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Regular Article

Effects of subphase pH, temperature and ionic strength on the aggregation behavior of PnBA-*b*-PAA at the air/water interface

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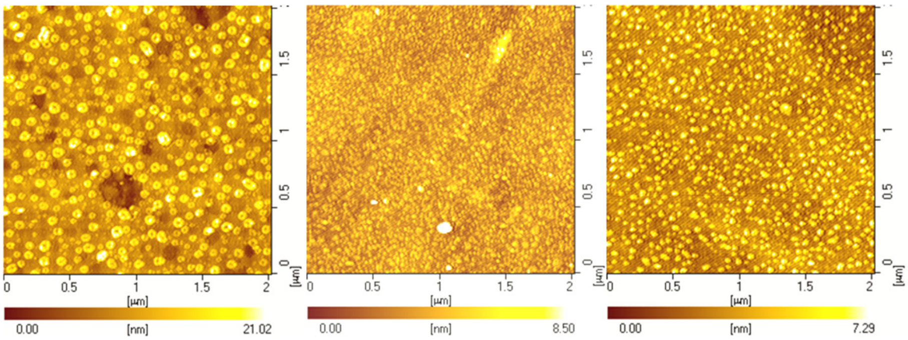
GRAPHICAL ABSTRACT

The LB films of diblock polyelectrolyte PnBA-*b*-PAA prepared from alkaline subphase with medium ionic strength exhibit ringlike nanostructures, while those under other conditions exbihit condensed or isolated micelles and wormlike structures, respectively.



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ABSTRACT

Aggregation behavior of an amphiphilic diblock polyelectrolyte poly(*n*-butylacrylate)-*b*-poly(acrylic acid) (PnBA-*b*-PAA) at the air/water interface and morphologies of its LB films were characterized by the Langmuir monolayer technique and atomic force microscopy (AFM), respectively. Effects of subphase pH, temperature and ionic strength on the isotherms and hysteresis curves of the PnBA-*b*-PAA monolayers and the morphologies of its LB films were systematically studied. With the increase of subphase pH, the isotherms shift negatively and the quasi-plateaus disappear under neutral and alkaline conditions. Hysteresis phenomena of the PnBA-*b*-PAA monolayers on acidic and neutral subphases are quite obvious and similar, while the compression and expansion isotherms under alkaline condition are almost overlapped. The LB films of PnBA-*b*-PAA transferred from acidic subphase exhibit isolated circular micelles with large size, while those from alkaline subphase exhibit condensed ones with small size. With the rise in subphase temperature, PnBA blocks on the water surface are more likely to aggregate into large cores due to the higher molecular mobility. Furthermore, the totally ringlike nanostructures prepared from alkaline subphase with medium ionic strength are observed for the first time in LB films of block copolymers.

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1. Introduction

Amphiphilic block copolymers have the ability to self-assemble into various ordered monolayer structures at the air/water interface [1–4]. Isotherms and hysteresis curves of copolymer monolayers and morphologies of their LB films have been widely studied in recent years [5–14]. Silva et al. studied the aggregation behavior of polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) at the air/water interface, and found there was a critical length of the PEO_n block ($48 < n < 90$) required to promote the hysteresis [8]. Seo et al. investigated the effect of subphase temperature on the isotherms of polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA), and suggested that PMMA blocks moved more freely and removed the free space more easily with the rise in temperature [9]. Our group once studied the effect of spreading solvents on the Langmuir monolayers and LB films of polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP), and found that the LB films prepared with a selective solvent exhibited different morphologies including planar structure, rod-like structure, circular micelles, and labyrinth pattern [10].

Amphiphilic block polyelectrolytes with stimuli-responsive behavior are known for their special characteristics, which can capture tiny stimulation from the environment and trigger tremendous changes in their physical or chemical properties [15–19]. Therefore, they are also called the environment-sensitive/responsive amphiphilic polyelectrolytes which have been applied to biosensors, protection of metals against corrosion, and room temperature sensors, etc. [20–29]. Hu et al. used molecular dynamics simulations to investigate the physical deposition behavior of the charged amphiphilic diblock polyelectrolytes, and found a flat amphiphilic bilayer structure and separate spherical clusters in nonselective and selective solvents, respectively [17]. Sprouse et al. investigated the micelles of poly(N, N-dimethylaminoethyl methacrylate)-*b*-poly(*n*-benzyl methacrylate) (PDMAEMA-*b*-PBMA) in aqueous solutions, and found that the cores were kinetically trapped and the coronas contracted with the increase of subphase pH and ionic strength [18].

On the other hand, amphiphilic block polyelectrolytes have also been widely studied at the air/water interface [30–42]. Claro et al. systematically studied the effects of subphase pH and ionic strength on the aggregation behavior of the PBMA-*b*-PDMAEMA monolayers at the air/water interface [32]. They concluded that at low pH the monolayer isotherms were condensed because the effects of the solubility and electrostatic repulsion prevail over hydrophobic interactions, while at high pH it was expanded due to the strong repulsion interaction between hydrophobic aggregates. Furthermore, with the increase of subphase ionic strength, polyelectrolyte brushes changed from an extended conformation to a coiled conformation. Geng et al. investigated the LB films of polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP), and found that the protonation/deprotonation procedures caused the reversibility of surface topological and chemical transition [33]. Chung et al. observed that the LB films of PS-*b*-P2VP exhibit isolated circular micelles at pH 5.3, while those at pH 1.8 exhibit the laced network structures [34]. Moreover, Wang et al. studied the effects of surface pressure and spreading solution concentrations on the aggregation behavior of polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA), and observed a variety of morphologies such as wormlike, porous, reticulate structures and dots in the LB films [35].

In this work, the aggregation behavior of the Langmuir monolayers of an amphiphilic diblock polyelectrolyte poly(*n*-butylacrylate)-*b*-poly(acrylic acid) (PnBA-*b*-PAA) at the air/water interface were investigated. PAA block is hydrophilic and responsive to pH, and the effective surface p*K*a (acid dissociation constant) of PAA brushes at room temperature is ~ 4.4 according to the results of Dong et al. determined by contact angle titration [43]. Nano-sized hydrophobic elastomeric PnBA cores form on the water surface to avoid the unfavorable interaction with water and PAA coronas, anchoring PAA coronas at the air/water interface. Effects of subphase pH, temperature and ionic strength on the structures and properties of Langmuir monolayers and LB films of PnBA-*b*-PAA were systematically studied.

2. Experimental section

2.1. Materials and reagents

The sample PnBA-*b*-PAA was synthesized by the reversible addition fragmentation chain transfer (RAFT) polymerization methodology, and characterized by size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR). The weight-average molecular weights (M_w) of PnBA and PAA blocks were respectively 12,000 and 28,000. Polydispersity index (M_w/M_n) of the sample was 1.35, and thus its number-average molecular weight (M_n) was calculated as 29,630 which was used at the following isothermal experiments. For more details on the block copolymer synthesis by RAFT, see the two references [44,45].

Spectrograde tetrahydrofuran (THF) was used to prepare the spreading solution of PnBA-*b*-PAA (0.50 mg/mL). Fresh aqueous solutions of H_2SO_4 and NaOH were used as acidic (pH 3) and alkaline subphases (pH 9), respectively, and fresh ultrapure water (pH 7) was used as neutral subphase. The subphase water (resistivity of 18.25 MΩ cm) was purified and deionized by a purification system (Molecular 1810C, China). NaCl (0.15, 0.30 and 0.75 mol/L) and $BaCl_2$ (0.05, 0.10 and 0.25 mol/L) were used to control alkaline subphase ionic strengths (I) of 0.15, 0.30 and 0.75 mol/L, respectively. All these reagents were analytical grade except THF and used without further purification. Ionic strength is used to describe the activity coefficients of strong electrolytes, where $I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2$ (c_i and z_i represent molar concentration and charge number of ion i, respectively).

2.2. $\pi{-}A$ experiments

Surface pressure versus mean molecular area (π–A) isotherms were measured with a KSV minitrough (Finland) with an effective area of $324 \times 75\ \mathrm{mm}^2$. A refrigerated bath circulator (THD-0510, China) was used to control subphase temperature. In an experiment, PnBA-*b*-PAA solution of appropriate volume (listed in Table 1) was dropwisely spread onto the air/water interface to obtain an initial surface pressure of ~0.3 mN/m using a gas-tight Hamilton microliter syringe, and a 15-min interval was allowed to evaporate the spreading solvent completely. The Langmuir monolayer was symmetrically compressed with two mobile barriers at a relative speed of 10 mm/min. A rectangular filter paper ($25 \times 10\ \mathrm{mm}^2$) and an iron hook suspending on the balance were used as a sensor to measure surface pressure. All the π–A isotherms were run at least two or three times with good reproducibility. The conditions in hysteresis experiments (compression–expansion cycles) were similar to those in the isothermal experiments. Maximum pressures were selected as 8, 15 and 10 mN/m at pH 3, 7 and 9, respectively, where the barriers were almost close to paper

Table 1
Spreading volumes (μL) of PnBA-*b*-PAA at different subphase pH and temperatures.

Conditions	10 °C	20 °C	30 °C
pH 3	10	8	11
pH 7	10	11	11
pH 9	9.5	7.5	9