



Effects of surface wetting induced segregation on crystallization behaviors of melt-miscible poly(*L*-lactide)-*block*-poly(ethylene glycol) copolymer thin film



Jingjing Yang^{a,b}, Yongri Liang^{a,*}, Weichao Shi^{a,b}, Han Sup Lee^c, Charles C. Han^{a,*}

^a State Key Laboratory of Polymer Physics and Chemistry, Joint Laboratory of Polymer Science and Materials, The Beijing National Laboratory for Molecular Sciences, and Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

^b Graduate School of Chinese Academy of Sciences, Beijing 100049, China

^c Department of Nano-Systems Engineering, INHA University, Incheon 402-751, South Korea

ARTICLE INFO

Article history:

Received 26 February 2013

Received in revised form

7 May 2013

Accepted 13 May 2013

Available online 20 May 2013

Keywords:

Surface wetting

Crystallization

Poly(*L*-lactide)-*block*-poly(ethylene glycol) (PLLA-*b*-PEG) thin film

ABSTRACT

The effects of wetting induced surface segregation on the crystal nucleation, growth rate, morphology and crystal orientation of melt-miscible crystalline–crystalline diblock copolymer of poly(*L*-lactide)-*block*-poly(ethylene glycol) (PLLA-*b*-PEG) thin films (~90 nm) were investigated in this work with reflection optical microscopy (ROM), atomic force microscopy (AFM), and two-dimensional grazing incident wide angle X-ray scattering (2D GIWAXS) methods. The XPS results demonstrated that the wetting induced surface enrichment of PLLA block on the free surface of PLLA-*b*-PEG thin films occurred when the thin films annealed at 160 °C (molten state). When the PLLA-*b*-PEG thin film annealed at 160 °C for 30 min, the fraction of PLLA block (f_{PLLA}) on the free surface could reach to ~90%. The ROM, AFM and 2D GIWAXS results indicated that the nucleation, crystal growth, morphology and crystal orientation of PLLA block in PLLA-*b*-PEG thin films were significantly influenced by prior wetting process. For the PLLA-*b*-PEG thin film with wetting time shorter than 15 min ($\sim 52\% < f_{\text{PLLA}} < \sim 75\%$), the O-shaped flat-on nucleus preferentially formed on the free surface of thin films. However, for the thin film with wetting time longer than 15 min ($f_{\text{PLLA}} > \sim 75\%$), the S-shaped edge-on nucleus preferentially formed on the free surface at early stage of crystallization and then grew into tilted flat-on lamella. Furthermore, the overall spherulite growth rate of PLLA in PLLA-*b*-PEG thin films decreased with increase of wetting time. We found that the crystallization behavior of PLLA on the free surface in the PLLA-*b*-PEG thin films was strongly influenced by surface wetting induced changes of surface energy, composition and chain alignments. Our results demonstrated that the crystallization kinetics, morphology and crystal orientation of crystalline block copolymer thin films can be controlled by prior wetting process.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Recently, crystalline block copolymer thin films have received much attention; because these systems can produce much more special superstructures. The crystalline block copolymer thin film is one kind of polymer thin films, which have become an integral part in modern hi-tech applications such as optoelectronics, biotechnology, nanolithography, novel sensors and actuators [1]. In contrary to bulk system, the surface wetting effects are known to have significant influence on pattern evolution in the polymer thin films,

accompanied by phase transitions such as crystallization and phase separation. For example, the phase separated morphology of polymer blend thin films is governed by interplay between phase separation process and wetting process, which is referred to as surface-directed phase separation (SDPS) [2–5]. Therefore, understanding the interplay between wetting process and phase transition process is a key issue for controlling the structure and morphology of the polymer blend and block copolymer thin films.

Generally, the surface segregation in polymer blend or block copolymer thin films is one of the phenomena of surface wetting, which is induced by preferential wetting of one component in the thin films during the annealing process. It is believed that the component with lower surface free energy or with shorter or with more flexible chains in polymer blends or block copolymer thin

* Corresponding authors. Tel.: +86 10 82618089; fax: +86 10 62521519.
E-mail addresses: liangry@iccas.ac.cn (Y. Liang), c.c.han@iccas.ac.cn (C.C. Han).

films will preferentially segregate onto the surface during the annealing process [6–8]. In the past decades, the surface wetting induced surface segregation in the polymer blend or block copolymer thin films has been extensively investigated theoretically [2,4,9–13] and experimentally [3,6,7,14–20]. For example, Ton-That et al. [6] investigated the effects of annealing on the surface composition and morphology of polystyrene/poly (methyl methacrylate) (PS/PMMA) blend (50/50 wt/wt). They found that the component with a lower surface free energy, PS, segregated to the surface to form surface segregation morphology, when the films annealed at a temperature above their glass transition temperatures. But as annealing time was longer than 14 h, the surface enrichment and morphology change (continuous PS layer on the surface) was mainly due to the phase separation between PMMA and PS. Russell et al. [16] investigated the effect of the air/copolymer and copolymer/substrate interfaces on the morphology of PS-b-PMMA copolymer films using dynamic secondary ion mass spectroscopy. Their results demonstrated that surface or preferential wetting of the two blocks at the polymer/substrate and the polymer/air interfaces greatly affected the morphology of the films.

However, the effect of surface wetting induced segregation on the crystallization has seldomly been reported so far. The crystallization process is one of the most basic processes of self organization and is utilized for controlling the structure and morphology of crystalline block copolymer thin films [21]. In this work, we used the double-crystalline diblock copolymer of poly(*L*-lactide)-block-poly(ethylene glycol) (PLLA-b-PEG) thin film as a model material to investigate the effect of surface wetting induced segregation on the crystal nucleation, spherulite growth, morphology and crystal orientation in crystalline block copolymer thin films. The reason is that PLLA-b-PEG copolymer is one of the biodegradable crystalline–crystalline diblock copolymers with excellent properties, such as biodegradability, biocompatibility, innocuity, tissue absorbability, and so on [22].

2. Experimental

2.1. Materials

The PLLA-b-PEG copolymer sample was provided by Ji'nang Daigang Co, Ltd, in China. The polydispersity index (PDI) of this PLLA-b-PEG copolymer was 1.25, and the number average molecular weight (M_n) of PLLA and PEG were 4900 and 5000, respectively [22]. The melting temperatures of PLLA and PEG in the PLLA-b-PEG copolymer were measured as 130 and 52.5 °C by differential scanning calorimetry (DSC) with a heating rate of 2 °C/min, respectively.

2.2. Thin film preparation

The PLLA-b-PEG thin films were prepared by spin coating a solution of about 15 mg/mL PLLA-b-PEG/chloroform onto silicon substrates at 3000 rpm for 60 s. The silicon wafer, which was N type (100) of single-side polished silicon wafer, with about 0.5 mm of thickness were treated with Piranha solution ($H_2SO_4:H_2O_2 = 3:1,v/v$) for 1 h to make a hydrophilic surface before use. The thicknesses of PLLA-b-PEG thin films were about 90 nm, which were measured by Ellipsometry (Woolam Co., Inc.). And thin films were dried at vacuum oven at room temperature for several hours to completely remove the residual solvent before experiments.

2.3. Surface wetting and crystallization process

The wetting and crystallization processes of the PLLA-b-PEG thin films were performed with a hot stage (Linkam LTS350)

under nitrogen atmosphere. The PLLA-b-PEG thin films were heated at 160 °C for different time for wetting and then rapidly quenched to 70 °C (i.e. $T_{m,PLLA} > 70\text{ °C} > T_{m,PEG}$, where $T_{m,PLLA}$ and $T_{m,PEG}$ are melting temperatures of PLLA and PEG, respectively) for isothermal crystallization of PLLA block for 6 h. Subsequently, the samples were quickly quenched to 30 °C ($<T_{m,PEG}$) for isothermal crystallization for 2 h.

2.4. Reflection optical microscopy

The reflection optical microscopy (ROM) observations were performed with an Olympus BX51 optical microscope equipped with a hot stage (Linkam CS350) under nitrogen atmosphere and the ROM images were recorded by a C-5050ZOOM camera.

2.5. Atomic force microscopy

Atomic force microscopy (AFM) images of PLLA-b-PEG thin films were obtained by a Nanoscope multimode V8 (Bruker Co.) with tapping mode at room temperature. A silicon cantilever tip was used for measurements of the AFM images. The resonance frequency was about 330 KHz and the scan rate was 20 $\mu\text{m/s}$. The scanning density was 512 lines per frame.

2.6. Two-dimensional grazing incident wide angle X-ray scattering (2D GIWAXS)

2D GIWAXS measurements were performed at room temperature on the BX14B1 beamline in the Shanghai synchrotron radiation facility (SSRF), China. The incident angle, α_i was set as 0.15° (the critical angle of silicon substrate is 0.2° ($\lambda = 0.1381\text{ nm}$) [23] and the critical angle of PLLA was about 0.15° ($\lambda = 0.154\text{ nm}$) [24] and the exposure time was 60 s. A Mar345 (3450 × 3450) detector was used to record the 2D GIWAXS patterns. The wavelength of the incident X-ray was 0.124 nm and sample to detector distance (SDD) was 273.7 mm. The silicon powder was used as standard material to calibrate the scattering vectors. The air scattering was subtracted before analysis of all 2D GIWAXS patterns.

2.7. X-ray photoelectron spectroscopy (XPS)

Surface chemical compositions of PLLA-b-PEG thin films were measured by ESCALab220i-XL electron spectrometer (VG Scientific) with Aluminum (Al) $K\alpha$ radiation (300W) using normal incidence angle. The binding energies were calibrated by the C1s (284.8 eV) from adventitious carbon. The XPSPEAK software (Version 4.0) was used to fit the XPS spectra.

3. Results and discussion

3.1. Surface wetting induced surface segregation

The spin-coated PLLA-b-PEG thin films were annealed at 160 °C for wetting. In our previous work [22], using small angle X-ray scattering method we demonstrated that PLLA and PEG blocks in bulk PLLA-b-PEG copolymer were absent of microphase separation (i.e. completely miscible) at 160 °C. The wetting time dependent surface morphologies were observed by reflection optical microscopy (ROM), as shown in Fig. 1. The ROM images showed that the whole silicon substrate was uniformly wetted by PLLA-b-PEG copolymer at 160 °C. However, the air surface brightness of thin film gradually changed as wetting time increased. It indicated that the reflectivity, which is dependent on chemical compositions and their structure on the free surface of PLLA-b-PEG thin film, was somewhat changed by wetting. These results reveal that the surface

Download English Version:

<https://daneshyari.com/en/article/5182138>

Download Persian Version:

<https://daneshyari.com/article/5182138>

[Daneshyari.com](https://daneshyari.com)