

Crystallization Behavior of “Wet Brush” and “Dry Brush” Blends of PS-*b*-PEO-*b*-PS/h-PEO

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ABSTRACT: The crystallization behavior of the blending system consists of homopolymer poly(ethylene oxide) (h-PEO) with different molecular weights, and polystyrene-*block*-poly(ethylene oxide)-*block*-polystyrene (PS-*b*-PEO-*b*-PS) triblock copolymer has been investigated by DSC measurements. The crystallization of PEO block (b-PEO) in block copolymer occurs under much lower temperature than that of the h-PEO in the bulk ($\Delta T > 65$ °C), which is attributed to the homogeneous nucleation crystallization behavior of the b-PEO microdomains. In both the “dry-brush” and the “wet brush” blending systems, the homogeneous nucleation crystallization temperature of PS-*b*-PEO-*b*-PS/h-PEO blends increases due to the increase of the domain size. The heterogeneous nucleation crystallization temperatures of h-PEO in the wet brush blending systems are higher than that of the corresponding h-PEO

in the bulk. At the same time, the heterogeneous nucleation crystallization temperature of b-PEO10000 decreases from 43 °C to 30 °C and 40 °C in the h-PEO600 and h-PEO2000 blending systems, respectively, because of the stretching of the PEO chains in the wet brush. However, this kind of phenomenon does not happen in the dry brush blending systems. The self-seeding procedure was used to further ascertain the nucleation mechanism in the crystallization process. As a result, the self-seeding domains have been confirmed, and the difference between the dry brush and wet brush systems has been observed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 907–915, 2009

Key words: block copolymer; crystallization; blending; wet brush; dry brush

INTRODUCTION

The confined crystallization of copolymers and blends consist of immiscible semi-crystalline polymer, and amorphous polymer has attracted great interest in recent years.^{1–18} Because of the immiscibility of different blocks, different morphologies of the segregated block copolymer including lamellae, gyroids, cylinders, and spheres, depending on the volume fraction of the block copolymer, have been revealed.¹⁹ The crystallization behavior of the amorphous-crystalline block copolymer is related to

the interplay between micro-phase separation of copolymer and crystallization of crystalline block. Due to the nanoscale microdomains formed during phase separation, the crystallization behavior of the confined crystalline blocks is different from that of the crystalline homopolymer. Factors such as the interaction between different blocks, temperature of order-disorder transition (T_{ODT}), microdomain structure, glass transition temperature (T_g) of amorphous block, and crystallization temperature (T_c) of crystal block have an important effect on the crystallization process of semi-crystalline copolymer. To study the crystallization of semi-crystalline PEO-*b*-PS copolymers with a PEO crystal block, the concepts of hard and soft confined crystallization were introduced by Cheng et al.^{2–6} If $T_{ODT} \gg T_g^{PS} > T_c^{PEO}$, the crystallization of PEO is under hard PS confinement, and if $T_{ODT} > T_c^{PEO} \geq T_g^{PS}$, the crystallization of PEO is under soft PS confinement. Depending on the segregation strength, there are three modes of crystallization in semi-crystalline block copolymer, i.e., breakout crystallization, template crystallization, and confined (fractionated) crystallization. Müller et al. built a clear concept on the confined crystallization and homogeneous nucleation crystallization of a

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series of block copolymer and polymer blends.^{20,21} In semi-crystalline copolymers, nucleation in the bulk usually occurs on the heterogeneities, and the homogeneous nucleation may occur in isolated microdomains of the microphase separation of block copolymers. The number of droplets formed by microphase separation is so large that each droplet cannot possess the same kind of nuclei (the heterogeneities may be the catalyst debris, impurities, and some other unknown substances, which have different activities). Those droplets containing the active heterogeneities can crystallize at the lowest supercooling condition, where the crystallization temperature is identical with that in the bulk. A stronger supercooling condition should be reached to make the droplets containing the heterogeneities with less activity crystallize. For the droplets that do not contain heterogeneities, homogeneous crystallization must be adopted at the highest supercooling.

According to the molecular weight ratio of homopolymer B (h-B) to block B (b-B) ($\alpha = M_{h-B}/M_{b-B}$), A-*b*-B block copolymer/B homopolymer blending systems can be divided into three cases: the complete phase separation system ($\alpha \gg 1$) [as shown in Fig. 1(a)], “dry-brush” blending system ($\alpha \geq 1$) [Fig. 1(b)], and “wet-brush” blending system ($\alpha < 1$) [Fig. 1(c)].^{22,23} Although the original concepts of dry brush and wet brush are based on the amorphous polymers, they can be adopted in the system of this work because both components are flexible polymers at the temperature of about 150°C. In the dry-brush system, h-B chains will form an isolated region in the middle of the B domains instead of mixing in the B block because of the high conformational entropy penalty. In the wet-brush system, the added h-B will be uniformly dissolved in the corresponding b-B microdomains, thus changing the microdomain size or even the morphologies. The phase structure of the blending system is different from the neat semi-crystalline block copolymer A-*b*-B; thus the crystallization behavior changes. For example, Chen et al.⁷⁻⁹ investigated the melting and crystallization behavior of the poly(ethylene oxide)-*block*-poly(1,4-butadiene)/poly(1,4-butadiene) (PEO-*b*-PB/PB) dry brush and wet brush systems. It was found that the morphologies of the blending systems changed from lamellae to cylinder and even sphere with the increasing of the added h-PB in the wet brush system, which indicated an increase in the curvature of PEO microdomains. Eventually, the homogeneous crystallization occurred, which was caused by the decrease of the size of the isolated b-PEO domain. In the dry brush system, the lamellar structure was detected in all compositions as well as in the cylinders and spherical vesicles. With the increasing of h-PB contents, undercooling homogeneous crystallization occurred. In most of the works on the confined

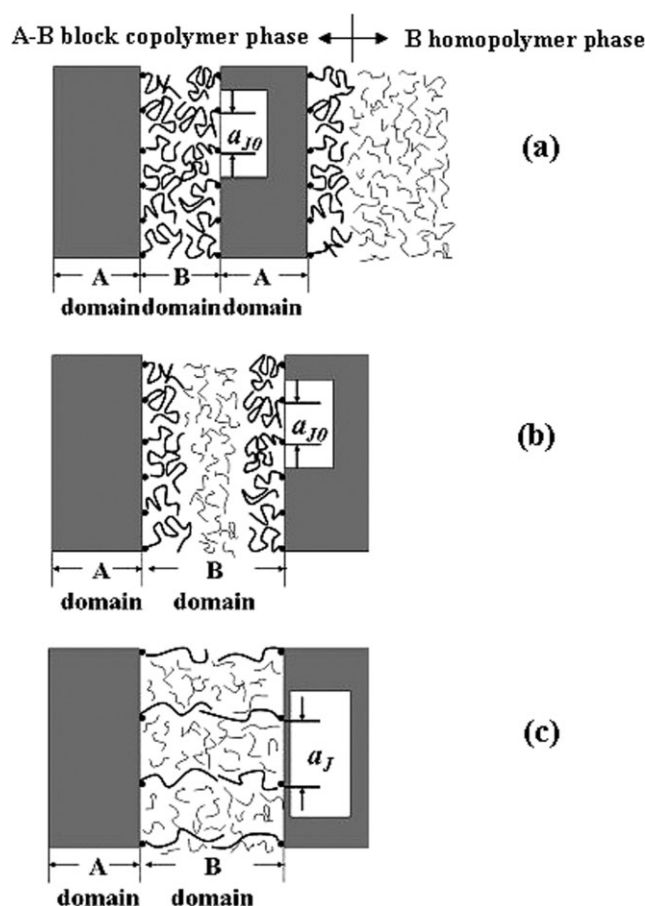


Figure 1 Schematic diagram by Hashimoto showing the possible structures of the mixtures of A-B block copolymer and the B homopolymer: (a) the complete phase separation; (b) the “dry brush” blending; (c) the “wet brush” blending.

crystallization of A-*b*-B/h-B blend systems, A is crystalline block and B is noncrystalline block or homopolymer.

The miscibility of polymer blend consisting of block copolymer and homopolymer has been investigated widely. All reports have pointed out that the miscibility of blends largely depends on the molecular weight of the polymers. Koizumi and Hashimoto et al.²⁴⁻²⁷ investigated the effects of the molecular weight of homopolymer ($M_{n,h-PS}$) on the interface structure and the miscibility of the polystyrene-*block*-polyisoprene/polystyrene (PS-*b*-PI/h-PS) blends. Feng et al.²⁸⁻³⁰ pointed out that the miscibility of the polystyrene-*block*-polybutadiene-*block*-polystyrene/polystyrene (SBS/PS) blends and PS/PS-*b*-PB-4-arm blends depended on the $M_{n,h-PS}$, whereas it was independent of the structure of block copolymer. The miscibility between the asymmetric PS-*b*-PB star block copolymer (ST2) and 20% PS homopolymer was investigated by Adhikari et al.³¹ The miscibility, structure, and mechanical properties of SIS/h-I (50/50) blending systems have been researched by Kane et al.³²

In our previous work, the crystallization behavior of the dry brush blending system of PS-*b*-PEO-*b*-PS and h-PEO10000 (A-*b*-B-*b*-A/h-B) was studied,³³ in which both *b*-PEO (*b*-B) and h-PEO (*h*-B) can crystallize. It indicates that the homogeneous nucleation crystallization occurs in the neat block copolymer, and the adding of PEO homopolymer into PS-*b*-PEO-*b*-PS copolymer cannot totally erase the homogeneous nucleation crystallization of PS-*b*-PEO-*b*-PS copolymer but increases the homogeneous nucleation crystallization temperature. In this work, the crystallization behaviors of the blending systems of PS-*b*-PEO-*b*-PS and h-PEO with different molar masses (600, 2000, 10,000 and 20,000 g/mol) were studied by DSC measurements. The confined crystallization for the blending system of PS-*b*-PEO-*b*-PS and h-PEO was investigated, and the difference in the crystallization behavior of h-PEO and *b*-PEO in the dry-brush and wet-brush blending systems has been discussed.

EXPERIMENT

The synthesis and purification of ABA triblock copolymer PS-*b*-PEO-*b*-PS strictly followed the method described by Jankova et al.³⁴ The molar mass of PEO macromolecular initiator is 10,000 g/mol, whereas that of each arm of PS block is about 64,500 g/mol, which consists the PS-*b*-PEO-*b*-PS copolymer with molar mass of 139,000 g/mol and the polydispersity of 1.68. PEO homopolymers with different molar masses ($M_{h\text{-PEO}} = 600, 2000, 10,000, 20,000$ g/mol) were obtained from Sinopharm Chemical Reagent (China, China) and used without further purification. All the characterization data of molecular weights were obtained by gel permeation chromatography (GPC). The blending of PS-*b*-PEO-*b*-PS copolymer and PEO homopolymer with different compositions was carried out by dichloromethane in a beaker. After stirring for 20 min, the solution was left to evaporate in a fume hood at room temperature. Solvent was removed drastically in a vacuum oven overnight.

A Perkin-Elmer Diamond DSC was used to characterize the melting and crystallization behavior of the blends. The calibration was carried out with indium and zinc. Without specification, the entire heating and cooling scans were performed at the rate of 10°C/min. Ultrapure nitrogen was used as purge gas.

RESULTS AND DISCUSSION

The crystallization processes of PS-*b*-PEO-*b*-PS and PS-*b*-PEO-*b*-PS/h-PEO systems

Samples of h-PEO ($M_{h\text{-PEO}} = 600, 2000, 10,000, 20,000$), PS-*b*-PEO-*b*-PS copolymer, and their blends

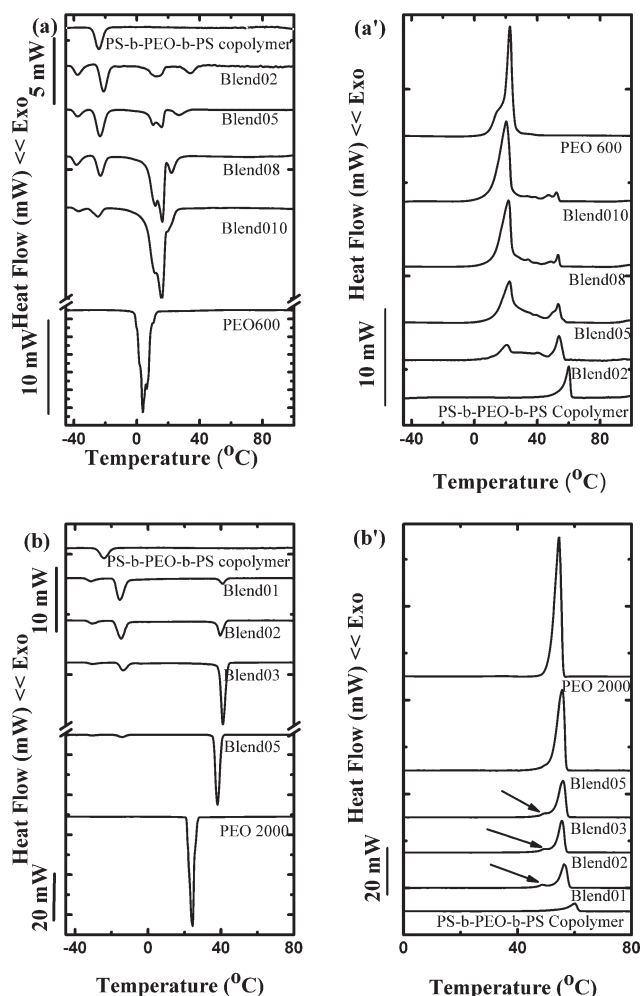


Figure 2 The crystallization curves of h-PEO, copolymer, and their “wet brush” blends for h-PEO600 (a) and 2000 (b) blending systems, respectively; (a') and (b') show the successive melting curves correspondingly. (Blend0*x* indicates that the weight ratio of h-PEO/PS-*b*-PEO-*b*-PS is *x*/10, and the value of *x* is 1, 2, . . . 10. The break on the *x* axis is for better viewing. The explanatory caption is applied equally for following figures.)

with different fractions were heated up to 150°C and kept for 3 min, then cooled down to -50°C. The corresponding cooling scans were recorded as shown in Figures 2(a,b) and 3(a); the immediate subsequent heating scans are presented in Figures 2(a',b') and 3(a').

Melting and crystallization behavior in “wet brush” blending systems

The wet brush blending systems were obtained by adding of h-PEO600 and h-PEO2000 into the PS-*b*-PEO-*b*-PS block copolymer. Figure 2(a,a') shows the standard cooling scans of crystallization and the subsequent heating scans of melting, respectively, in the DSC experiment for neat PS-*b*-PEO-*b*-PS copolymer, h-PEO600 homopolymer, and their blends with

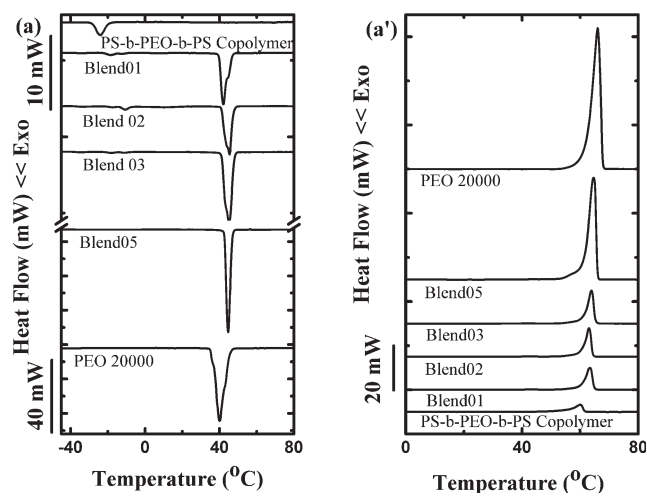


Figure 3 The crystallization (a) and melting (a') curves of h-PEO, copolymer, and their “dry brush” blends for h-PEO20000 blending systems.

different compositions. In the cooling scan curve of the PS-*b*-PEO-*b*-PS copolymer, only one crystallization peak at a very low temperature of about -24°C was observed, and the corresponding melting peak appears at about 60°C . It means that the melting hysteresis ($T_m - T_c$) of the b-PEO10000 domain is 84°C , which is greatly larger than that of the h-PEO10000 in the bulk ($\sim 20^{\circ}\text{C}$). This is attributed to the homogeneous nucleation crystallization of b-PEO10000.³⁵ When h-PEO600 is added into the block copolymer, four crystallization peaks at 30°C (T_{c1}), 12°C (T_{c2}), -20°C (T_{c3}), and -38°C (T_{c4}) can be observed (the detail presentation of the notations are shown in Table I), which are attributed to the heterogeneous nucleation crystallization of b-PEO10000 and h-PEO600, the homogeneous nucleation crystallization of b-PEO10000, and h-PEO600, respectively. When only a small amount of h-PEO600 is added, they are uniformly dissolved into the brushes of b-PEO10000 and the b-PEO10000 chains are not extended as much and still maintain soft. Thereby when active heterogeneity exists, the soft b-PEO10000 chains are capable of crystallization locally at normal temperature. With the increase

amount of added h-PEO600, more and more h-PEO600 molecules can be distributed into the b-PEO10000 domains. The b-PEO10000 chains are stretched and the interspaces between them are expanded [as illustrated in Fig. 1(c)], which will hinder the chains from folding and crystallizing. Therefore, the crystallization temperature T_{c1} decreases closer to T_{c2} and finally they are almost merged. In the subsequent heating scans for each blending system, as shown in Figure 2(a'), two main melting peaks can be found. Additionally, a halo formed between the two peaks raises the curve away from the baseline. It suggests that crystallographic defects are formed in these blend systems by chain entanglement of the b-PEO10000 and h-PEO600.

The crystallization and melting curves of the PS-*b*-PEO-*b*-PS/h-PEO2000 blends with different weight percentages of homopolymer are shown in Figure 2(b,b'). Three crystallization peaks at about 40°C (T_{c1}), -15°C (T_{c2}), and -31°C (T_{c3}) were observed in all blending systems. With the increasing of the added h-PEO2000, the area of the peak T_{c2} decreases, whereas that of T_{c1} increases simultaneously. Temperature at peak T_{c2} in blends, the homogeneous nucleation crystallization temperature of b-PEO10000, is about 9°C higher than that in neat PS-*b*-PEO-*b*-PS copolymer due to the enlargement of the b-PEO domains by adding h-PEO2000.^{3,36} The crystallization peak T_{c1} at 40°C , attributed to the heterogeneous nucleation crystallization of h-PEO2000 and b-PEO10000, is absolutely higher than the crystallization temperature of h-PEO2000, at about 24°C in the bulk. That is, h-PEO2000 can crystallize at a higher temperature under the inducement of the crystallization of b-PEO10000 at 40°C .

In both of the wet brush systems, we can find a crystallization peak at temperatures lower than -30°C (-37°C and -31°C for the h-PEO600 and h-PEO2000 added systems, respectively). This is attributed to the homogeneous nucleation crystallization of the h-PEO600 and h-PEO2000, which are distributed in the blend systems with a much smaller microdomain size. Their self-seeding and annealing

TABLE I
The Crystallization Temperature (T_c) for Different Blending Systems

Nucleation blends	Hetero-(b-PEO)	Hetero-(h-PEO)	Homo-(b-PEO)	Homo-(h-PEO)
h-PEO600	$T_{c1} (^{\circ}\text{C})$	$T_{c2} (^{\circ}\text{C})$	$T_{c3} (^{\circ}\text{C})$	$T_{c4} (^{\circ}\text{C})$
Blending systems	($\sim 30^{\circ}\text{C}$)	($\sim 12^{\circ}\text{C}$)	($\sim -20^{\circ}\text{C}$)	($\sim -38^{\circ}\text{C}$)
h-PEO2000	$T_{c1} (^{\circ}\text{C})$		$T_{c2} (^{\circ}\text{C})$	$T_{c3} (^{\circ}\text{C})$
Blending systems	($\sim 40^{\circ}\text{C}$)		($\sim -15^{\circ}\text{C}$)	($\sim -31^{\circ}\text{C}$)
h-PEO10000	$T_{c1} (^{\circ}\text{C})$		$T_{c2} (^{\circ}\text{C})$	-
Blending systems	($\sim 45^{\circ}\text{C}$)		($\sim -11^{\circ}\text{C}$)	
h-PEO20000	$T_{c1} (^{\circ}\text{C})$		$T_{c2} (^{\circ}\text{C})$	-
Blending systems	($\sim 45^{\circ}\text{C}$)		($\sim -11^{\circ}\text{C}$)	

behavior also can be observed at much lower temperatures in the self-seeding process, which will be discussed in another article.

Comparing the two wet brush blending systems, we find that the homogeneous nucleation crystallization temperature (T_{c3} , -20°C) of b-PEO10000 domains in the h-PEO600 blending systems is lower than that in the h-PEO2000 blending system (T_{c2} , -15°C). Due to the smaller molecular weight of h-PEO600, more h-PEO600 molecules can get into the b-PEO domains, and the b-PEO10000 chains can be greatly stretched and the distances between chains will be largely increased, which will have greater hindrance for the chains to crystallize. Thus, the increase of temperature for the homogeneous nucleation crystallization caused by size increase in the h-PEO600 blending system is smaller than that in h-PEO2000 blending systems.

Two distinct heterogeneous nucleation crystallization peaks, T_{c2} (12°C) and T_{c1} (30°C), can be found in h-PEO600 blending systems, whereas only one (at 40°C) appears in the h-PEO2000 blending systems. Although the heterogeneous nucleation crystallization temperatures of the two h-PEO polymers increase several degrees after blending with the PS-*b*-PEO-*b*-PS copolymer, the crystallization temperature of h-PEO600 ($<10^{\circ}\text{C}$) is too far away from the peak of b-PEO10000 to cause them to merge in these blends like that in h-PEO2000 blends. The corresponding melting curves shown in Figure 2(a',b') also present a similar phenomenon.

Melting and crystallization behavior in "dry brush" blending systems

The h-PEO10000 and h-PEO20000 polymers were added into the block copolymer to prepare the dry brush blending systems, and the former one has been discussed in our previous work.³³ The results indicate that the homogeneous nucleation crystallization occurs in block copolymer, and the homogeneous nucleation crystallization temperature is increased by blending h-PEO10000 into the PS-*b*-PEO-*b*-PS copolymer. Similar results have been obtained for PS-*b*-PEO-*b*-PS/h-PEO20000 blending system in this work, as shown in Figure 3(a). In the dry brush blending systems with different compositions, a homogeneous nucleation crystallization peak at about -10°C can be observed, 14°C higher than that of the block copolymer because of the enlargement of the domain size. Besides the homogeneous nucleation crystallization, the heterogeneous nucleation crystallization peaks can be observed at about 45°C in both dry brushes.

The TEM images of h-PEO10000 blending systems are shown in our previous article.³³ Based on the images, the droplet-matrix structure can be found in

the neat PS-*b*-PEO-*b*-PS block copolymer. When the PEO homopolymer is added into block copolymer, the small droplets of PEO block still exist, whereas some larger droplets corresponding to h-PEO also can be observed. It indicates that part of the added h-PEO molecules can enter the b-PEO droplets and the other part of h-PEO molecule forms its own droplets. In the range of the amount of homopolymer added in this experiment, the b-PEO spheres can be retained with larger sizes without being destroyed.

Comparing the DSC results of the wet brush and dry brush blending systems of PS-*b*-PEO-*b*-PS and h-PEO, an obvious difference between these systems can be found, i.e., the increment of the homogeneous nucleation crystallization temperature is different from each other and the temperature increment of wet brush blending systems is smaller than that of dry brush blending systems. It can be seen in Figures 2 and 3 that the temperature increases from -24°C to around -20°C and -15°C for PS-*b*-PEO-*b*-PS/h-PEO600 (Blend01) and PS-*b*-PEO-*b*-PS/h-PEO2000 blending systems (Blend01), respectively, whereas it increases to about -10°C for both of the PS-*b*-PEO-*b*-PS/h-PEO10000 and PS-*b*-PEO-*b*-PS/h-PEO20000 dry brush blending systems. The crystallization behavior of b-PEO10000 in blending systems is affected by two factors: one is the domain size and the other is the degree of the chains stretched, i.e., the increase of the domain size leads to the increase of the crystallization temperature; whereas the crystallization temperature can be decreased by the stretched molecular chains. The obtained crystallization temperature can be determined by the competition of these two factors. In the wet brush blending systems, more homopolymer molecules can enter into the b-PEO10000 chains; thus the chain stretch is the dominant factor that decreases the crystallization temperature, whereas the increased domain size is the dominant factor in dry brush blending systems in which crystallization temperature is increased. Therefore, the increment of the homogeneous nucleation crystallization temperature in the wet brush blending systems is smaller than that in the dry brush blending systems.

The self-seeding procedure

The self-seeding procedure designed by Fillon et al.³⁷ has been used to investigate the crystallization behavior of these blending systems. Different self-seeding domains have been presented. The samples will be in different states at different self-seeding temperatures, T_s : completely molted, only self-seeded, or self-seeded and annealed, corresponding to Domain I, Domain II and Domain III, respectively. Under a high enough T_s , no self-seeds or crystals

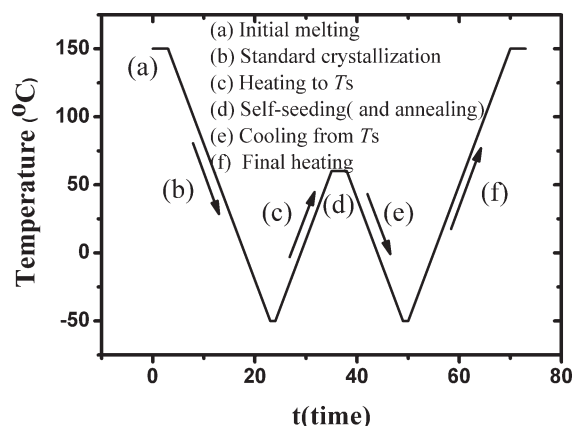


Figure 4 Schematic representation of the self-seeding procedure conducted by DSC. (a) Erasure of any previous thermal history by heating the sample up to 150°C and maintaining for 3 min. (b) Creation of a “standard” thermal history by cooling at a rate of 10°C/min to -50°C. (c) Partial melting up to a self-seeding temperature T_s at a rate of 10°C/min. (d) Thermal condition at T_s for 3 min. (e) DSC cooling scans from T_s to -50°C at a rate of 10°C/min. (f) DSC heating scans from -50°C to 150°C at a rate 10°C/min.

can survive, and the sample will be completely melted, in which Domain I can be defined. When T_s is high enough to melt almost all samples completely but leaves some small crystal fragments unmelted, which acts as the self-seeds in the followed cooling scans, the sample is considered to be in Domain II. At lower T_s , only part of the crystals can be melted, then the unmelted crystals will be annealed, and the rest of the polymer will be self-seeded in the cooling scans, which is assigned to be Domain III. The self-seeding procedure is schemed in Figure 4. Based on the self-seeding experiments in this work, different self-seeding domains have been ascertained.

Self-seeding procedure of the “wet brush” blending systems

Figure 5(a) shows the self-seeding results for Blend02 of the h-PEO600 blending system at different self-seeding temperatures. No difference was observed in crystallization curves at T_s higher than 59°C, nor in the melting curves in Figure 5(a'). When the T_s decreases down to 58°C, the crystallization peak becomes rather wide and nearly divides into two peaks [indicated by arrows in Fig. 5(a)], one is still at the original position and the other shifts to a higher temperature. It is suggested that some of the crystals remain at the original state, i.e., Domain I, whereas the others are self-seeded under this T_s , i.e., Domain II. The peak T_{c1} shifts to a higher temperature at about 41°C when T_s is down to 57°C or 56°C, which indicates that the samples

are totally in Domain II. Peak T_{c1} goes on shifting to higher temperatures when T_s is down to 55°C and the crystallization seems to start just at the beginning of the cooling run, which usually means that the self-seeding and the annealing behavior occur simultaneously. Furthermore, a small high-temperature melting peak appears in the corresponding melting curve (indicated by arrow) because of thicker and more perfect crystals formed during the annealing process. From this T_s temperature (55°C) downward, Domain III has been reached. Further decrease in the T_s means larger amounts of unmelted and annealed crystals and higher melting temperatures. During the self-seeding process, the T_{c3} peak also changes. When the T_s decreases from 56°C to 55°C, the T_{c3} peak sharply decreases until disappears at $T_s = 54°C$, which means all crystals are self-seeded below this temperature. Additionally,

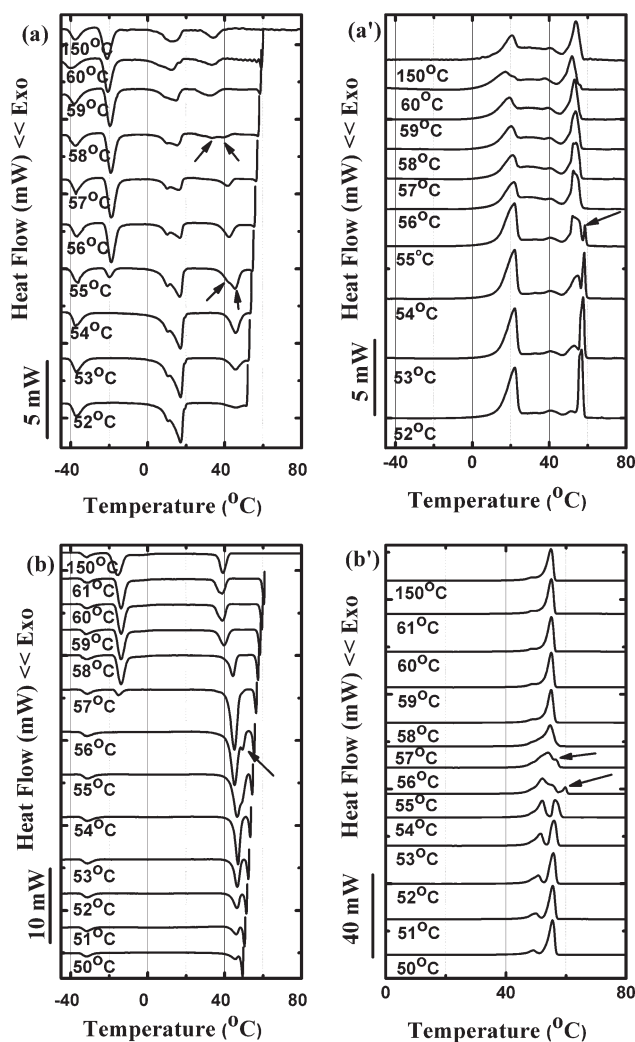


Figure 5 The cooling DSC curves from indicated T_s for Blend02 with h-PEO 600 (a) and h-PEO 2000 (b) and the subsequent heating DSC curves (a', b') after self-seeding at the indicated temperatures, respectively.

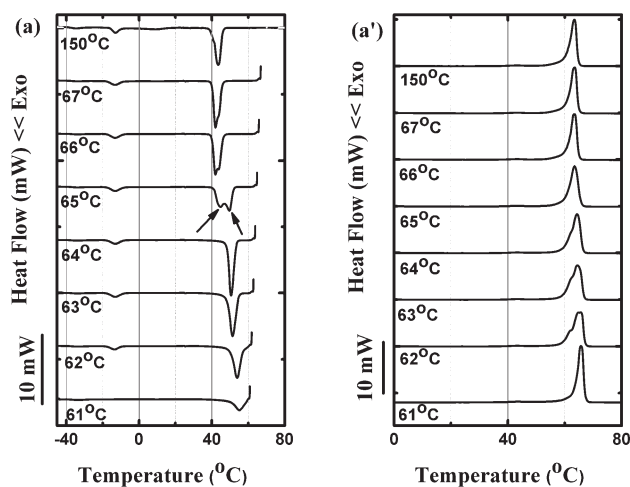


Figure 6 The cooling DSC curves from indicated T_s for Blend01 with h-PEO 20,000 (a) and the subsequent heating DSC curves (a') after self-seeding at the indicated temperatures.

with the decrease of T_s , both melting peaks become sharper at the expense of the halo between them. The reason is that the phase separation between homopolymer and block copolymer occurs during this process, and the details will be presented in another report.

Figure 5(b) shows the self-seeding results for the Blend02 of the h-PEO2000 blending system. Similar to that in the h-PEO600 blending system, this system will be in Domain I at high T_s ($\geq 59^\circ\text{C}$) and in Domain II at $T_s = 58^\circ\text{C}$ and 57°C . When the T_s is down to 56°C , the crystallization peak T_{c1} divides into two peaks (indicated by arrow) and the successive melting peak becomes broad, as shown in Figure 5(b'). It indicates that Domain III has been reached. The division of the peak T_{c1} suggests that there are two kinds of crystal microdomains in the state of Domain II and Domain III, respectively. The detailed interpretation has been pointed out by Gao et al.³³ With further decreasing of the T_s , the high-temperature melting peak becomes obvious and the area of the higher melting peak increases, which indicates a more drastic annealing behavior. The T_{c3} peak disappears at $T_s = 56^\circ\text{C}$ due to the self-seeding behavior of the crystallized polymers.

Self-seeding procedure of the “dry brush” blending systems

Figure 6(a,a') shows the self-seeding results of the dry brush blending systems (Blend01) containing h-PEO20000. The self-seeding behavior of the h-PEO20000 blending systems is similar to that of the h-PEO10000 blending systems reported in our previous work,³³ in which self-seeding domains are confirmed. It is clear that the system is assigned to be in

Domain I when the T_s is higher than 66°C . When the T_s is at 65°C , peak division occurs in the peak T_{c1} , and both of the two peaks are higher than their original temperatures. Correspondingly, the successive melting peak becomes broad. As we discussed in the wet brush blending systems, self-seeding occurs at this temperature and the divided peaks are correspondingly attributed to the self-seeded crystals and the self-seeded and annealed crystals. That means Domain II and Domain III are coexistent when the self-seeding temperature is 65°C . When the T_s is at 64°C , the peak T_{c1} shifts to a higher temperature at about 50°C , which means that Domain III has been achieved. When the T_s is further down to 61°C , the T_{c2} peak disappears and the corresponding melting peak shifts to higher temperature and becomes sharper.

Comparing the self-seeding results of the wet brush and dry brush blending systems, an obvious difference can be distinguished in the melting curves. For the wet brush blending systems, a higher temperature peak appeared in the melting curves during the self-seeding procedure when the Domain III was achieved, as shown by arrows in Figure 5(a',b'), whereas it cannot be observed in the dry brush blending systems. The appearance of the higher temperature melting peak, a typical character of “annealing behavior” in the wet brush blending systems, comes from the annealing of the crystals under a proper self-seeding temperature. In the dry brush blending systems, the annealing behavior does not perfect the crystallization much, thus the increment of the melting temperature is small, and the melting peak only becomes broad without the appearance of a new melting peak at a higher temperature. For the wet brush blending system, when the sample was heated from -50°C to T_s , h-PEO600 with the lower melting point will be melted first. At proper T_s , the crystal of PEO block will be significantly perfected by the annealing behavior; this results in the appearance of the conspicuous higher temperature melting peak in the melting curve. It is the same for the h-PEO2000 added systems. For the dry brush blending, the entanglement between the copolymer and homopolymer is much less than that in the wet brush blending, so the crystals of both components are relatively more perfect. The annealing behavior has less influence on the corresponding melting curves.

Furthermore, the homogeneous nucleation crystallization peak in the wet brush (peak T_{c3} in the h-PEO600 blending systems and T_{c2} in h-PEO2000 blending systems) in the self-seeding process is also different from that in the dry brush blending systems (peak T_{c2} in h-PEO10000 and h-PEO20000 blending systems). When the crystals, assigned to peak T_{c3} or T_{c2} , are totally self-seeded under a

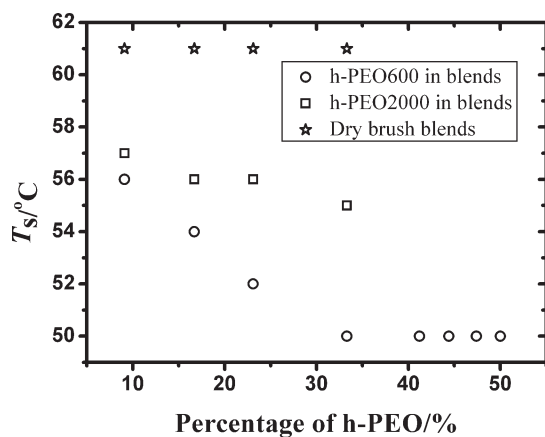


Figure 7 The T_s for the homogeneous nucleation crystallization peak in totally self-seeded blending systems.

certain value of T_s , the homogeneous nucleation crystallization peak will disappear. For all dry brush blending systems with different h-PEO percentages, the T_s is identical at 61°C, whereas in the wet brush blending systems, the T_s decreases with the increase of the h-PEO percentages, as shown in Figure 7. This phenomenon is related to the weight of the h-PEO in the b-PEO10000 domains. For the dry brush blending systems, the microdomain seems to be saturated by the homopolymer, even adding 9.1% h-PEO (Blend01). The exact crystallization enthalpy at peak T_{c2} (peak T_{c3} for h-PEO600 blending systems) is almost the same²⁴ in dry brush blends, whereas it decreases in the wet brush blends as the amount of h-PEO increases from 9.1% to 33.3%. Thus, the self-seeding behavior for peak T_{c2} is independent of the h-PEO percentage in the dry brush blends.

CONCLUSIONS

The crystallization behavior for the wet brush and dry brush blending systems of PS-*b*-PEO-*b*-PS/h-PEO ($M_{h-PEO} = 600, 2000, 10,000, 20,000$ g/mol) with different fractions was studied in this work. For the neat block copolymer, only homogeneous nucleation crystallization peak was observed at -24°C . For both the wet brush and the dry brush blending systems, the homogeneous nucleation crystallization temperature increases with the increase of the domain size caused by adding h-PEO. The temperature increment in the wet brush blending systems is smaller than that in the dry brush blending systems because of the stretches of the b-PEO10000 chains and the increasing of the distance between the chains in the wet brush blending, which is a disadvantageous factor for crystallization. However, the b-PEO10000 chains will not be affected in the dry brush blending system. In all of the blending systems, the heterogeneous nucleation crystallization behavior of b-

PEO10000 can be observed. The heterogeneous nucleation crystallization peaks for b-PEO10000 and h-PEO are incorporated in all systems except the h-PEO600 blending systems because of the much lower crystallization temperature of h-PEO600. In the wet brush blending systems, the heterogeneous nucleation crystallization temperature for b-PEO10000 is lower than that of h-PEO10000 in the bulk. At the same time, the crystallization of b-PEO10000 at higher temperatures initiates the h-PEO600 and h-PEO2000 molecules to crystallize at higher temperatures than that in the bulk, whereas in the dry brush blending systems, the heterogeneous nucleation crystallization temperature is almost the same as that in the bulk. During the self-seeding procedure, a new higher temperature melting peak appears when the Domain III has been achieved. However, in the dry brush blending systems, the division of the melting peak is not observed. Furthermore, different self-seeding domains were confirmed in all of the blending systems.

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References

- Müller, A. J.; Balsamo, V.; Arnal, M. L. *Adv Polym Sci* 2005, 190, 1.
- Zhu, L.; Cheng, S. Z. D.; Calhoun, B. H.; Ge, Q.; Quirk, R. P.; Thomas, E. L.; Hsiao, B. S.; Yeh, F.; Lotz, B. *J Am Chem Soc* 2000, 122, 5957.
- Zhu, L.; Calhoun, B. H.; Ge, Q.; Quirk, R. P.; Cheng, S. Z. D. *Macromolecules* 2001, 34, 1244.
- Zhu, L.; Cheng, S. Z. D.; Calhoun, B. H.; Ge, Q.; Quirk, R. P.; Thomas, E. L.; Hsiao, B. S.; Yeh, F.; Lotz, B. *Polymer* 2001, 42, 5829.
- Zhu, L.; Mimnaugh, B. R.; Cheng, S. Z. D.; Ge, Q.; Quirk, R. P.; Thomas, E. L.; Lotz, B. *Polymer* 2001, 42, 9121.
- Zhu, L.; Huang, P.; Chen, W. Y.; Ge, Q.; Quirk, R. P.; Cheng, S. Z. D.; Thomas, E. L.; Lotz, B.; Hsiao, B. S.; Yeh, F. J.; Liu, L. *Macromolecules* 2002, 35, 3553.
- Chen, H. L.; Hsiao, S. C.; Lin, T. L.; Yamauchi, K.; Hasegawa, H.; Hashimoto, T. *Macromolecules* 2001, 34, 671.
- Chen, H. L.; Wu, J. C.; Lin, T. L.; Lin, J. S. *Macromolecules* 2001, 34, 6936.
- Lee, W. C.; Chen, H. L.; Lin, T. L. *J Polym Sci Part B: Polym Phys* 2002, 40, 519.
- Loo, Y. L.; Register, R. A.; Ryan, A. J. *Macromolecules* 2002, 35, 2365.
- Chen, H. L.; Lin, S. Y.; Huang, Y. Y.; Chiu, F. C.; Liou, W.; Lin, J. S. *Macromolecules* 2002, 35, 9434.
- Müller, A. J.; Balsamo, V.; Arnal, M. L.; Jakob, T.; Schmalz, H.; Abetz, V. *Macromolecules* 2002, 35, 3408.
- Huang, P.; Zhu, L.; Cheng, S. Z. D.; Ge, Q.; Quirk, R. P. *Macromolecules* 2001, 34, 6649.
- Huang, P.; Guo, Y.; Quirk, R. P.; Ruan, J.; Cheng, S. Z. D. *Polymer* 2006, 47, 5457.
- Huang, P.; Zhu, L.; Guo, Y.; Ge, Q.; Cheng, S. Z. D. *Macromolecules* 2004, 37, 3689.
- Vasilev, C.; Reiter, G.; Pispas, S.; Hadjichristidis, N. *Polymer* 2006, 47, 330.

17. Balsamo, V.; Paolini, Y.; Ronca, G.; Müller, A. J. *Macromol Chem Phys* 2000, 201, 2711.
18. Lu, S.; Liu, Y. X.; Zhu, L.; Benjamin, S. H.; Carlos, A. A. *Polymer* 2004, 45, 8181.
19. Bates, F. S.; Frederickson, G. H. *Annu Rev Phys Chem* 1990, 41, 525.
20. Manaure, A. C.; Müller, A. J. *Macromol Chem Phys* 2000, 201, 958.
21. Arnal, M. L.; Müller, A. J.; Maiti, P.; Hikosaka, M. *Macromol Chem Phys* 2000, 201, 2493.
22. Hashimoto, T.; Koizumi, S.; Hasegawa, H. *Phys B* 1995, 213, 676.
23. Tanaka, H.; Hasegawa, H.; Hashimoto, T. *Macromolecules* 1991, 24, 240.
24. Koizumi, S.; Hasegawa, H.; Hashimoto, T. *Macromolecules* 1994, 27, 7893.
25. Koizumi, S.; Hasegawa, H.; Hashimoto, T. *Macromolecules* 1994, 27, 6532.
26. Hashimoto, T.; Hideaki, T.; Hasegawa, H. *Macromolecules* 1990, 23, 4378.
27. Hashimoto, H.; Fujimura, M.; Hashimoto, T.; Kawai, H. *Macromolecules* 1981, 14, 844.
28. Feng, H. Q.; Feng, Z. L.; Yuan, H. Z.; Shen, L. F. *Macromolecules* 1994, 27, 7830.
29. Feng, H. Q.; Feng, Z. L.; Shen, L. F. *Macromolecules* 1994, 27, 7835.
30. Feng, H. Q.; Feng, Z. L.; Shen, L. F. *Macromolecules* 1994, 27, 7840.
31. Adhikari, R.; Michler, G. H.; Godehardt, R.; Ivan'kova, E. M. *Polymer* 2003, 44, 8041.
32. Kane, L.; Norman, D. A.; White, S. A.; Matsen, M. W.; Satkowski, M. M.; Smith, S. D.; Spontak, R. J. *Macromol Rapid Commun* 2001, 22, 281.
33. Gao, Y.; Liu, H. L. *J Appl Polym Sci* 2007, 106, 2718.
34. Jankova, K.; Chen, X. Y.; Kops, J.; Batsberg, W. *Macromolecules* 1998, 31, 538.
35. Huang, Y. Y.; Chen, H. L.; Li, H. C.; Lin, T. L.; Lin, J. S. *Macromolecules* 2003, 36, 282.
36. Massa, M. V.; Veress, K. D. *Phys Rev Lett* 2004, 92, 25509.
37. Fillon, B. W.; Wittmann, J. C.; Lotz, B.; Thierry, A. *J Polym Sci Part B: Polym Phys* 1993, 31, 1383.