

Ideal Spread Monolayer of Fully Hydrophobic Polysilane, Poly(methyloctylsilane), with the Assist of Liquid Crystal Monolayer

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Fully hydrophobic polymer, poly(methyloctylsilane) [PMOS], formed an ideal spread monolayer on water surface by cospreading method with liquid crystal molecule, 4'-pentyl-4-cyanobiphenyl [5CB]. The PMOS/5CB hybrid monolayer were characterized by surface pressure – area (π -A) isotherm measurements, Brewster angle microscopy (BAM), and atomic force microscopy (AFM). Pure PMOS do not exhibit a pressure increase in π -A isotherms and can not form a stable monolayer on a water surface. The mixed film of two components, PMOS and 5CB, gave a characteristic pressure lift-off attributed to the hybrid monolayer above the 5CB plateau. The lift-off area of the PMOS/5CB hybrids was exactly in proportion to the mixing ratio, $R = [\text{Si unit of PMOS}]/[\text{5CB}]$. BAM and AFM observation revealed the highly homogeneous feature with monomolecularly smooth surface at the lift-off area for the PMOS/5CB hybrid.

Key words: polymer spread monolayer, conjugated polymer, Langmuir-Blodgett film, polysilane

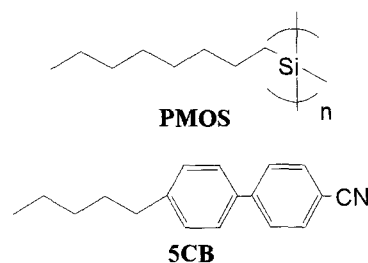
1. INTRODUCTION

The properties and morphologies of ultrathin film are crucially affected by the chain conformation and organization near the substrate [1-6]. The study on conformational states and orientation of polymer main chains adjacent to solid surfaces is an interdisciplinary field of research with important practical application. These phenomena, in particular, are encountered with devices for photofunctional polymers and semiconducting polymers, which perform generally in ultrathin films on a substrate or an electrode [3, 6-9]. Their conjugated systems are strongly dependent on the conformation and orientation [9, 10]. Thus evaluating and fabricating the electronic structure of conjugated polymers at interfacial regions in films are significant in improving and advancing device performance.

Spread monolayers of macromolecules extended at air-water interface with every monomer unit, play an important role in our understanding of interactions of polymer/water surface, polymer/polymer and polymer/substrate interface [11-15]. Details of conformation and orientation of polymer ultrathin film at interface have been characterized by the Langmuir film balance method and Langmuir-Blodgett (LB) technique with ancillary spectroscopy. For spreading on a water surface, polymers generally require a hydrophilic or polar moiety in the side or main chain [4, 15]. Evidently, not all engineering plastics and functional polymers can form Langmuir monolayers since many polymers usually have a hydrophobic substituents such as long alkyl chains and a phenyl group. Fully nonpolar hydrocarbon-based polymers, for example polyethylene [16] and polystyrene [2, 17], can not be spread on water. Recent works have revealed that the deposition of hydrophobic polymers on a water surface provides ultrafine particles [17] or ultrathin films with a thickness of a few tens nanometers

[2]. Some studies attained LB deposition of hydrophobic polymers such as poly(alkylthiophene)s [18] and poly(dialkylsilane) [19, 20] via co-spreading with fatty acids, nevertheless the polymer chains were folded and three-dimensional aggregated state in the LB films.

Our recent work demonstrated that the fully hydrophobic polymer, poly(dihexylsilane) [PDHS], can spread on a water surface with the assist of a liquid crystal monolayer having dynamic fluidity and spreading nature [21, 22]. Moreover we attain the precise evaluation of conformational state for polymer chains near a solid surface by the stepwise LB depositions of the monolayer [23]. The notable finding is that the different conformation from the bulk state is omnipresent in adjacent to a solid surface for any film [23]. We report here that the spread monolayer formation of another type of fully hydrophobic polysilane, poly(methyloctylsilane) [PMOS], by cospreading method with 4'-pentyl-4-cyanobiphenyl [5CB] (Scheme). Polysilanes have a unique conjugated system with both high backbone flexibility and UV absorption properties which strongly depends on the main chain conformation [24, 25]. Therefore, studies on monolayers and ultrathin films of polysilanes provide



Scheme. Chemical structures of the materials used in this work.

valuable information in scientific and technological research.

2. EXPERIMENTAL

PMOS was synthesized by the Wurtz condensation of an methyloctyldichlorosilane with sodium metal in dry toluene [24]. 5CB was purchased from Dainippon Ink and Chemicals, Inc. Pure water was of Millipore grade (18 M Ω cm).

Spreading behavior of mixed monolayers were characterized using a Lauda FW-1 film balance at 15 °C. Two mother solutions, PMOS dissolved in hexane and 5CB dissolved in chloroform, were prepared, and then mixed at target ratios R ($= [\text{Si unit}] / [\text{5CB}]$). The mixed solutions were spread onto a pure water surface (cospreparing method). The morphologies of the Langmuir monolayer were observed by Brewster angle microscopy (BAM) using an NLE EMM633 (Filgen, Inc.). Atomic force microscopic (AFM) observation was carried out on a SPA300/SPI3700 system (Seiko Instruments) in the noncontact mode. Transferred monolayers for AFM studies were prepared onto a freshly cleaved mica substrate by the conventional vertical dipping method.

3. RESULTS AND DISCUSSION

3.1 Surface Pressure-Area Isotherms

Figure 1 indicates the surface pressure (π)-area (A) isotherms of pure 5CB monolayer, pure PMOS, and PMOS/5CB mixed films at various R on a water surface at 15 °C. Pure 5CB monolayer exhibited the plateau at 5 mN m $^{-1}$ with the lift-off area at 0.45 nm 2 . Pure PMOS did not show a considerable expansion, judging from the too small limiting area for a PMOS monomer unit. PMOS did not form a stable monolayer on the water surface due to the lack of polarity in the polymer structure. On the contrary, all of the PMOS/5CB mixed films gave the surface pressure rising above 10 mN m $^{-1}$ which appeared on that of the 5CB plateau. The high pressure in π - A curves for the PMOS/5CB mixed film indicate that the co-spreading with 5CB attained the stable hybrid films of PMOS at the constant pressure on water without 2-dimensional phase separation. In the case of $R = 1.0$, the PMOS/5CB hybrid film showed a two step pressure lift-offs, which provided the essential views of the hybrid monolayer on water. The first gradual lift-off from ca. 0.49 nm 2 with the plateau at 5 mN m $^{-1}$ is probably due to 5CB monolayer, and the second uprise at ca. 0.2 nm 2 above the pressure region of 5 mN m $^{-1}$ could be ascribed to the PMOS/5CB hybrid monolayer. The limiting area of ca. 0.2 nm 2 was fairly consistent with that of the monolayer composed of amphiphilic polysilanes having ether-containing side chain [26].

The systematic π - A studies with increasing the mixing ratios R present the appending evidence for the monolayer formation of this hydrophobic polymer. At $1.0 \leq R \leq 2.0$, the same behavior was essentially observed as for $R = 1.0$. In the case of $R = 4.0$, the feature of the 5CB monolayer was not observed any more and the hybrid film apparently exhibited a single pressure increase reaching to 10 mN m $^{-1}$ followed by a plateau. At $R = 3.0$, we infer the intermediate state between the former and the latter case. We estimated

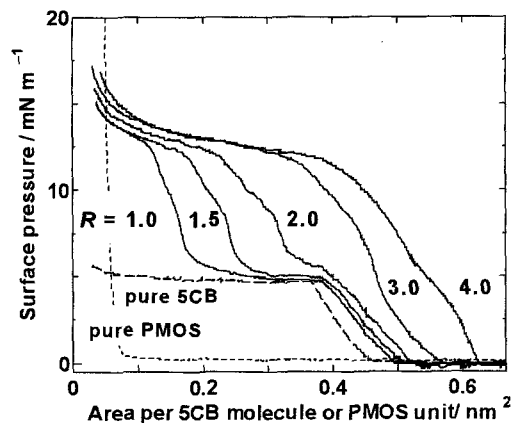


Figure 1. Surface – pressure isotherms of pure 5CB monolayer, pure PMOS and PMOS/5CB hybrid monolayers at various mixing ratios R on a pure water surface at 15 °C.

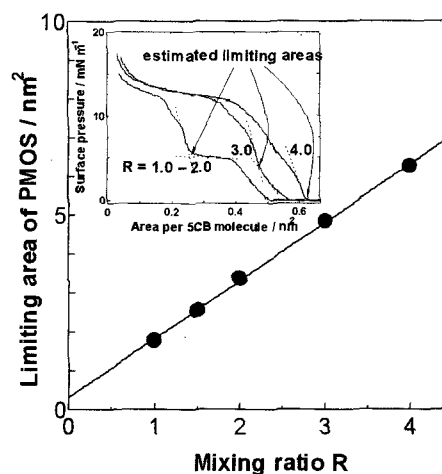


Figure 2. Estimated limiting area of PMOS versus R . The inset in figure depicts the schematic definitions from the experimental π - A isotherms

the limiting area of PMOS in the hybrid films from the π - A isotherms as schematically depicted in the inset of Figure 2. Figure 2 shows the limiting areas of the PMOS/5CB hybrid films as a function of the mixing ratio R . The estimated limiting area of PMOS/5CB hybrids was obviously in exact proportion to R and the linear regression line almost extrapolated close to zero. These facts imply that PMOS could be spread monomolecularly on water with the assist of 5CB monolayer and shows the coincident behavior of the PDHS/5CB hybrid systems. The hydrophobic polymer / long fatty acids cospread systems did not exhibit the linear extension behavior of the limiting areas with the increase of mixing ratio for π - A studies [18-20]. In these cases, the hydrophobic polymers are not miscible with fatty acids [18-20] and 3-dimensional aggregations of hydrophobic polymers are formed on top of fatty acid monolayer [19-20].

3.2 Brewster Angle Microscope Observations

Figure 3 depicts BAM images of the hybrid monolayers of $R = 3.0$ taken at areas for 0.8 (a), 0.5 (b) and 0.45 (c) nm 2 . The pure 5CB monolayer was hardly observed at the area larger than the plateau region of ca.

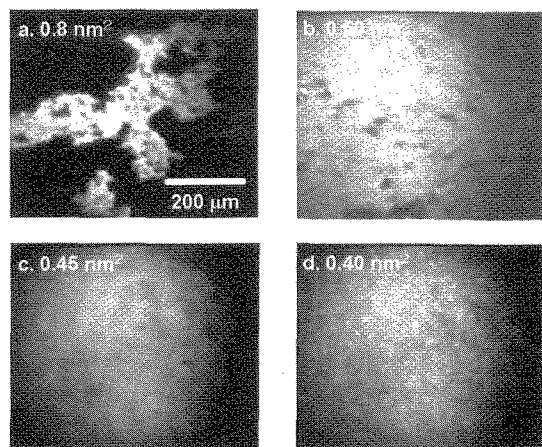


Figure 3. BAM images of the PMOS/5CB hybrid monolayer at $R = 3.0$ for 0.8 (a), 0.5 (b), 0.45 (c) and 0.4 nm² (d) on the water surface at 15 °C.

0.35 nm² owing to the weak reflectance for the highly expanded nature on water surface [21, 22]. In the case of pure PMOS, the floating blocks of the aggregated PMOS with extremely high reflectivity were observed (data not shown). This indicates that pure PMOS can not be spread monomolecularly on water. On the contrary, the PMOS/5CB exhibited strongly reflection and the solid like domains on a water surface at the large area of 0.8 nm² (Figure 3a). Upon compression, the bright regions were gathered without any collapse to disappear the darker area (Figure 3b). Around ca. 0.45 nm² for the limiting area of the PMOS/5CB hybrid monolayer, it was found that the floating film became highly homogeneous feature suggesting a monomolecularly smooth surface (Figure 3c). The hybrid film at 0.4 nm² and 9-10 mN m⁻¹ finally showed heterogeneous morphology with many dots of collapsed points (Figure 3d). We discriminated that these observable domains and the homogeneous monolayer on water were attributed to the monomolecularly spread PMOS with adequate density and reflectivity. Essentially the same behavior was observed for the hybrid films at other mixing ratios. These BAM observations directly justified that PMOS in the hybrid

formed the spread monolayer with 5CB molecule on the water surface.

This solid-like feature of the PMOS/5CB monolayer exhibits a marked difference in our previous results of the PDHS/5CB mixed monolayer, which showed fluid-like morphology observed at all area conditions without the boundaries [21, 22]. It is noteworthy that PDHS with the symmetric substituents is in a crystalline state at room temperature, whereas PMOS with asymmetric structure is in a rubbery elastic state in bulk [24, 25]. In the monolayered state, it appeared that both polysilanes indicate the opposing rheological feature from the bulk state. It is interesting that these antithetic behaviors are just ascribable to the difference in the rather minor structural change in the alkyl substituents. The miscibility of both polysilanes with LC molecule is almost the same since the monolayer formation of the two hydrophobic polymers was attained similarly. Therefore, the discrepancies observed in the bulk and the monolayer states are essential and should be considered in terms of thermodynamic issues.

The above regard was confirmed by the fact that the both polysilanes in monolayer on water exhibit the antithetic conformation to that in their bulk state characterized by UV absorption spectroscopy [23]. In bulk, elastic PMOS and crystalline PDHS adopt the random-gauche and the trans-zigzag conformation respectively [24, 25]. In the PMOS/5CB monolayer, PMOS gave the 'rigid' transoid conformer which appeared at low temperatures in the thermochromic study [23-25]. On the other hand, PDHS in the hybrid monolayer adopted the 'flexible' helical-gauche conformation as the liquid crystalline state in bulk above ca. 40 °C [22-25]. These manners were in accord with the results of BAM observations. The transoid conformation in the PMOS/5CB monolayer is probably induced by the long octyl side chains facing alternately on a two-dimensional plane. The helical-gauche conformation of the monolayered PDHS is ascribed to the state of the main chain free from the three-dimensional crystalline state.

3.3 Atomic Force Microscopy

AFM studies of the hybrid monolayers revealed the

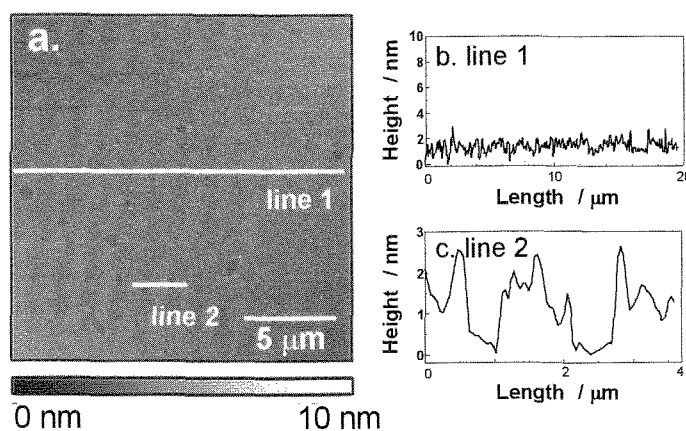


Figure 4. The topographical AFM image of the PMOS/5CB hybrid monolayers transferred onto a cleaved mica substrate at a surface pressure of 6 mN m⁻¹ at $R = 3.0$. The height reference is shown in the bottom of the figure. The right figures indicate the height profiles of the AFM images which were taken along the white lines drawn in the left AFM figure.

conclusive evidence for the ideal spread monolayer formation of hydrophobic PMOS. Figure 4 demonstrates the AFM image of the PMOS/5CB monolayer for $R = 3.0$ transferred at 6 mN m^{-1} onto a mica substrate. Under these conditions, the PMOS/5CB hybrid monolayer fully covered the water surface as estimated from the π -A isotherm and BAM images. As expected, the surface morphologies of the PMOS/5CB monolayer gave almost a flat surface with some small dimples as defects. The higher area gave a highly uniform and molecularly smooth surface with a roughness of below ca. 2 nm (Figure 4b) and the depths of the dimples ranged from 0.5 to 1.5 nm (Figure 4c). The depth of these dimples agreed quite well with a molecular dimension of PMOS unit, strongly suggesting the spread monolayer formation similar to the PDHS/5CB system [22]. The results of AFM are in good agreement with the conclusions drawn from the π -A isotherms and BAM data.

Present work attained the monolayer formation for another type of fully hydrophobic polysilane, PMOS, by the cospreading method with 5CB which we previously developed for the first time [21, 22]. This indicates that the method proposed here should have wide applicability to various hydrophobic polymers. We also demonstrated that polymers at interface shows different conformation in bulk state and the interfacial conformation invariably exists in any films by the layer-by-layer deposition studies of these hybrid monolayers [23]. The polymer field effect transistors perform in ultrathin films with a thickness below 50 nm [27] and monomolecularly film [8]. The electroluminescence devices have many interfacial situations due to many layers of semiconducting polymers [9, 28-30]. Now, understandings of the polymer chain behavior at interfaces become prime importance for these polymer advanced devices. As proposed here, the fabrication of the spread monolayer of hydrophobic polymers which are the ultimate form of polymer thin film will offer new opportunity for studying on properties and assembly of functional polymers.

4. CONCLUSION

The spread monolayer of the hydrophobic polysilane, PMOS, was prepared by simple cospreading with liquid crystal molecule on a water surface. The resulting film exhibited the highly homogeneous feature by BAM observation. AFM observation revealed the ideal spread monolayer of PMOS with the monomolecularly smooth surface for the PMOS/5CB hybrid. We anticipate that the present method is applicable to other types of hydrophobic conjugated polymers.

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REFERENCES

[1] M. Stamm, *Adv. Polym. Sci.*, 100, 357 (1992).

[2] T. Kajiyama, Y. Oishi, *Trends. Polym. Sci.*, 3, 30 (1995).

[3] C. W. Frank, V. Rao, M. M. Despotopoulou, R. F. W. Rease, W. D. Hinsberg, R. D. Miller and J. F. Rabolt, *Science*, 273, 912 (1996).

[4] C. W. Frank, Ed. *Organic Thin Films Structure and Applications ACS Symp. Series 695*; American Chemical Society: Washington, DC (1998).

[5] R. L. Jones, S. K. Kumer, D. L. Ho, R. M. Briber and T. P. Russel, *Nature*, 400, 146 (1999).

[6] H. Mensinger, M. Stamm and C. J. Boeffel, *J. Chem. Phys.*, 96, 3183 (1992).

[7] M. Onoda, K. Tada and H. Nakayama, *J. Appl. Phys.*, 86, 2110 (1999).

[8] H. G. O. Sandberg, G. L. Frey, M. N. Shkunov, H. Sirringhaus, R. H. Friend, M. M. Nielsen and C. Kumpf, *Langmuir*, 18, 10176 (2002).

[9] G. Hadziioannou and P. F. van Hutten, *Semiconducting Polymers, Chemistry, Physics and Engineering*, Wiley-VCH (2000)

[10] K. Ichimura, *Chem. Rev.*, 100, 1847 (2000).

[11] G. L. Gaines Jr., *Insoluble Monolayers at Liquid-Gas Interfaces*, Wiley, New York (1966).

[12] G. L. Gaines Jr., *Langmuir*, 7, 834 (1992).

[13] K. Kawaguchi, S. Komatsu, M. Mitsuzumi and A. Takahashi, *J. Colloid Interface Sci.*, 102, 356 (1984).

[14] T. Seki, M. Sakuragi, Y. Kawanishi, Y. Suzuki, T. Tamaki, R. Fukuda and K. Ichimura, *Langmuir*, 9, 211 (1993).

[15] A. Ulman, *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-assembly*, Academic Press, New York, (1991).

[16] D. J. Crisp, *J. Colloid Sci.*, 1, 49, 191 (1946).

[17] J. Kumaki, *Macromolecules*, 19, 2258 (1988).

[18] I. Watanabe, K. Hong and M. F. Rubner, *Langmuir*, 6, 1164 (1990).

[19] T. Seki and K. Ichimura, *Langmuir*, 13, 1361 (1997).

[20] T. Seki, A. Tohnai, N. Tanigaki, K. Ichimura, *Macromol. Chem. Phys.* 1999, 200, 1446.

[21] S. Nagano, T. Seki and K. Ichimura, *Chem. Lett.*, 613 (2000)

[22] S. Nagano, T. Seki and K. Ichimura, *Langmuir*, 17, 2199 (2001).

[23] S. Nagano and T. Seki, *J. Am. Chem. Soc.*, 124, 2074 (2002).

[24] R. D. Miller and J. Michl, *Chem. Rev.*, 89, 1359 (1989).

[25] R. G. Jones, W. Ando and J. Chojnowski, Ed. *Silicon-Containing Polymers, The Science and Technology of Their Synthesis and Applications*, Kluwer Academic Publishers (2000).

[26] R. Kani, Y. Nakano, Y. Majima, S. Hayase, C. -H. Yuan and R. West, *Macromolecules*, 27, 1911 (1994).

[27] G. Xu, Z. Bao and J. T. Groves, *Langmuir*, 16, 1384 (2000)

[28] X. Zhang and A. Jenkhe, *Macromolecules*, 33, 2069 (2000).

[29] X. Zhang, D. M. Kale and A. Jenkhe, *Macromolecules*, 35, 382 (2002).

[30] P. K. H. Ho, J.-S. Kim, J. H. Burroughes, H. Becker, S. F. Y. Li, T. M. Brown, F. Cacialli and R. H. Friend, *Nature*, 404, 481 (2000).