Nanoscale Pattern Formation in Langmuir−Blodgett Films of a Semifluorinated Alkane and a Polystyrene−Poly(Ethylene Oxide) Diblock Copolymer

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ABSTRACT

A novel example of the self-assembling capabilities of semifluorinated *n*-alkanes is presented: nanoscale periodic structures were revealed in mixed Langmuir−Blodgett films of a semifluorinated *n*-alkane with a polystyrene−poly(ethylene oxide) diblock copolymer by atomic force microscopy. The surface structures, resembling honeycombs with a hump at the center, have a periodicity of ∼40 nm. The same qualitative morphological features were found in all mixed films, independently of the polymer grafting density. Evidence suggests these structures arise from the organization of the semifluorinated alkane molecules segregated to the surface of the polymer layer.

The value of fluorinated compounds as low surface energy materials has long been acknowledged; in particular, surfaces consisting of close-packed arrangements of −CF$_3$ groups have some of the lowest surface energies known.[1] In this context, semifluorinated *n*-alkane oligomers, F(CF$_2$)$_n$(CH$_2$)$_m$H, constitute an important class of self-assembling materials. Perfluoroalkyl and alkyl chains have been amply demonstrated to be "mutually phobic".[2,3] Structurally, the helical configuration of perfluoroalkyl chains contrasts with the plane zigzag character of alkyl chains,[4] conferring conformational rigidity to the former as opposed to flexibility of the latter. Being made up of the above two chemically and structurally distinct blocks covalently bonded to form a single chain, semifluorinated *n*-alkanes gather the requisites to combine the "dual character" of amphiphilic molecules and the physics of orientational ordering of smectogenic liquid crystals. Accordingly, aggregation in solvents selective for one of the blocks[5,6] and smectic liquid crystalline phases were reported.[7−9] Also, organization in the solid state was evidenced by data consistent with the existence of layered structures.[10−13]

Recently, the self-organizing capabilities of semifluorinated *n*-alkanes have been exploited to yield polymers of low surface energy. Introduced as side groups in homopolymers and block copolymers, either as single chains or two- and three-arm monodendrons, they were shown to retain their smectogenic character,[14−18] giving rise to very low energy surfaces that are also stable against reconstruction in a polar environment.[15,18]

Semifluorinated *n*-alkanes distinguish themselves further by being a new class of Langmuir film-forming materials,[19,20] as traditionally the presence of an hydrophilic group was required for a molecule to form Langmuir films.[21] The detailed structure of the films, however, is still subject of controversy, and both monolayer and bilayer interleaved structures have been discussed.[19,20]

In this work, a new approach was used in order to create a low energy surface. A semifluorinated *n*-alkane was "blended" with an amphiphilic block copolymer and the "blend" confined at the air−water interface by the Langmuir technique. A polystyrene (PS)-poly(ethylene oxide) (PEO) diblock copolymer was used. The system is prone to organization on multiple length scales[22,23] due to the interplay between phase separation within the PS−PEO, phase separation within the semifluorinated alkane, the smectogenic character of the latter, and competing interactions between the two molecules. The picture generally accepted for the behavior of PS−PEO, of block size similar to that used here, as Langmuir film is as follows.[24−27] The polymer is physically grafted to the air−water interface by the hydrophobic PS block, which is a glass at room temperature. At low

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number of grafts per unit area, PEO is adsorbed at the interface. Upon compression, excluded volume interactions lead to its progressive desorption and stretching into the water subphase, eventually resulting in a "brush" configuration. PS should not contribute to the surface pressure, and no evidence for a first-order transition has been reported. Some predictions can then be made concerning the behavior of the semifluorinated alkane molecules in the mixed films. Being hydrophobic, it is expected that they vertically segregate to the top of the PS−PEO film. Being the component of lowest surface energy among the four blocks present in the system, it is expected also that the surface will be enriched in the fluorinated block. And, as PS is constrained to the air−water interface and given the difference in surface energy between this block and the fluorinated block,[28] lateral segregation between PS and the semifluorinated alkane is also likely to occur.

We shall now briefly describe the materials and methods used in this work. The semifluorinated n-alkane $F(CF_2)_8$-$(CH_2)_{18}H$ (SFA) was synthesized according to the procedure described by Rabolt et al.[10] PS−PEO with a PS block of 40 monomers and a PEO block of 123 monomers was purchased from Polymer Source, Quebec, and used as received. The reported polydispersity is 1.06. Solutions of SFA and PS−PEO of concentrations 1 mg/mL were prepared in chloroform and mixed to the desired proportions. Films were prepared on deionized water using a NIMA 601 film balance (Wilhelmy plate method) with a single barrier (compression speed 20 cm²/min) and transferred via the Langmuir−Blodgett (LB) technique onto hydrophilic glass substrates (dipping speed 1 mm/min). A single layer was transferred. Atomic force microscopy (AFM) was performed within 1 day after film preparation, with a Digital Instruments D3100 scanning probe microscope operating in tapping mode and using etched silicon probes. Surface roughness of the glass substrates was less than 0.3 nm. All experiments were performed at ambient conditions.

All surface pressure vs area curves for Langmuir films of the pure PS−PEO, SFA, and their binary mixtures showed no hysteresis before collapse. The surface pressure−area curve for the pure PS−PEO (Figure 1a, curve 6) is in good agreement with previous experiments.[24] The semiplateau is attributed to the gradual desorption of the PEO chains, until a brush is formed at a limiting area of 3 nm². The surface pressure−area curve for the pure SFA (Figure 1b, curve 7) shows a limiting area of 0.32 nm², similar to the cross-sectional area of a perfluoroalkyl chain[4,29] and therefore consistent with a close-packed arrangement of the perfluoroalkyl blocks.

Picturing that SFA vertically segregates to the top of the polymer, proportions of PS−PEO and SFA in the mixed films were chosen which would correspond to a close-packed layer of SFA covering a layer of PS−PEO in different grafting density regimes. It is observed that the surface pressure vs area "fingerprint" of the polymer is significantly altered by the presence of the SFA for all compositions studied (Figure 1a) and resembles the curve of the pure SFA. The same curves plotted per SFA area reveal that the mixed
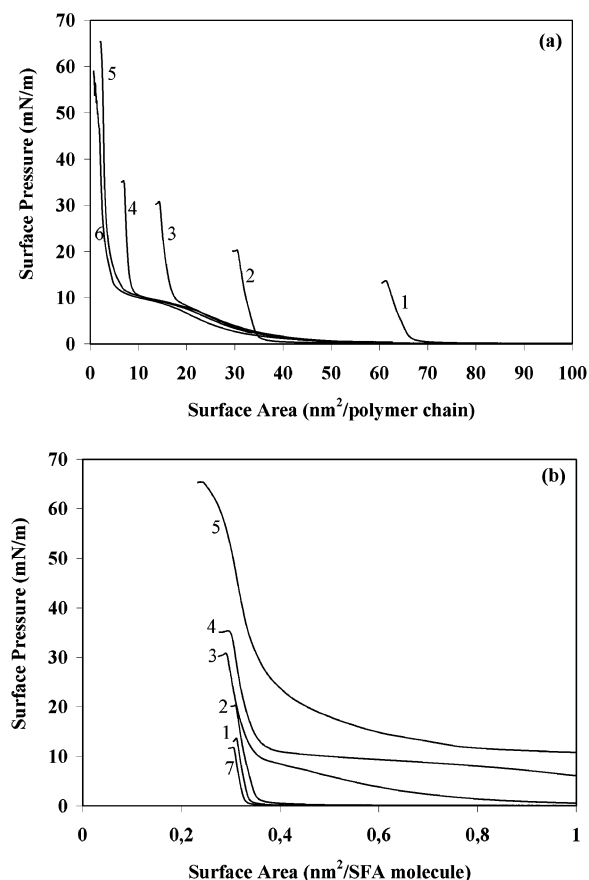

Figure 1. Surface pressure vs area curves for Langmuir films of the pure PS−PEO, SFA, and their binary mixtures at the air−water interface, plotted (a) against area per PS−PEO chain and (b) area per SFA molecule. Numbers in the curves correspond to different SFA:PS−PEO molar proportions: (1) 200:1; (2) 100:1; (3) 50:1; (4) 20:1; (5) 9:1; (6) 0:1; (7) 1:0.

films always reach roughly the same limiting area value as the pure SFA film (Figure 1b). As the PS−PEO grafting density increases, the maximum surface pressure attained by compression of the mixed films increases. These observations are consistent with the existence of a film of SFA on top the PS−PEO film at the air−water interface.

AFM images of size ranging from 200 nm to 2 μm were obtained for all the films whose surface pressure−area curves are depicted in Figure 1, transferred by the LB technique onto glass substrates. For the pure PS−PEO film transferred at surface coverage corresponding to the semiplateau in the surface pressure−area curve, a two-phase stripe structure is shown clearly by the phase image, even if it is not so apparent in the topography (Figure 2a). For the PS−PEO film transferred in the brush configuration, no phase separation was evidenced on the scales investigated here (Figure 2b). Transferred films of the pure SFA show aggregates of ∼40 nm diameter (Figure 2c). The films are disturbed by the tip after a single scan. Clustering on similar length scales was observed in films of the semifluorinated acid $F(CF_2)_8$-$(CH_2)_{16}COOH$, transferred onto glass slides by a modified LB procedure ("horizontal scooping up method").[30]

The mixed films exhibit surface structures that can be described as honeycombs with a hump at the center (Figures
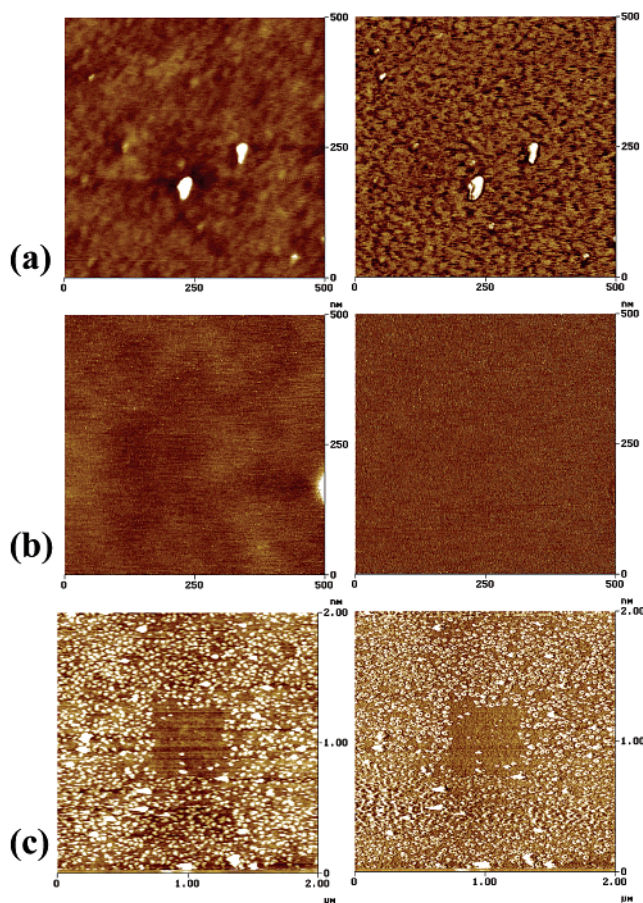
Figure 2. AFM tapping mode 500 × 500 nm images of pure PS–PEO LB films transferred at (a) 9 mN/m and (b) 25 mN/m, and (c) 2 × 2 μm images of pure SFA film transferred at 8 mN/m, showing a squared hole produced by a first 500 nm scan. Images on the left-hand side show the topography (z-range 5 nm), and images on the right-hand side show the phase.

3 and 4). The same qualitative pattern is observed independently of the polymer grafting density, but increased order is observed in the images as the brush regime is approached. The structures have a periodicity of ~40 nm, equal to the external diameter of the honeycombs. The thickness of the honeycomb walls, 6–7 nm, is too close to the lateral resolution of the measurement, 5 nm. The diameter of the inner humps is ~30 nm, except for the film of composition corresponding to PS–PEO in the brush regime, where it becomes ~20 nm. The maximum height difference found is ~1.7 nm, smaller than the contour length of the SFA molecule, 3.65 nm.

Whether the structures observed exist in the Langmuir films or are induced by the transfer process is still to be determined. After transfer to the solid substrate, the area available to the film molecules is no longer constrained as it was at the air–water interface. Therefore, the structure of the transferred films may differ from the films at the water surface. This is especially true for the diblock copolymer layer, as the compression restricted the chains conformational freedom resulting in a loss of entropy. Furthermore, while PEO is grafted to the air–water interface via the PS blocks in the Langmuir film, upon LB deposition the PEO chains are adsorbed on the glass surface. Also, it is important to
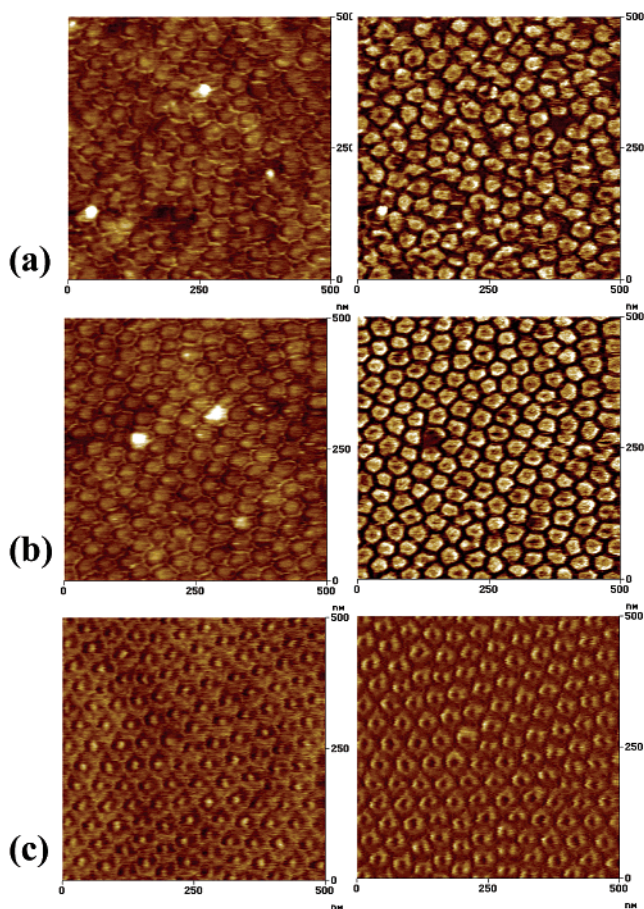
Figure 3. AFM tapping mode 500 × 500 nm images of mixed LB films for different SFA:PS–PEO molar proportions, corresponding to different grafting densities of PS–PEO: (a) 200:1, transfer pressure 9 mN/m; (b) 50:1, transfer pressure 25 mN/m; (c) 9:1, transfer pressure 40 mN/m. Images on the left-hand side show the topography (z-range 5 nm), and images on the right-hand side show the phase.
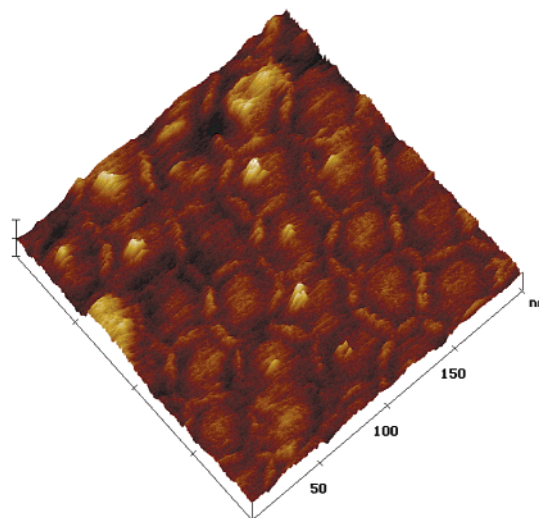

Figure 4. 3D topographical higher resolution (200 × 200 nm) tapping mode AFM image of a mixed film of SFA:PS–PEO molar proportion 50:1, transfer pressure 25 mN/m.

stress that in either of the two cases the grafting/adsorbing blocks can be considered immobile a priori.[31] The surface

coverage upon transfer may rather be expected to adjust itself to minimize the total free energy. Such adjustment may lead to the formation of domains.[31−33] In any case, one can predict a two-phase structure in the Langmuir film before the brush is formed and an homogeneous film once the chains attain the brush configuration, which are indeed observed in the LB films (Figures 2a and 2b). Analogously to diblock copolymers adsorbed on a flat surface,[32,33] the diblock SFA molecules can be anticipated to phase separate at the water surface and at the glass surface, also in agreement with the aggregates observed (Figure 2c). Because none of the blocks are polar, the chains should be loosely held to the surface, which is consistent with the LB film being easily disturbed, even in tapping mode AFM. As mentioned previously, competing interactions between the two self-assembling molecules under study may lead to both vertical and lateral segregation in the mixed films. Surface pressure−area curves indicate that SFA is segregated to the top of the PS−PEO layer at the air−water interface. From AFM results, the fact that the same pattern is obtained irrespective of polymer grafting density, while ordering increases with increasing polymer grafting density (Figure 3) also supports this conclusion. The same fact seems to contradict the expected lateral segregation between SFA and PS at the PEO surface; it rather suggests that the SFA domains cover the PS−PEO layer for all grafting densities.

In summary, this work reports on a novel approach to prepare surface nanoscale periodic structures, playing with the self-assembling capabilities of a diblock copolymer and a short diblock fluorinated molecule, and competing inter-actions between the two. Further work is in progress to elucidate the composition of the structures found (composition of the humps and honeycomb walls), determine whether they are formed already at the air−water interface, and establish a systematic route for obtaining such structures.

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