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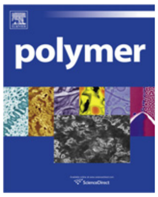

Polymer communication

Nanodroplet formation and exclusive homogenously nucleated crystallization in confined electrospun immiscible polymer blend fibers of polystyrene and poly(ethylene oxide)

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ABSTRACT

By utilizing electrospun blend fibers of polystyrene (PS) and poly(ethylene oxide) (PEO) with diameters in sub-microns, nanodroplets of the minor component (PEO) were obtained by annealing the blend fibers above the glass transition temperature (T_g) of the matrix polymer (PS), as a result of the Rayleigh-Plateau instability in the melt. However, direct thermal annealing of the PS/PEO blend fibers led to poor Rayleigh breakup of the PEO fibers in the PS matrix, and fractionated crystallization with both homogeneous and heterogeneous nucleation was observed, probably due to a broad size distribution of PEO particles. On the contrary, after confining the PS/PEO blend fibers with a high T_g polymer, poly(4-*tert*-butyl styrene) (P4tBS, $T_g \sim 143$ °C), well-defined Rayleigh breakup of the PEO fiber was achieved by annealing the P4tBS-coated PS/PEO blend fibers at 150 °C. Consequently, exclusive homogeneously nucleated PEO crystallization was observed at −20 °C. This report could provide a universal method to achieve nano-sized droplets for the study of nanoconfinement effect by utilizing electrospun immiscible polymer blend fibers without addition of any compabitilizers.

1. Introduction

Nanostructured polymers have attracted growing attention because they are recognized as an efficient way to obtain novel polymeric materials with synergistic and superior mechanical, electrical, and optical properties due to nanoconfinement effects. In addition to amorphous polymers [1], polymers with long or quasi-long range order have demonstrated nanoconfined properties. These polymers include crystalline polymers, liquid crystalline polymers, and block copolymers. When they are confined in nanoscale spaces, novel ordered morphologies with unique orientations are observed [2]. First, when block copolymers are confined into nanoscale spaces, single crystalline domains with specific orientations can be obtained [3–12]. These single crystalline domains have good potentials for next generation nanolithography and microelectronics applications. Second, when liquid crystalline polymers are confined into nanoscale spaces, the ordered mesogens adopt a specific orientation conforming to the confinement geometry [13–16]. In the above two kinds of ordered polymers, the commensurability between the polymer long period and the confinement dimension plays an important role in the final domain (for block copolymers) and mesogen (for liquid crystals) orientations. Third, when crystalline polymers are confined into nanoscale spaces, crystallization behavior, crystal orientation, polymorphism, phase transformation, and even melting behavior can be drastically altered [2,17]. Finely dispersed immiscible polymer blends [18], polymers in nanopores [19–22], and microphase-separated crystalline block copolymers [17] have been used to achieve the confined polymer crystallization with uniform crystal orientation, and thus novel properties [23,24].

Among the above effects for nanoconfined polymer crystallization, the most pronounced change is the crystallization behavior. Homogeneous nucleation, which is rarely observed in bulk polymers, can occur when the confined geometry changes from three-dimensional (3D) to two-dimensional (2D), one-dimensional (1D), and finally to zero-dimensional (0D), and the corresponding confined space decreases from the bulk to nanometer scales. The following mechanism has been proposed [25]: the number of droplets per unit volume is much higher than the number density of heterogeneous nuclei (i.e., there are no existing nuclei in most of the

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droplets), and thus homogeneous or self nuclei have to be generated for crystallization, which usually happens at a large supercooling (ca. 60–100 °C). For example, homogeneous nucleation of poly(ethylene oxide) (PEO) was observed at ca. −23 °C in miniemulsions, which is much lower than that of heterogeneous nucleation in the bulk PEO (ca. 40 °C) [26,27]. The critical size of the droplets for the appearance of homogeneous nucleation depends on the density of heterogeneities in the specific polymer. It is reported that exclusive homogeneous nucleation can be observed when isotactic polypropylene (PP) is finely dispersed at a density of ca. 10^{12} droplets/cm^3 [28].

Closely related to the crystallization behavior, uniform crystal orientation can be achieved by confining the crystal growth in nanoscale lamellae and cylinders [2]. Moreover, polymorphic phases and phase transformation may also be affected by confined crystallization, although the effects are much less pronounced. For example, after confining a small molecule liquid crystal, 4-*n*-octyl-4′-cyanobiphenyl (8CB), in 30 nm cylindrical nanopores, a rich polymorphism with at least four different low temperature phases in addition to the smectic A is observed [29]. Also, when nylon 6 is confined in nanofibers (200 nm diameter), the Brill transition (i.e., from the monoclinic α-form to a high-temperature monoclinic form) is observed at 180–190 °C, which is at least 20 °C higher than that (160 °C) in the bulk sample [30].

In our recent report, nanodroplets and fractionated crystallization were achieved for the first time for poly(vinylidene fluoride) (PVDF) by thermal annealing of electrospun PVDF/polysulfone (PSF) blend fibers above both the melting temperature (T_m) of PVDF (170 °C) and the glass transition temperature (T_g) of PSF (185 °C) [31]. The nanodroplet formation was attributed to the Rayleigh-Plateau instability [32] of the co-continuous PVDF/PSF blend fibers in the melt. Nevertheless, homogeneously nucleated crystallization always co-existed with heterogeneously nucleated crystallization in the thermally annealed PVDF/PSF electrospun blend fibers, because nanodroplets from the Rayleigh breakup of strained PVDF nanofibers in the PSF matrix had a broad size distribution ranging from 100 to 800 nm. In this work, we studied nanodroplet formation in thermally annealed electrospun polystyrene (PS)/PEO blend fibers. Instead of using the direct thermal treatment as reported in Ref. [31], the electrospun PS/PEO blend fibers were confined with a high T_g polymer, poly(4-*tert*-butylstyrene) (P4tBS, $T_g \sim 143$ °C), before thermal annealing. It was found that after coating the electrospun blend fibers with P4tBS, the Rayleigh breakup in confined blend fibers became better controlled, and/or coalescence of the nanodroplets from the Rayleigh breakup was effectively prevented. As a result, exclusive homogeneously nucleated crystallization was achieved in these thermally annealed and confined PS/PEO blend fibers.

2. Experimental

2.1. Materials

A PEO standard with the number-average molecular weight (M_n) of 36,500 g/mol, the weight-average molecular weight (M_w) of 41,500 g/mol, and the molecular weight distribution $M_w/M_n = 1.14$, was purchased from Fluka. PS (M_n = 170,000 g/mol and $M_w/M_n = 2.06$) and P4tBS (M_w = 50,000–100,000 g/mol) samples were purchased from Sigma–Aldrich. Tetrahydrofuran (THF, HPLC grade, Fisher Scientific) and *N,N*-dimethylformamide (DMF, anhydrous, purity ~99.8%, Sigma–Aldrich) were used as received.

2.2. Electrospinning of PEO/PS fibers and subsequent coating with P4tBS

The mixed solution for electrospinning was obtained by dissolving 15 wt.% polymers (i.e., PS and PEO with PS/PEO = 70/30 wt./wt.) in a mixture solvent of 50/50 (wt./wt.) THF/DMF. A uniform milk-like suspension was obtained by strong agitation at 80 °C for 3 h. Fibers of the PS/PEO 70/30 blend were prepared via electrospinning under the following conditions: a DC voltage of 15 kV, a collector-to-needle tip distance of 18 cm, and a pump rate of 1.0 mL/h. The total electrospinning time was about 0.5 h to obtain an overlaid fiber mat.

The electrospun PS/PEO blend fibers were further coated with a high T_g polymer, P4tBSt ($T_g \sim 143$ °C [33]), in order to study the confinement effect. The as-spun PS/PEO fibers were dipped into a 3 wt.% P4tBS/hexane solution followed by being dried at ambient temperature for three cycles. The final P4tBS-coated PS/PEO fiber mat was further dried in a vacuum oven at room temperature for 2 d to completely remove residue solvents. The weight percentage of P4tBS in the fiber mat was approximately 67 wt.%. Because the T_g of P4tBS was higher than the T_m of PEO (ca. 63 °C) and T_g of PS (~100 °C), the PS/PEO blend fibers were effectively confined by P4tBS. To study the evolution of phase morphology, the P4tBS-coated PS/PEO blend fibers were annealed at different temperatures for 15 min, ranging from 85 to 225 °C.

2.3. Instrumentation and characterization

To study the nonisothermal and isothermal crystallization behaviors of PS/PEO blend fibers before and after being coated with P4tBS, differential scanning calorimetry (DSC) was carried out on a TA Instruments Q-100 DSC. About 3 mg of sample was used for the DSC study, and the cooling process was carried out at a rate of −5 °C/min after annealing the samples at different temperatures for 15 min. The as-spun PS/PEO fibers were sputter coated with gold for the scanning electron microscopy (SEM) study using a JEOL JSM-6510 SEM. The transmission electron microscopy (TEM) study was carried out using a JEOL 1200EX at an accelerating voltage at 120 kV. The sputter coated P4tBS-confined PS/PEO fibers were first embedded in standard epoxy using a silicone mold (Ted Pella, Inc.), and then the standard epoxy was cured at 60 °C for 12 h. Thin sections (~80 nm) were obtained by microtoming the epoxy block using a diamond knife and were floated onto the water surface before picking up with a 400-mesh TEM copper grid.

3. Results and discussion

Nonisothermal crystallization was first performed for the unconfined PS/PEO blend fibers after annealing at different temperatures. The corresponding DSC results are shown in Fig. 1A. When the blend fibers were annealed below the T_g of PS (e.g., at 85 and 95 °C), a major crystallization peak was observed at 40 °C and a small crystallization peak was seen at −20 °C. On the basis of previous studies [34,35], we assumed that the high and low temperature crystallization processes were induced by (unconfined) heterogeneous and homogeneous nucleation, respectively. When annealed above the T_g of PS (e.g., at 105 and 115 °C), the intensity of the low temperature crystallization peak slightly increased and the major heterogeneously nucleated crystallization peak appeared almost unchanged. With further increase of annealing temperature (e.g. 125 and 135 °C), the major heterogeneously nucleated crystallization peak at 40 °C started to decrease its intensity and the homogeneously nucleated crystallization peak kept nearly the same. Meanwhile, a broad peak seemed to appear between 40 and −20 °C, which could be attributed to heterogeneously nucleated confined crystallization [36]. When the blend fiber was annealed at 150 °C for 15 min, multiple crystallization peaks at −20, −2.5, and 12 °C were observed along with the unconfined heterogeneous crystallization peak at 40 °C. This is typical for fractionated crystallization [36]. Further increasing the