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Self-Nucleation Behavior of the Polyethylene Block as Function of the Confinement Degree in Polyethylene-*Block*-Polystyrene Diblock Copolymers

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Summary: A series of well defined polyethylene-b-polystyrene diblock copolymers ($E_xS_y^z$, where x and y represent the composition in weight % and z the molecular weight in Kg/mol) has been synthesized in a wide composition range by sequential anionic polymerization. The molecular weight of the PE block was kept constant. A fractionated crystallization behavior was observed for the PE block within $E_{26}S_{74}^{105}$ (PE cylinders) and $E_{11}S_{89}^{244}$ (PE spheres). When the PE blocks form a continuous or percolated phase (PE, $E_{79}S_{21}^{41}$ and $E_{53}S_{47}^{51}$), a "classic" self-nucleation behavior (where the usual three self-nucleation domains are obtained) was observed. When the PE block is located within isolated microphases (having dimensions on the nanometer scale) and a fractionated crystallization was detected ($E_{26}S_{74}^{105}$ and $E_{11}S_{89}^{244}$), the fraction of crystals formed at higher temperatures exhibits a "classic" self-nucleation behavior, while those crystals that crystallized at the largest supercooling (lower exotherms) can only be self-nucleated at lower temperatures where annealing of unmolten material has already started. An unusual fractionated crystallization behavior for isolated, spherical PE microphases ($E_{11}S_{89}^{244}$) is reported.

Keywords: confinement; crystallization; diblock copolymers; self-nucleation

Introduction

The crystallization of PA-*b*-PB diblock copolymers with one crystallizable block has been extensively studied[1–12]. Structure formation during crystallization from a microphase-separated melt is determined by whether or not the self-assembly is disrupted by crystallization. The microdomain can either change its shape (if there is break out), or can retain it during crystallization (strong confinement). In strongly segregated block copolymers with a glassy amorphous component, crystallization may not be able to disturb the microphase structure because it is frozen in by the glassy domain. When a crystallizable block is subdivided into isolated microdomains (MDs) whose number is significantly (several orders of magnitude) greater than the number of usually active heterogeneities, a fractionated crystallization phenomenon occurs that could even lead to exclusive homogeneous nucleation[10–16]. The fractionated crystallization process was reported indiblock copolymers[11,12,17], polymer blends[19–23] and more recently in triblock terpolymers[6–8,10–16]. The occurrence of the fractionated crystallization phenomenon for a wide range of copolymers has been recently reviewed[12].

In a self-nucleation (SN) experiment[24], a polymer with an initial crystalline "standard" state is heated to a given temperature, denoted self-nucleation temperature (T_s). If T_s is high enough to melt most of the polymer except for a certain amount of crystal fragments, recrystallization takes place upon subsequent cooling, using as

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nuclei those crystallographically "ideal" seeds which are left unmolten during heat treatment at T_s. When T_s is lower, partial melting can occur and a large population of crystals is not melted and therefore anneals during heat treatment at T_s. Normally, three self-nucleation domains can be defined depending on the applied T_s. In Domain I or "complete melting Domain", the crystallization temperature (T_c) upon cooling from T_s remains constant and no self-nucleation can be detected. Domain II or "self-nucleation Domain" occurs when heat treatment at T_s causes a shift in crystallization temperature (during subsequent cooling from T_s) to higher temperatures with decreasing self-nucleation temperature. Finally, in Domain III or "self-nucleation and annealing Domain", annealing and self-nucleation take place simultaneously[24]. The self-nucleation technique has been applied to crystallizable block copolymer systems and has also been the subject of a recent review[12].

In this work, we study the self-nucleation behavior of the crystallizable block within well defined polyethylene-*b*-polystyrene linear AB diblock copolymers with different confinement degree.

Experimental Section

Synthesis

Solvents and monomers were purified according to common procedures[1,6–8]. The synthesis of poly(1,4-butadiene)-*b*-polystyrene diblock copolymers (PB-*b*-PS), and poly(1,4-butadiene) (PB) homopolymer was accomplished by sequential anionic polymerization of butadiene (in benzene at 60 °C) and styrene (in benzene at 40 °C) with sec-BuLi as initiator. The use of benzene as a solvent results in a high 1,4-addition for butadiene, which is necessary to get a model linear low density polyethylene structure after hydrogenation. Styrene was added as a second monomer. By this strategy, the homopolymer and all block copolymers have the identical PB (and finally PE) block. The polymerization was terminated using degassed isopropanol followed by precipitation in the same non-solvent. The following notation is employed here: $A_xB_y^m$, where the subscript number denotes the mass fraction in weight percent and the superscript gives the number-average molecular weight, M_n, in Kg/mol of the entire block copolymer (see Table 1). The molecular weight of the PB homopolymer was determined by SEC (Waters Instruments) calibrated with narrowly distributed 1,4 PB Standard at 30 °C, the measurement was performed in THF with a low rate of 1mL/min using toluene as internal standard. The copolymer compositions and molecular weights were obtained using ^{1}H-NMR spectroscopy (Bruker AC 250 spectrometer) in $CDCl_3$. The % (1,2) units for the polybutadiene was also calculated using ^{1}H NMR. The synthesis process for all the diblock copolymers was designed in order to obtain a PB block in the block copolymers with the same molecular weight and similar content of 1,2 units as in the PB homopolymer (see Table 1).

Hydrogenation

The polyethylene-*b*-polystyrene diblock copolymer (PE-*b*-PS), and PE homopolymer (PE) were obtained by hydrogenation of the corresponding precursors. Homoge-

Table 1.
Characteristics of the samples employed.

Copolymers	Mn (Kg/mol) Butadiene block	PB % 1,2 Units	Polydisp. D	After Hydrogenation Copolymers	TEM Morphology
PB^{24}	24.4	11.0	1.01	PE^{25}	—
$B_{78}S_{22}^{41}$	31.0	12.6	1.02	$E_{79}S_{21}^{41}$	PS cylinders
$B_{49}S_{51}^{51}$	26.4	11.3	1.04	$E_{53}S_{47}^{51}$	lamellae
$B_{25}S_{75}^{105}$	26.4	11.3	1.05	$E_{26}S_{74}^{105}$	PE cylinders
$B_{11}S_{89}^{244}$	27.6	11.3	1.02	$E_{11}S_{89}^{244}$	PE spheres

neous catalytic hydrogenation was carried out in degassed toluene (1.5–2 wt% polymer solution) at 60 °C and 60 bar H_2 pressure for 3 days using a Wilkinson catalyst $(Ph_3P)_3$-Rh(I)Cl (Aldrich, 1 mol % with respect to the number of double bonds present in the PB blocks). Under the employed conditions the PB blocks were completely hydrogenated as revealed by ^{1}H-NMR (Bruker AC 250 spectrometer, results not shown). Purification was accomplished by precipitation into isopropanol. Further purification was performed in order to remove residual Wilkinson catalyst by refluxing the homopolymer or block copolymer solution in toluene with a small amount of concentrated hydrochloric acid, again followed by precipitation into isopropanol.

Differential Scanning Calorimetry (DSC)

All samples were analyzed with a Perkin-Elmer Pyris 1 DSC instrument calibrated with cyclohexane and indium under high purity nitrogen atmosphere. The DSC scans were obtained at 10 °C/min using a sample mass between 5 and 7 mg. All DSC cooling curves were recorded after the samples were held in the melt at 140 °C for 3 min in order to erase previous thermal history. The crystallization and melting enthalpies values were normalized with respect to the PE fraction in the block copolymers.

Self-nucleation experiments were also performed. The detailed procedure used here is described as follows:

a.- Erasure of thermal history by heating the sample to 140 °C for three minutes. This step erases all crystalline memory of the material as far as the dynamic experiments in the DSC are concerned. In other words, only temperature-resistant heterogeneous nuclei remain, and upon subsequent cooling the polymer will always crystallize at the same peak crystallization temperature (if the same cooling rate is used). This last observation suggests that the nucleation density remains constant under these conditions.

b.- Creation of a "standard" thermal history by cooling at a rate of 10 °C/min to 0 °C. During such controlled cooling the material will crystallize up to a certain extent.

c.- Heating at 10 °C/min to a self-nucleation temperature, that shall be termed T_s. The thermal conditioning at T_s is performed for five minutes. Depending on T_s, according to Fillon et al.[24], the sample will be completely molten (Domain I), self-nucleated (Domain II), or self-nucleated and annealed (Domain III), as mentioned in the introduction. If T_s is too high, no self-nuclei or crystal fragments can survive, and the sample is said to be in Domain I or complete melting domain. When T_s is high enough to melt the sample almost completely, but low enough to leave some small crystal fragments that can act as self-nuclei during the subsequent cooling from T_s, the sample is said to be in Domain II or self-nucleation domain. When T_s is too low, only part of the crystals will melt. Therefore, the unmelted crystals will be annealed during the 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 said to be in Domain III or self-nucleation and annealing domain. Isothermal crystallization of a certain chain population during the 5 min at T_s can also occur when T_s is within Domain III. In block copolymers, it could be possible that Domain III splits into two domains[17]: Domain III_A, where annealing without previous self-nucleation occurs and Domain III_{SA}, where self-nucleation and annealing are simultaneously observed. Domain III_{SA} would be the exact equivalent to the standard Domain III explained before.

d.- DSC cooling scans from T_s at a rate of 10 °C/min, where the effects of the thermal treatment will be reflected on the crystallization of the material. If the polymer has been self-nucleated, a shift of the peak crystallization temperature to higher temperatures as compared to the standard cooling run (step b) is expected.

e.- DSC heating scans from 0 to 140 °C, where the effects of the entire thermal treatment will also be reflected in the melting of the material. For instance, if annealing took place at T_s, then a second, higher melting peak will be seen.

The distinction between the domains can be ascertained by careful observations of the cooling runs (step d) from T_s and the final heating runs (step e).

Results and Discussion

Classical Self-Nucleation Behavior[25]

Figure 1 shows cooling and heating DSC scans for PE^{25} during self-nucleation over a broad range of T_s temperatures. As detailed in the experimental section, three self-nucleation domains can be recognized in crystallizable polymers depending on the applied T_s. The PE^{25} is in Domain I when complete melting occurs, in this case complete melting was found to persist down to 113 °C, since no change was detected in the crystallization temperature as compared to the standard crystallization temperature obtained with a T_s of 120 °C, indicating that a constant nucleation density was achieved. For $101\,°C < T_s \leq 112\,°C$ the homopolymer is in Domain II, the crystallization temperature shifts to higher values pinpointing the higher nucleation density upon cooling from T_s, while in the subsequent heating scans no changes could be detected (see Figure 1). Finally, at $T_s \leq 101\,°C$ the polymer is said to be in Domain III, as indicated by the existence of an annealing signal at higher temperature (a second melting peak) on the heating scan in Figure 1.

Figure 2 presents the T_s temperatures at which self-nucleation Domains are located for PE^{25} (left); in a similar way, the transition between different self-nucleation domains are plotted on a representative melting DSC scan (right).

In Figure 2, vertical lines have been drawn to show the limits between the different Domains. It is clear, that at least in the PE^{25} case, Domain II extends to temperatures well above the final melting temperature detected by DSC. Therefore, the increase in nucleation density encountered within the higher temperature range in Domain II indicates that 5 minutes at those high T_s temperatures may not be enough to erase its crystalline memory or to relax the residual segmental orientation in

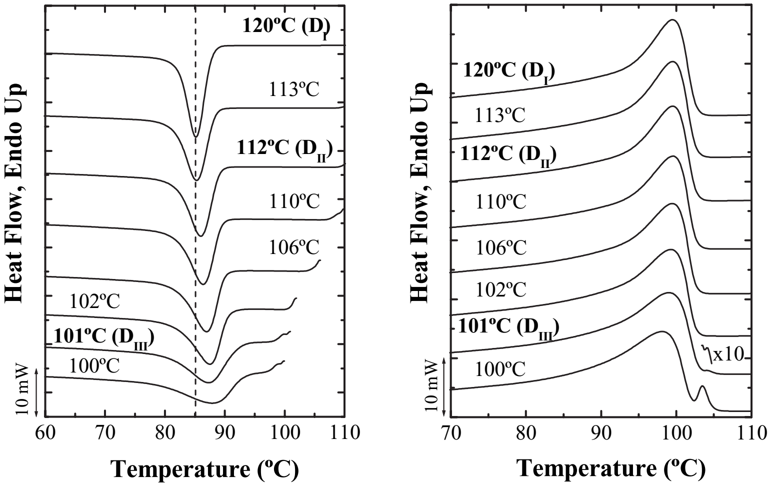

Figure 1.

DSC cooling scans (left) (10 °C/min) for PE^{25} after self-nucleation at the indicated *Ts*, and subsequent heating scans (right) (10 °C/min).

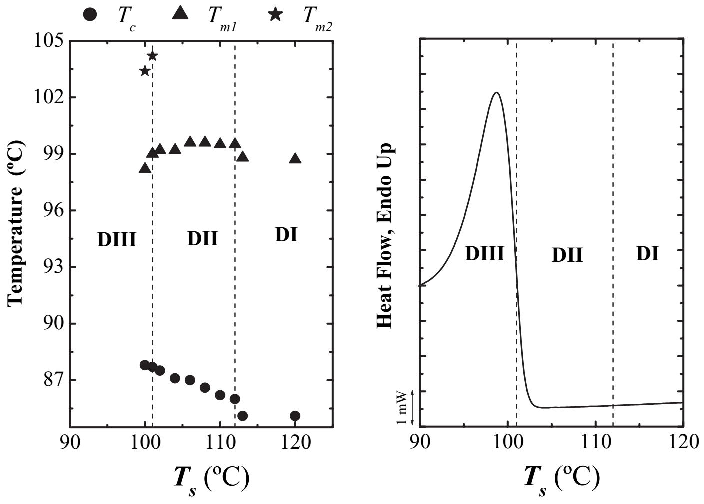

Figure 2.
Variation of crystallization temperature (Tc_{peak}) and melting temperatures (Tm_{peak1} and Tm_{peak2}) (left), and location of the self-nucleation domains (right) for PE^{25} as function of T_s. The dashed line corresponds to changes in self-nucleation domains.

the melt. The effect of increasing the time during self-nucleation experiments and the origin of the memory that self-nuclei can have, will be reported in the near future[26]. Regardless of the origin of the effect, the experimental fact remains that when the sample is within Domain II, an increase in nucleation density is obtained as indicated by the increase in T_c. This increase in nucleation density can be exponential for polymers with intrinsically low nucleation densities. In the case of PP, as the T_s decreases only a few degrees, the nucleation density increases from 10^6 nuclei/cm^3 in Domain I until 10^{12} nuclei/cm^3 for the lowest T_s within Domain II[24]. Since polyethylene has a much higher nucleation density than PP[24], typically 10^9 active heterogeneities/cm^3, the effects of self-nucleation on T_c and on the increase of nucleation density are less pronounced as it can be seen in the PE^{25} case[24]. The characteristic behavior of the self-nucleation of PE^{25} presented in Figure 2 indicates that the maximum temperature that induces self-nucleation without any annealing is the minimum T_s temperature within Domain II, i.e., 102 °C.

The morphology of the diblock copolymers employed here has been observed by transmission electron microscopy and the results have been recently published[27]. They are summarized in Table 1.

The PE blocks within $E_{79}S_{21}{}^{41}$ and $E_{53}S_{47}{}^{51}$ diblock copolymers samples were found to exhibit a ''classic'' self-nucleation behavior. Table 2 lists the temperatures at which the three domains can be observed. The classic self-nucleation behavior was expected for $E_{79}S_{21}{}^{41}$ since it is a diblock copolymer where the PE crystallizable block forms a continuous matrix (Table 1). In the case of $E_{53}S_{47}{}^{51}$, the classic self-nucleation behavior could be explained as a direct consequence of defects present in the lamellar morphology developed by this copolymer, in other words, the percolation level in this type of morphology is high and

Table 2.
T_s temperatures range for the self-nucleation domains of selected materials.

Sample	Domain I	Domain II	Domain III
PE	$T_s > 112$	$101 < T_s \leq 112$	$T_s \leq 101$
$E_{79}S_{21}{}^{41}$	$T_s > 114$	$99 < T_s \leq 114$	$T_s \leq 99$
$E_{53}S_{47}{}^{51}$	$T_s > 116$	$99 < T_s \leq 116$	$T_s \leq 99$

this allows the spread of secondary nucleation through out the PE crystallizable material, in an analogous way as it happens in the $E_{79}S_{21}^{41}$ block copolymer and in the PE^{25} homopolymer[24].

Table 2 shows that the temperature limit between Domain I and Domain II for $E_{79}S_{21}^{41}$ and $E_{53}S_{47}^{51}$ is located at higher T_s values ($T_s \leq 114$ and $T_s \leq 116\,^{\circ}C$, in that order) than that found for the PE homopolymer ($T_s \leq 112\,^{\circ}C$). This result could indicate crystalline memory retention induced by the PS microphase (with a T_g value of 107 °C).

In this section, the results have shown that in the absence of strict morphological confinement (i.e., a continuous matrix or a high percolation level of the non-crystalline block) the PE block shows a "classic" self-nucleation behavior with some differences, due to the presence of the PS block, in the T_s values limiting the self-nucleation domain transitions.

Non-Classical Self-Nucleation Behavior

Müller et al.[12] have recently reviewed the self-nucleation behavior of a large number of block copolymer systems, like polystyrene-*b*-polyethylene-*b*-poly(ε-caprolactone) (PS-*b*-PE-*b*-PC) and polyethylene-*b*-poly(ethylene-*alt*-propylene)-*b*-poly(ethylene oxide) (PE-*b*-PEP-*b*-PEO), that have shown a mixed self-nucleation behavior due to the fractionated crystallization process. The authors established that the fraction of crystals formed at higher temperatures exhibits the three classical self-nucleation domains and those crystals that crystallize at the largest supercoolings can only be self-nucleated at temperatures where the Domain III has already started and therefore that Domain II disappears for such populations.

Figure 3 shows DSC cooling and heating scans during self-nucleation treatments at the indicated T_s values (steps (d) and (e)). $E_{26}S_{74}^{105}$ (where the PE block forms cylinders within the PS matrix) exhibits a self-nucleation behavior that totally differs from the "classic" behavior, as reported by Fillon et al.[24] and exhibited by PE^{25}, $E_{79}S_{21}^{41}$ and $E_{53}S_{47}^{51}$ in the above section.

The $E_{26}S_{74}^{105}$ diblock copolymer exhibits two crystallization exotherms ("α" and "β") with two different self-nucleation behaviors. Upon close examination, the "α" crystallization exotherm shows a "classic" behavior with the presence of the three self-nucleation domains: Domain I at $T_s > 112\,^{\circ}C$, Domain II at $99\,^{\circ}C < T_s \leq 112\,^{\circ}C$ and Domain III at $T_s \leq 99\,^{\circ}C$, Figure 3. The

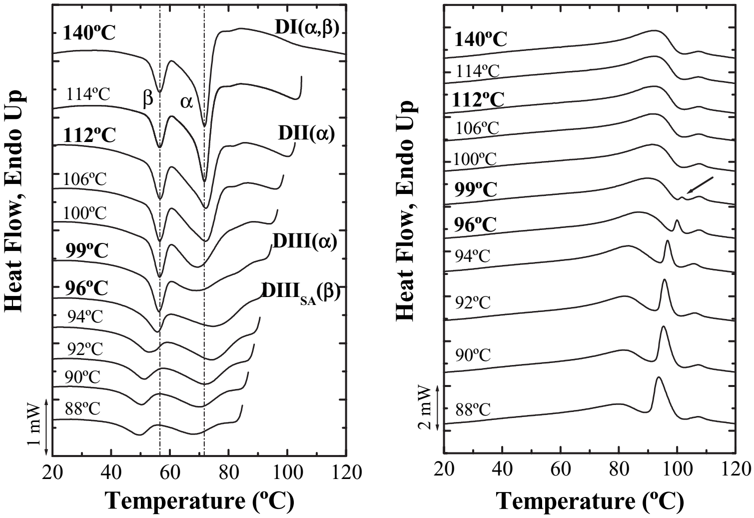

Figure 3.
DSC cooling scans (right) (10 °C/min) for $E_{26}S_{74}^{105}$ after self-nucleation at the indicated Ts, and subsequent heating scans (left) (10 °C/min).

existence of the three classical self-nucleation domains for this high temperature exotherm could be provoked by some degree of percolation present in a fraction of the cylindrical microdomains (MDs) population. As a result, the crystallization process can begin in one MD and spread through out other MDs that are interconnected with one another.

For the "β" exotherm no considerable changes were observed in the crystallization temperature (T_c) and in the associated enthalpy of crystallization (ΔH_c) in a T_s range from 112 to 99 °C (see Figure 3). From a T_s value of 96 °C, a progressive decrease in T_c and in ΔH_c was observed as T_s values were decreased. This behavior is completely different to the one observed in a classic Domain II behavior, because the T_c shifts to lower values as T_s decreases. However, the reduction noted in the crystallization enthalpy of the "β" exotherm is caused by the crystallization at lower supercooling of a fraction of the material (within the MDs involved in this process) that has been self-nucleated and is overlapped with the "α" crystallization exotherm. Therefore, the "β" exotherm does not exhibit the exclusive self-nucleation domain; it exhibits a direct transition from Domain I to Domain III_{SA}, similar to other types of block copolymers reported in previous publications[11,14–17].

Various block copolymer systems with a crystallizable component have shown absence of Domain II after the self-nucleation treatment. This peculiar behavior has been studied in PE and PCL blocks within triblock terpolymers of PS-*b*-PE-*b*-PCL where the crystallizable block (PE or PCL) was strongly confined into small isolated microdomains[17]. Similar results[11,16] have been found for the self-nucleation behavior of the crystallizable PEO block within PB-*b*-PI-*b*-PEO, the corresponding hydrogenated PE-*b*-PEP-*b*-PEO triblock terpolymers and for PEO and PCL for PS-*b*-PEO-*b*-PCL triblock terpolymers[14–18].

The absence of Domain II, for the β exotherm, is a direct consequence of the extremely high MDs density ($\sim 10^{12}/cm^3$ for $E_{26}S_{74}{}^{105}$) that need to be self-seeded in comparison with the number of heterogeneities usually active in a bulk sample of the crystallizable block ($10^9/cm^3$ for a typical PE). Therefore, to increase the density of "self-nuclei", the self-nucleation temperature has to be decreased to values so low that some unmelted crystals can be annealed.

Figure 4 shows the DSC cooling and heating scans during self-nucleation at the T_s values indicated for $E_{11}S_{89}{}^{244}$ (PE microspheres within a PS matrix). A fractionated crystallization behavior for a sphere forming component within a diblock copolymer is not usual. Generally, when the component is dispersed into well isolated MDs, only superficial or homogeneous crystallization can be achieved[12]. Furthermore, the behavior is very atypical for exotherms "β" and "γ".

The "α" exotherm corresponds to the crystallization of a certain population of PE spheres within $E_{11}S_{89}{}^{244}$. This population of spheres shows the three classic domains of self-nucleation: Domain I at $T_s > 112\,°C$, Domain II at $94\,°C < T_s \leq 112\,°C$ and Domain III at $T_s \leq 94\,°C$. In this case, this relatively high temperature crystallization exotherm cannot be explained by percolated MDs and therefore must be caused by the crystallization of a small fraction of droplets that contain highly active heterogeneities (like Wilkinson catalyst remains)[12].

The very small "β" crystallization signal did not show any changes until the T_s reached a value of 94 °C, where this signal started to disappear, while at the same time an annealing peak appeared in the subsequent melting run. In view of previous studies[11,14–17], a transition from Domain I to Domain III_{SA} was established for the self-nucleation behavior of this exotherm. The origin of this exotherm must be related to the existence of a second droplet population that contains less active heterogeneities[12].

In the case of the dominant "γ" exotherm (the one with the largest enthalpy of

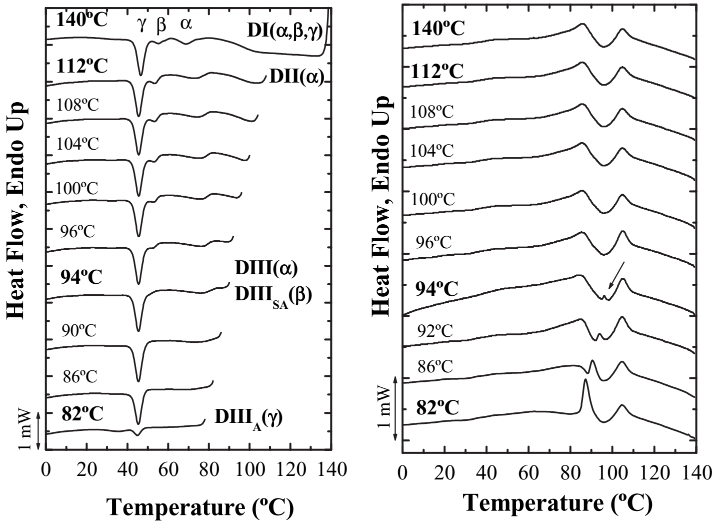

Figure 4.

DSC cooling scans (right) (10 °C/min) for $E_{11}S_{89}^{244}$ after self-nucleation at the indicated Ts, and subsequent heating scans (left) (10 °C/min).

crystallization), where most of the PE spheres within $E_{11}S_{89}^{244}$ crystallize, the self-nucleation is even more restricted as indicated by its invariant shape and enthalpy down to T_s temperatures of 86 °C where extensive annealing has already occurred in the sample (as judged by the size of the annealed melting peak). Therefore, a transition from Domain I to Domain III_A has been assigned and finally, at lower temperatures, Domain III_{SA} can be appreciated by a reduction in the crystallization enthalpy associated with exotherm "γ" (see DSC trace for $T_s = 82\,°C$). This case agrees with previous reports; in those cases where the injection of self-nuclei in every MD is most difficult in view of the very large number of MDs, Domain III is split into Domain III_A and Domain III_{SA} as explained in the experimental part. The origin of exotherm "γ" is related to the crystallization of heterogeneity free droplets whose nucleation can either start at the surface of the droplet or homogeneously[12,27].

Conclusions

The crystallization process of the PE block within PE-*b*-PS diblock copolymers is increasingly restricted as the PS content in the diblock copolymers increases. A fractionated crystallization behavior was observed for the confined PE MDs within $E_{26}S_{74}^{105}$ (PE cylinders) and $E_{11}S_{89}^{244}$ (PE spheres) which is caused by the high density of MDs in comparison with the heterogeneity density present in the PE block. The self-nucleation experiments in these copolymers showed different behaviors. When the PE blocks form a continuous or percolated phase (PE, $E_{78}S_{22}^{41}$ and $E_{53}S_{47}^{51}$), a "classic" behavior (where the three self-nucleation domains are obtained) was observed.

When the PE block is located in isolated MDs and a fractionated crystallization was detected ($E_{26}S_{74}^{105}$ and $E_{11}S_{89}^{244}$), the fraction of crystals formed at higher temperatures exhibits a "classic" self-nucleation behavior, while those crystals that crystallize at the largest supercooling (lower exotherms) can only be self-nucleated at temperatures where the Domain III has already started and hence Domain II disappears for this fraction of material. A peculiar fractionated crystallization behavior for spherical PE MDs is reported in this work, with two low temperature exotherms β and γ.

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