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KSV NIMA [Application Note] #10

Nanostrand Formation of Block Copolymers at the Air/Water Interface

This Application Note describes controlled fabrication of nanostrand block copolymer structures using a Langmuir-Blodgett trough.

Introduction

Fabricating thin layers using nanotechnology relies on the ability to build structures with precise control of the thickness, packing, and particle organization. Langmuir-Blodgett (LB) and Langmuir-Schaefer (LS) techiques have been widely used for nanoparticle film fabrication of materials including graphene, metals, semiconductors and colloidal particles [1-7]. The advantages of the LB and LS techniques include highly controlled deposition, a variety of substrates, the abililty to alternate layer structures and use under ambient conditions. Additionally, the deposition speed, layer number and temperatures can be controlled.

Block copolymers are frequently used to achieve nanostructures based on phase separation between dissimilar blocks and are commonly used in nanoporous membranes and components in active nanodevices. To achieve optimal performance, the block copolymers in these materials must form a well-ordered nanopattern. In the following study, nanostrand networks were fabricated and analyzed using Langmuir-Blodgett deposition with different spreading solvents and polymer concentrations. The goal was to optimize experimental conditions to achieve reproducible patterns of long nanostrands and nanostrand networks with high surface coverage. The full study was published in ACS Nano 2010, 4 (11), pp 6825-6835 by Perepichka et al [4].

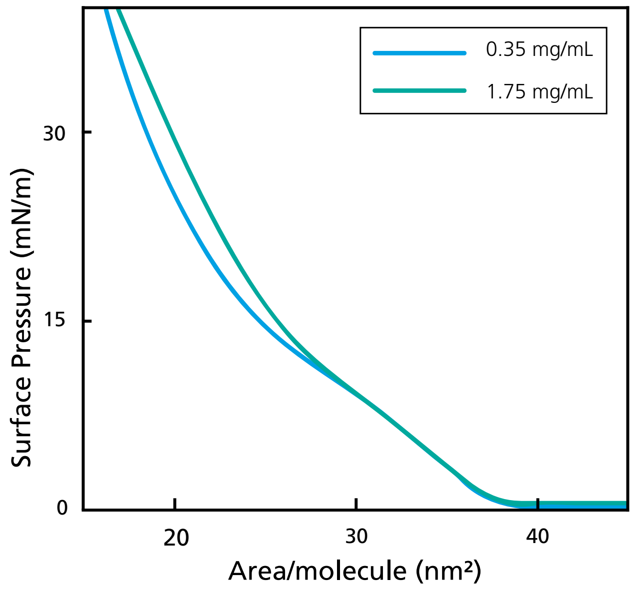
Experimental

Methods

Block copolymers of polystyrene-b-poly(4-vinyl pyridine)/3-n-pentadecylphenol (PS-P4VP/PDP) in different solvents were deposited on hydrophilic mica substrates using a KSV NIMA Langmuir-Blodgett trough. Before the deposition, the polymers were mixed in the desired solvent with different molar ratios and concentrations. During monolayer compression, the temperature was kept at 20 °C using a water circulator. During deposition, the quality of the transfer was followed by measuring a transfer ratio of 1.0 ± 0.2. The resulting layers were analyzed using atomic force microscopy (AFM).

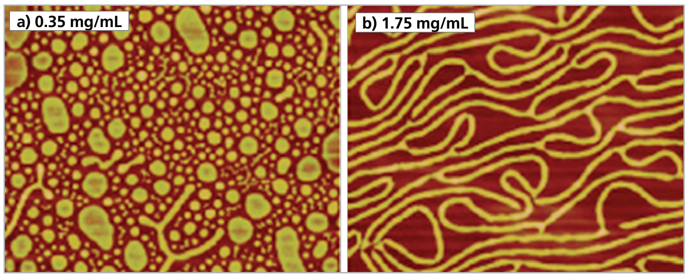
Results

When nanostructured polymers are compressed in a Langmuir trough, the polymers organize to form patterns depending on their hydrophobic and hydrophilic properties. Typically, the relatively large hydrophilic blocks surround the condensed and smaller hydrophobic regions of the polymers, which generates an elongated, ribbon-like structure, with various length-to-width aspect ratios. Figure 1 presents the surface pressure - area isotherm for the copolymer, spread from a chloroform solution. The Langmuir isotherms for low and high polymer concentrations are very similar, including the pressures of 5 and 10 mN/m typically employed for film transfer. This indicates that the morphological differences in the films do not impact on the surface pressure evolution at these concentrations.



[Fig. 1]: Isotherm of PS-P4VP/PDP with different concentrations on the water surface. Adapted with permission from ACS Nano 2010, 4 (11), pp 6825-6835. Copyright 2010 American Chemical Society

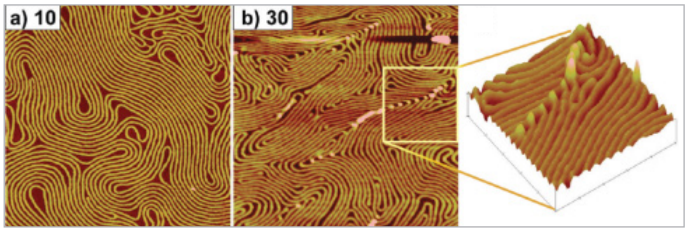
In Figure 2, the effect of the spreading solution concentration on the transferred layer structure is presented through atomic force microscopy images. The deposition surface pressure was 10 mN/m. At low concentrations in Figure 2a nanodot and planar aggregates dominated, but at high concentrations in Figure 2b a clear nanostrand network was present.



[Fig. 2]: AFM height images of LB monolayers of PS-P4VP/PDP formed at 20 °C from chloroform solutions at copolymer concentrations of a) 0.35 mg/mL and b) 1.75 mg/mL and transferred to mica at a surface pressure of 10 mN/m. Adapted with permission from ACS Nano 2010, 4 (11), pp 6825-6835. Copyright 2010 American Chemical Society.

The effect of different spreading solvents, such as 1,1,2,2 -tetrachloroethane, and subphase temperature were examined. Generally, both low vapor pressure spreading solvents and lower temperatures led to slower evaporation from the water surface and helped the polymers to maintain their mobility at the air/water interface for longer periods. This resulted in a higher degree of nanostrand alignment, maximal nanostrand density and fewer strand ends. The effect of lower subphase temperature was enhanced when low vapor pressure spreading solvents were used.

An increase in the deposition surface pressure from 10 mN/m to 30 mN/m increased the strand density (Figure 3a) and also resulted in a buckled film in some regions (Figure 3b), especially where the nanostrands were sharply angled. For these experiments, it was essential that the concentration was high, since low concentration solutions did not yield the nanostrand network morphology even at higher surface pressures. It can be seen from Figure 3 that only the strand density increased with surface pressure, with separated strand widths and heights unaffected. This indicates that the network forms soon after solution deposition and barrier compression simply pushes the network strands closer together. Barrier expansion showed open cracks within the dense nanostructures areas, indicating irreversible sticking.



[Fig. 3]: AFM height images of LB monolayers of PS-P4VP/PDP spread from a 1.90 mg/mL 1,1,2,2 –tetrachloroethane solutions at subphase temperature of 9 °C and transferred to mica at surface pressures of a) 10 mN/m and b) 30 mN/m. Adapted with permission from ACS Nano 2010, 4 (11), pp 6825-6835. Copyright 2010 American Chemical Society.

Conclusions

The study illustrates how a structured network morphology with relatively few strand ends can be obtained reproducibly and uniformly over large surface areas using a Langmuir-Blodgett trough. The resulting morphology was found to be dependent on the polymer concentration, choice of spreading solvent, temperature and deposition pressure. The optimized experimental conditions for nanostrand deposition included relatively high polymer concentration, low vapor pressure spreading solvent and low subphase temperature. Langmuir-Blodgett deposition enables careful control and adjustment of the experimental conditions in ambient conditions.

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