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Characteristic phase-separated monolayer structure observed for blends of rodlike and flexible polymers

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Abstract

Monolayers of polymer blends composed of a rodlike polymer (tetra(methoxy)-tetra(octyloxy)-phthalocyaninato-polysiloxane (PcPS) or poly(γ-benzyl-L-glutamate)(PBLG)) and a flexible polymer (poly(isobutylvinyl ether)(PIBVE)) were studied by atomic force microscopy (AFM), transmission electron microscopy (TEM) and the surface pressure–area isotherm measurements. These blends were completely phase-separated into two pure monolayer phases at the air–water interface, a quasi-2D system. The AFM observation showed that anisotropic string-shaped domains of PcPS formed a networklike structure in the PIBVE matrix monolayer. In the PcPS domains, polymer chains were observed to be aligned parallel to each other along the domain contour, forming a 2D nematic phase. The domain-shape anisotropy decreased with decreasing chain length of PcPS. In addition, PBLG, another rodlike polymer also formed similar anisotropic domains in the PIBVE matrix, indicating the universality of the observed morphologies. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Rodlike polymer; Phase separation; Monolayer

1. Introduction

A monolayer of polymer blends spread at the air–water interface and its Langmuir–Blodgett (LB) film transferred on a solid substrate have attracted much attention, for potential applications as high-function ultrathin films. In addition to this practical interest, surface monolayers are of fundamental interest as a model of a 2D polymer system. Since the conformations and interactions of polymers will be dimension dependent, the phase behavior and phase-separated structure of polymer blends in a 2D system should be different from those in a 3D system. In this regard, a number of studies have been made on the miscibility of polymer blends in a monolayer state. In most of these studies, the surface pressure (π)-area (A) isotherm and ellipsometric measurements were carried out, and the polymer–polymer miscibility was discussed in comparison with the miscibility in the bulk state [1–12].

On the other hand, the process and structure of phase separation of polymer blends in a monolayer have been less sufficiently characterized. For this purpose, direct microscopic observations of the monolayer structures would be the best way, but the usually poor microscopic contrast between phases in the monolayer and the difficulty of phase separation due to the poor fluidity of polymer chains at the air–water interface have brought about limited success. Nevertheless, several important results have been reported: Kawaguchi et al. [13] observed LB films of poly(vinyl acetate) (PVAc)/poly(methyl acrylate) (PMA) blends by atomic force microscopy (AFM), noting that PMA components were squeezed out on top of the PVAc film (the "vertical" phase separation). Wu et al. [14,15] made transmission electron microscopic (TEM) observations of the monolayer of a tetra(methoxy)-tetra(octyloxy)-phthalocyaninato-polysiloxane (PcPS) and isopentyl cellulose (IPC) blend at the air–water interface, and found that each component was laterally phase-separated into two nematic phases. Both of these components are rigid polymers with flexible side chains, so-called "hairy-rod" polymers [16]. This type of polymer, including polypeptides, polysiloxanes, cellulose derivatives and polysilanes, has been extensively studied as advanced LB materials with high thermal and mechanical stabilities. These polymers, locally oriented in a monolayer on the water surface, were reported to be macroscopically aligned by the dipping process [17], giving a highly oriented LB film. The orientation behavior of hairy-rod polymers is considered to originate from the excluded volume effect of the rodlike polymer [18,19].

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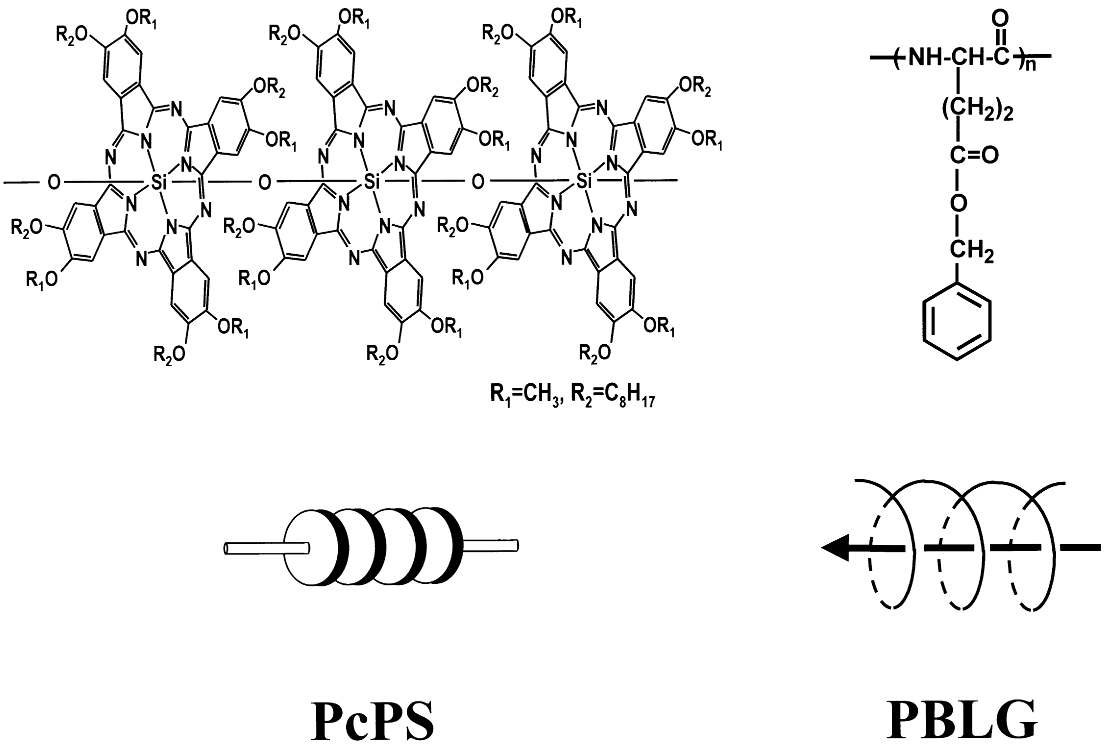

Fig. 1. Chemical structures and schematic illustrations of molecular shape of PcPS and PBLG.

This work focuses on the phase behavior and phase structure of the blend of a rodlike polymer and a flexible polymer on the water surface. In this work, we will study two different types of rodlike polymers, PcPS [20–22] and poly(γ-benzyl-L-glutamate) (PBLG) [23,24], blended with poly(isobutylvinyl ether) (PIBVE). PIBVE is a flexible polymer, which is known to have a high fluidity on the water surface, and forms a stable monolayer [25]. As schematically shown in Fig. 1, the rodlike characters of PcPS and PBLG come from the dense stacking of the bulky phthalocyanine moieties and the helical conformation, respectively. The former is decorated with "hairs" of flexible side chains, while the latter has benzyl groups. The phase-separated structures of these blends will be thoroughly characterized by direct observations by AFM and TEM, and discussed in terms of the molecular shape anisotropy of the rodlike polymers.

2. Experimental

Materials. The PcPS samples were generously donated by Professor Gerhard Wegner of Max Planck Institute for Polymer Research in Germany: two samples, $PcPS_H$ and $PcPS_L$, with an average degree of polymerization of approximately 80 and less than 30, respectively, were investigated. The PIBVE sample was synthesized by living cationic polymerization using a HI/ZnI_2 initiating system [26–29]. Its number-average molecular weight (M_n) and polydispersity index (M_w/M_n), estimated by a polystyrene-calibrated gel permeation chromatographic analysis, were 27800 and 1.37, respectively. The PBLG sample, which has a nominal weight-average molecular weight (M_w) of 26,000, was purchased from Sigma and used without further purification.

Preparation of Surface Monolayer. The sample polymer was spread from a solution of chloroform on the clean water surface in a Teflon-coated rectangular Langmuir trough ($200 \times 500 \times 3\ mm^3$). Chloroform (Spectrograde, Dojindo Laboratories) was used without further purification. Blend monolayers were prepared by spreading a mixture solution of PcPS (or PBLG) and PIBVE. The total polymer concentration in the solutions was adjusted to about 0.01 wt%, unless otherwise noted. The subphase water was purified by means of a Mitamura Riken model PLS-DFR automatic still, which consisted of a reverse-osmosis module, an ion-exchange column, and a double distiller. By circulating thermostated water, the temperature of the subphase for the PcPS/PIBVE blend monolayers was kept at 20°C unless otherwise noted. For the PBLG/PIBVE blend monolayers, the temperature of the subphase was kept at 5°C to obtain stable and transferable monolayers since PBLG/PIBVE blend monolayers were not transferred on mica surface with a good transfer ratio at 20°C. In each experiment, 0.5 ml of sample solutions was spread on the water surface. After spreading the solution, 30 min was allowed for the solvent to evaporate. The π–A isotherms were recorded at a constant compression speed of $14\ cm^2/min$; π was measured by means of a Whilhelmy-type film balance.

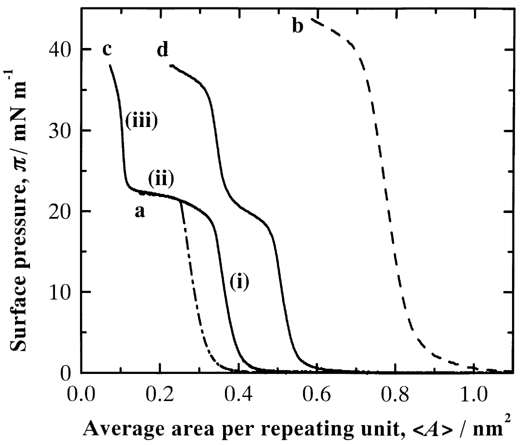

Fig. 2. Surface pressure–area isotherms of the single component (broken curves): (a) PIBVE, and (b) $PcPS_H$; their blends (solid curves), $f_{PcPS} = $ (c) 0.14, and (d) 0.46.

For the deposition, surface monolayers were compressed up to a desired surface pressure at a constant compression speed of 14 cm^2/min, unless otherwise noted.

Atomic Force Microscopy (AFM). At a constant surface pressure, surface monolayers were deposited as a single layer on a freshly cleaved mica by vertically lifting up the mica, which had been immersed in the water before spreading the sample solution. The deposition (lifting up) speed was 6 mm/min. The transfer ratio was close to unity, independent of the blend composition, thus confirming a successful deposition. AFM observations were performed at room temperature with a contact-mode atomic force microscope (Seiko Instruments Inc., Japan, SFA300 controlled by SPI3600) using a V-shaped Si_3N_4 cantilever (Park Scientific Instruments, Sunnyvale, CA, spring constant 0.064 N/m). Topographic images were taken in the air under the constant-force mode with an applied force of 0.2 nN at a scanning speed of 25 μm/s unless otherwise noted. At least four samples were prepared for each blend composition, and several images were taken at different locations on each sample.

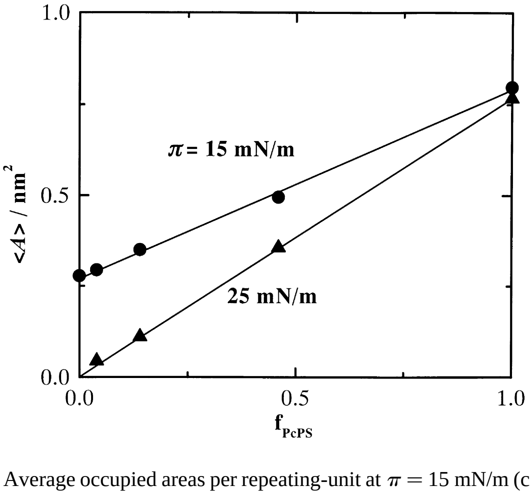

Fig. 3. Average occupied areas per repeating-unit at $\pi = 15$ mN/m (circles) and 25 mN/m (triangles) in $PcPS_H$/PIBVE blend monolayers as a function of f_{PcPS}.

Transmission Electron Microscopy (TEM). The fine structures of blend monolayers were observed in the bright-field imaging mode at a direct magnification of 80,000× using a JEOL JEM 1010D. The dark-field imaging mode was also used to observe the phase-separated structures of blend monolayers at a direct magnification of 5000×. The sample specimens for the TEM observation were prepared by transferring the surface monolayer onto a specimen copper grid (3 mm in diameter, 400 mesh) covered with a carbon film (7 nm in thickness) according to the procedure of Uyeda et al. [30]. In brief, the carbon-film side of the grid placed strictly parallel to the water surface was allowed to just touch the monolayer surface from the air side, it was then withdrawn by using an elevation apparatus with the hydrophobic side of the monolayer adhered on the carbon film. The area of the carbon grid was so small that a drop of water was lifted up together, which was removed off by use of filter paper. This procedure allowed the surface monolayer to be transferred as a single layer.

3. Results and discussion

Fig. 2 shows the π–A isotherms of $PcPS_H$, PIBVE and their blends, where $\langle A\rangle$ is the average occupied area per repeating unit. As previously reported, $PcPS_H$ and PIBVE formed a stable monolayer by itself, in which polymer chains essentially lie flat on the water surface. The collapse pressures for the $PcPS_H$ and PIBVE monolayers were approximately 33 and 22 mN/m, respectively. Unlike these single-component monolayers, the $PcPS_H$/PIBVE blend monolayers showed the isotherms in which π increased in two steps with decreasing A, giving an intermediate plateau region. The plateau pressure was nearly equal to the collapse pressure of the PIBVE monolayer, independent of the blend composition. In Fig. 3, $\langle A\rangle$ at 15 mN/m (below the plateau) and 25 mN/m (above the plateau) are plotted as a function of the mole fraction of PcPS repeating unit (f_{PcPS}). Below the plateau, $\langle A\rangle$ of the blend monolayer was found to satisfy the following relationship

$$\langle A\rangle = A_{PcPS} f_{PcPS} + A_{PIBVE}(1 - f_{PcPS}) \tag{1}$$

where A_{PcPS} and A_{PIBVE} are the occupied area per repeating unit in the single-component monolayers of $PcPS_H$ and PIBVE, respectively. This relationship was proposed for an immiscible as well as an ideally miscible blend by Goodrich [31] and Gaines [3]. Above the plateau, $\langle A\rangle$ was proportional to f_{PcPS}, suggesting that the PIBVE component there has little contribution to the surface pressure. These results suggest the following structural changes to take place on the water surface; taking curve c in Fig. 2 as an example, below

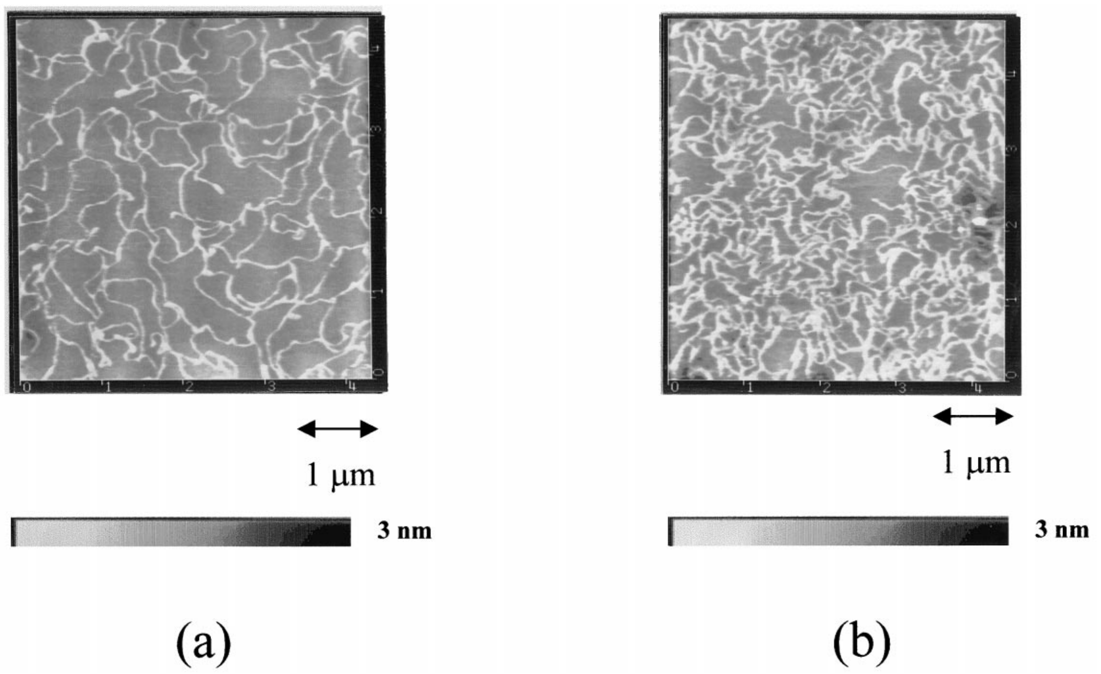

Fig. 4. Topographic AFM images of the $PcPS_H$/PIBVE blend monolayers deposited at $\pi = 15$ mN/m, f_{PcPS} = (a) 0.03 and (b) 0.14.

the plateau (region i), the two components are phase-separated into microdomains, which will be discussed below, and each domain is composed of a monolayer of one component or the other. At the plateau region (region ii), the PIBVE monolayer collapses in its domain. With further compression (region iii), the water surface is covered only by the PcPS monolayer with the PIBVE component having completely been squeezed up on top of the PcPS layer. This is consistent with the fact that π steeply increased up to the value nearly equal to the collapse pressure of the PcPS (single-component) monolayer on the water surface.

Now, we focus on the phase-separated structure in the blend monolayer at $\pi = 15$ mN/m (below the plateau), where each component forms a stable monolayer. Fig. 4 shows AFM images of the monolayer deposited on the mica at this surface pressure. These images showed that the blends form quite a unique phase-separated structure, "string"-shaped domains connected with each other like a network. This characteristic structure was also observed by the dark-field imaging mode of TEM for the monolayer transferred on a different substrate (carbon film) by a different deposition technique. This means that the observed phase-separated structures were not formed at the transfer process, but on the water surface. The average and standard deviation of the height difference between the "string" and the matrix were estimated to be 1.1 ± 0.1 nm independent of the blend composition ($f_{PcPS} = 0.03$ and 0.14) by analyzing the cross-sectional images at totally 140 locations of three different samples for each blend composition. These values are comparable to the difference in the thickness d of the PcPS (2.0–2.2 nm [21,22]) and PIBVE (about 0.7 nm [25]) monolayers. In addition to this, the area fraction of the string domain increased with increasing f_{PcPS}, in approximate agreement to the theoretical value calculated by assuming a complete separation into the two pure monolayer phases. These observations suggest that almost all PcPS chains were squeezed out from the PIBVE domain (and vice versa), forming essentially pure string-shaped domains.

The string-shaped domain of PcPS was also characterized by a narrow distribution of the domain width. An increase in f_{PcPS} caused significant changes in the total area of PcPS domains, but only a minor change in the domain width was observed: Fig. 5 gives the distribution histograms of the domain width, which was measured at totally 140 locations of three different samples for each blend composition. The average and standard deviation of the PcPS domain width are 87 ± 12 and 114 ± 15 nm in the blend monolayer of $f_{PcPS} = 0.03$ and 0.14, respectively. Since PcPS molecules are aligned parallel to each other with interchain spacing of about 2.2 nm along the domain contour (see below), these values of the average domain width correspond to 40–50 of the rodlike molecules, tightly aligned parallel with each other. This unique structure was formed with a high reproducibility, independent of the deposition position in the trough. Such a reproducibility of monolayer morphology is usually difficult to achieve in polymer blend monolayers because of the generally poor fluidity of polymer chains on the water surface. Presumably, our systems owe their essentially uniform and reproducible domain morphologies to the exceptionally high fluidity of the PIBVE phase. PIBVE is thus an excellent matrix for a polymer blend system at the air–water interface. The string-shaped domain structure was not significantly changed in the studied range of

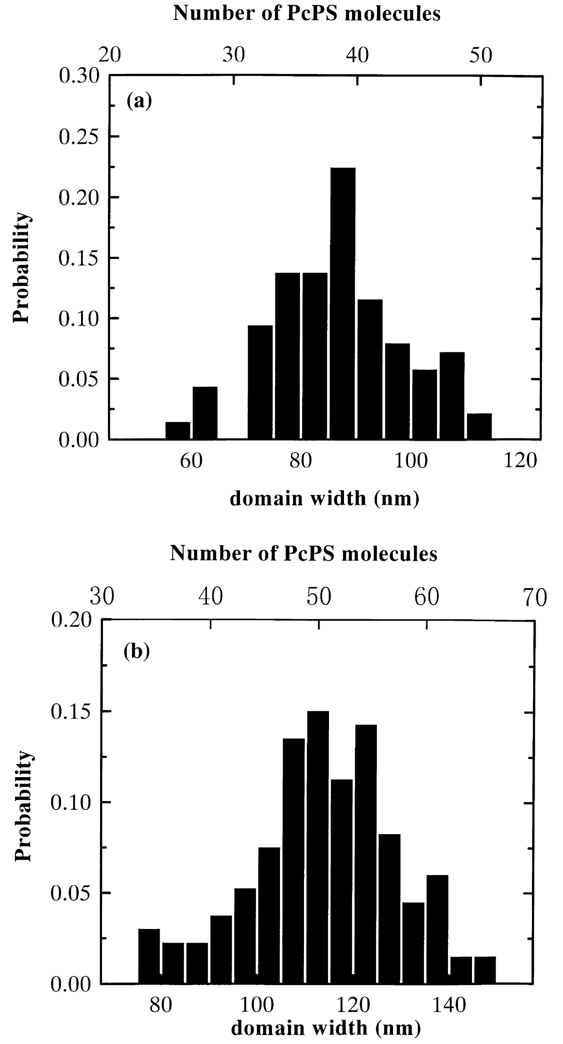

Fig. 5. Probability distribution histograms in width of the string-shaped domain of the $PcPS_H$/PIBVE blend monolayer, $f_{PcPS} =$ (a) 0.03 and (b) 0.14.

concentration of sample solution (0.003–0.01 wt%) and subphase temperature (5–30°C).

Bright-field TEM observation was performed to investigate the aggregation state of the PcPS chains in the domain. Fig. 6 shows a high-resolution TEM image together with its schematic illustration for the $PcPS_H$/PIBVE blend monolayer ($f_{PcPS} = 0.14$ and $\pi = 15$ mN/m). The figure directly reveals that PcPS chains are aligned parallel to each other along the domain contour, forming the so-called "2D nematic phase". A 2D nematic order was firstly observed for the PcPS/IPC blend system [14,15].

In order to confirm that the anisotropic shape of the PcPS domain arises from the anisotropic molecular shape of PcPS, we investigated the effect of PcPS chain length on the domain structure. The sample $PcPS_L$, which has a lower molecular weight than $PcPS_H$, blended with PIBVE showed almost the same π–A isotherm and the same linear relationship between $\langle A \rangle$ and f_{PcPS} at $\pi = 15$ mN/m (below the plateau) as the $PcPS_H$/PIBVE blend. Fig. 7 shows the AFM image of the blend monolayer ($f_{PcPS} = 0.03$) deposited at $\pi = 15$ mN/m. The area fraction of the $PcPS_L$ domain also suggests a complete phase separation into each domain. Clearly, $PcPS_L$ is observed to form domains whose shapes are much less anisotropic than those formed by $PcPS_H$ (comparison with Fig. 4(a)). This confirms that the shape anisotropy of the PcPS *molecules* is reflected on the shape anisotropy of the PcPS *domains*.

Further, we conducted an additional experiment in which another rodlike polymer, PBLG, was blended with PIBVE in order to confirm that the observed anisotropic shape of PcPS domain arises from the shape anisotropy of PcPS molecule. Fig. 8 shows the π–A isotherms of PBLG, PIBVE and their blend with $f_{PBLG} = 0.13$, where f_{PBLG} denotes the mole fraction of PBLG repeating unit. As previously reported, PBLG formed a stable monolayer by itself, in which polymer chains essentially lie flat on the water surface. The π–A isotherm of the PBLG/PIBVE blend showed a shoulder at $\pi = 13$ mN/m, which corresponded to the collapse of the PBLG monolayer. With further compression π increased, reaching a plateau region

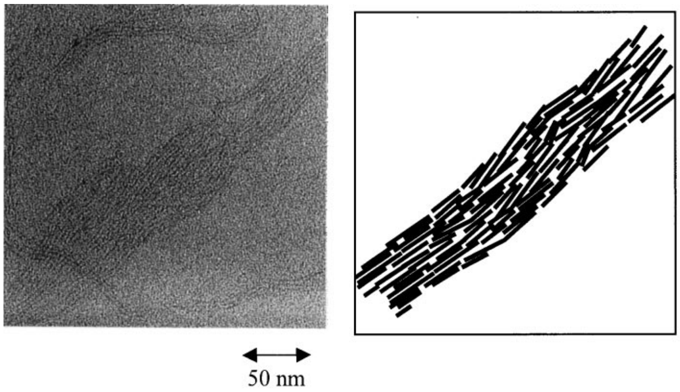

Fig. 6. Bright-field TEM image of the $PcPS_H$/PIBVE blend monolayer ($f_{PcPS} = 0.14$) deposited at $\pi = 15$ mN/m and its schematic illustration of molecular arrangement.

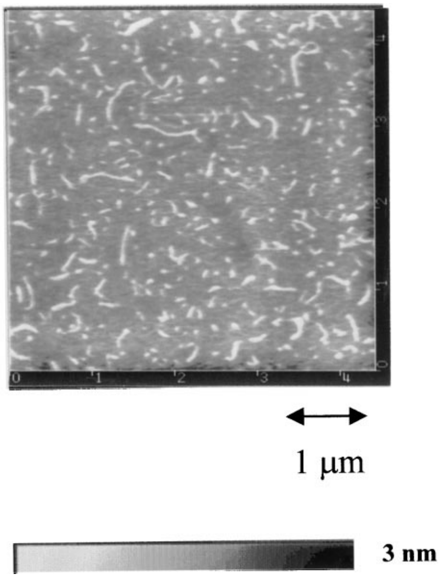

Fig. 7. Topographic AFM image of the $PcPS_L$/PIBVE blend monolayer ($f_{PcPS} = 0.04$) deposited at $\pi = 15$ mN/m.

which corresponded to the collapse of the PIBVE monolayer. Fig. 9 shows an AFM image of the blend monolayer deposited at $\pi = 10$ mN/m, which is a pressure below the shoulder. Again, string-shaped phase-separated morphologies are clearly observed. This suggests universality of the string-shaped anisotropic phases of rodlike polymers dispersed in the matrix of flexible polymers.

4. Conclusions

The π–A isotherm, AFM measurements and dark-field TEM observations revealed that the blends of rodlike and flexible polymers (PcPS/PIBVE and PBLG/PIBVE blends) formed a stable monolayer at the air–water interface, where the rodlike polymer was segregated into a network of string-shaped domains in the matrix of the PIBVE monolayer. The bright-field TEM observation of the PcPS/PIBVE blend monolayer revealed that PcPS chains were aligned parallel to each other along the domain contour, forming a 2D nematic phase. The shape anisotropy of the domain formed by PcPS seemed to vanish for very short PcPS chains. Thus, the anisotropic string-shaped domains are characteristic of (sufficiently long) rodlike polymers blended with a monolayer forming flexible polymer like PIBVE.

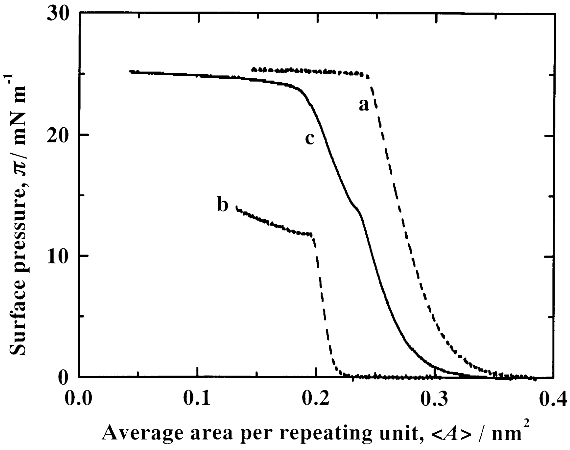

Fig. 8. Surface pressure–area isotherms of the single component (broken curves), (a) PIBVE, (b) PBLG, and (c) their blend ($f_{PBLG} = 0.13$) (solid curve).

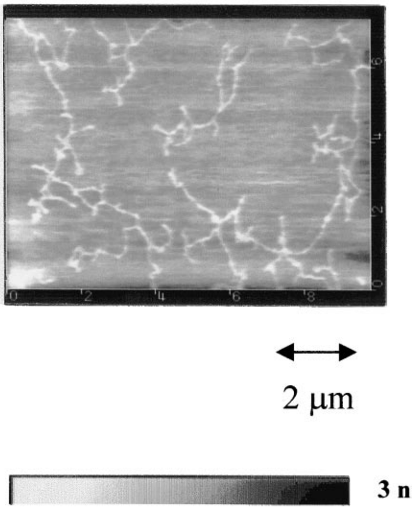

Fig. 9. Topographic AFM image of the PBLG/PIBVE blend monolayer ($f_{PBLG} = 0.13$) deposited at $\pi = 10$ mN/m obtained at a scanning speed of 50 μm/s.

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