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Structural change with blending of crystalline/amorphous block copolymers having different types of microphase separations

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ABSTRACT

Two kinds of polystyrene/polyethylene diblock copolymers exhibiting bicontinuous and spherical microphase separations were blended at different ratios. Initial films were prepared by hot xylene dissolution, followed by casting and drying. The obtained films were melted and isothermally crystallized at various temperatures. Differential scanning calorimetry melting peak temperatures for the isothermally crystallized films suggested that characteristic crystal growth occurred at critical bicontinuous/spherical blend ratios of 90/10 and 85/15. The crystalline structure consisted of interior pure crystals and exterior defective crystals. Transmission electron microscopy observations of these blended films indicated the progressive isolation of the amorphous phase with increases in the spherical component. Specifically, the mixed morphologies of both the bicontinuous and spherical structures were obtained for the above critical blend ratios. Analysis implied that this unique morphology was formed as a result of the combination of the crystal nucleus effect and the competitive growth effect.

1. Introduction

The semicrystalline polymer alone contains both crystalline and amorphous phases of nanometer sizes, which are controllable by crystallization conditions. If one of the segments of the block copolymer is a semicrystalline polymer, the formation of various morphologies is expected, depending on the crystallization conditions, which cannot be introduced for usual amorphous sets. Recently, we reported that the polystyrene/polyethylene diblock copolymer (PS-*b*-PE), in which the PE segment was semicrystalline but the PS segment was always amorphous, exhibited a bicontinuous network structure (i.e., interconnected crystalline and amorphous components) under suitable crystallization conditions [1–4]. Namely, the crystalline/amorphous microphase separation was controlled by the isothermal crystallization temperature (T_c). This was quite different from general polymerization-controlled phase separation. This bicontinuous PS-*b*-PE film became an electrolyte membrane with both low water uptake and high proton conductivity by selective sulfonation of PS segment [4], which was recently reviewed by Elabd et al. [5] Furthermore, a flexible nanoporous PE film was obtained from this bicontinuous PS-*b*-PE precursor by fuming nitric acid etching, which selectively removed the amorphous phase [2,3].

The blending technique has been applied to block copolymer systems to prepare various morphologies. Most attempts were sets of an amorphous/amorphous block copolymer with homopolymer bases because the amorphous segments were easily mixed together at the molecular level. Bates and Lodge et al. [6] prepared a nanoporous material with a range of 50 nm from a bicontinuous microemulsion precursor for the blending of polyisoprene (PI) and PS homopolymers with PI-*b*-PS, followed by selective removal of the PS segment after selective cross-linking of the PI segment. With this method, microphase separation could be controlled by the blend ratio on film preparation, independent of the polymerization condition. Additionally, blending between amorphous/amorphous block copolymers was extensively performed to control the nanostructure [7–12]. He et al. [8,11] reported the effect of solvent treatment on the morphology of blended thin films containing two amorphous/amorphous block copolymers with different blend ratios. In contrast, undesirable phase separation at a submicrometer scale occurred for a crystalline/amorphous set [13–15]. Indeed, no bicontinuous structure has been obtained for the blending of PS and PE homopolymers with PS-*b*-PE, although the phase size was reduced and the blend morphology was stabilized [14,15]. Takeshita et al. [16] investigated the microphase separation structure in the molten state and the structure formation in crystallization from the melt for the blends consisting of two kinds of PS-*b*-PEs with different

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copolymer compositions by synchrotron small-angle X-ray scattering (SAXS) measurements.

In this study, we focus on the improvement of the connectivity of the crystalline phase when similar blending of crystalline/amorphous block copolymers of PS-*b*-PEs was made. Namely, the enhancement of connectivity of the PE segment was tried by blending PS-*b*-PEs exhibiting a bicontinuous network structure and the PS spheres in a PE matrix. This approach was expected to achieve the control of multiple morphologies by not only crystallization condition but also blend ratio.

The formation of a microphase separation of block copolymer meant that the spatial restriction between both segments effectively affected structural formation. Thus, non-equilibrium crystallization behavior under such restricted conditions would be reasonably notable if a block copolymer contained a crystalline segment [16–26]. Müller et al. [22,23] considered the microdomain structure in the microphase separation of the PE segment within diblock copolymers using a successive self-nucleation/annealing technique, a thermal fractionation method based on the sequential application of self-nucleation and annealing steps. In the present study, the effect on structural formation of blending of crystalline/amorphous block copolymers was comprehensively investigated by combined morphological observation using transmission electron microscopy (TEM) and crystallization behavior estimated by differential scanning calorimetry (DSC) measurement.

2. Experimental section

2.1. Materials

Two kinds of PS-*b*-PEs having different types of microphase separations were purchased from Polymer Source Inc. (Quebec, Canada): one exhibited a bicontinuous network structure, and the other exhibited PS spheres in a PE matrix, reflecting the ratio of the segmental lengths of PS and PE blocks. The former bicontinuous morphology has been reported in our previous studies [1–4]. The latter spherical microphase separation was confirmed by TEM observation (not shown here). The number-average molecular weights (MWs) of PS and PE segments and MW distributions of each material are listed in Table 1. It should be noted that the same MWs of the PE segment for each material were chosen in order to avoid macrophase separation within the crystalline phase.

2.2. Film preparation

Blended films were prepared with component ratios (wt %) of 100/0, 95/5, 90/10, 85/15, 50/50, and 0/100 for both bicontinuous and spherical materials. Appropriate amounts of these blended materials, 1 wt %, were dissolved in *p*-xylene at the boiling point for 10 min under a nitrogen gas flow with antioxidants, 0.5 wt % (based on polymer) of both octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propanoate and bis(2,4-di-*tert*-butylphenyl)pentaerythritol diphosphite, followed by casting and drying at room temperature (RT) in a vacuum. The obtained cast films, which had a thickness of 50 μm, were melted at 180 °C for 10 min, and then quenched and isothermally recrystallized at various T_cs of 50–105 °C for 12 or 24 h, followed by quenching at RT. The following melt-recrystallization procedure was carried out in the DSC furnace. Fuming nitric acid etching of the film was performed at RT for 30 min. An excess amount of fuming nitric acid was added to the sample film in a glass bottle. Following this etching procedure, the treated film was washed with distilled water and then acetone, and dried well at RT.

Table 1
MWs and MW distributions of each PS-*b*-PE material.

Material	Number-average MW (× 10^3)		MW distribution
	PS segment	PE segment	
Bicontinuous	54.00	67.00	1.07
Spherical	5.80	48.60	1.05

2.3. Measurements

A Perkin Elmer Pyris 1 DSC was used for DSC measurements. DSC scans were performed from RT to 180 °C in the heating process and from 180 °C to RT in the cooling process at a rate of 10 °C/min under a nitrogen gas flow. The sample melting temperature (T_m) was evaluated as the peak temperature of the melting endotherm. The temperature was calibrated using indium and tin standards. Obtained DSC thermograms were normalized considering the total weight of PE segment in films. ^{1}H-NMR measurements were made for the 1.0 vol% deuterated chloroform solution of the prepared film, using Bruker Avance DSX 300 operated at 300 MHz.

TEM observations of the films were conducted with the use of a JEOL JEM-1200EX electron microscope operated at 80 kV. The samples were stained by RuO_4 vapor and embedded in an epoxy resin, causing the amorphous phase to appear as a darker region in the image. The assembly was cut into thin sections 50 nm thick with a Reichert Ultracut S microtome for TEM observation. Scanning probe microscopy (SPM) observations of the etched films were performed by an SPA-400 multi-function unit with an SPI3800N probe station (SII NanoTechnology Inc.). A rectangular cantilever with a tetrahedral silicon tip (SII NanoTechnology Inc., SI-DF20) was applied in the tapping mode measurement. The scan rate was 1 μm/s.

3. Results and discussion

The melting characteristics for isothermally crystallized films with different blend ratios were examined by DSC measurement. Fig. 1 presents the melting endotherms of films isothermally crystallized at 90 °C for 12 h, which is the optimum T_c to form a bicontinuous network structure for the 100/0 film [2]. By comparison, blended films exhibited a higher melting peak and a lower melting peak at approximately 95 °C. In Fig. 1, the lower and

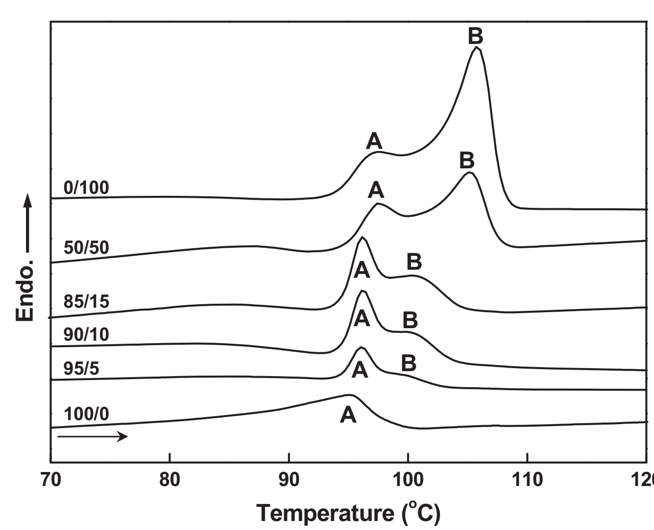

Fig. 1. DSC heating curves of films isothermally crystallized at 90 °C for 12 h. The index on each curve represents the blend ratio of bicontinuous/spherical components. The heating temperature direction is indicated by the arrow. Lower and higher melting peaks are indexed by A and B, respectively.