European Polymer Journal 47 (2011) 2063–2068

Contents lists available at SciVerse ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Surface segregation of polypeptide-based block copolymer micelles: An approach to engineer nanostructured and stimuli responsive surfaces

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ARTICLE INFO

Article history:
Received 18 April 2011
Received in revised form 8 July 2011
Accepted 12 July 2011
Available online 27 July 2011

Keywords:
Polymer blends
Block copolymers
Surface morphology
Polypeptides

ABSTRACT

We describe the surface segregation of polypeptide-based block copolymer micelles to produce stimuli-responsive nanostructures at the polymer blend/air interface. Such structures were obtained by simultaneous surface migration and self assembly at the surface of diblock copolymer/homopolymer blends. We employed blends composed of homopolymer (PS) and an amphiphilic block copolymer polystyrene-b-poly(L-glutamic acid) (PS-b-PGA). The surface was functionalized based on the preferential segregation to the polymer blend/air interface of the hydrophilic PGA block of the diblock copolymer upon annealing to water vapor. The surface migration of the diblock copolymer to the interface was demonstrated both by XPS and contact angle measurements. As a consequence, the PGA interfacial attraction leads to a large surface excess on diblock copolymer which in turn, through macrophase and microphase separation, produced separated domains at the surface with regions composed either of homo or block copolymer. Herein we demonstrate that the use of asymmetric diblock copolymers with a higher content in PS lead to spherical micellar assemblies randomly distributed at the surface. As observed by AFM imaging the blend composition, i.e. the amount of block copolymer within the blend influences the density of micelles at the surface. Finally, when exposed to water, the pH affects the surface morphology. The PGA segments are collapsed at low pH values and extended at pH values above 4.8, thus inducing variations on the topography of the films at the nanometer scale.

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1. Introduction

The preparation of nanostructured surfaces and thin films with ordered moieties below 100 nm is a current center of interest as these materials can be employed in a wide range of applications such as electronic, biological or sensing applications [1]. Such structures have been mainly obtained by using the 'bottom up' approach that usually concerns the self-assembly of block copolymers [2]. This methodology allow us to control the type of morphology varying from lamellar, cylindrical to cubic in a nanometer scale range depending on the chemical nature of the blocks, the topology or the chain length [3]. A particular case of self-assembly concerns the case of homopolymers and block copolymer blends that allow us to obtain rather complex morphologies in a straightforward manner. The variety of morphologies exhibited by homopolymer/copolymer (A/A–B) blends was explained by deGennes in terms of solubility of the copolymer brushes by the homopolymer [4]. Three different situations can be, thus, found in these systems [5–7]: situation (i) in which the homopolymer (generally a low molecular weight) can be completely or "uniformly" solubilized into the A domains of similar chemical nature. The situation (ii) concerns the partial or "localized" solubilization of the homopolymer in the block copolymer. In these two cases the increase of the volume of the B phase changes the interfacial curvature

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doi:10.1016/j.eurpolymj.2011.07.011

thus leading to morphological transformations. This strategy has been, for instance, employed for the elaboration of materials with a variety of morphologies ranging from lamellar phase or the intriguing OBDD (Ordered bicontinuous double-diamond) to hexagonal lattices exclusively depending on the % of homopolymer in the mixture [8]. Finally, in situation (iii), the low solubility of the homopolymer induces the formation of macrophase separated domains rich in diblock copolymer (in which additionally microphase separation may be observed) randomly distributed in a homopolymer host. Situation (iii) is generally found in blends with diblock copolymers with large incompatibility between the blocks (given by the Flory–Huggins parameter (χ) or in blends in which the molar masses of homopolymer and diblock copolymer differs significantly) [9–11]. Equally, the relative ratio between the segments in the block copolymer is expected to play an important role in the final morphology.

Whereas the behavior of homopolymer/copolymer blends have been extensively studied both in thin films and in bulk both from a theoretical and experimental point of view [12], the potential of these blends to control the surface properties of polymeric materials has been somehow neglected. Herein, we describe the preparation of functional and nanostructured interfaces by using blends of homopolymer/amphiphilic diblock copolymer in the complete segregation regime, i.e. the homopolymer and amphiphilic diblock copolymer have very different sizes. Taking advantage of the surface micelle surface migration and by exposure to different environments we will vary the chemical composition at the surface. Thus, both surface chemistry and functional group distribution can be simultaneously modified. Finally, the use of stimuli-responsive hydrophilic PGA block confers to the surface additional advantages. Polypeptides have in comparison with other hydrophilic blocks several major advantages including their response to several stimuli such as pH, temperature or ion strength [13]. In addition polypeptides are able to modify the secondary structure between rigid rodlike α-helical conformation and a rather disordered coil conformation as a function among others of the chain length of the chain. The use of this polymer will afford not only nanostructured surfaces with controlled chemistry but also with pH stimuli responsive properties.

2. Experimental section

^{1}H NMR spectra of the copolymers were recorded at room temperature on a Bruker Avance 400 MHz spectrometer using the residual proton resonance of the deuterated solvent as an internal standard. Average molar masses and molar mass distributions of the samples were determined by Size Exclusion Chromatography (SEC), using a Varian 9001 pump with both a refractive index (Varian RI-4) and a UV detector (Spectrum Studies UV 150). Calibration was obtained using narrowly-distributed polystyrene standards and THF as the mobile phase at a flow rate of 0.5 ml min^{-1}.

The synthesis of similar diblock copolymers has been already reported [14,15] and was carried out in several steps. First, styrene was polymerized by atom transfer radical polymerization (ATRP). By adequately tuning the conversion to values lower than 40% a large percentage of end-brominated polystyrene groups should be obtained. The end-terminal bromo group was easily modified into an amine function by reaction with 1,4-diaminoethane. The amine modified PS was employed, in turn, as macroinitiator for the ring-opening polymerization of γ-benzylester-L-glutamate N-carboxyanhydride. Finally, deprotection under basic conditions (KOH/H_2O/THF) lead to the amphiphilic PS-b-PGA diblock copolymers. Throughout this study a series of different block copolymers were prepared with the following compositions (resulting from ^{1}H NMR analysis): PS_{49}-b-PGA_{17} (PDI: 1.23), PS_{49}-b-PGA_{62} (PDI: 1.31) and PS_{27}-b-PGA_{70} (PDI: 1.28).

Films were prepared by spin casting from concentrated (60 mg/ml) THF solutions containing homopolystyrene (M_n: 600.000 g/mol) and the diblock copolymer in the appropriate amount. The films were supported on silicon wafers previously cleaned with a piranha solution. The samples were dried for an additional hour and exposed either to dry or humid air. The dry air atmosphere was obtained in a closed oven working at 95 °C for 48 h. The humid environment was produced in a tightly closed stainless steel vessel having a bottom reservoir with water and a platform to place the films. Annealing in a humid environment was carried out during 36 h at 90 °C.

2.1. Contact angle measurements

Water contact angles were measured using a KSV Theta goniometer. The volume of the droplets was controlled to be about 3 μl. The pH of the water employed was either 3 or 11.

Dynamic Light Scattering (DLS) experiments were performed using a Malvern NanoS. The samples were kept at constant temperature (25.0 ± 0.2 °C) during all the experiments. Measurements were done at 173° and the counting time varied for each sample from 300 s up to 600 s. Millipore water was thoroughly filtered through 0.1 μm membranes and directly employed for the preparation of the solutions.

2.2. X-ray photoelectron spectroscopy (XPS) experiments

The surface composition of selected blends was obtained by XPS. XPS spectra were recorded with a 220i-XL ESCALAB from VG (The Netherlands). The films, supported on silicon wafer, were put under UHV to reach the 10^{-8} Pa range. The Non-monochromatized Mg X-ray source was used at 100 W, as well as a flood gun to compensate for the nonconductive samples. The spectra were calibrated in relation to the C1s binding energy (284.6 eV), which was applied as an internal standard. Fitting of the high-resolution spectra was provided through the AVANTAGE program from VG.

2.3. Atomic force microscopy (AFM)

The AFM images recorded in tapping mode were measured using a Digital Instruments NanoScope IIIa Multimode. The solution was held in a standard fluid cell

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