Monolayer Formation of a Hydrophobic Polysilane on Water Surface Assisted by Liquid Crystal Molecule

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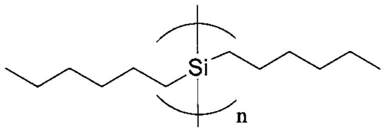
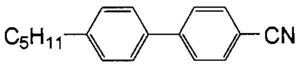
A mixed solution of poly(dihexylsilane) and 4'-pentyl-4-cyanobiphenyl (5CB) was spread on pure water. Surface pressure-area isotherm data and Brewster angle microscopy showed that a monomolecular stretching of this hydrophobic polysilane is performed with the assist of 5CB molecule.

Polymer ultrathin films whose thickness approaches to the levels of a polymer coil or even to a stretched monomolecular state have been attracted considerable attention due to the emergence of modified thermophysical properties stemming from the two dimensional restriction.[1-4] The Langmuir-Blodgett (LB) technique is a fascinating tool to attain the monolayer stretching of chains at the interface for polymers having an amphiphilic or polar structure. However, in cases of hydrophobic polymers, direct adaptation onto water provides associated states of polymers yielding ultrafine particles[5] or ultrathin films with a thickness having a few tens of nanometers.[3] Some LB film studies using hydrophobic polymers such as poly(alkylthiophene)[6] and poly(dihexylsilane)[7,8] (PDHS) have been undertaken via co-spreading with a long chain fatty acid, however, it is confirmed that the polymer chain in such films adopts a folded and aggregated state to form a microphase separated structure.



PDHS



5CB

We show herein that the main chain of the hydrophobic PDHS can be ideally stretched on a water surface with an assist of 4'-pentyl-4-cyanobiphenyl (5CB) molecule. To our knowledge, this is the first example of the spread monolayer formation of a hydrophobic polymer possessing no polar group. With respect to polysilanes, they have unique electronic absorption properties that strongly depend on the backbone conformation and orientation.[9] Therefore, studies on ultrathin films and monolayers of polysilanes are of particular value from both the scientific and technological viewpoints.[4,9] Amphiphilic polysilanes have been synthesized with great efforts, and their structures and properties of LB films have been explored.[10-12] To date, monolayer formation of polysilanes with pure hydrocarbon substituents, which constitute the majority part of polysilane research, have not been reported.

The surface pressure-area (π–A) isotherms of pure 5CB monolayer, pure PDHS ($M_w = 4.2 \times 10^5$, $M_w/M_n = 2.1$) film and a PDHS/5CB mixed film at 15 °C[13] are depicted in Figure 1. In this case, the molar ratio (R) defined as [PDHS unit]/[5CB] was 1.0. Pure PDHS did not form a stable monolayer on the water surface (a), judging from the too small limiting area for an Si unit. The monolayer of pure 5CB exhibited a lift-off area at 0.45 nm^2 and a plateau at 5 mN m^{-1} below 0.35 nm^2 upon compression (b), as commonly observed for 4'-*n*-alkyl-4-cyanobiphenyl series.[14] On the other hand, the mixed film by co-spreading method gave two step plateau regions (c). The first pressure lift-off area exactly corresponded to that of pure 5CB. The steep second uprise around 0.25 nm^2 followed by a plateau at 11-12 mN m^{-1} was a newly observed behavior. The limiting area of ca. 0.25 nm^2 for the second pressure lift was comparable to that for hitherto known amphiphilic polysilanes having a hydroxyalkyl or alkoxyalkyl group.[11]

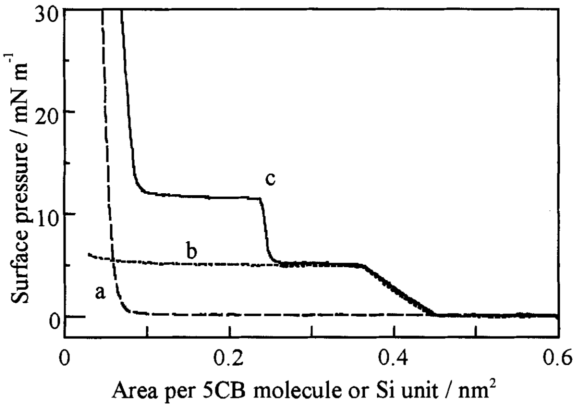


Figure 1. The π-A isotherms of pure PDHS (a), pure 5CB (b), and PDHS/5CB mixed film (R = 1.0, c) on pure water at 15 °C. The abscissa indicates the area per Si unit for (a) and 5CB molecular for (b) and (c).

π-A isotherms of the PDHS/5CB mixed films at various R were shown in Figure 2. The variation of R led to systematic results. At 0.5≤ R ≤ 1.5, essentially the same behavior was observed as for R = 1.0 except for the position of the second step. With the increase in R the second step shifted to larger areas. At larger R (2.0 ≤ R), the feature of π-A isotherm of 5CB was not observed any more, but only the steep step was obtained at the first lift-off. The inset of Figure 2 displays the area of the steep uprises vs R ranging 0.5 – 3.0. As shown, the area of the new step was in exact proportion to R. The overall π-A profile after the steep step coincided well with each other. This strongly suggests that the molecular mixing (hybridization) was attained in the PDHS/5CB films, and that they behave like a single component material. Mixing with a long chain fatty acid gave only a slight expansion at low pressures and did not show such systematic expansions with R.[7,8]

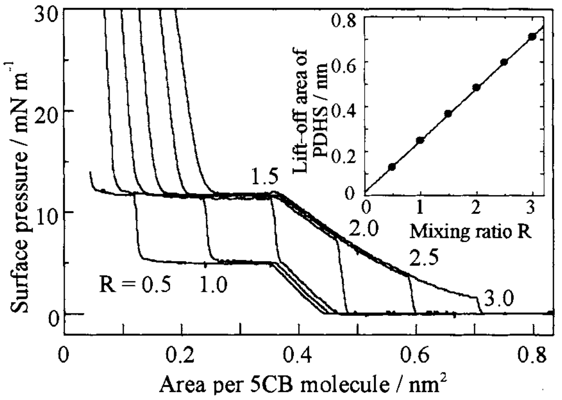


Figure 2. The π-A isotherms of the PDHS/5CB mixture at various mixing ratio R on pure water at 15 °C. The inset depicts the lift-off area of PDHS vs. R.

Explorations using PDHS with other two different molecular weights ($M_w = 3.7 \times 10^4$ $M_w/M_n = 2.2$ and $M_w = 1.7 \times 10^4$ $M_w/M_n = 2.1$) were also achieved, and essentially the identical results were obtained (data not shown). These facts as well as the coincidence of the molecular occupying area with that of non-ionic amphiphilic polysilanes[10,11] obviously indicate that the occupying area is not determined by the overall mass of the polymer but by the individual Si unit.

Brewster angle microscopic (BAM) observation revealed a molecularly smooth surface of the hybrid films. Figure 3 indicates BAM images of the PDHS/5CB hybrid films taken at areas of 0.70 (a) and 0.48 nm^2 (b), and at 0.35 nm^2 (c) for the film of R = 2.0.[13] The monolayer of pure 5CB at areas larger than the plateau region is hardly observed due to highly suppressed light reflection.[15,16] The PDHS/5CB hybrid film, on the other hand, exhibited strongly reflecting fluid portions far before the pressure lift-off (a). Upon compression, these bright areas were gathered without any collapse to diminish the dark round area. When the area approached to the pressure lift-off region at 0.48 nm^2, the hybrid film became highly homogeneous (b). The homogeneity of the film was retained even in the regime of the second plateau at 11 – 12 mN m^{-1} (c). Essentially the same behavior was observed for the films at other mixing ratios. Thus the BAM observation directly proofs the smooth surface of the hybrid film.[17]

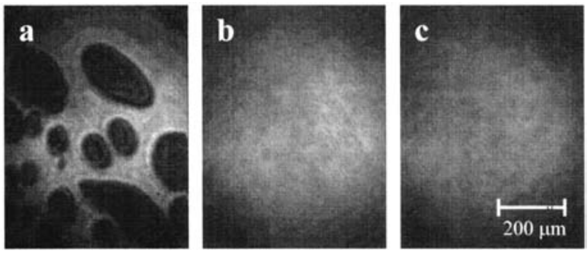


Figure 3. BAM images of PDHS/5CB mixed film of R = 2.0 for 0.70 (a), 0.48 nm^2 (b), and 0.35 nm^2 (c) on the water surface at 15 °C.

Hydrophobic polymers, such as poly(alkylthiophene)s[6] and PDHS,[8] and long chain fatty acids are not miscible at the molecular level in the co-spread monolayer as confirmed by the π-A isotherms measurements with addition of the polymer. In the present system, in contrast, both π-A data and BAM images provide the evidence of molecular mixing in the monolayer. In fact, the polarized microscopy and differential scanning calorimetry justify the remarkable miscibility of these two components in the bulk.[18] The cyano group in 5CB acts as the hydrophilic function of PDHS, and hence the PDHS/5CB hybrid can be regarded as a "supramolecular" amphiphilic polymer. Examinations using other types of liquid crystal (LC) molecule provided essentially the same results (data not shown). We assume at present that the highly fluid and dynamic nature of LC monolayers on water together with the high miscibility is responsible for the monolayer formation of PDHS.

In summary, monomolecularly spread PDHS on water can be prepared by simple co-spreading with 5CB. We anticipate that, after the LB deposition, the films can provide much information on the polymer chain behavior on a solid substrate. The work in this direction is now underway.

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13 PDHS was prepared by reductive condensation of the dihexyldichlorosilane with sodium metal in dry toluene. 5CB was purchased from Dainippon Ink and Chemicals, Inc. Two mother solutions, PDHS dissolved in hexane (1.0×10^{-3} mol (Si unit) dm^{-3}) and 5CB dissolved in chloroform (1.0×10^{-3} mol dm^{-3}) were prepared. Mixed solutions were prepared from these solutions at the various target ratios, R = [PDHS unit] / [5CB], (co-spreading method). The mixed solution was spread onto pure water surface in a Lauda FW-1 film balance. π-A isotherms and BAM (Nippon Laser Electronics, EMM633) images were obtained at 15 °C.

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