

NUCLEATION AND CRYSTALLIZATION OF H-SHAPED (PS)₂PEG(PS)₂ BLOCK COPOLYMERS*

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Abstract A series of H-shaped (PS)₂PEG(PS)₂ block copolymers with different PS chain lengths were prepared. The influence of different confinements active on the crystallization and self-nucleation (SN) behavior of the PEG blocks was investigated by differential scanning calorimetry (DSC). When the content of the crystalline block was high, a classical SN behavior was obtained. The block copolymer with PEG content of 49% (by weight) showed a classical SN behavior with a narrow self-nucleation domain and had bimodal crystallization exotherms. When the PEG dispersed as separated microdomains in the block copolymer, the self-nucleation domain disappeared and only annealing was observed.

Keywords: Block copolymers; Crystallization; Differential scanning calorimetry (DSC); H-shaped; Self-nucleation.

INTRODUCTION

Polymer crystallization is one of the mainly studied aspects of polymer physics. Crystallization within confined dimensions is attracting more and more interests. Various well-defined block copolymers with at least one crystalline block have been investigated in different confined environments. In strongly segregated block copolymers, the crystalline block can be confined within small isolated microdomains under certain volume fractions.

Linear block copolymers containing polystyrene (PS) and poly(ethylene oxide) (PEO) such as PS-*b*-PEO and PS-*b*-PEO-*b*-PS have been investigated extensively^[1–5]. The phase behavior of PS-*b*-PEO copolymers with different microdomain structures has been studied by Cheng *et al.*^[1, 3–7] using SAXS, WAXD and DSC. Recently, non-linear block copolymers containing crystalline blocks^[8] and diblock copolymers containing two different crystalline blocks have been reported^[9, 10]. Crystallization under confinement is becoming more fascinating.

In terms of crystallization, homogeneous nucleation needs a higher supercooling than heterogeneous nucleation does. The self-nucleation (SN) technique developed by Fillon *et al.*^[11] can be used as a powerful tool to study the nucleation behavior of various polymers, and in the past a lot of homopolymers^[11, 12] as well as copolymers^[12–17] have been investigated. Müller *et al.*^[13] have synthesized different PS-*b*-PEO and polystyrene-*block*-poly(ethylene oxide)-*block*-poly(ϵ -caprolactone) (PS-*b*-PEO-*b*-PCL) block copolymers and studied their self-nucleation behaviors. They found that for PS-*b*-PEO-*b*-PCL triblock copolymers when either one or two

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crystalline blocks was present in contents greater than 35 wt%, standard self-nucleation behavior was encountered. When both the PCL and PEO contents were equal to or below 21 wt%, homogeneous nucleation took place, and the resulted self-nucleation behavior showed the difficulty in generating enough self-seeds to nucleate isolated microdomains which caused the disappearance of “domain II”. Abetz *et al.*^[14] have studied the influence of different confinements active during crystallization within polybutadiene-*block*-polyisoprene-*block*-poly(ethylene oxide) (PB-*b*-PI-*b*-PEO) and the corresponding hydrogenated polyethylene-*block*-poly(ethylene-*alt*-propylene)-*block*-poly(ethylene oxide) (PE-*b*-PEP-*b*-PEO) triblock copolymers on the self-nucleation behavior of the crystalline PEO and PE blocks. It is commonly accepted that poly(ethylene oxide) (PEO) and poly(ethylene glycol) (PEG) have the same repeat unit and similar crystallization behavior.

H-shaped (PS)₂PEG(PS)₂ block copolymers were first synthesized by Pan *et al.*^[18]. They also studied the thermal behavior of the novel block copolymers and found that the degree of crystallinity of PEG increased with the increase of its weight fraction in the copolymers. However, the crystallization and nucleation of the H-shaped block copolymers were not well investigated.

In this contribution, we synthesized several (PS)₂PEG(PS)₂ block copolymers with the same PEG chain length and different PS chain lengths, and studied the self-nucleation behavior of the crystalline PEG block by applying the SN technique. The influence of different PS chain lengths, *i.e.*, different confinements active during crystallization of PEG on the self-nucleation behavior is discussed.

EXPERIMENTAL

Synthesis

The synthesis of H-shaped (PS)₂PEG(PS)₂ block copolymers was reported in our earlier communications^[19, 20]. In brief, the macroinitiator was obtained by esterification of hydroxyl-ended poly(ethylene glycol) with dichloroacetyl chloride. The copolymer was synthesized by atom transfer radical polymerization (ATRP) using macroinitiator, CuCl, 2,2'-bipyridine and styrene. Tetrahydrofuran (THF) was used as solvent.

The architecture of H-shaped block copolymers was confirmed by the relationship between the degrees of polymerization of H-shaped and linear copolymers^[19]. The copolymer composition and molecular weight were determined from ¹H-NMR spectra, which were obtained on a Bruker AV-400 spectrometer with CDCl₃ as solvent and TMS as an internal standard. The polydispersity was determined on a Waters 410 GPC calibrated with polystyrene standards at 35°C. THF was used as an eluent with a flow rate of 1 mL/min. The data for (PS)₂PEG(PS)₂ copolymers are listed in Table 1.

Table 1. Basic characteristics of the materials used in this study

No.	Copolymer ^a	$M_{n, \text{NMR}}$ (PS)	$M_{n, \text{NMR}}$ (copolymer)	M_w/M_n (GPC)	f_{PEG} (wt%)	f_{PEG} (vol%)
H15	(PS ₈) ₂ PEG ₂₂₇ (PS ₈) ₂	3328	13328	1.19	75.0	73.8
H13	(PS ₂₅) ₂ PEG ₂₂₇ (PS ₂₅) ₂	10400	20400	1.22	49.0	47.5
H11	(PS ₄₀) ₂ PEG ₂₂₇ (PS ₄₀) ₂	16640	26640	1.24	37.5	36.1

^a The subscripts of PS and PEG represent the number of repeat units of each block.

Differential Scanning Calorimetry (DSC)

Thermal analysis was performed on a TA DSC Q100. All experiments were performed at a scanning rate of 10 K/min in N₂ atmosphere.

Self-nucleation (SN) Experiments

Self-nucleation measurements were performed in analogy to the procedure described by Fillon *et al.*^[11]. Figure 1 shows the complete thermal treatment and is explained in detail as follows:

(a) Initial melting to erase any previous thermal history of the sample. In this step, all crystals are melted when heated to 120°C. Only temperature-resistant heterogeneous nuclei remain. Upon subsequent cooling the crystalline block (PEG) always crystallizes at the same crystallization temperature if under the same cooling rate, which means that the nucleation density remains constant.

(b) Creation of a “standard” thermal history by cooling at a rate of 10 K/min to -60°C (or -40°C). This step ensures that the crystallization of the copolymer under investigation occurs under the same dynamic condition.

(c) Heating to a predetermined self-nucleation temperature, which is denoted as T_s in what follows.

(d) Thermal conditioning at T_s for five minutes. Depending on different T_s s, the sample will be completely melted, only self-nucleated, or self nucleated and annealing. If T_s is too high, the sample is completely melted (as in step (a) above) and no self-nuclei or crystal fragments will survive. In this condition, the sample is said to be under “Domain I”. When T_s is high enough to melt almost all the sample, but low enough to leave small crystal fragments that can act as self-nuclei (more recently it has been proposed that such self-nuclei could also arise from “precursors” or local segmental orientation which may retain crystalline memory^[21]) during the subsequent cooling from T_s , the sample is under “Domain II” or self-nucleation domain. If T_s is too low, only part of the crystal will melt. The unmelted crystals will be annealed during five minutes at T_s , while the rest of the polymer will be self-nucleated during the subsequent cooling from T_s , then the sample is under “Domain III” or self-nucleation and annealing domain.

(e) A subsequent cooling scan from T_s at a rate of 10 K/min. The effects of the thermal treatment will be reflected by the crystallization of PEG. If self-nucleation takes place, the peak crystallization temperature will locate at a higher temperature as compared to the standard cooling run (step (b)).

(f) Final DSC heating scan from -60°C (or -40°C) to 120°C , where the effects of the entire thermal history will be reflected in the melting of PEG. Steps (e) and (f) can help us to distinguish the three domains.

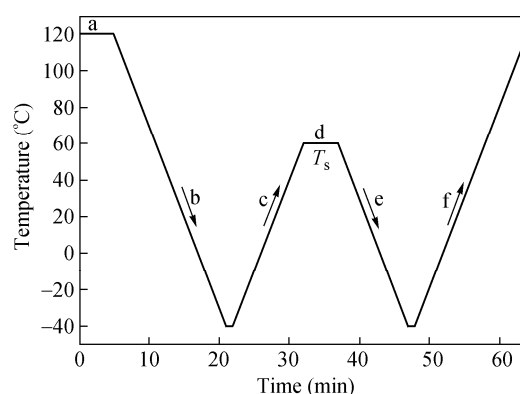


Fig. 1 Schematic representation of the self-nucleation experiments conducted by means of DSC

RESULTS AND DISCUSSION

Standard DSC Scans

Figure 2 shows cooling and subsequent heating scans (at 10 K/min) of PEG ($M_n = 10000$) and H-shaped block copolymers with different end PS chain lengths. The samples were used as synthesized. There was a strong dependence between the end PS chain length and the crystallization or melting temperatures. The crystallization temperature of copolymer H15 was a little lower than that of PEG homopolymer, which meant that the PS blocks, although very short, imposed an obstacle on the crystallization of PEG block. Both copolymers H11 and H13 crystallized at very high supercoolings ($T_c < -38^{\circ}\text{C}$) upon cooling from the melt, suggesting that homogeneous nucleation had taken place. Figure 2(b) shows that with decreasing end PS chain length, the melting temperatures increase gradually, namely, the crystals are more stable. Copolymer H11 melted at around 35°C , which suggested that the crystals were very thin and irregular, probably caused by the low content of the PEG block and the microdomain confinement.

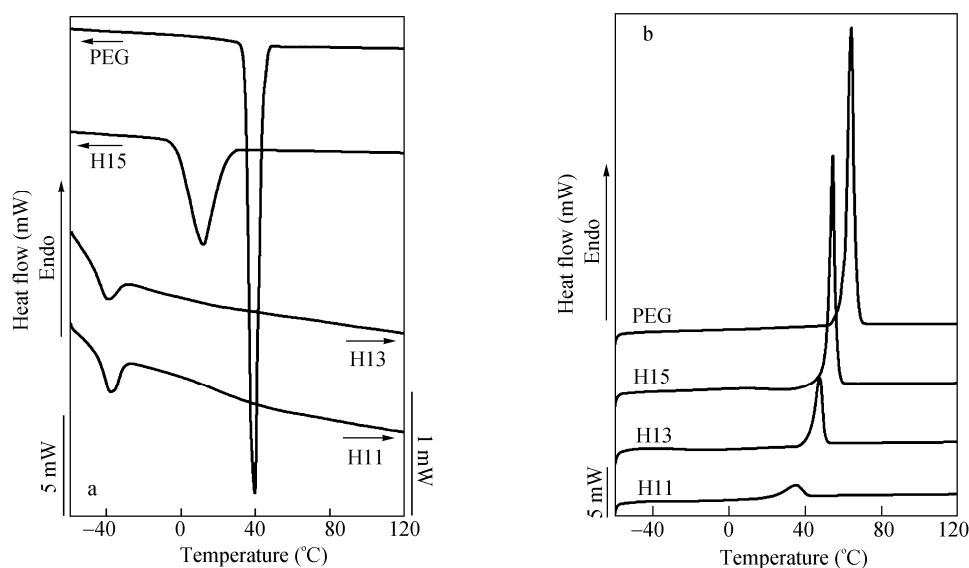


Fig. 2 DSC cooling (a) and heating (b) scans (at 10 K/min) of PEG ($M_n = 10000$) and different H-shaped block copolymers

Classical Self-nucleation Behavior

Crystalline homopolymers usually show all the three self-nucleation domains, which were confirmed by Fillon *et al.*^[11] and other groups. Actually, three domains mean three T_s ranges in which different crystallization behaviors take place. In “Domain I”, only thermally-stable heterogeneous nuclei remain in the polymer melt. Upon cooling, recrystallization always takes place at the same temperature as observed in the standard cooling scan. “Domain II” is the T_s range in which the polymers melt almost completely, but leave small crystal fragments. These small fragments act as self-nuclei in the subsequent cooling scan, and their concentration varies dramatically with T_s . The nucleation density increases significantly as a result of small reduction in T_s which makes the shifting of crystallization peak to a higher temperature in the subsequent cooling run. If only part of the crystal melts, we say that “domain III” has reached. The unmelted material anneals at T_s . Upon cooling, the crystallization starts almost immediately without a perfectly flat baseline. On the final melting, a sharp high-temperature peak appears. In the case of PEG ($M_n = 10000$), “Domain II” and “Domain III” starts at 76°C and 64°C, respectively. The self-nucleation domains usually denoted on the standard heating curve of the corresponding polymer^[12–14, 21], as depicted in Fig. 3. The meanings of symbols are listed in the figure and it is clear where the self-nucleation domains are located.

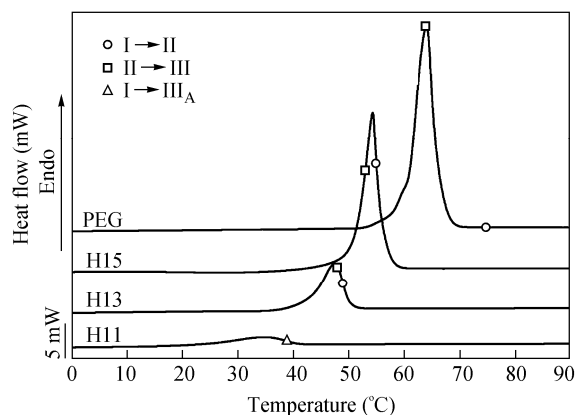


Fig. 3 DSC heating scans (at 10 K/min) for PEG homopolymer and indicated copolymers. The self-nucleation domains are indicated on the DSC traces by symbols.

Self-nucleation Behavior of Copolymer H15

Although the PEG weight fraction of H15 is higher than S₃₉EO₆₁⁴⁶ (The subscripts indicate the weight content of each block and the superscript denote the molecular weight of the copolymer) in Ref. [13], the T_c of H15 is lower than the diblock copolymers and it is due to the confinement on both ends of the PEG block. Figure 4 shows representative cooling and heating scans for H15 (PEG wt% is 75%) after thermal conditioning at the indicated self-nucleation temperatures (T_s s).

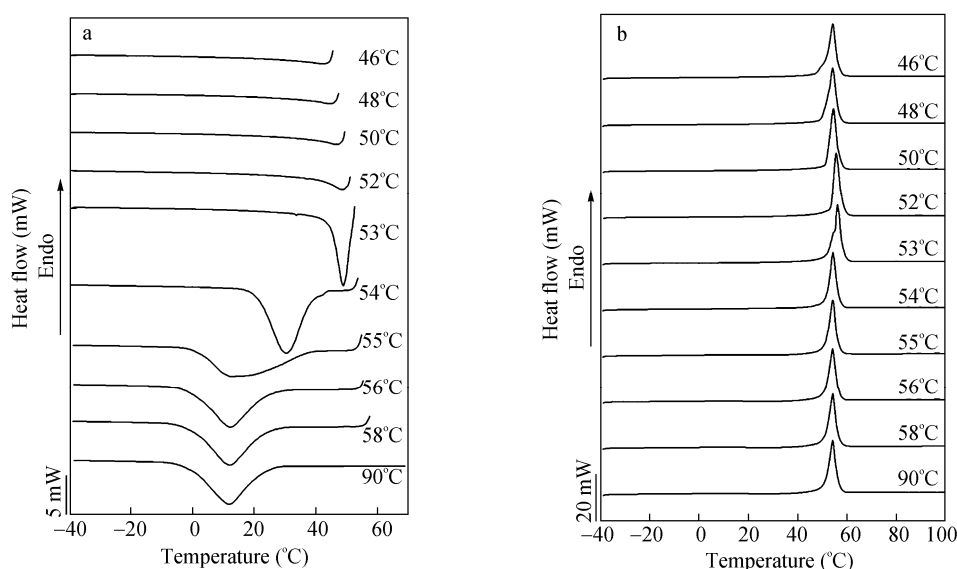


Fig. 4 DSC cooling scans (a) for H15 after self-nucleation at the indicated T_s , and subsequent heating scans (b)

We can see a similar behavior like the classical self-nucleation behavior of crystalline homopolymer. The cooling scan from $T_s = 90^\circ\text{C}$ represented a cooling run from “Domain I”. PEG was the major component of H15 copolymer and existed as a continuous phase in the bulk, so there were enough heterogeneous nuclei to intrigue nucleation. But the PS blocks at each end of the PEG block increased the steric hindrance to attach the PEG segments to the crystal growth front, which showed a decrease of the crystallization temperature in comparison with PEG homopolymer (the crystallization temperature of PEG ($M_n = 10000$) was *ca.* 42°C). Therefore, all the three self-nucleation domains for the PEG block could be located as depicted in Fig. 3 and since the limits of “Domain II” and “Domain III” were shifted to lower temperatures compared with PEG homopolymer, we speculated that the PEG block within copolymer H15 experienced greater difficulty to be self-nucleated and annealed.

Self-nucleation Behavior of Copolymer H13

When the PEG fraction in the copolymer decreases, the self-nucleation behavior changes enormously. Figure 5 shows the cooling and subsequent heating scans for H13 after self-nucleation at the indicated T_s . From $T_s = 60^\circ\text{C}$ to $T_s = 50^\circ\text{C}$, only one crystallization peak appeared at very high supercooling (labeled “1” in Fig. 5a), whose temperature did not change. When the T_s was 49°C , the crystallization exotherm split into two exotherms (the low-temperature one was labeled as “1” and the high-temperature one was labeled as “2” in Fig. 5a). While exotherm “2” shifted to higher temperature upon lowering T_s , a small fraction of PEG was left without self-nucleation in exotherm “1” and shifted to lower temperatures (though the change is tiny), which was opposite to the common trend. As T_s decreased from 49°C to 46°C , the enthalpy of exotherm “1” reduced and the enthalpy of exotherm “2” increased. When $T_s < 46^\circ\text{C}$, the exotherm “1” still existed but its enthalpy became so small that it was hard to determine the onset and peak temperatures due to the concerned error. The changes are more

obvious in the plot of T_c versus T_s as depicted in Fig. 6. On remelting after cooling from a specific T_s , only one endotherm was observed in Fig. 5(b) when $T_s > 48^\circ\text{C}$. An additional high-temperature endotherm became apparent if T_s was lower than or equal to 48°C .

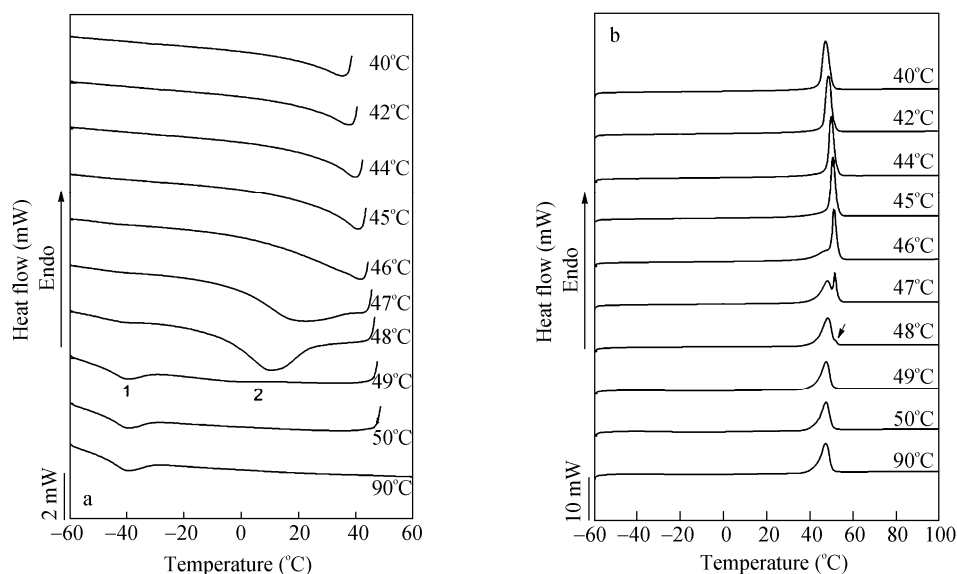


Fig. 5 DSC cooling scans (a) for H13 after self-nucleation at the indicated T_s , and subsequent heating scans (b)

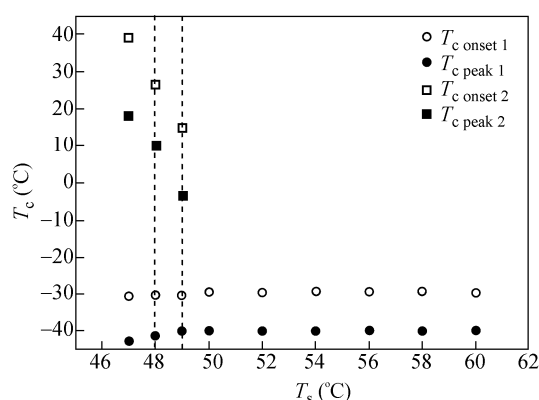


Fig. 6 Variation of the crystallization temperatures with T_s for H13
The dashed line corresponds to a change in the self-nucleation domain.

The bimodal crystallization of the PEG block came from the crystallization of two different parts of the PEG chains^[12]. Both the chain ends of the PEG block were connected with two PS chains each. Those parts of the PEG chains closer to the interfaces experienced greater difficulty in being self-nucleated because of their hindered diffusion. These PEG chain segments close to the interfaces with the PS blocks might always crystallize in exotherm “1” and could not self-nucleate (Fig. 5a). On the other hand, those chain segments located in the middle of the PEG block might crystallize initially in exotherm “1” along with the rest of the PEG block upon cooling from high T_s values ($T_s > 49^\circ\text{C}$). However, at lower T_s values, they could self-nucleate since these PEG chain segments have less diffusion hindrance. With increased density of the remaining crystal fragments they crystallized at lower supercoolings in exotherm “2”. As the T_s decreased, the crystallization enthalpy of exotherm “1” reduced while that of exotherm “2” increased. This observation indicated that part of the material which crystallized at $T_s = 48^\circ\text{C}$ could be self-nucleated at $T_s = 47^\circ\text{C}$, *i.e.*, at exotherm “2”. As T_s

decreased, the amount of material available for crystallization during cooling from T_s also decreased. This may be one of the reasons for the observed change in crystallization enthalpies^[12].

Based on the above results, all the three self-nucleation domains for the PEG block of H13 can be located as depicted in Fig. 3. The “domain II” is very narrow.

Self-nucleation Behavior of Copolymer H11

Figure 7 depicts the DSC cooling (a) and subsequent heating (b) scans for H11 after self-nucleation at the indicated T_s . The variation of the crystallization temperatures with T_s for H11 block copolymer is shown in Fig. 8. The $T_{c \text{ onset}}$ s remained almost the same, while the $T_{c \text{ peak}}$ s decreased with the decrease of T_s . As T_s lowering, the unmelted crystals experienced annealing even before any sign of self-nucleation was detected. Actually, the T_s at which self-nucleation could happen is so low that it was not found. In the whole T_s range of our experiment, no shift in T_c to higher temperatures with the decrease of T_s was observed, which meant that there was no sign of self-nucleation^[14]. On the heating scans, a new endotherm peak appeared when T_s was 39°C. This is different from the behavior of “Domain III” in the classical SN experiment, where self-nucleation and annealing happened simultaneously. We referred to the domain where only annealing has been detected as “Domain III_A”. (“Domain III_A” is a sub-domain of “Domain III”, where “A” means only annealing happened and there was no sign of self-nucleation.)

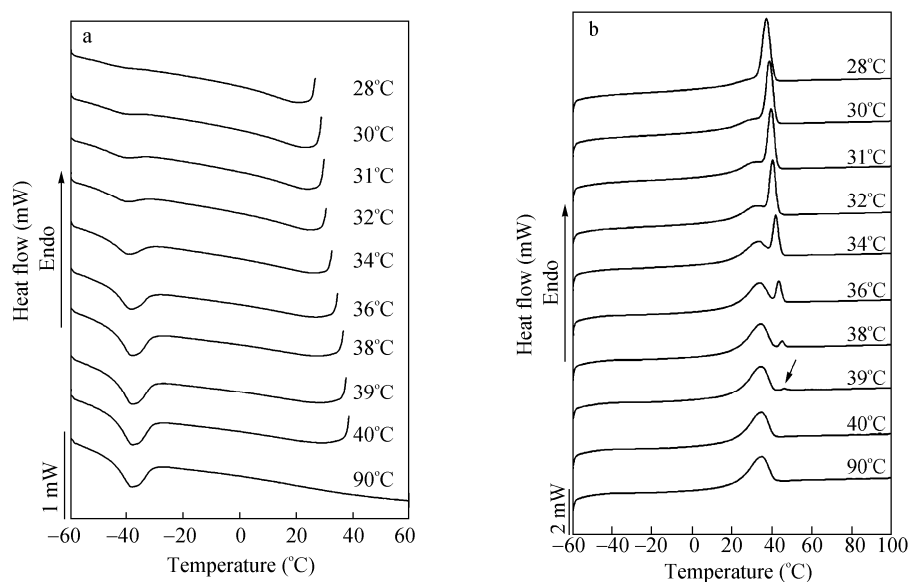


Fig. 7 DSC cooling scans (a) for H11 after self-nucleation at the indicated T_s , and subsequent heating scans (b)

PS and PEG were immiscible. When the content of PEG block was relative low in the block copolymer, it usually existed as isolated confined microdomains. Self-nucleation could take place unless there were crystal fragments in every microdomain, which indicated a huge number of crystal nuclei (of the order of 10^{25} nuclei/cm³^[13]), say, a large amount of unmelted PEG was needed. In this case, very low T_s was necessary. For H11, self-nucleation cannot occur even if the T_s was 24°C, so “Domain II” was absent (see Fig. 3).

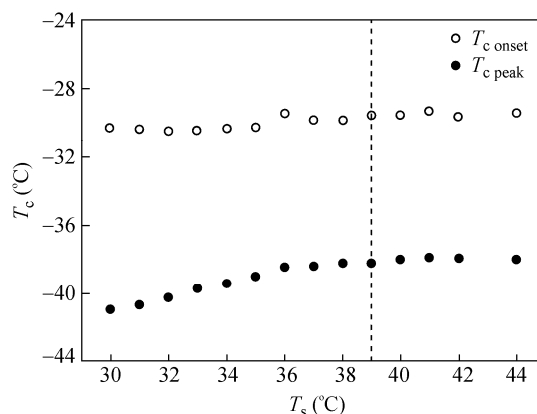


Fig. 8 Variation of the crystallization temperatures with T_s for H11
The dashed line corresponds to a change in the self-nucleation domain.

CONCLUSIONS

In this work, we studied the self-nucleation of H-shaped $(PS)_2PEG(PS)_2$ block copolymers. With the same PEG chain length, we obtained different self-nucleation behavior through changing the PS chain lengths, that is, changing the morphology of the block copolymers. When PEG is the major component, it exists as continuous phase. There are enough heterogeneous nuclei in it and the crystallization is triggered mainly by these nuclei, so its self-nucleation behavior is similar to the classical results. The copolymers with PEG content of 49% and 37.5% (by weight) both crystallize at very high supercoolings in the standard DSC cooling scans, but their self-nucleation behavior are completely different. As the PEG content equals to 49%, we speculate that the bulk phase morphology is lamella or PEG cylinder^[22]. PEG and PS domains appear by turns (the number of heterogeneous nuclei in every PEG domain decreases) and the confinement of PEG becomes larger which makes the mobility of PEG block decreases. As a result, in the self-nucleation experiment, there will be enough self-nuclei to trigger the crystallization only when T_s is low, which cause the narrowing of “domain II”. When the end PS chain length increases further, PEG exists as isolated microdomains in the PS continuous phase, and a huge number of nuclei, say, a very low T_s is needed to start the crystallization. In the whole T_s range of our experiment, no sign of self-nucleation is detected, so “domain I” goes directly into “Domain III_A”. Further studies about the crystallization of $(PS)_2PEG(PS)_2$ block copolymer and the difference between H-shaped and linear block copolymer are under progress.

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