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Two-Dimensional Microphase Separation of a Block Copolymer in a Langmuir−Blodgett Film

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As have been illustrated by many authors over the past decades, the Langmuir−Blodgett (LB) technique provides very powerful tool for building well-ordered thin films.[1] Due to the amphiphilic nature of the molecules commonly used in LB films, the structures perpendicular to the film surface have been controlled in the very sophisticated manner, while the structures parallel to the film surface still remain ill-controlled. In bulk, block copolymers which are composed of block chains immiscible to each other are known to form regular microphase-separated structures such as spheres, cylinders, and lamellae, etc., with the size of polymer chain dimensions.[2] We have made, for the first time, a LB film of a block copolymer, both of which blocks are known to form the monolayer on the water surface and successfully obtained a two-dimensionally microphase-separated monolayer, with each domain composed of the monolayer of the each block.[3] This new way to control the lateral morphology of LB films should be useful to construct highly functionalized LB films. The size of the domains was 1 order of magnitude larger than that expected for highly segregated chain, indicating that the chains in the domains are significantly elongated and interpenetrate with other chains.

The sample used was a poly(methyl methacrylate)-*block*-poly(octadecyl methacrylate) diblock copolymer (PMMA-*b*-PODMA) which was polymerized by the high-speed living anionic polymerization technique with metalloporphyrin as an initiator and a bulky Lewis acid as a polymerization promoter.[4] The number average molecular weights was 5.84×10^4 for PMMA and 1.75×10^5 for PODMA, and the polydispersity index was 1.04. The polymer solutions with a polymer concentration of 4×10^{-6} g/mL in benzene were spread onto a water surface[5] at 25 °C in a commercial LB trough (FSD-50, USI, Japan). The layer formed on the water surface was compressed to a state with a relatively large specific area, 0.70 m^2/mg, where the surface pressure was not detectable, kept for 8 h, and deposited onto a freshly cleaved mica by pulling it out of the water while compressing the film at 1 mN/m with a transfer ratio of 1 ± 0.1. The samples deposited on a mica were observed in air by a commercial atomic force microscope (AFM, NanoScopeIII, Digital Instruments) with a silicon cantilever (resonance frequency 300−400 kHz; spring constant 70−90 N/m) using the tapping mode. AFM images are shown in the height mode without any image processing except flattening.

The surface pressure vs area curves of the block copolymer showed monotonic increase with decreasing area. The conventional linear extrapolation of the high-pressure limb of the curve to zero pressure yields a limiting area, $A_0^{\text{copolymer}}$ of 0.55 m^2/mg, in good agreement with the value (0.56 m^2/mg) which is estimated on the basis of the additive rule of the two domain areas using the A_0 values measured for each homopolymer (A_0^{PMMA} 0.955 m^2/mg; A_0^{PODMA} 0.43 m^2/mg) and the copolymer composition (Φ_{PODMA} 75 wt %) as $A_0^{\text{PODMA}}\Phi_{\text{PODMA}} + A_0^{\text{PMMA}}(1 - \Phi_{\text{PODMA}})$. Figure 1 shows two representative AFM images of the LB film. Clearly phase-separated structures with the regular spacings were observed, where the bright area with a larger height from the substrate corresponds to PODMA domains and the dark with a smaller height corresponds to PMMA. A close look shows that there are two different sizes of domains: the larger (the major) ones are branched long rods, short rods, and disks with the width of 60 to 90 nm and the smaller (the miner) ones indicated by the arrows are interconnected into "network-like" structures of PODMA having a width of 20−50 nm coexisting with PMMA domains. The Fourier transform of the images show two peaks which correspond to the spacings of 155 and 125 nm for the larger and the smaller domains, respectively.

The heights, t, observed for the both domains were 2.3−2.5 nm and 0.8−1.0 nm, respectively. These are in good agreement with the height estimated for each monolayer domain ($t^{\text{PODMA}} = 2.31$ nm; $t^{\text{PMMA}} = 0.86$ nm) using the limiting areas of the homopolymers, A_0^{PODMA} and A_0^{PMMA}, and the bulk densities ($\rho^{\text{PMMA}} = 1.22$ g/cm^3; $\rho^{\text{PODMA}} = 0.96$ g/cm^3 [6]) as $t = \rho^{-1}A_0^{-1}$. The area ratio of PODMA domains in Figure 1 is 0.66, which is also in good agreement with the value (0.59) estimated assuming the additive rule of each domain area using the limiting areas of the homopolymers and the composition of the block copolymer as $(A_0^{\text{PODMA}}\Phi_{\text{PODMA}})/(A_0^{\text{PODMA}}\Phi_{\text{PODMA}} + A_0^{\text{PMMA}}\Phi_{\text{PMMA}})$. From the reasonable thickness and the area ratio of the domain, we conclude that each domain is composed of the monolayer of the each block.

de Gennes showed that in two-dimensional melt, a single ideal chain could build up the two-dimensional bulk density without interpenetrating into other polymer chains. In another word, the single chains may exist as perfectly segregated chains (2D segregated chain).[7] This makes a strong contrast to the well-known situation in the three-dimensional melt where a single polymer chain should interpenetrate significantly into other polymers to build up the bulk density. If polymer chains exist as perfectly segregated chains in the two-dimensionally microphase-separated domains, the domain size of microphase

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[1] Gaines, G. L. *Insoluble Monolayers at Liquid−Gas Interfaces*; Interscience: New York, 1966. Ulman, A. *An Introduction to Ultrathin Organic Films from Langmuir−Blodgett to Self-Assembly*; Academic Press: New York, 1991.

[2] Aggarwal, S. L., Ed. *Block Polymers*; Plenum Press: New York, 1970. Molau, G. E., Ed. *Colloidal and Morphological Behavior of Block and Graft Copolymers*; Plenum Press: New York, 1970.

[3] In the series of reports, Lennox and Eisenberg et al. reported surface micelle formation of some diblock copolymers on the water surface. Each block copolymer studied contains polystyrene as an essential block and a hydrophilic component such as poly(vinylpyridinum salt), poly(butyl methacrylate), and poly(dimethylsiloxane) as another block. Polystyrene is known not to be spread on the water surface as a monolayer but form flakes or particles due to the lack of hydrophilic group. Thus, although regular spheres, rods, and planar disks of polystyrene were observed, these were not formed via truly two-dimensional microphase separation in a monolayer which we report here. See, for example, references to their previous work included in the following: Li, S.; Hanley, S.; Khan, I.; Varshney, S. K.; Eisenberg, A.; Lennox, R. B. *Langmuir* **1993**, *9*, 2243−2246.

[4] The PMMA-*b*-PODMA sample was polymerized in methylene chloride at 0 °C in nitrogen atmosphere using methylaluminum 5,10,15,20-tetraphenylporphine as an initiator and methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) as a Lewis acid to promote polymerization. MMA and ODMA monomers were added sequentially. These conditions are based on the original paper: Sugimoto, H.; Kuroki, M.; Watanabe, T.; Kawamura, C.; Aida, T.; Inoue, S. *Macromolecules* **1993**, *26*, 3403−3410.

[5] The solution spread on water is very dilute, similarly to that used previously for obtaining the polystyrene (PS) *monomolecular* particles.[9−11] Thus, the structures of the LB films observed here are expected to be formed via a self-assembly of the single molecules spread on the water surface.

[6] Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley Publications: New York, 1991.

[7] de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: London, 1979; pp 60−61.

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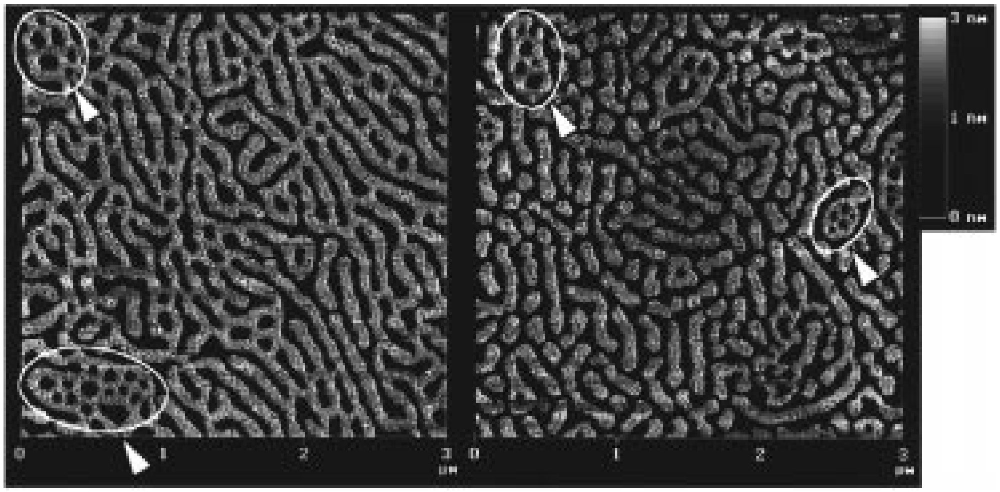

Figure 1. AFM images of a PMMA-*b*-PODMA monolayer deposited on mica. The bright area with a larger height corresponds to the monolayer domain composed of PODMA block, and the dark area with a lower height corresponds to that of PMMA block. There are two different sizes of domains. The arrows indicate the smaller (the miner) “network-like”structures. See the text for details.

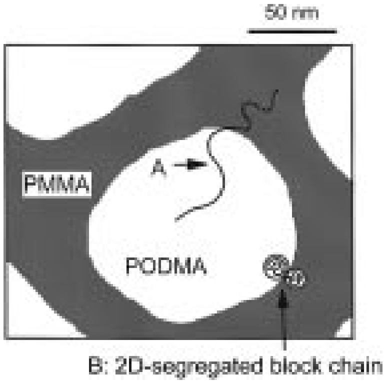

Figure 2. A schematic representation of a possible molecular conformation of the block copolymer (A) in the disk-like domain picked up from Figure 1. PODMA block chains and PMMA block chains are segregated in PODMA and PMMA domains, and the chemical junctions of the block copolymers are placed at the interface. The domain size is 1 order of magnitude larger than that expected for perfectly segregated chain (B), indicating that the block copolymer chains in the domains are elongated and significantly interpenetrate with other chains.

separation should be close to the size of perfectly segregated chain. The areas for the perfectly segregated block chains are 131 nm^2/block for the PODMA block and 92.6 nm^2/block for the PMMA block, judging from the molecular weights, A_0^{PODMA} and A_0^{PMMA}. In the schematic representation of Figure 2, we show a disk-like domain picked up from Figure 1 with a possible molecular arrangement (A). The size of the domain is 1 order of magnitude larger than that expected for 2D segregated chain (B), and the PODMA domain is estimated to contain 50 PODMA blocks. Thus, the chains in given domains should be highly elongated normal to the interface and interpenetrated significantly with neighboring chains,[8] contradictory to the de Gennes picture of the segregated chains with no interchain interpenetration in two-dimensional space. This unique chain elongation and interpenetration may be driven by repulsive interactions of PODMA and PMMA block chains across the microdomain interface and interactions of them with the water and air. The ODMA side groups in the PODMA block can crystallize due to its long hydrocarbon chain. A strong aggregation due to crystallization should affect the conformation of the PODMA backbone chains in 2D space and their packing in the PODMA domains. This fact may also account for the extraordinary large domain size observed here. This point should be confirmed by using perfectly amorphous block copolymers; this will be explored in future work.

In conclusion, from a block copolymer we have, for the first time, succeeded in obtaining two-dimensionally microphase-separated monolayer with each domain composed of the monolayer of each block. We expect that this will be a promising way to construct highly functional LB films with regular lateral morphology.

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(8) Although the domain sizes are much larger than that expected for 2D segregated chains, they are still reasonably smaller than the fully stretched chain lengths of the blocks. The fully stretched chain lengths are 132 nm for the PODMA block and 149 nm for the PMMA block.

(9) Kumaki, J. *Macromolecules* **1986**, *19*, 2258−2263.

(10) Kumaki, J. *Macromolecules* **1988**, *21*, 749−755.

(11) PS *mono-block* particles from which a PMMA monolayer is emanated were also obtained from poly(styrene)-*block*-poly(methyl methacrylate) in the similar conditions. See: Kumaki, J.; Nishikawa, Y.; Hashimoto, T. *J. Am. Chem. Soc.*, **1996**, *118*, 3321−3322.