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Molecular arrangement of symmetric and non-symmetric triblock copolymers of poly(ethylene oxide) and poly(isobutylene) at the air/water interface

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ABSTRACT

The behavior of a series of amphiphilic triblock copolymers of poly(ethylene oxide) (PEO) and poly(isobutylene) (PIB); including both symmetric (same degree of polymerization (DP) of the terminal PEO blocks) PEO_m-*b*-PIB_n-*b*-PEO_m and non-symmetric (different DP of the terminal PEO blocks) PEO_m-*b*-PIB_n-*b*-PEO_z, is investigated at the air/water interface by measuring surface pressure *vs* mean molecular area isotherms (π *vs mmA*), Langmuir–Blodgett (LB) technique, and infrared reflection–absorption spectroscopy (IRRAS). The block copolymer (PEO_{32}-*b*-PIB_{160}-*b*-PEO_{32}) with longer PEO segments forms a stable monolayer and the isotherm reveals a pseudo-plateau starting at $\pi \sim 5.7$ mN/m, also observed in the IRRAS, which is assigned to the pancake-to-brush transition related to the PEO dissolution into the subphase and subsequent PEO brush dehydration. Another plateau is observed at $\pi \sim 40$ mN/m, which is attributed to the film collapse due to multilayer formation. The pancake-to-brush transition could not be observed for samples with smaller PEO chains. The isotherms for block copolymers, with short PEO chains, both symmetric (PEO_3-*b*-PIB_n-*b*-PEO_3) and non-symmetric (PEO_{12}-*b*-PIB_n-*b*-PEO_3), reveal another transition at $\pi \sim 20$–25 mN/m. This is interpreted to be due to the conformational transition from a folded state where the middle PIB block is anchored to the water surface at both ends by the terminal hydrophilic segments to an unfolded state with PIB anchored to the water surface at one end. It is assumed that this transition involves the removal of PEO_3 chains from the water surface in case of non-symmetric PEO_{12}-*b*-PIB_{85}-*b*-PEO_3 and in case of symmetric, probably one PEO_3 of each PEO_3-*b*-PIB_{85}-*b*-PEO_3 chain. Because of the weaker interaction of the short PEO_3 chains with the water surface as compared with the relatively longer PEO_{12} chains, the film of PEO_3-*b*-PIB_{85}-*b*-PEO_3 collapses at much lower surface pressure after the transition as compared with the PEO_{12}-*b*-PIB_{85}-*b*-PEO_3. The AFM images reveal the formation of microdomains of almost uniform height (6–7 nm) in LB films of PEO_3-*b*-PIB_{85}-*b*-PEO_3 and PEO_{12}-*b*-PIB_{85}-*b*-PEO_3 after transferring onto silicon surfaces. These domains are assumed to be the mesomorphic domains of ordered and folded PIB chains.

1. Introduction

Amphiphilic block copolymers belong to a class of polymeric materials that have the ability to create self-assembled nanostructures in selective solvents, thin films, and bulk, which has led to many applications for amphiphilic block copolymers in areas ranging from water purification [1], surface modification [2], drug-delivery systems [3], as templates to achieve ordered nanostructures [4], to anti-fouling surfaces [5]. Additionally, amphiphilic block copolymers have been extensively investigated both theoretically and experimentally to understand their molecular arrangement and the formation of self-assembled nanostructures at the air/water interface [6–13].

Similar to low molar mass amphiphiles, amphiphilic block copolymers, composed of hydrophobic and hydrophilic segments, have the ability to form a monomolecular layer at the air/water interface. The hydrophilic block anchors the block copolymer to the water subphase, while the hydrophobic block grafts the copolymer chains to the air. By measuring the surface pressure as function of mean molecular area during compression of the monolayer, the so-called Langmuir isotherm also termed as surface pressure *vs* mean molecular area (π–*mmA*) isotherm is recorded. The π–*mmA* isotherm reveals various regimes corresponding to

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various transitions and conformations of the block copolymer chains at the interface during compression. For example, Langmuir isotherms of poly(ethylene oxide) (PEO) containing amphiphilic block copolymers show a pancake region at lower surface pressure where the PEO chains are adsorbed on the water surface with a flattened conformation, followed by a pseudo-plateau which is attributed to the dissolution of PEO chains into the water subphase. The PEO chains adopt a brush conformation at higher surface pressure and grafting density [14–16].

Amphiphlic block copolymers with PEO as the hydrophilic block and polystyrene (PS) [17–19], poly(methyl methacrylate) (PMMA) [14], poly(propylene oxide) [20], poly(*L*-lactide) [21], perfluorinated methacrylate [22–25], and many more [10,26,27] as the hydrophobic block have been extensively investigated at the air/water interface. More recently, our group has started investigations on a new series of PEO and polyisobutylene (PIB) containing block copolymers for monolayer and nanostructure formation at the air/water interface and has observed some unusual behavior [28,29]. The Langmuir isotherms for PIB-*b*-PEO diblock copolymers showed a typical plateau, corresponding to the pancake-to-brush transition of PEO; however, with decreasing length of the PEO chains, the plateau disappeared completely from the π–*mmA* isotherm. At higher surface pressures ($\pi \sim 41$ mN/m) all the isotherms exhibited an extended plateau, corresponding to the multilayer formation due to the so-called roll-over collapse of the monolayer [30], which is known for PIB based amphiphiles [31]. After transferring the monolayer of PIB_{130}-*b*-PEO_{19} to silicon substrate using the Langmuir–Blodgett (LB) technique, AFM images revealed the formation of columnar structures of specific heights perpendicular to the silicon substrate, which were ascribed to the organization of PIB chains into mesomorphic domains. The occurrence of mesomorphic PIB is surprising and interesting since PIB is an amorphous polymer which shows crystallization only in oriented fibers under external stress [32]. In another study on PIB-*b*-PEO three arm star block copolymers having very short PEO (3EO units per arm) segments, the monolayer apparently collapsed at relatively lower surface pressure (π = 22 mN/m) as indicated by a transition in the compression Langmuir isotherm. The typical plateau for the multilayer formation could not be observed. The Langmuir isotherm of PIB-*b*-PEO star block copolymers with relatively long PEO segments (16EO units per arm), without the plateau corresponding to pancake-to brush transition, revealed the formation of stable monolayer with a collapse pressure of ~39 mN/m, with surface pressure still slightly increasing with further compression. In the current study, we are aiming to extend our understanding by investigating a series of triblock copolymers of PEO and PIB (PEO-*b*-PIB-*b*-PEO) for their monolayer formation and various phase transitions at the air-/water interface by measuring the π–*mmA* isotherms, infra-red reflection–absorption spectroscopy (IRRAS), and atomic force microscopy (AFM) on LB films. The triblock copolymers under investigation differ in PIB–PEO ratio and have different chain architectures, including; **symmetric** PEO_{32}-*b*-PIB_{160}-*b*-PEO_{32}, PEO_{12}-*b*-PIB_{55}-*b*-PEO_{12}, PEO_3-*b*-PIB_{57}-*b*-PEO_3, and PEO_3-*b*-PIB_{85}-*b*-PEO_3 and **non-symmetric** PEO_3-*b*-PIB_{70}-*b*-PEO_{12}, and PEO_3-*b*-PIB_{85}-*b*-PEO_{12}. For comparison purposes, PIB homopolymers have also been investigated for their monolayer formation at the air/water interface.

2. Experimental

2.1. Materials

The investigated PEO-*b*-PIB-*b*-PEO triblock copolymers (Scheme 1 and Table 1) were synthesized and characterized as described elsewhere [33,34].

2.2. Surface pressure measurements

Langmuir isotherm measurements were performed with a KSV 2000 Langmuir trough system (KSV, Helsinki) with a maximal surface area of 76,050 mm^2 equipped with symmetrically movable barriers, a platinum Wilhelmy plate for surface pressure measurements, and a circulating water bath system for temperature control. The subphase was purified deionized water (TKA GenPure Labor&Reinstwassertechnick Christian Wiesenack, Jena) with a conductivity <0.056 μS cm^{-1}. The surface purity of water in the trough was checked before each measurement by surface pressure measurements to a maximum compression (π < 0.15 mN m^{-1}). Predetermined volumes (50 μl and 100 μl) of the block copolymer solution, prepared in HPLC grade chloroform (1.0–2.0 mg/mL) were spread evenly on the subphase with fully opened barriers using a digital microsyringe.

The Langmuir isotherm measurements started after a waiting period of 20 min to ensure the complete evaporation of chloroform and uniform diffusion of the block copolymer chains on the water surface. The compression rate was kept at 15 cm^2/min. The complete isotherm for each sample was obtained by multiple measurements with increasing amount of spread volume, ranging from 100 up to 900 μl for the homopolymer and 20 to 200 μl for the triblock copolymers, leading to different initial surface pressures. Thus, different regions of the isotherm were first recorded and later combined into one plot to produce a complete isotherm.

2.3. Infrared reflection absorption spectroscopy

Infrared reflection absorption spectroscopy (IRRAS) was performed on a BRUKER Vector 70 FT-IR spectrometer equipped with a nitrogen cooled MCT detector and an A511 reflection unit (Bruker Optics, Germany), placed over the Langmuir trough setup (Riegler & Kierstein, Germany). A trough with two compartments in a hermetically sealed box was used. The sample trough (30 × 6 cm^2) was equipped with a Wilhelmy balance and two barriers. A circular reference trough (r = 3 cm) placed next to the sample trough can be brought into the focus of the IR beam by means of a shuttle. The filling levels of both troughs were kept equal and constant by means of an automated, laser reflection controlled, pumping system connected to reservoirs of purified, deionized water. The IR beam can be focused to the water surface in different angels of incidence with respect to the surface normal and was polarized with a KRS-5 wire-grid polarizer. The reflectance absorbance spectra (RA) were calculated from the single-beam reflectance spectra recorded on the reference (R_0) and sample trough (R) according to RA = $-\log(R/R_0)$. The resolution and scanner speed in all experiments were 4 cm^{-1} and 80 kHz. 1000 scans or 500 scans were accumulated for measurements in *p*- or s-polarization, respectively. A zero filling factor of 2 was applied before Fourier transformation, resulting in a final data point distance of 2 cm^{-1}.

Two types of IRRAS experiments were performed:

(i) Spectra were recorded at 45 different areas during a PEO_{32}–PIB_{160}–PEO_{32} monolayer compression from 1150 $Å^2$/molecule (2.5 mN/m) to 280 $Å^2$/molecule (18 mN/m). The compression speed was 30 $Å^2$/(molecule min). However, during spectra accumulation the barriers were stopped. Spectra were recorded in p- and s-polarization at an angle of incidence of 40°.

(ii) Angle dependent measurements were performed on PEO_{32}-*b*-PIB_{160}-*b*-PEO_{32} monolayer at three different surface pressures (4; 10; 20 mN/m). The spectra were recorded in p- and s-polarization and at various angles of incidence, ranging from 25° to 70° in increments of 3° excluding 52°, 55° and 58° due to the low reflectivity in the range of the Brew-