S0	187	42	2.16	2.91	0.52	1.94
	191	38	2.18	0.94	0.87	1.15
	195	34	2.42	0.20	1.69	0.59
	199	30	2.41	0.05	3.02	0.33
S5	180	43	2.26	6.22	0.38	2.63
	184	39	2.31	4.04	0.46	2.15
	188	35	2.40	0.73	0.98	1.02
	194	29	2.40	0.22	1.60	0.62
S10	170	43	2.84	13.48	0.35	2.85
	175	38	2.91	8.12	0.43	2.33
	180	33	3.30	2.02	0.72	1.38
	185	28	3.68	0.61	1.04	0.96

$$K^{1/n} = k_0 \exp\left(\frac{-\Delta E}{RT_c}\right) \quad (6)$$

$$\frac{1}{n} \ln K = \ln k_0 - \frac{\Delta E}{RT_c} \quad (7)$$

where ΔE is the crystallization activation energy, R is the gas constant and k_0 is the temperature-independent pre-exponential factor. Figure 6 shows the plots of $(1/n)\ln K$ versus $1/T_c$ for S0, S5, and S10. From Figure 6, it is found $(1/n)\ln K$ versus $1/T_c$ is linear and the slope is used to calculate the ΔE . The values of ΔE are -266.29 , -191.67 , and -123.32 kJ/mol for S0, S5, and S10, respectively. As the polymers have to release energy while transforming from the melt to the crystalline state, the value of ΔE is negative.²⁵

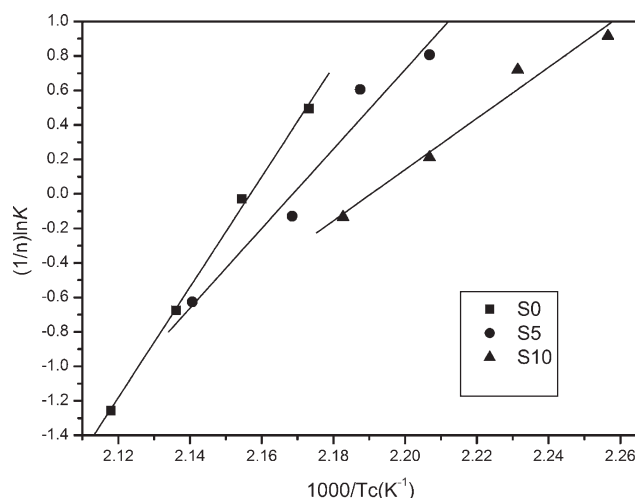


Figure 6 The plots of the Avrami parameters $(1/n)\ln K$ versus $1/T_c$ for the acquisition of the isothermal crystallization activation energy for S0, S5, and S10.

Spherulite growth analysis

The classic Lauritzen-Hoffmann equation is adopted to describe the spherulite growth rate in the isothermal crystallization process of the homopolymer and copolymers for higher degrees of supercooling.²⁶ The overall crystallization rate G , is defined as the reciprocal of $t_{1/2}$, i.e. $G = \tau_{1/2} = (t_{1/2})^{-1}$, should not be interpreted as simple spherulitic radial growth because of the combination of nucleation and growth phenomena. That is:

$$G = G_0 \exp\left[-\frac{U^*}{R(T_c - T_\infty)}\right] \exp\left[-\frac{K_g}{fT_c\Delta T}\right] \quad (8)$$

where G_0 is a pre-exponential factor, U^* is the transport activation energy, which characterizes molecular diffusion across the interfacial boundary between melt and crystals. T_∞ is the hypothetical temperature below which all viscous flow ceases, K_g is a nucleation parameter, ΔT is the degree of supercooling ($\Delta T = T_m^0 - T_g$) and $f = 2T_c / T_m^0 + T_c$ is a correction factor accounting for the variation in the enthalpy of fusion of the perfect crystal. The double logarithmic relation of above equation is presented:

$$\ln G + \frac{U^*}{R(T_c - T_\infty)} = \ln G_0 - \frac{K_g}{fT_c\Delta T} \quad (9)$$

Using the half-time of crystallization $t_{1/2}$ instead of the growth rate G ,²⁷ the above equation can be written as follows:

$$\ln(1/t_{1/2}) + \frac{U^*}{R(T_c - T_\infty)} = \ln G_0 - \frac{K_g}{fT_c\Delta T} \quad (10)$$

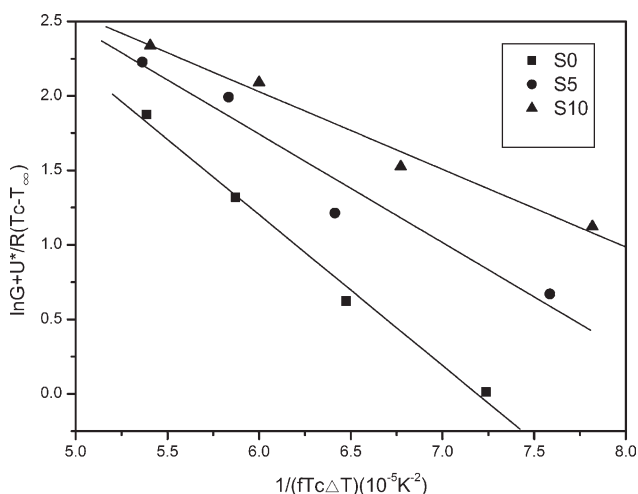


Figure 7 The plots of $\ln G + U^*/R(T_c - T_\infty)$ versus $1/fT_c\Delta T$ for S0, S5, and S10.

TABLE IV
The Crystallization Parameters of S0, S5, and S10 Samples

Copolymer	T_m^0 (K)	T_g (K)	$T_m^0 - T_g$ (K)	K_g (K^2)	$\ln G_0$
S0	502.35K	341.25K	161.1	101190	7.2739
S5	496.25K	340.05K	156.2	72833	6.1137
S10	486.95K	333.15K	153.8	52170	5.1588

Hoffman et al.²⁸ found $U^* = 1500$ cal/mol by fitting the crystallization rate data for various polymers and $T_\infty = (T_g - 30)$ K.

The plots of $\ln G + U^*/R(T_c - T_\infty)$ versus $1/fT_c\Delta T$ for the homopolymer and copolymers yield good straight lines in Figure 7, indicating that the L-H equation can describe the crystallization process of the homopolymer and copolymers. The values of K_g and G_0 were determined from the slope and intercept of the plots, and listed in Table IV. It is noticed that for all different conditions, S0 presents higher K_g value when compares to other copolymers, meaning a higher barrier for nucleation resulting to the lower crystallization rate mentioned before.

CONCLUSIONS

The isothermal crystallization kinetics of homopolymer PBT and its copolymers PBTS with 5 mol % and 10 mol % content of sebacate were examined using DSC at supercooling degree ranging from 30°C to 43°C. The melting equilibrium temperatures (T_m^0) for the three samples were 229.2, 223.1, and 213.8°C determined by Hoffman-Weeks method, respectively. The Avrami equation can well describe the isotherm crystallization. The values of n are around 2.1 ~ 2.4 for PBT and are close to 3 for other two copolymers, indicating that the crystallization mode of these polymers may follow two- and three-dimensional and nucleation-controlled crystal growth with thermal nucleation mechanism. The introduction of sebacate into PBT enhances crystallization of PBT in PBTS under the same supercooling degree. The isothermal crystallization activation energies of the homopolymer and copolymers were determined to be -266.29, -191.67, and -123.32 kJ/mol using the Arrhenius equation, respectively.

References

- Pratt, C. F.; Hobbs, S. Y. *Polymer* 1976, 17, 12.
- Righetti, M. C. *Macromol Chem Phys* 1997, 198, 363.
- Chisholm, B. J.; Zimmer, J. G. *J Appl Polym Sci* 2000, 76, 1296.
- Pillin, I.; Pimbert, S.; Feller, J. F.; Levesque, G. *Polym Eng Sci* 2001, 41, 178.
- Dilorenzo, M. L.; Righetti, M. C. *Polym Eng Sci* 2003, 43, 1885.
- Lee, J W.; Lee, S. W.; Lee, B.; Ree, M. *Macromol Chem Phys* 2001, 202, 3072.

7. Wu, T. M.; Lin, Y. W. *J Polym Sci Part B: Polym Phys* 2004, 42, 4255.
8. Wu, T. M.; Chang, C. C.; Yu, T. L. *J Polym Sci Part B: Polym Phys* 2000, 38, 2515.
9. Ueberreiter, K.; Steiner, N. *Makromol chem* 1964, 74, 158.
10. Marrs, W.; Peters, R. H.; Still, R. H. *J Appl Polym Sci* 1979, 23, 1063.
11. Marrs, W.; Peters, R. H.; Still, R. H. *J Appl Polym Sci* 1979, 23, 1077.
12. Marrs, W.; Peters, R. H.; Still, R. H. *J Appl Polym Sci* 1979, 23, 1095.
13. Marrs, W.; Peters, R. H.; Still, R. H. *J Appl Polym Sci* 1979, 23, 1105.
14. Papageorgiou, G. Z.; Bikiaris, D. N.; Achilias, D. S.; Nanaki, S.; Karagiannidis, N. *J Polym Sci Part B: Polym Phys* 2010, 48, 672.
15. Mulla, A.; Mathew, J.; Shanks, R. *J Polym Sci Part B: Polym Phys* 2007, 45, 1344.
16. Chuah, H. *Polym Eng Sci* 2001, 41, 308.
17. Papageorgiou, G. Z.; Nanaki, S. G.; Bikiaris, D. N. *Polym Degrad Stabil* 2009, 95, 627.
18. Zou, H. T.; Li, G.; Jiang, J. M.; Yang, S. L. *Polym Eng Sci* 2008, 48, 511.
19. Golike, R. C.; Cobbs, W. H., Jr. *J Polym Sci Part B: Polym Phys* 1961, 54, 227.
20. Zhu Kui; Zhu Weipu; Gu Yanbo; Shen Zhiqian; Chen Wei; Zhu Guixiang. *Chinese J Chem* 2007, 25, 1581.
21. Pratt, C. F.; Hobbs, S. Y. *Polymer* 1975, 16, 462.
22. Hoffman, J.; Weeks, J. *J Res Natl Bur Stand A66* 1962, 13, 13.
23. Runt, J.; Miley, D. M.; Zhang, X.; Gallagher, K. P.; McFeaters, K.; Fishburn, J. *Macromolecules* 1992, 25, 1929.
24. Cebe, P.; Hong, S. *Polymer* 1986, 27, 1183.
25. Neil, L. A.; Cecil, G. A.; Tony, M. *J Appl Polym Sci* 2008, 110, 1043.
26. Lauritzen, J. I.; Hoffman, J. D. *J Appl Phys* 1973, 44, 4340.
27. Chan, T. W.; Isayev, A. I. *Polym Eng Sci* 1994, 34, 461.
28. Hoffman, J. D. *Polymer* 1983, 24, 3.