Investigation on Isothermal Crystallization, Melting Behaviors, and Spherulitic Morphologies of Multiblock Copolymers Containing Poly(butylene succinate) and Poly(1,2-propylene succinate)

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ABSTRACT: In this article, isothermal crystallization, melting behaviors, and spherulitic morphologies of high-impact multiblock copolymers, comprising of PBS as hard segment and poly(1,2-propylene succinate) (PPSu) as soft segment with hexamethylene diisocyanate as a chain extender, were investigated. The results from differential scanning calorimetry (DSC) suggest that the two segments of multiblock copolymers are miscible in amorphous region. The crystallization kinetics were analyzed by the Avrami equation. The effect of PBS segment length as well as the introduction of PPSu segment on the crystallization kinetics and melting behaviors of block copolymers was studied. Both crystallization rate (G) and spherulitic growth rate (g) are markedly increased with the increase of PBS segment length or decreased with the incorporation of PPSu segment. All the multiblock copolymers show the multiple melting behaviors, whose position and area depend on PBS segment length and the presence of PPSu segment. The melting peaks shift to higher temperature region with increasing PBS segment length. Spherulitic morphologies of the multiblock copolymers after being isothermally crystallized were examined by polarized optical microscopy. It is the first time to investigate the effect of one segment length on crystallization behavior of block copolymers based on a fixed weight ratio systematically. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2124–2134, 2011

Key words: melting behaviors; crystallization; block copolymers; poly(butylene succinate); poly(1,2-propylene succinate)

INTRODUCTION

Biodegradable aliphatic polyesters have been actively studied as an alternative to some traditional nondegradable polymers. PBS is one of the most promising members in the family of aliphatic polyesters because of its combined mechanical properties and processability. However, as compared with conventional nondegradable polymers, its higher cost and poorer mechanical properties, especially the unsatisfactory impact strength, restrict its widespread application. To improve the physical properties, reduce the production cost so as to extend its application, various random copolymers based on PBS have been synthesized.[1–3] Unfortunately, melting point (T_m) of these copolymers decreased markedly.[1–3] In our previous work,[4] multiblock copolymers were synthesized by chain-extension of crystallizable PBS and amorphous PPSu with hexamethylene diisocyanate (HDI). The multiblock copolymers possess good thermal and mechanical properties (impact strength was increased by 18-fold as compared with PBS).[4]
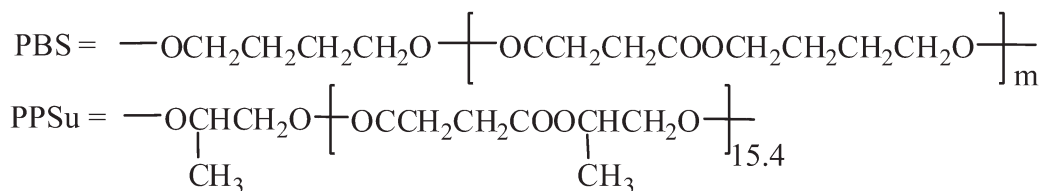
It is well-known that physical properties and biodegradability of semicrystalline biodegradable polymers strongly depend upon their crystal structures, morphologies and crystallinity degree. Therefore, much more attention should be directed to study the crystallization kinetics and morphologies of biodegradable polyesters for a better understanding of the relationship between structure and properties.

In recent decades, the crystallization behaviors of PBS homopolymer[5–14] and random copolymers[15–22] have been extensively studied. The crystal structure,[5] morphology,[8,9] bulk crystallization,[6,8,10] and melting behaviors[6,7,11–13] of PBS have been reported. Crystallization behaviors of PBS random copolymers, such as poly(butylene succinate-*co*-butylene terephthalate),[15] poly(butylene succinate-*co*-adipate),[18] poly(butylene succinate-*co*-butylene carbonate),[19] poly(butylene succinate-*co*-L-lactate)[20] and poly(butylene succinate-*co*-14 mol% ethylene succinate),[21] have also

- PBS (or PPSu) -CO- $HNCH_2CH_2CH_2CH_2CH_2CH_2NH$ -CO- PPSu (or PBS) -

Multiblock copolymer

$PBS =$ $-OCH_2CH_2CH_2CH_2O$ $-[OCCH_2CH_2COOCH_2CH_2CH_2CH_2O]_m$

$PPSu =$ $-OCHCH_2O$ $-[OCCH_2CH_2COOCHCH_2O]_{15.4}$ with CH_3 groups

The values of m are 11.6, 24.6 and 45.3 for PBS20, PBS40 and PBS80, respectively.

Scheme 1 Structure of multiblock copolymers.

been investigated. However, crystallization behaviors of PBS based block copolymers have not been well studied. Soccio et al.[23] obtained block copolymers of poly(butylene/diethylene succinate) by melt blending of PBS with poly(diethylene succinate) and studied the effect of transesterification reactions on the crystallization behaviors and morphologies of PBS. Park et al.[24] prepared the block copolymers composed of PBS and poly(butylene terephthalate) by melt processing and studied transesterification and crystallization behaviors of the copolymers. Actually, random copolymers were formed due to the transesterification reactions in these cases.[24] Therefore, self-synthesized multiblock copolymers were employed to systematically investigate the crystallization kinetics during the isothermal crystallization process. On the other hand, it is significant to study the crystallization behaviors of the multiblock copolymers because of their regular sequential structure, desirable thermal properties and mechanical properties.[4] In this work, the miscibility between PBS segment and PPSu segment in amorphous domain and the effect of PBS segment length and presence of PPSu segment on the crystallization kinetics and melting behaviors of multiblock copolymers were studied by differential scanning calorimetry (DSC) and polarized optical microscopy (POM) in detail. Spherulitic morphologies of multiblock copolymers were also observed by POM. It is expected that the results will give us a better understanding of the relationship between structure and properties of block copolymers derived from different polyesters.

EXPERIMENTAL

Materials

The synthesis of multiblock copolymers has been reported in our previous article[4] in detail. The co-

polymer 40-25-10, representing copolymer based on PBS40 (dihydroxytelechelic PBS with a molecular weight around 4000) and PPSu25 (dihydroxytelechelic PPSu with a molecular weight around 2500) with their weight ratio of 10/100, is used as an example to interpret the nomenclature of multiblock copolymers. The structure, molecular weights and glass transition temperatures (T_g) of the polymers are shown in Scheme 1 and Table I.

Differential scanning calorimetry

All the measurements were conducted under a high purity nitrogen atmosphere. Samples of 5 ± 0.1 mg were used in the tests. The DSC heating scans of polymers were examined on a Pyris Diamond DSC (Perkin-Elmer instrument) equipped with a CryoFill liquid nitrogen cooling system, according the following procedures: specimens were heated to 170°C and kept there for 5 min to eliminate thermal histories, then cooled to −80°C as soon as possible using liquid nitrogen as cooling agent and held there for 5 min. After that, the samples were heated to 170°C at a rate of 20°C/min. The endothermal curves were recorded for analysis. For studying isothermal crystallization behaviors, a Perkin-Elmer DSC-7, calibrated with indium and zinc standards, was used. The studies were performed as follows: the samples

TABLE I
Characteristics of Copolymers and Homopolymer

Sample	M_n ($\times 10^4$)	PDI	$M_{n(PPSu)}$	$M_{n(PBS)}$	T_g (°C)
20-25-00	9.0	3.02	2513	2092	−40.7
20-25-10	7.5	4.40	2513	2092	−37.6
40-25-10	13.5	3.45	2513	4322	−35.5
80-25-10	9.8	2.24	2513	7882	−32.8

M_n, determined by GPC with polystyrene as a standard; $M_{n(PPSu)}$ and $M_{n(PBS)}$, determined by titration of the end groups.
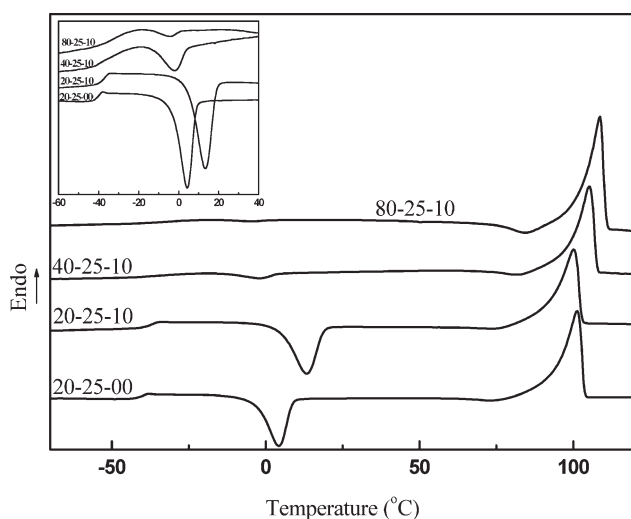
Figure 1   DSC heating scans of the polymers.

were heated to 170°C and held there for 5 min to erase any thermal history, and then cooled to the designated crystallization temperature (T_c) as soon as possible for isothermal crystallization. After the completion of crystallization, the samples were heated to 170°C at a rate of 20°C/min. The endothermal curves and exothermal curves of heat flow as a function of time were recorded for isothermal crystallization studies.

Polarized optical microscopy

Spherulitic morphologies of polymers after being isothermally crystallized at the stated temperature were examined with POM (Olympus Bx 51, Japan). Polymer ultrathin films with a thickness of 10 µm were employed. Before observation, samples were heated to 170°C in a hot stage and held there for 5 min, then cool to desired T_c as soon as possible for isothermal crystallization.

RESULTS AND DISCUSSION

Miscibility between PPSu segment and PBS segment

Though the thermal properties have been reported in another article,[4] the DSC curves of heating scans for various polymers are presented in this article (Fig. 1) to study the miscibility between the soft segment and hard segment. The inset in the top left corner of this figure enlarges the thermograms in the range of −60 to 40°C so that it can be more clearly seen. This article only gives values of T_g (in Table I) to analyze the miscibility and crystallization because other thermal parameters have been reported. Evidently, as displayed in Figure 1 and Table I, all the multiblock copolymers show single T_g, irrespective of chain

length. Furthermore, T_g of 20-25-10 lies between T_g of PPSu ($T_g = -5.3°C$) and T_g of 20-25-00, suggesting the presence of a homogenous amorphous state. Therefore, it is reasonable to reach a conclusion that PPSu segment is miscible with PBS segment in the amorphous region. On the other hand, value of T_g increases gradually with increasing PBS segment length. It is attributed from the fact that with the increase of PBS segment length, crystallinity degree is evidently increased[4] and subsequently amount of PBS segment (low-T_g fraction) located in the amorphous region is diminished. It thus further supports the conclusion that PBS segment is miscible with PPSu segment in amorphous region.

Isothermal crystallization

The DSC exothermic curves of polymers during isothermal crystallization process at different crystallizations temperatures are shown in Figure 2. The development of relative degree of crystallinity (X_t) for each exothermal curve was evaluated using the following expression:

$$X_t = \frac{\int_0^t (dH/dt)dt}{\int_0^\infty (dH/dt)dt} \qquad (1)$$

where dH/dt denotes the rate of heat evolution, the limits t and ∞ denote the elapsed time during the course of crystallization and at the end of the crystallization process, respectively. Once the values of X_t versus t are obtained, the well-known Avrami equation[25,26] was utilized to analyze the isothermal crystallization kinetics of polymers as following:

$$X_t = 1 - \exp(-Kt^n) \qquad (2)$$

$$\ln[-\ln(1 - X_t)] = n\ln t + \ln K \qquad (3)$$

where K is the overall crystallization rate constant and n is the Avrami exponent, which is correlated with the nucleation mechanism and grown dimension.

Figure 3 gives the plots of X_t versus t of polymers at various T_c. By plotting $\ln[-\ln(1 - X_t)]$ versus $\ln t$, the values of n and K could be obtained from the slope and intercept, respectively. Figure 4 shows the Avrami plots of polymers at various T_c.

The values of n and K for polymers are summarized in Table II. As indicated in Table II, values of Avrami exponent n show a weak dependence on the structure, implying that the crystallization mechanism does not change significantly with the introduction of PPSu segment or the change in PBS segment length.

The crystallization half-time ($t_{1/2}$), i.e., the time at which the relative degree of crystallinity achieves
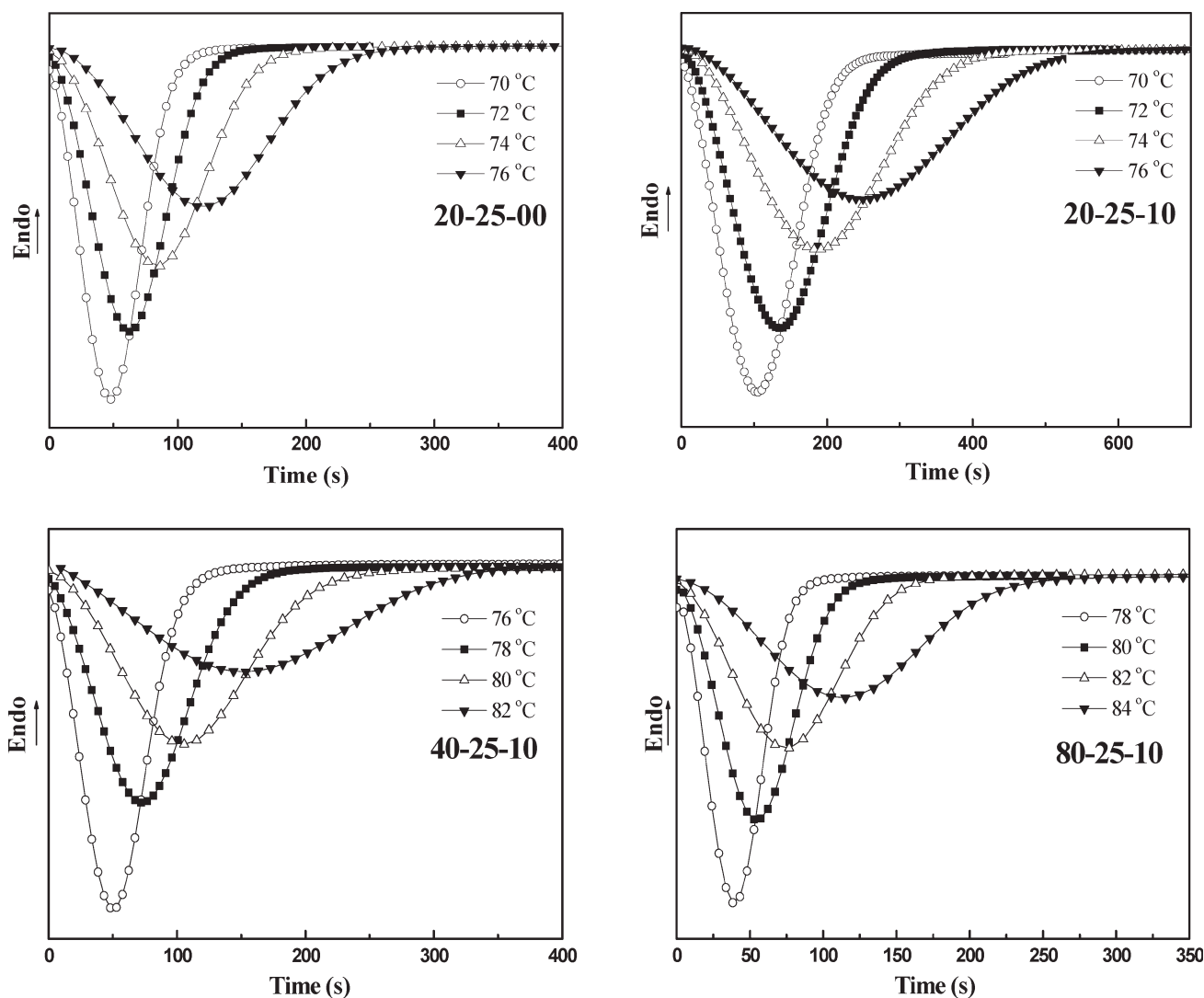
Figure 2 DSC exotherms of the isothermal crystallization of polymers at various T_c.

50%, can be determined from Figure 3 or by the following equation:

$$t_{1/2} = \left(\frac{\ln 2}{K}\right)^{1/n} \qquad (4)$$

From Table II, it is evident that the values of $t_{1/2}$ calculated by the equation 4 are in good agreement with those determined from the experimental data. $t_{1/2}$ is a significant parameter for the discussion of crystallization kinetics as the crystallization rate (G) is proportional to the reciprocal of $t_{1/2}$. The plots of $1/t_{1/2}$, which was measured directly from Figure 3, as a function of T_c are depicted in Figure 5.

Effect of PPSu segment on the isothermal crystallization kinetics

The effect of structure on the crystallization rate is complicated. As displayed in Figure 5, value of $1/t_{1/2}$

of 20-25-10 is smaller than that of 20-25-00 at a given crystallization temperature, suggesting that the presence of PPSu segment noticeably reduces the crystallization rate. This slow-down in the crystallization rate may be caused by the following reasons. Similar to crystallization process of other crystalline-amorphous binary copolymer,[27,28] completely uncrystallizable PPSu segment should be excluded from crystals and resided between lamellae of PBS segment. Another reason is the dilution effect caused by amorphous PPSu segment. In addition, as discussed before, the introduction of high-T_g PPSu leads to an increase in T_g, which results in a decrease in the spherulitic growth rate and a retardation in the crystallization rate.

Effect of PBS segment length on the isothermal crystallization kinetics

It is well-known the segment length is one of the key variables that governs crystallization kinetics of
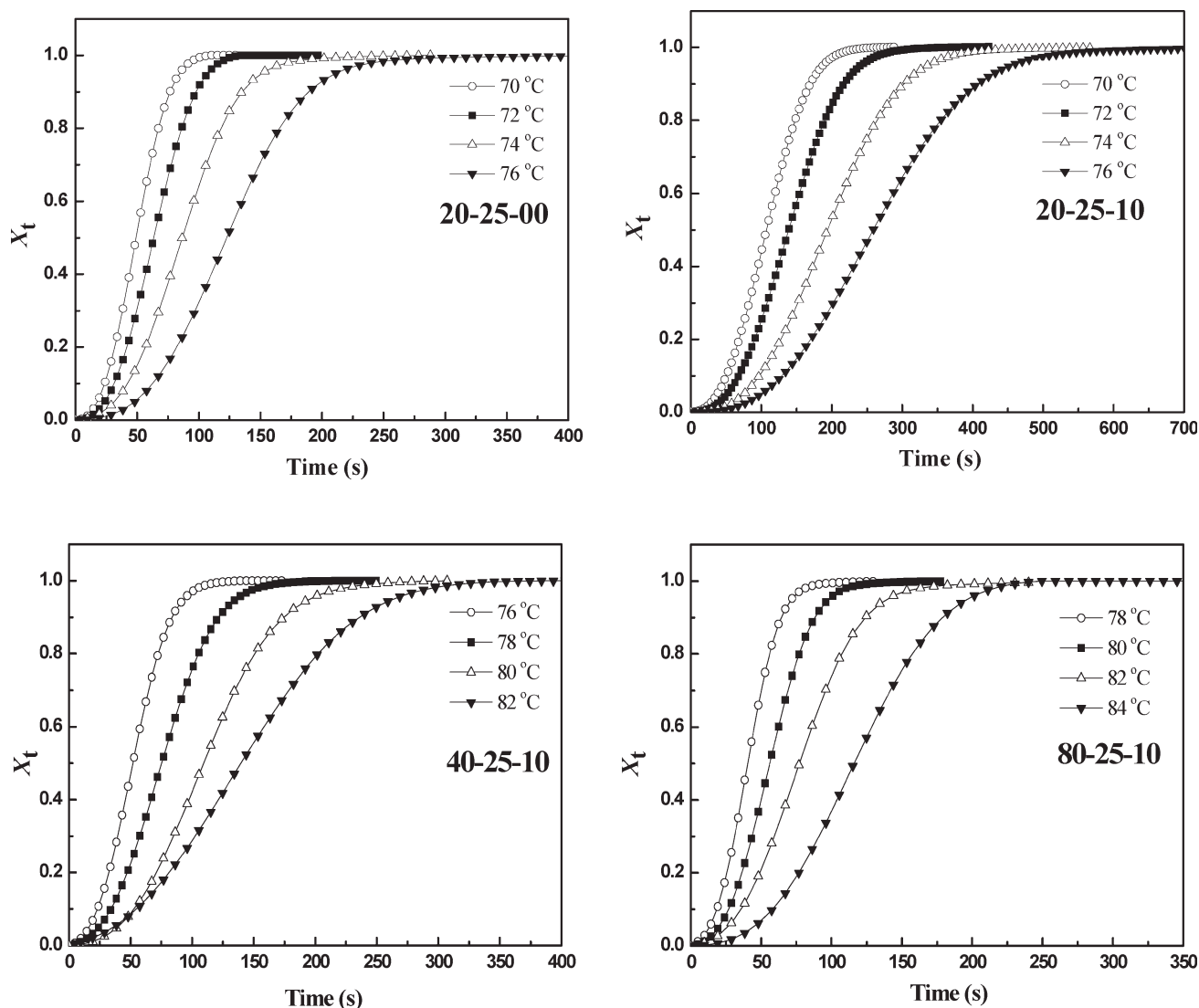
Figure 3 $X(t)$ values as a function of crystallization time t of polymers at various T_c.

block polymers. The influence of one segment length on crystallization behaviors of two-block and three-block copolymers has been widely reported.[29–32] However, in the case of these block copolymers, there is an inevitable variation in the weight ratio of one segment with a change in its segment length. Thus, it is a complicated and difficult work to evaluate how segment length affects the crystallization behavior of block copolymers individually. Self-synthesized multiblock copolymers enable us to systematically investigate the effect of PBS segment length on the crystallization behavior of block copolymers based on a fixed weight ratio. As illustrated in Table II and Figure 5, PBS segment length, which largely depends on PBS molecular weight, plays an important role in the crystallization kinetics of copolymers. Crystallization rate, G, which is proportional to $1/t_{1/2}$, increases substantially with the increase of PBS segment length at any given T_c. It can be interpreted

in terms of the supercooling degree (ΔT), which can be calculated from $\Delta T = T_m^0 - T_c$, where T_m^0 is the equilibrium melting point. As shown in Figure 7 (see the following), value of T_m^0 for copolymers increases evidently with increasing molecular weight of PBS segment when molecular weight of PBS segment is less than 4000, then increases slightly with further increase in the molecular weight. Hence, copolymer with longer PBS segment actually undergoes crystallization at a higher ΔT at a same T_c. ΔT is a key parameter for crystallization driving force and greater ΔT means faster nucleation rate. Besides, spherulitic growth rate also increases with an increase in ΔT, which has been verified by data from POM in all cases (see the following). As a result, crystallization rate becomes faster as PBS segment becomes longer in the discussed range. Urethane group generated from the chain-extension with HDI is another significant structural factor for copolymer
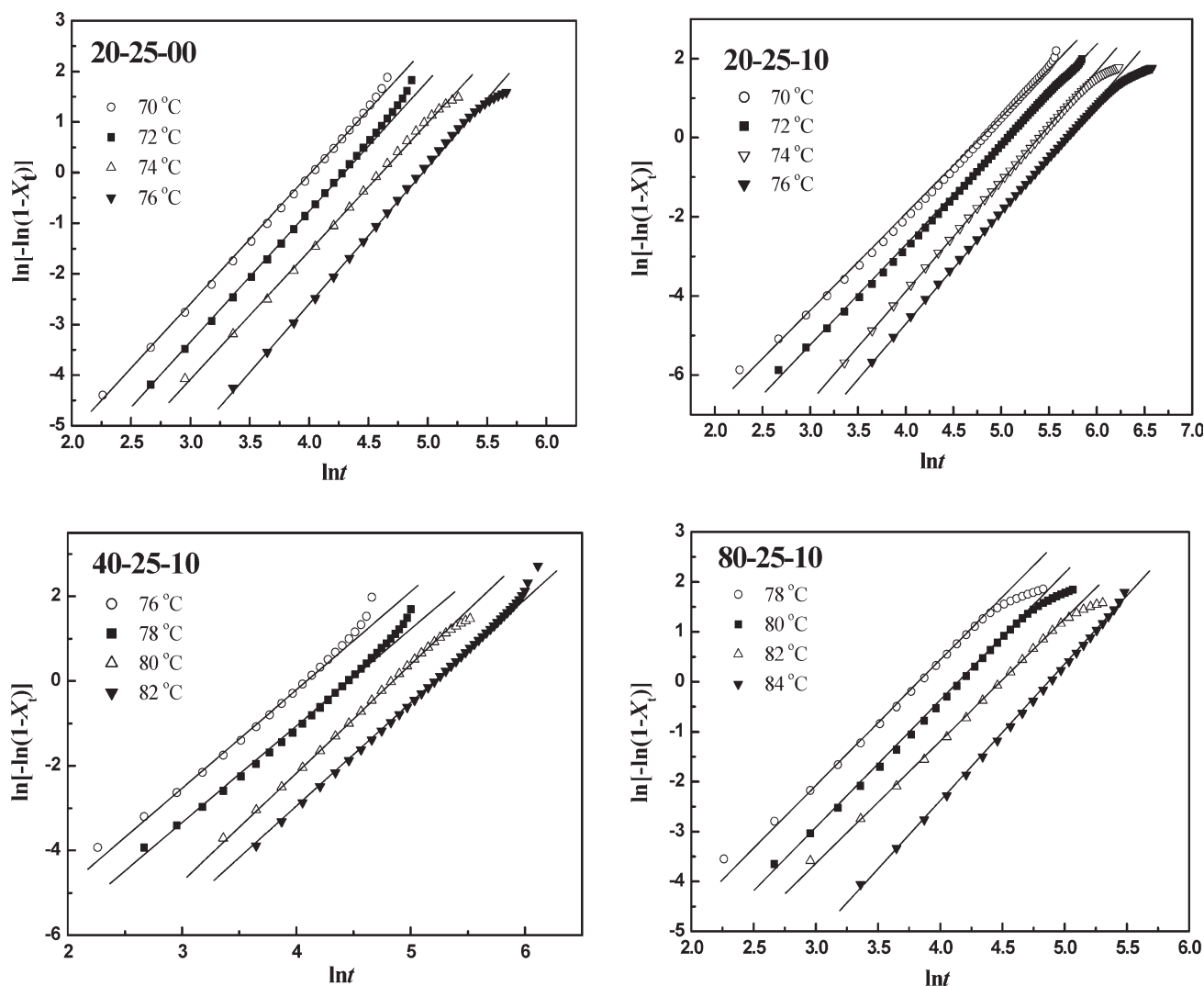
Figure 4 Avrami plots of polymers at various T_c.

crystallization. It is well established that the introduction of urethane groups disturbs the macromolecular backbone regularity[33,34] and thus depresses the crystallization of the copolymer seriously. This becomes more pronounced for copolymer with shorter PBS segment as more urethane groups are introduced (more HDI needed for chain-extension).

Subsequent melting behaviors

Figure 6 presents the typical subsequent heating curves of 20-25-10 after being isothermally crystallized at different temperatures. The main parameters are listed in Table III. Obviously, triple melting peaks appear in the heating scans and are identified with T_{mA}, T_{mL}, and T_{mH} from low temperature to high temperature. The multiple melting phenomenons of PBS homopolymer and copolymers have been intensively studied[11–13,23] and have been ascribed to the melting/recrystallization or reorganization proc-

esses taking place during the DSC heating scan. Similar viewpoint is adopted to interpret the multiple melting behaviors of multiblock copolymers.

T_{mA}, which appears $\sim 5°C$ higher than T_c, is the typical annealing peak,[23] arising from the melting of poorer or smaller crystals between the larger crystals grown during the isothermal process at T_c; T_{mL} is attributed to the fusion of primary crystals formed at T_c; while T_{mH} is ascribed to the melting of crystals with highest perfection and stability, i.e., the crystals developed by recrystallization or reorganization of the crystals grown at T_c during the heating process. Both from Figure 6 and Table III, it is readily apparent that the position and area of the melting peaks depend on T_c. As the area of annealing peak is small and hardly varies with T_c, it is considered to be insignificant for the multiple melting behaviors. Hence, they are not discussed later on. The position of peak T_{mL} regularly shifts to a higher temperature region with increasing T_c, implying that the

TABLE II
Crystallization Kinetic Parameters of Multiblock Copolymers and Homopolymer at Various Crystallization Temperature

Samples	T_c (°C)	n	K (s^{-n})	$t_{1/2}$ (s)[a]	$t_{1/2}$ (s)[b]
20-25-00	70	2.60	2.90×10^{-5}	48.78	47.96
	72	2.71	9.63×10^{-6}	63.36	62.22
	74	2.56	7.58×10^{-6}	86.52	86.17
	76	2.64	1.99×10^{-6}	122.74	124.82
20-25-10	70	2.48	7.00×10^{-6}	106.47	104.28
	72	2.56	2.39×10^{-6}	138.90	138.28
	74	2.71	4.29×10^{-7}	194.48	196.82
	76	2.75	1.63×10^{-7}	258.29	258.88
40-25-10	76	2.40	6.11×10^{-5}	51.03	48.90
	78	2.41	2.30×10^{-5}	76.72	71.78
	80	2.48	5.89×10^{-6}	109.38	111.19
	82	2.43	3.59×10^{-6}	153.12	148.57
80-25-10	78	2.38	1.45×10^{-4}	39.92	39.72
	80	2.52	2.80×10^{-5}	56.13	55.78
	82	2.42	1.87×10^{-5}	77.62	77.30
	84	2.67	2.08×10^{-6}	116.60	116.18

[a] $t_{1/2}$, determined from Figure 3.
[b] $t_{1/2}$, calculated from $t_{1/2} = (\ln 2/K)^{1/n}$.

perfectness of primary crystals increases with the increase of T_c. Furthermore, the value of ΔH_{mL} increases gradually with the increase of T_c, contrary to the trend of ΔH_{mH}. With respect to the position of peak T_{mH}, it remains almost unchanged with T_c. T_{mL}, the melting temperature of primary crystals grown at T_c and presented before the heating scan, was employed to calculate T_m^0. T_m^0 was obtained by extrapolating the line of T_{mL} versus T_c to the line of $T_m = T_c$ according to the well-known theory proposed by Hoffman-Weeks,[35] as illustrated in Figure 7.

Besides, the influence of structure on the multiple melting behaviors has been studied. As displayed in Figure 6 and Table III, T_{mL} and T_{mH} of 20-25-10 are slightly lower than that of 20-25-00 at a particular T_c, suggesting that amorphous PPSu segment just
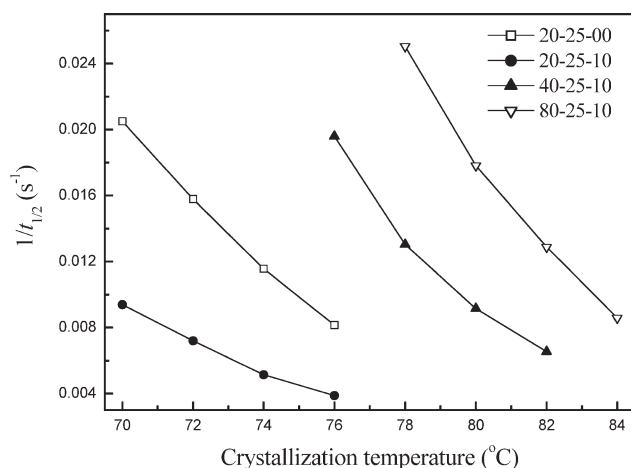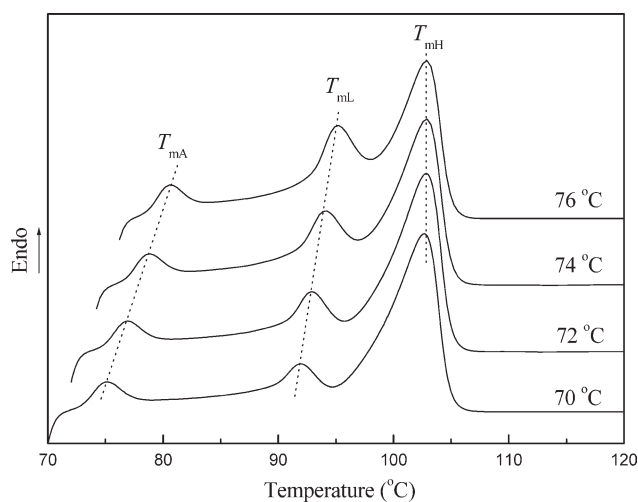

Figure 6 Subsequent melting behaviors of 20-25-10 at various T_c.

slightly disturbs the crystal perfection. It may be attributed to the fact that PPSu segment, which needs to be excluded from the crystals of PBS, retards lamellar reorganization or crystal recrystallization process. On the other hand, values of T_m, including T_{mA}, T_{mL}, and T_{mH}, and ΔH_{mH} tend to increase with increase in the PBS segment length at any given T_c. Since higher T_m implies thicker lamellae or more perfect and stable crystals, the higher T_m for copolymer with longer PBS segment is possibly resulted from the fact that longer PBS segment favors the lamellar reorganization or crystal recrystallization. Owing to the same reason, the value of ΔH_{mH} increases with increasing PBS segment length.

Spherulitic morphologies

The spherulitic morphologies of 40-25-10 crystallized at 76°C at different times are shown in Figure 8. It

Figure 5 Crystallization rate as a function of crystallization temperature.

TABLE III
Melting Endotherm Parameters of Various Samples

| Samples	T_c (°C)	T_{mA} (°C)	T_{mL} (°C)	T_{mH} (°C)	ΔH_{mL} (J/g)	ΔH_{mH} (J/g)
20-25-00	70	75.8	91.9	104.6	2.3	44.0
	72	76.8	92.9	104.6	3.7	42.1
	74	78.5	93.9	104.6	5.6	39.2
	76	80.5	95.2	104.6	8.4	35.4
20-25-10	70	75.1	91.5	102.7	5.9	34.4
	72	76.9	92.6	102.8	7.8	32.7
	74	78.8	93.7	102.9	9.9	29.2
	76	80.5	94.8	102.9	13.0	25.3
40-25-10	76	81.5	97.6	108.3	3.5	39.9
	78	83.2	98.6	108.3	5.9	36.4
	80	85.2	99.6	108.3	8.4	33.1
	82	87.2	100.9	108.3	11.9	29.2
80-25-10	78	82.2	98.9	110.9	0.7	52.0
	80	84.2	99.9	110.9	1.6	49.6
	82	86.2	100.9	111.2	4.6	46.1
	84	87.9	102.2	111.2	7.6	42.5
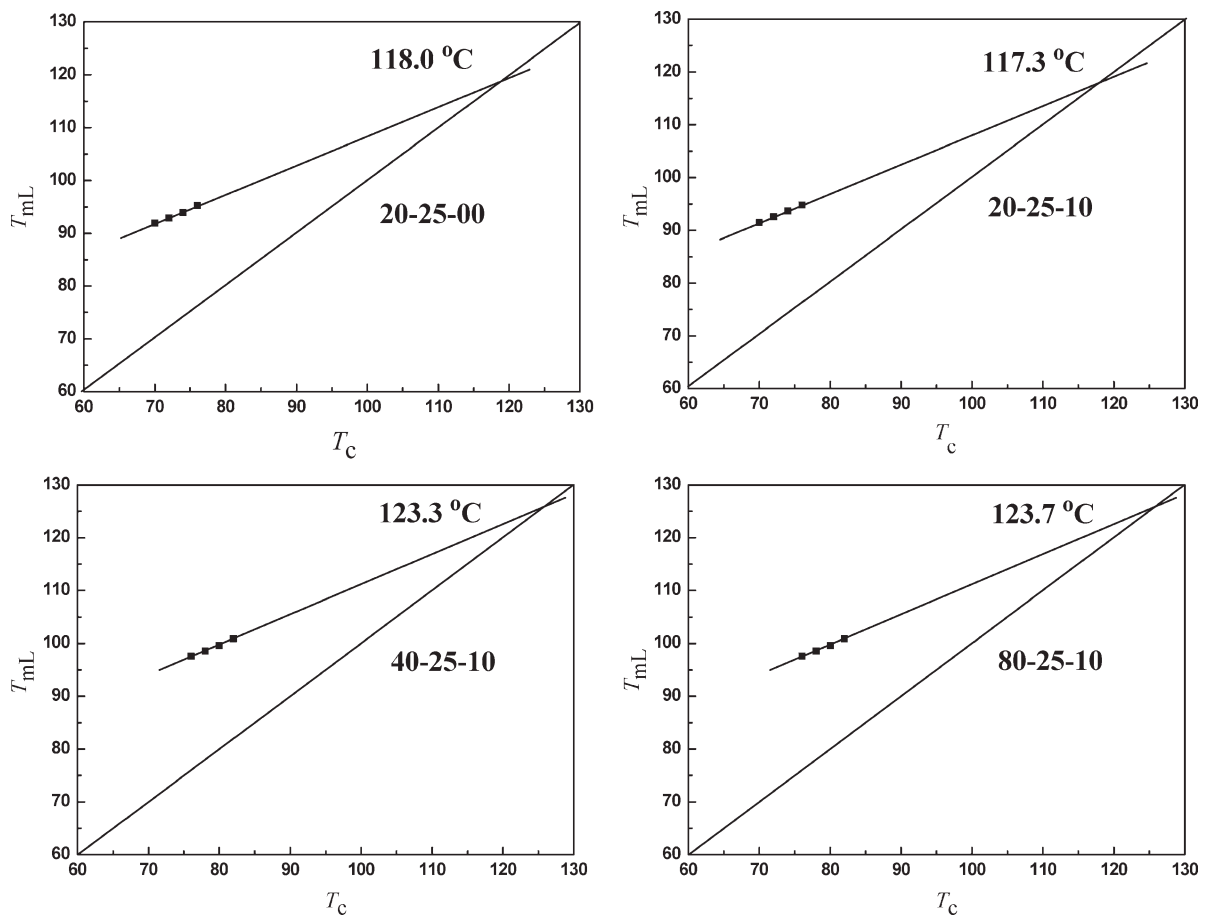
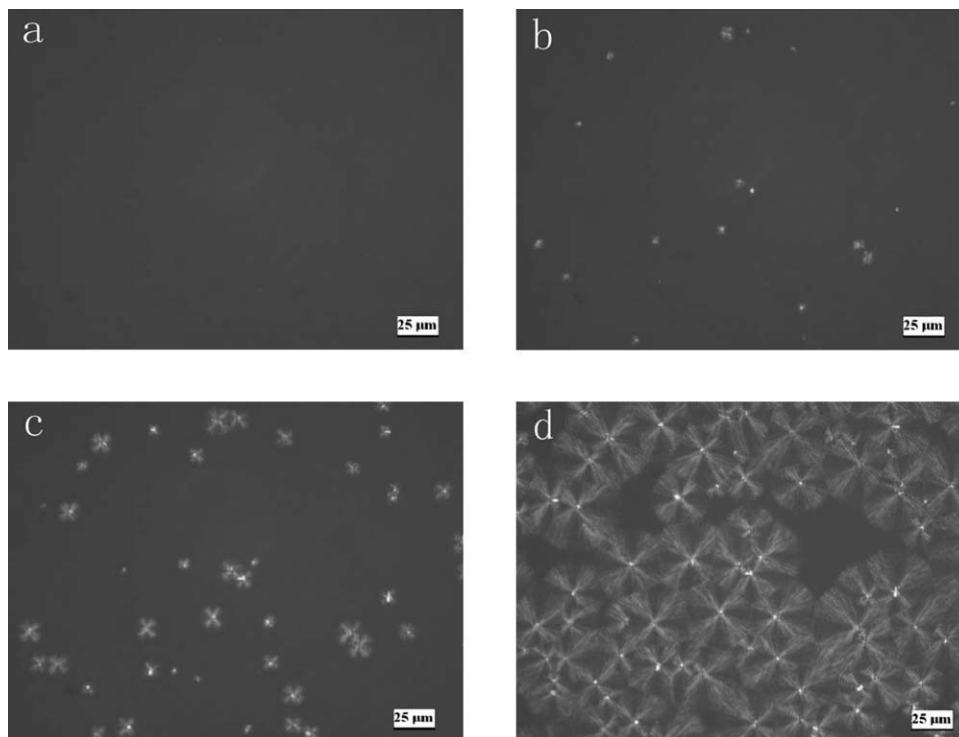**Figure 7** Holffman-Week's plot for polymers.

Figure 8 POM micrographs of 40-25-10 crystallized at 82°C at (a)30 s; (b) 45 s; (c) 60 s; (d) 90 s from the melt.
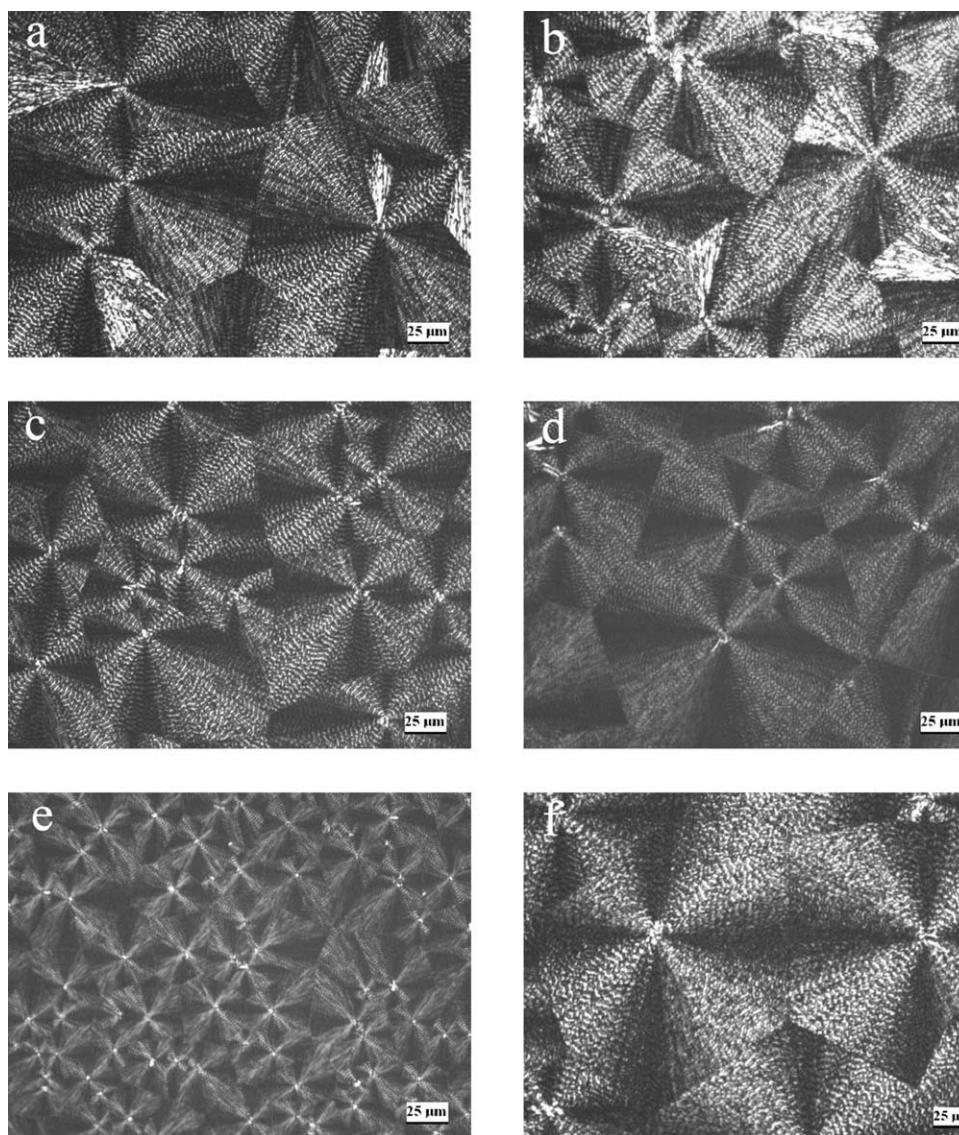
Figure 9 Reprensentive POM micrographs of polymers isothermally crystallized (a) 20-25-00 at 82°C; (b) 20-25-10 at 82°C; (c) 40-25-10 at 82°C; (d) 80-25-10 at 82°C; (e) 40-25-10 at 76°C; (f) 40-25-10 at 92°C from the melt.

can be found that nuclei formation is time-dependent and then the nucleation can be ascribed to the thermal kinetics.

Figure 9 gives the spherulitic morphologies of polymers crystallized at different temperatures under polarizer. It can be observed that all the polymers exhibit typical Maltese cross pattern. As far as spherulitic size is concerned, it shows a weak dependence on PBS segment length. As revealed in Figure 9, 40-25-10 demonstrates smallest spherulites among these three copolymers. It is not surprising since spherulitic size is the result of the competition between nucleation and growth. The smaller spherulites of 40-25-10, as compared with that of 20-25-10, originate from its evidently higher degree of supercooling at a particular T_c, which favors nucleation and thus increases the number of nucleis. However, there is no distinct difference in the degree of super-

cooling between 40-25-10 and 80-25-10. The slightly bigger spherulites of 80-25-10 owe to its apparently faster growth rate (described below) and thus lesser time for spherulites to grow before impinging, which produces fewer nucleis that can grow larger. In addition, spherulite size becomes bigger and nucleation density becomes smaller at higher crystallization temperatures. It is a natural consequence of the difficulty in nucleation under lower degree of supercooling.

Spherulitic growth rate

Spherulitic growth rate, g, of polymers was determined by measuring spherulitic radii from POM micrographs taken at successive intervals during isothermal crystallization before impingement. The temperature dependence of g for various polymers
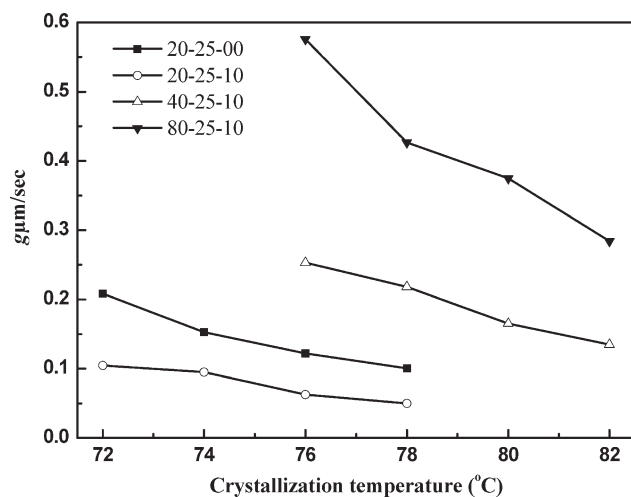
Figure 10 Spherulitic growth rate of polymers as a function of crystallization temperature.

is shown in Figure 10. As expected, with a decrease in T_c and subsequent increase in ΔT, value of g increases, which supports the previous discussion. Besides, the value of g for 20-25-10 is smaller than that of 20-25-00 at a particular T_c, indicating that the presence of PPSu segment retards the spherulitic growth. It is reasonable since the crystallization of PBS segment needs to exclude PPSu segment. Simultaneously, dilution effect caused by PPSu segment also reduces g. The increased T_g by the incorporation of PPSu also slows down the spherulitic growth process. As far as PBS segment length is concerned, value of g (Fig. 10) increases substantially with increasing PBS segment length, originating from the difference in ΔT and urethane groups as previously discussed. Therefore, a conclusion can be reached that the results of g by POM (Fig. 10) are completely consistent with that of G obtained by means of DSC (Fig. 5).

As discussed above, both crystallization rate and spherulitic growth rate increase greatly with the increase of PBS segment length, resulting in higher crystallinity degree for the copolymer with longer PBS segment.[4] It is generally regarded that higher crystallinity degree improves tensile strength but deteriorates impact strength. Consequently, the tensile strength is gradually enhanced, while the impact strength is prominently deteriorated with increasing PBS segment length.[4] 40-25-10, with satisfactory tensile strength, impact strength and crystallization rate, is considered as the optimal sample for the balance of crystallization and mechanical properties.

CONCLUSIONS

The isothermal crystallization, melting behaviors and spherulitic morphologies of high-impact multi-block copolymers have been studied. The PPSu segment is found to be miscible with PBS segment in amorphous region from the analysis of DSC results. The incorporation of PPSu segment decreases both the crystallization rate and spherulitic growth rate because of exclusion of PPSu segment, dilution effect and increased T_g caused by PPSu segment. While the increase of PBS segment length increases both the crystallization rate and spherulitic growth rate, owing to the increased supercooling degree and decreased amount of urethane groups. Multiple melting behaviors have been observed for all the multiblock copolymers, which have been ascribed to melting/recrystallization or reorganization mechanism. Increasing PBS chain length favors the lamellar reorganization or crystal recrystallization, crystal perfection and crystallinity degree; while the introduction of PPSu segment has a contrary influence. The results of spherulitic growth rate agree well with overall crystallization rate.

References

1. Tserki, V.; Matzinos, P.; Pavidou, E.; Vachliotis, D.; Panayiotou, C. Polym Degrad Stab 2006, 91, 367.
2. Cao, A. M.; Okamura, T.; Ishiguro, C.; Nakayama, K.; Inoue, Y.; Masuda, T. Polymer 2002, 43, 671.
3. Chae, H.; Park, S.; Kim, B.; Kim, D. J Polym Sci Part B: Polym Phys 2004, 42, 1759.
4. Zheng, L. C.; Li, C. C.; Huang, W. G.; Huang, X.; Zhang, D.; Guan, G. G.; Xiao, Y. N.; Wang, D. J. Polym Adv Technol, to appear.
5. Ichikawa, Y.; Kondo, H.; Igarashi, Y.; Noguchi, K.; Okuyama, K.; Washiyama, J. Polymer 2000, 41, 4719.
6. Papageorgiou, G. Z.; Bikiaris, D. N. Polymer 2005, 46, 12081.
7. Qiu, Z.; Komura, M.; Ikehara, T.; Nishi, T. Polymer 2003, 44, 7781.
8. Miyata, T.; Masuko, T. Polymer 1998, 39, 1399.
9. Wang, H. J.; Gan, Z. H.; Schultz, J. M.; Yan, S. K. Polymer 2008, 49, 2342.
10. Qiu, Z. B.; Fujinami, S.; Komura, M.; Nakajima, K.; Ikehara, T.; Nishi, T. Polym J 2004, 36, 642.
11. Yoo, E. S.; Im, S. S. J Polym Sci Part B: Polym Phys 1999, 37, 1357.
12. Yasuniwa, M.; Tsubakihara, S.; Satou, T.; Iura, K. J Polym Sci Part B: Polym Phys 2005, 43, 2039.
13. Yasuniwa, M.; Satou, T. J Polym Sci Part B: Polym Phys 2002, 40, 2411.
14. Papageorgiou, G. Z.; Achilias, D. S.; Bikiaris, D. N. Macromol Chem Phys 2007, 208, 1250.
15. Li, F.; Xu, X.; Hao, Q.; Li, Q.; Yu, J.; Cao, A. J Polym Sci Part B: Polym Phys 2006, 44, 1635.
16. Papageorgiou, G. Z.; Bikiaris, D. N. Biomacromolecules 2007, 8, 2437.
17. Qiu, Z. B.; Yan, C. Z.; Lu, J. M; Yang, W. T. Macromolecules 2007, 40, 5047.
18. Ren, M. Q.; Song, J. B.; Song, C. L.; Zhang, H. L.; Sun, X. H.; Chen, Q. Y.; Zhang, H. F.; MO, Z. S. J Polym Sci Part B: Polym Phys 2005, 43, 3231.
19. Qiu, Z. B.; Miao, L. Q.; Yang, W. Y. J Polym Sci Part B: Polym Phys 2006, 44, 1556.
20. Shibata, M.; Inoue, Y.; Miyoshi, M. Polymer 2006, 47, 3557.

21. Gan, Z. H.; Abe, H.; Doi, Y. Biomacromolecules 2001, 2, 313.
22. Gan, Z. H.; Abe, H.; Kurokawa, H.; Doi, Y. Biomacromolecules 2001, 2, 605.
23. Soccio, M.; Lotti, N.; Finelli, L.; Munari, A. Eur Polym J 2009, 45, 171.
24. Park, S. S.; Chae, S. H.; Im, S. S. J Polym Sci Part A: Polym Chem 1998, 36, 147.
25. Avrami, M. J Chem Phys 1939, 7, 1103.
26. Avrami, M. J Chem Phys 1940, 8, 212.
27. Ho, R. M.; Hseih, P. Y.; Yang, C. C.; Lin, J. J. J Polym Sci Part B: Polym Phys 2001, 39, 2469.
28. Ho, R. M.; Chi, C. W.; Tsai, C. C.; Lin, J. J. Polymer 2002, 43, 1365.
29. Huang, C. I.; Tsai, S. H.; Chen, C. M. J Polym Sci Part B: Polym Phys 2006, 44, 2438.
30. Shin, D.; Shin, K.; Aamer, K. A.; Tew, G. N.; Russell, T. P.; Lee, J. H.; Jho, J. Y. Macromolecules 2005, 38, 104.
31. Chen, H. L.; Hsiao, S. C.; Lin, T. L.; Yamauchi, K.; Hasegawa, H.; Hashimoto, T. Macromolecules 2001, 34, 671.
32. Sun, J. R.; Hong, Z. K.; Yang, L. X.; Tang, Z. H.; Chen, X. S.; Jing, X. B. Polymer 2004, 45, 5969.
33. Coffey, D. H.; Meyrick, T. J. Rubber Chem Technol 1957, 30, 283.
34. Sun, X. H.; Ni, X. Y. J Appl Polym Sci 2004, 94, 2286.
35. Hoffman, J. D.; Weeks, J. J. J Res Natl Bur Stand Sect A 1962, 66, 13.