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Nucleation and Crystallization of PS-*b*-PEO-*b*-PCL Triblock Copolymers

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Summary: We have recently prepared a series of Polystyrene-*b*-Poly(ethylene oxide)-*b*-Polycaprolactone (PS-*b*-PEO-*b*-PCL or SEOCL) triblock copolymers of varying compositions and molecular weights. These ABC triblock copolymers present the peculiarity that two of the three blocks are able to crystallize upon cooling from an already phase segregated melt. When either of the crystallizable blocks or both are a minor phase, a fractionated crystallization process develops. The confinement of crystallizable blocks in the nanoscopic scale enables the clear observation in some cases of exclusive crystallization from homogeneous nuclei of two components within the triblock copolymer. The homogeneous nature of the nucleation was deduced since the supercooling attained is the maximum possible before vitrification of the material takes place. The self-nucleation domains were also found to depend on the composition and molecular weight of the copolymers. The block copolymers exhibited a marked decrease in crystalline memory and when the crystallizable blocks constitute minor phases, the self-nucleation domain disappears. The reason behind this behavior is that only at lower self-nucleation temperatures the density of self-nuclei becomes high enough to include at least one crystal fragment per confined microdomain in view of their vast numbers (e.g., $10^{16}/cm^3$).

Introduction

The crystallization of block copolymers has attracted recent attention in view of its many differences with the crystallization of bulk polymers [1]. In particular, the effect of confinement into microphase separated phases (that in block copolymers are in the nanometers range or on the same order of magnitude of the chain end-to-end distance) can affect the nucleation and crystallization kinetics of crystallizable components and the thermodynamic stability of the processes involved, such as chain folding [1-3].

In the case of immiscible polymer blends, a dispersion of one component into the matrix of another can be achieved in the microns range. The nucleation of bulk polymers is generally performed on heterogeneities or impurities since the free energy penalty is much smaller than that of creating homogeneous nuclei by spontaneous aggregation of polymer chains [4]. If the number of microscopic droplets of the dispersed polymer is greater than the number of heterogeneities that are usually active at low supercoolings

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then a fractionated crystallization phenomenon takes place [5-6]. This means that the confined crystallizable polymer can display one or a series of crystallization exotherms when cooled from the melt in a Differential Scanning Calorimeter (DSC) that can be located at lower temperatures than the temperature at which the bulk polymer crystallizes. The origin of multiple exotherms has been attributed to the crystallization of different groups of droplets at specific and independent supercoolings. The droplets that contain heterogeneities usually active at low supercoolings in the bulk polymer will crystallize at identical temperatures to that polymer in the bulk. Those droplets that contain other types of less efficient heterogeneities will nucleate at the supercooling necessary for those heterogeneities to become active. Finally, those droplets that do not contain any heterogeneities will only nucleate at the largest supercooling, since a greater supercooling is usually needed in order to generate homogeneous nuclei. [5-6].

The homogeneous nucleation phenomena were first studied by droplet crystallization experiments performed in metals, alcanes and polymers when dispersed in inert low molecular weight media [4-6]. Nevertheless, some authors found that the greatest supercooling needed for the crystallization of a certain droplet population was dependent on the superficial characteristics of the droplets. Both the crystallization of polymer droplets in inert low molecular weight media and in high molecular weight polymer matrices share the same limitations from the point of view of being susceptible to surface nucleation phenomena [4-7]. In the case of block copolymers, two factors contribute to make them an ideal system to study homogeneous nucleation: the purity involved in anionic synthesis and the presence of well-defined interphases in strongly segregated systems. The finding of extremely large supercoolings attributable to crystallization starting from homogeneous nuclei in diblock copolymers minor phase components dates back to 1969 [5-8] and has been the subject of recent attention [3, 9-10]. In the case of ABC triblock copolymers, only a few works have reported fractionated crystallization of one crystallizable component [11-12]. In this work, we present results on an ABC triblock copolymer system where two crystallizable components can exhibit fractionated crystallization depending on the composition.

Experimental

The Polycaprolactone (PCL) was supplied by Aldrich and SEC measurements indicated that its Mw was 16.000 g/mol (Mw/Mn=1.53). The Polyethylene oxide (PEO) was supplied by Polysciences as a narrow molecular weight standard of Mw=1.000 g/mol

(Mw/Mn=1.1). The PS-*b*-PEO and PS-*b*-PEO-*b*-PCL copolymers employed in this work were synthesized in a previous work [12]. We will only refer in detail to two samples that exhibit fractionated crystallization: a $S_{81}EO_{19}^{18.5}$ diblock copolymer (Mw/Mn=1.07) and a $S_{63}EO_{16}C_{21}^{24}$ triblock copolymer (Mw/Mn=1.12). Data for the other block copolymers of this series [13] will be reported in the near future [14]. The subindices indicate the amount of each component in weight % and the superindices the average number molecular weight in Kg/mol. All DSC runs were performed in a Pyris 1 from Perkin-Elmer under ultra pure nitrogen atmosphere calibrated with cyclohexane and Indium. The self-nucleation technique designed by Fillon et al. [15] was employed in order to ascertain the self-nucleation Domains for the homopolymers and copolymers, details of experimental procedure can be found in previous works [6-7]. Samples are first heated to a high enough temperature in order to erase thermal history, then they are cooled at 10 °C/min down to –100 °C to provide them with a standard thermal history. Then they are heated to a temperature denoted Ts (or self-nucleation temperature) and isothermally kept there for 5 min. After treatment at Ts, the sample is cooled down to –100 °C and subsequently heated at 10 °C/min until full melting occurs. Depending on Ts, 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-nucleated since Ts 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; in Domain III the sample is partially molten so that self-nucleation and annealing of unmelted crystals will take place at Ts [6-7, 15].

Table 1 Self-nucleation experiments in homopolymers

Material	Ts (°C)	Molten Fraction (%)	Tc (°C)	ΔHc (J/g)	Tm (°C)	ΔHm (J/g)	Domain
PEO	100	100	21	-126	40	153	I
	50	100	32	-114	42	155	IIa
	45	99.9	35	-120	41	181	IIa
	43	99.7	35		41	184	II
	41	98.0	35		41	186	II
	39	69.1	36		**42.1**	192	III
	37	47.7	34	-91	42; **44**	194	III
PCL	120	100	35.9	-72	55.7	80	I
	63	100	38.3	-71	56.2	79	IIa
	62	100	39.1	-71	56.2	79	IIa
	60	99.9	40.0	-70	56.2	80	II
	59	97.8	46.3	-66	56.3	80	II
	58	88.9	46.3	-67	57.7; **60.7**	82	III
	57	74.3	47.7	-48	57.5; **60.5**	84	III

Results and Discussion

Table 1 presents the results of self-nucleation experiments performed on the homopolymers that will allow us to establish the basic behavior of these polymers in the bulk. It can be seen that both PEO and PCL clearly exhibit the usual three nucleation domains [15], however, since they both exhibit a temperature range where nucleation is encountered beyond temperatures where the melting endotherm is no longer present, this Domain has been classified in Table I as Domain IIa or self-nucleation due to crystalline memory. Once Ts is low enough for crystal fragments to be present, then the sample is labeled as being in Domain II or self-nucleation domain. When the samples are in Domain III, Ts causes annealing of unmelted crystal fragments and the melting of such annealed crystals is highlighted with Tm values in bold in Tables 1 and 2.

Table 2 Self-nucleation experiments in block copolymers.

Material	**Ts**	**Molten Fraction (%)**	**Tc (°C)**	**ΔHc (J/g)**	**Tm (°C)** PEO; PCL	**ΔHm (J/g)**
$S_{81}EO_{19}$	120	100	-40	-6; -9*	37	15
	44	99	-40	-6; -9*	37	14
	42	98	-40	-5; -8*	37; **46**	14
	36	57	-42	-2; -6*	35; **41**	15
	30	14	-45	0; -5*	37	15
$S_{63}EO_{16}C_{21}$	90	100	-42	-9	32; 52	17
	60	100	-42	-9	31; 52	15
	56	99	-42	-9	30; 52; **59**	15
	52	85	-42; 41	-5	33; 51; **56**	16
	42	31	-42; 39	-3	33; 50	17
	26	18		-3	**32**; 52	20

*Estimated enthalpy of crystallization during heating (i.e., cold crystallization)

Figure 1 presents cooling scans for the two block copolymers and their subsequent heating scans. From the location of the crystallization exotherms that peak at –40 °C and –42 °C for the $S_{81}EO_{19}^{18.5}$ and the $S_{63}EO_{16}C_{21}^{24}$ respectively, it is clear that fractionated crystallization is present. In the case of the $S_{81}EO_{19}^{18.5}$ the PEO block must be crystallizing from homogeneous nuclei as a result of its confinement into either cylinders or spheres, this can be inferred from the vicinity of the Tg of the PEO block, which was found at – 58 °C. The Tg of the PS block can be clearly seen in the heating scan of the diblock copolymer as well as cold crystallization of PEO that is present as a broad exotherm. In the case of the triblock copolymer, both crystallizable blocks are experiencing coincident crystallization from homogeneous nuclei (the Tg of the PCL is located at –60 °C) since both are confined into the PS matrix.

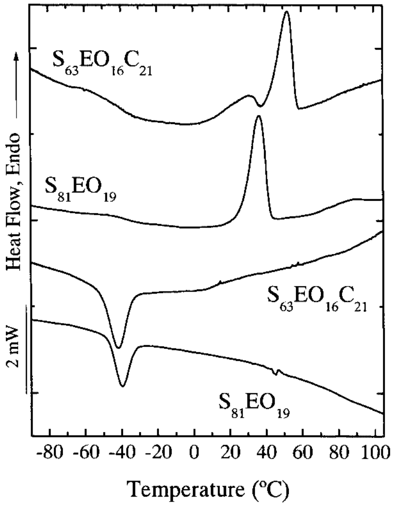

Figure 1. DSC cooling and heating scans of the block copolymers.

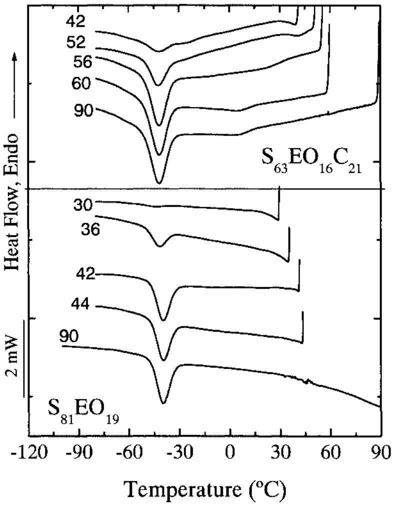

Figure 2. DSC cooling scans from the indicated Ts values.

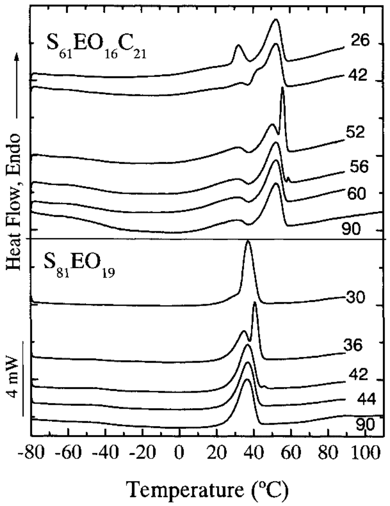

Figure 3. DSC heating scans from the indicated Ts values.

The DSC heating scan of the $S_{63}EO_{16}C_{21}$[24] triblock copolymer also exhibits a very clear cold crystallization exotherm before the double endotherm corresponding to the melting of the PEO block and the PCL block respectively (Fig. 1 and Table 2). Figure 2 shows cooling scans from selected Ts temperatures for the two block copolymers. The subsequent heating scans are presented in Figure 3 while Table 2 highlights important changes experienced by the materials at selected Ts temperatures. The self-nucleation results indicate that when the materials crystallize within phase segregated microdomains, the crystalline memory can not be retained, this was also observed for copolymers with compositions where no fractionated crystallization was present [14].

In the diblock copolymer, Figs. 2 and 3 and Table 2 show that annealing starts before self-nucleation at 42 °C, this means Domain II has been suppressed [16-17]. Self-nucleation is only clearly apparent at lower Ts temperatures, like 36 °C, when crystallization is observed immediately upon cooling. The reason for this behavior is that self-nuclei concentration increases sharply as Ts is decreased [15], therefore, since the phases are confined into cylinders or spheres of densities aproaching $10^{16}/cm^3$ [3, 9, 17], it is necessary to go to Domain III in order to generate enough self-nuclei to seed every crystallizable microdomain. For the triblock copolymer a fractionated crystallization process is clearly present. There is a small population of crystals that are formed in a small exotherm between 0 and 10 °C in Fig. 2, but most of the crystallization occurs in a coincident fashion after homogeneous nucleation at –42 °C. As in the case of the diblock, annealing starts before self-nucleation can affect the population that crystallizes at –42 °C, but the crystals formed between 0 and 10 °C experienced domain II self-nucleation. Finally, detailed analysis [14] of Figs. 2 and 3 indicates that the independent self-nucleation of each crystallizable block demonstrates that the PCL block does not nucleate the PEO block even if they are covalently bonded.

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