

Crystallization Behavior of Dry-Brush PEO-PS Block Copolymer and PEO Homopolymer Blend

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Received 17 September 2006; accepted 11 May 2007

DOI 10.1002/app.26812

Published online 1 August 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The crystallization behavior of semicrystalline PEO homopolymer/triblock PS-PEO-PS copolymer blend system, which exhibited "Dry-Brush" in the melt. A symmetric polystyrene-poly(ethylene oxide)-polystyrene triblock copolymer was blended with PEO homopolymer (h-PEO) having the same molecular weight as that of the PEO block in the copolymer. Considering the composition of the blend ($W_{ps} \geq 0.8$), PEO spheres were formed in the blend. Because of the dry-brush phase behavior of this blend, h-PEO added was localized in the PEO microdomains, which increases the domain size without changing

the microdomain morphology. The crystallization of PEO block was confined within the microdomains and the crystallization temperature was about 60°C lower than normal. Self-seeding tests were performed to clarify the nucleation mechanism of the blend. Because the droplets size varies greatly, multicrystallization peaks were witnessed in the self-seeding process. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2718–2723, 2007

Key words: blending; differential scanning calorimetry (DSC); crystallization; nucleation

INTRODUCTION

The confined crystallization behavior of copolymers and blends consisting of immiscible semicrystalline component and amorphous component has attracted great interests in recent years.^{1–24} When confined crystallization happens in a multiphase system, mesophase might be formed in the melt. Microphase separation in a system may generate long-range ordered microdomain: lamellar, cylinder, sphere, etc. But the final morphology after solidification is mainly based on the interplay between microphase separation and crystallization of a crystalline phase. Depending on the segregation strength, the mode of crystallization in block copolymer was distinguished into breakout crystallization, template crystallization, and confined crystallization. Mesophase morphology in melt and the chain length of copolymer play an important role on the mode of crystallization, such as breakout or confinement. The glass transition temperature (T_g) of amorphous block, the crystallization temperature (T_c) of the semicrystalline block, and the temperature of order-disorder transition (T_{ODT}) are very important for the confined crystallization of a block copolymer.

The concept of hard and soft confined crystallization was introduced by Cheng and coworkers when they studied the crystallization of PEO-co-PS copolymers.^{19–24} 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. Muller et al. have built clear concept on the confined (fractionated) crystallization and homogeneous nucleation of a series of block copolymer and polymer blends.^{25,26} When amorphous blocks are in the confinement, the nucleation mode of semicrystalline blocks is different from that of a PEO homopolymer. The number of droplets formed by microdomain separation is so great that each droplet couldn't possess the same kind of nuclei. Those droplets containing the heterogeneities that are active at lowest supercooling can crystallize at the same temperature as in the bulk. Those droplets containing the heterogeneities that are less effective can crystallize at larger supercooling. And those droplets that do not contain heterogeneities have to adopt homogeneous crystallization at largest supercooling.

In our study, PS-PEO-PS ABA triblock copolymer is synthesized through ATRP method and blended with homopoly(ethylene oxide) having the same molecular weight as that of the PEO block. In this situation, the blend is called "dry-brush" system.^{27,28} If the molecular weight of homopolymer is smaller than that of a block, it is called "wet-brush" system.

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For “wet-brush” system, homopolymer added to the system will be solubilized uniformly in the corresponding microdomains, thus causing changes of the microdomain morphologies.²⁹ Differential scanning calorimeter (DSC) was used to reveal the morphology changes in the dry-brush blend. Observing from DSC crystallization curves, the crystallization of PEO block in triblock copolymer occurs under much greater supercooling than that of the h-PEO ($\Delta T > 65^\circ\text{C}$). Due to the strong phase separation and the composition of the blend, PEO blocks spheres are formed in block copolymer. PEO blocks are confined inside this structure and separated from each other. This structure suggests that the crystallization only occurs under the initiate of homogeneous nucleation.

Adding h-PEO does not change the morphology type of triblock copolymer because of the feature of dry-brush blending. But an increase in the microdomain size of PEO phase is observed in the blends. The homogeneous nucleation crystallization temperature of h-PEO/triblock copolymer blend increases from -25 to 10°C . According to recent literatures,^{8,30–33} the homogeneous nucleation crystallization temperature of PEO varies from -50 to -3°C depending on the size of dispersion phase or the size of microdomain. And there has a clearly connection between the homogeneous nucleation crystallization temperature and the microdomain size.^{7,34} In this study, the homogeneous nucleation crystallization temperature of PEO in the blend is 15°C higher than that of PEO block in the copolymer. This suggests that the domain size increases upon adding h-PEO in the blend because of the dry-brush blending. But the compatibilization effect exerted by dry-brush blending is far less effective than the corresponding wet-brush blending, and so the h-PEO is not totally confined inside the microdomains formed by copolymer. Part of h-PEO forms droplets because of macrophase separation and crystallizes at the same supercooling as that of bulk h-PEO. Self-seeding tests are performed to study the nucleation and crystallization of the copolymer and blends. The self-seeding crystallization peaks are observed to split into two peaks at the boundary of self-seeding domain II and domain III. This is likely because of the dispersion on the size of PEO droplets and microdomains.

EXPERIMENTAL

The synthesis and purification of PS-PEO-PS ABA copolymer is strictly followed the method described by Jankova et al.³⁶ The molecular weight of PEO macromolecular initiator is 10,000 g/mol whereas the molecular weight of each arm of PS block is about 64,500 g/mol, which consists the PS-PEO-PS copolymer with molecular weight of 139,000 g/mol

and the polydispersity of 1.68. All the molecular weight characterization data is obtained by GPC (gel permeation chromatography). All the samples used in this article are prepared by solvent evaporation from dichloromethane solution. The blending of PS-PEO-PS copolymer and PEO homopolymer is conducted in solution. Copolymer and homopolymer with different compositions are dissolved by dichloromethane inside a beaker. After continual stirring for 20 min, the solution is cast into a plate and left to evaporate in a fume hood at room temperature. Solvent is removed by transferring the sample in a vacuum oven overnight.

A Perkin-Elmer Diamond DSC is used to characterize the melt and crystallization behavior of the blends. The calibration is carried out with indium and zinc. Without specification, the entire heating and cooling scans are performed at the rate of $10^\circ\text{C}/\text{min}$. Ultra pure nitrogen is used as purge gas.

TEM (Transmission Electron Microscopy) observation is performed by a JEOL JM1011 microscope. The acceleration voltage is 100 KV. The solution of 1% polymer is dropped on the TEM grid with carbon film on it. The TEM grid is dried in vacuum oven over night to remove solvent. The blend is stained with RuO_4 vapor to increase the contrast between PS and PEO.

RESULTS AND DISCUSSION

Figure 1(a) presents the crystallization curves of PEO, PS-PEO-PS copolymer, blend A, blend B, and blend C. All the samples were heated up to 150°C and kept for 3 min, while the cooling scans were recorded in Figure 1. Immediate subsequent heating scans were presented in Figure 1(b). Considering the T_g of PS at about 100°C and the confinement of PS blocks to the crystallization of PEO block, it is not surprising to witness the crystallization temperature of PEO block decrease from 43°C (PEO homopolymer) to -25°C (PS-PEO-PS copolymer). While, it is quite remarkable that the blends A, B, and C exhibit two crystallization peaks at both -10 and 43°C , the crystallization temperature of PEO block increases from -25 to -10°C . According to literature,^{7,34} the confined crystallization temperature increases with the expanding of the microdomain size. The dry-brush blending can increase the microdomain size without changing the morphology of this blend. The PEO microdomains remain isolated from each other, which can be approved by the existence of the crystallization peak at -10°C . And the crystallization peak at 43°C suggests that the nucleation method of h-PEO is obviously heterogeneous. Judging from DSC data, the morphologies of blend A, B, and C are typical droplet-matrix (Table I). Small amount of h-PEO is

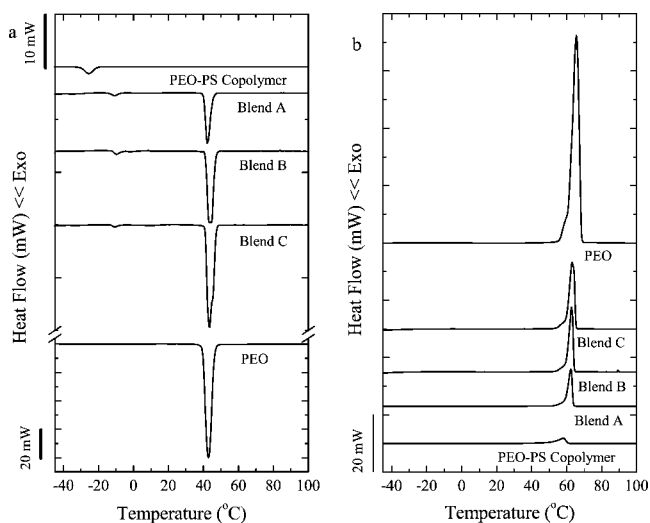


Figure 1 (a) The crystallization curves of PEO, copolymer, and their blends; (b) the successive melt curves of PEO, copolymer, and their blends.

trapped into the microdomains of PS-PEO-PS ABA triblock copolymer, thus increasing the microdomain size. Most h-PEO forms droplets in the blend. Comparing with PS-PEO-PS copolymer, the ΔH_{c2} decreases from 10.3 to 2.3 J/g and then remains almost constant for blends A, B, and C. (There is a little decrease in the crystallization enthalpy ΔH_{c2} from blend A to B to C. But when the weight fraction of PEO copolymer is considered, the exact crystallization enthalpy at -10°C is almost the same.) The content of h-PEO in the blend increases from 9.1% (blend A) to 16.7% (blend B) to 23.1% (blend C), whereas ΔH_{c2} remains almost constant. Adding more h-PEO into the blend cannot increase h-PEO content inside the microdomains of the triblock copolymer. The microdomain seems already saturated by the h-PEO even adding 9.1% h-PEO into the blend (blend A) because of the poor dry-brush blending effect. The dry-brush blending limits the compatibilizing effect between copolymer and h-PEO.

According to the study of Chen et al.⁷ on the crystallization behavior of the blends of PEO-PB block copolymer and PB homopolymer, when the content

of weight fraction of PEO block lower than 19%, a bcc packed PEO spheres were formed. Under this circumstance, these PEO spheres are isolated by PS matrix. From Figure 2(a), the morphology of PS-PEO-PS copolymer can be easily identified as a sphere-matrix structure. TEM images of PS-PEO-PS copolymer show that the PEO blocks forms spheres at the scale of less than 100 nm. For instance, if the radius of PEO spheres are 50 nm, the number of these spheres will be 1.5×10^{15} particles/cm³. This is much greater than the number of normal highly active heterogeneous nuclei in the bulk, which is at the scale of 10^9 nuclei/cm³. The number of PEO spheres is so great that most of them do not have a highly active heterogeneous nucleus in them. So, homogeneous nucleation is the only possible crystallization method for them.

To further verify the assumption, self-seeding was performed on blends A and B. As shown in Figure 3(a), a series of self-seeding tests were compared. The self-seeding technique designed by Fillon et al.³⁵ was employed to ascertain the self-seeding domains for the homopolymers and copolymers. Samples are first heated to a high enough temperature to erase thermal history. (A temperature of at least 25°C higher than the melting peak of the highest melting peak temperature in the sample was used, typically 150°C for 3 min.) Then they are cooled at $10^\circ\text{C}/\text{min}$ down to -50°C to provide them with a "standard" thermal history. Subsequently, they are heated to a temperature denoted T_s (or self-seeding temperature) and isothermally kept there for a constant time of 3 min. After treatment at T_s , the sample is cooled to -50°C and heated again at $10^\circ\text{C}/\text{min}$ until full melting occurs. Depending on T_s , the sample can be in one of three general domains: In domain I the sample is completely molten; in domain II the sample is self-seeding since T_s is high enough to melt almost all crystals, but small fragments that can act as self-nuclei remain and the nucleation density can be enormously increased by small changes in T_s ; in domain III the sample is partially molten so that self-nucleation and annealing of unmelted crystals will take place at T_s .³⁵

TABLE I
The Peak Melt and Crystallization Temperature and Enthalpy of PEO, PS-PEO-PS Copolymer, and Their Blends

Blends	Composition of PS-PEO-PS/PEO (by weight)	Crystallization and Melt Data					
		T_{c1} ($^\circ\text{C}$)	T_{c2} ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	ΔH_{c1} (J/g)	ΔH_{c2} (J/g)	ΔH_m (J/g)
PEO	0/10	42.86		65.53	-193.919		198.006
PS-PEO-PS	10/0		-25.60	57.91		-10.309	8.595
Blend A	10/1	42.27	-10.73	62.35	-28.673	-2.304	37.328
Blend B	10/2	43.45	-9.75	62.67	-48.586	-2.095	61.784
Blend C	10/3	43.45	-10.57	62.99	-66.873	-1.558	75.344

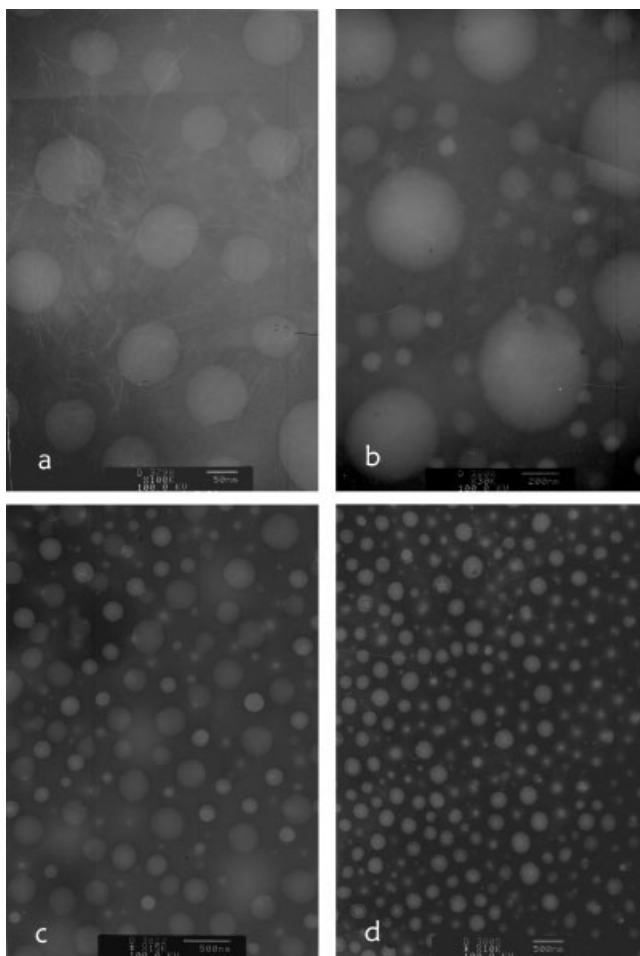


Figure 2 TEM images of (a) PS-PEO-PS copolymer; (b) blend A; (c): blend B; (d): blend C.

Figure 3 shows a series of crystallization and successive melting curves of blend A. When T_s decreases from 65 to 64°C, an obvious peak division occurs in the crystallization curve (peak A and peak B). This division clearly indicates that there are two different kinds of PEO crystal when the blend is cooled down from T_s . Both peak temperatures are higher than the “normal” crystallization temperature at about 43°C. The corresponding melting peak becomes broader, which also suggests the melting of two kinds of crystals. The two crystallization peaks indicate the different crystallization conditions: crystallization of PEO at peak A is under the initiation of partly molten PEO “seed” and annealed to form a thicker crystal; the crystallization of peak B is under the initiation of PEO “seed” but no annealing occurs. In this domain both characters of domain II and III coexists. Because of poor confinement applied by dry-brush blend, the microdomain size varies greatly. It is quite possible that some droplets are in domain II and some are in domain III. In this situation, the self-seeding thermogram will show both peaks at the same time. For blend B, self-seed-

ing test reveals similar results in Figure 4. But the peak division occurs when T_s is 65°C. It is 1°C higher than blend A. In Figure 3(a), the peak crystallization temperature of blend A has bigger displacement to 51°C when T_s are 63 and 62°C. When T_s reaches 61°C, the crystallization peak at -10°C was erased by the self-seeding process and the crystallization shifts to 53°C. The shoulder in the melting curves confirms that there are two kinds of PEO crystal existing in the blends. Decrease in T_s will keep more unmelted polymer in the system, which will act as nuclei during the successive crystallization process. That part of unmelted PEO will anneal at this process, thus increasing the melting temperature as shown in Figures 3 and 4. For blend B, the confined crystallization peak also disappears when T_s is 61°C in Figure 4.

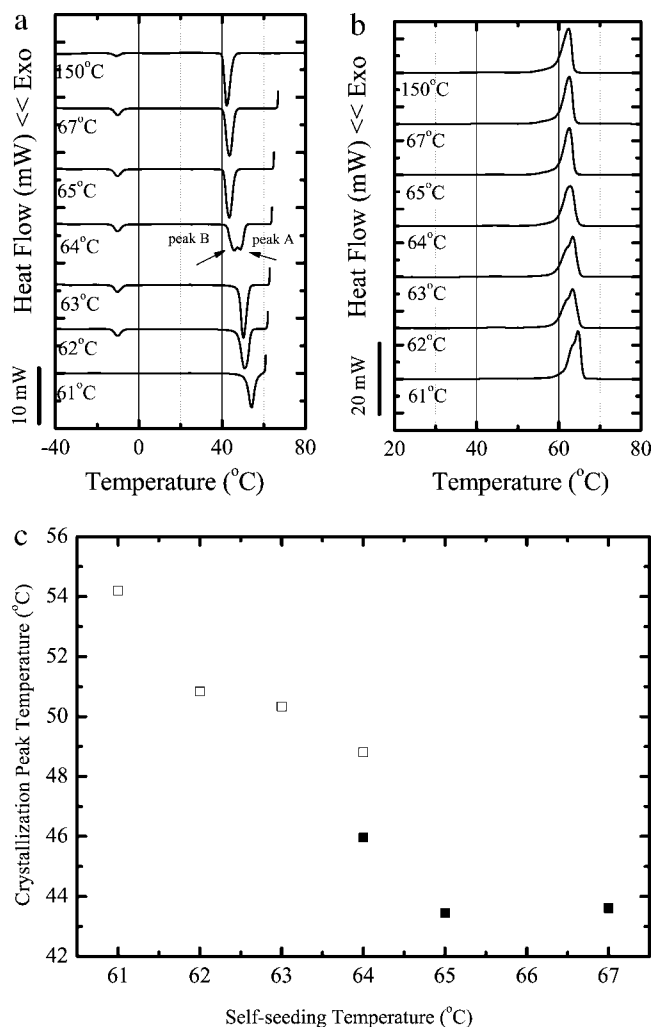


Figure 3 (a) The cooling DSC curves from indicated T_s temperatures for blend A. (b) Subsequent heating DSC curves after self-seeding at the indicated temperatures. (c) The crystallization peak temperature of PEO at different self-seeding temperature. The two symbols at 64°C indicate the peak division.

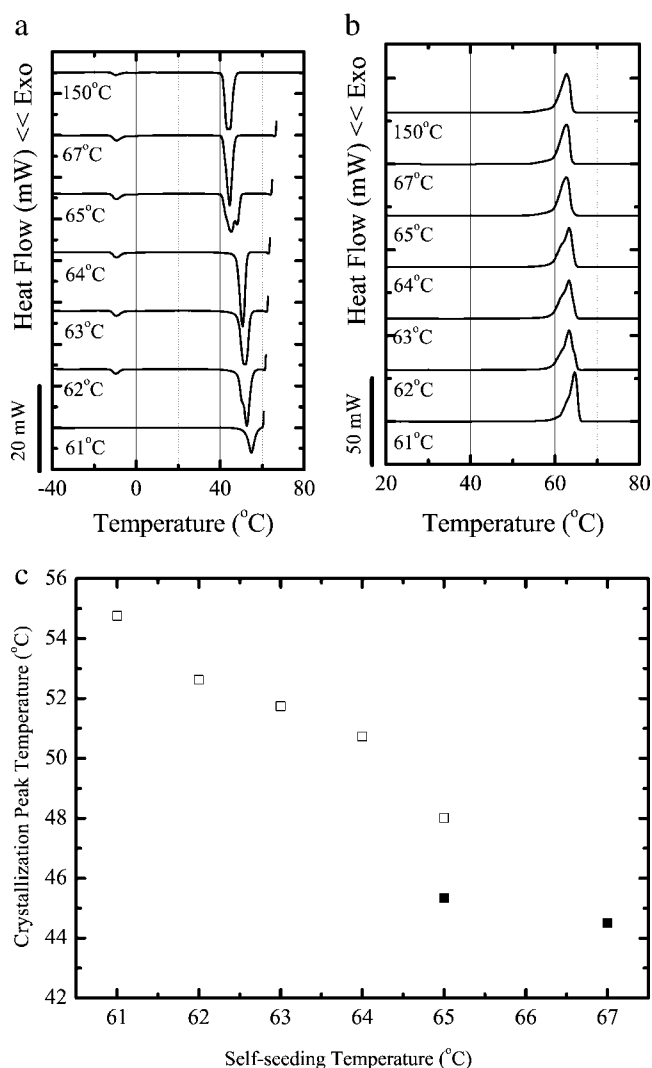


Figure 4 (a) The cooling DSC curves from indicated T_s temperatures for blend B. (b) Subsequent heating DSC curves after self-seeding at the indicated temperatures. (c) The crystallization peak temperature of PEO at different self-seeding temperature. The two symbols at 65°C indicate the peak division.

Judging from the self-seeding data, it can be concluded that the confined crystallization peak temperature at -10°C is initiated by homogeneous nucleation. The increase in the microdomain size also increases the crystallization temperature of PEO copolymer. Dry-brush blending enlarges the domain size without changing the matrix-droplet morphology. This conclusion can also be corroborated by TEM photography. As shown in Figure 2(d), even when the fraction of PEO in the blends reaches about 29% (blend C), the morphology is still a typical droplet-matrix structure. And most droplets are spheres, no cylindrical or lamellar morphology is observed. Even under solution blending, it is still hard to achieve a uniform dispersion in the blend.

Some droplets are in the scale of micron, whereas some are less than 50 nm.

The crystallization peak temperatures of PEO versus the self-seeding temperatures are shown in Figures 3(c) and 4(c). For blend A, the peak division occurs when self-seeding temperature (T_s) is 64°C . When T_s is higher than 64°C , the system is in domain I and the crystallization peak temperatures are 44°C . When T_s is 64°C , the crystallization peak is divided into two peaks which at the temperature of 45.9 and 48.8°C . The peak at 45.9°C is in domain II and the peak at 48.8°C is in domain III. When T_s is lower than 64°C , the crystallization temperatures are higher than 50°C and the system is in domain III. It is an interesting phenomenon that some droplets are in domain II and others are in domain III when T_s is 64°C for blend A. There is no doubt that there must be some difference between these two groups of droplets. Now in the system, there should be three groups of dispersed phase. One group is the microdomains of PS-PEO-PS copolymer swelled by h-PEO, but they are still in the range of microphase separation, which crystallize at -10°C . The second group is the droplets of pure h-PEO dispersed in the PS rich phase, which crystallize at 48.8°C (peak A) when T_s is 64°C . The origin of the third group, which crystallizes at 45.9° (peak B) when T_s is 64°C is interpreted as the following: some h-PEO droplets are compatibilized by PS-PEO-PS copolymer and the size of these droplets are smaller than uncompatibilized h-PEO droplets. The PEO in bigger droplets will have thicker lamellar than those in small droplets and thicker lamellar will only melt at higher temperature. So, self-seeding for blend A at 64°C , some bigger droplets are partly molten (domain III) and smaller droplets are self-seeding (domain II). Similar results are observed in blend B (Fig. 4), but the peak division temperature is at 65°C .

CONCLUSION

The confined crystallization of PS-PEO-PS copolymer and dry-brush blend with different fraction h-PEO was studied. In a wide range, confined crystallization phenomena were observed. Due to the immiscible and microphase separation, microdomain structures at nanoscale were found in the copolymer and blends. The number of these domains is much greater than the heterogeneous nuclei in the system, and so homogeneous nucleation is the only method for crystallization of PS-PEO-PS copolymer.

Blending PEO homopolymer with PS-PEO-PS copolymer could not totally erase the confined crystallization of PS-PEO copolymer but increase the confined crystallization temperature. Because of the effect of dry-brush blending, the size of microdo-

mains increases and the confined crystallization temperature is 15°C higher than the normal confined crystallization temperature of PS-PEO-PS copolymer.

From self-seeding test results, peak division was observed. When self-seeding process is at 64°C for blend A, a mixture of both domain II and domain III can be observed. Because of the size dispersion of h-PEO droplets, the melting points are different. The bigger and smaller droplets cannot melt at the same temperature to get into a same self-seeding domain.

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