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Abrupt Interfacial Transitions of Hydrophobic Polysilanes As Probed via Liquid Crystal-Assisted Stepwise Deposition

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The conformational and morphological behavior of ultrathin polymer films at interfaces is of fundamental importance to a large number of technological applications such as electric packaging, dielectric layers, coating, composites, and lubrication. Recently, considerable theoretical and experimental progress has been made in describing polymers in contact with surfaces and interfaces.[1−3] When the thickness of a polymer film reaches to a level of a few radius of gyration, thermophysical properties[4] (widely discussed with glass transition temperature) and structures (molecular orientation,[5] aggregation state,[6] and crystallinity,[7] etc.) are modified from those in a bulk state by the two-dimensional (2D) geometrical constraint. Such ultrathin films of polymers are mostly prepared by the solvent-spincast method.[4−7] This method is widely applicable for many sorts of soluble polymers, however it does not render precise thickness controls at nanometer levels. On the other hand, the Langmuir−Blodgett (LB) method utilizing the monolayer formation on water allows precise nanometer thickness controls via layer-by-layer deposition ("bottom up" approach).[8] However this method has an inconvenient restriction that the polymers need to possess polar moieties. Fully hydrophobic soluble polymers such as polystyrene and polysilanes (Si-catenated polymers) having hydrocarbon substituents[9] cannot be applied. Some attempts of LB deposition have been made for such polymers by mixing with monolayer-forming long chain carboxylic acid,[10,11] nevertheless the polymers are segregated within the LB films[11b] and the monolayer spreading of such polymers has not been realized.

Our recent work indicated that monolayer spreading of a fully hydrophobic polysilane, poly(di-*n*-hexylsilane) (PDHS), can be attained with the assist of a dynamic 2D spreading action of liquid crystal molecules on water.[12] Cospreading of PDHS with 4′-pentyl-4-cyanobyphenyl (5CB) on water provides a hybrid molecular layer in which an ideally spread monolayer of PDHS is formed on top of the 5CB monolayer. For ordinary amphiphilic polymers, the repeated LB deposition results in proportional increases of film thickness without changing the packing or conformational states because of their strong self-structuring (layering) nature;[8] however, this common concept would not be the case for polymers without polar interactions. In this communication, we propose a new supramolecular approach based on the modified LB technique for exploration of the conformations of hydrophobic polymers in ultrathin states. It is found here that *the chain conformation of hydrophobic polysilanes reflecting the 2D-constrained state abruptly changes to that of the bulk with a thickness increase at a monolayer level*.

Two types of fully hydrophobic polysilanes were employed, PDHS ($M_w = 4.2 \times 10^5$, $M_w/M_n = 2.1$) having two symmetric substitutents at each Si atom and poly(methyl-*n*-octylsilane) (PMOS, $M_w = 2.9 \times 10^5$, $M_w/M_n = 3.2$) with asymmetric ones. In the bulk state, PDHS mostly adopts a crystalline state,[9] and in contrast, PMOS shows a highly elastic character. Such properties were confirmed from the UV absorption spectra taken for a thick film (thickness = ca. 50 nm, Figure 1a). As seen, the *all-trans-zigzag* conformation exists predominantly at room temperature. The elastic PMOS, on the other hand, showed a broad absorption band around 308 nm, indicating a noncrystalline disordered state including gauche conformations of the Si backbone.

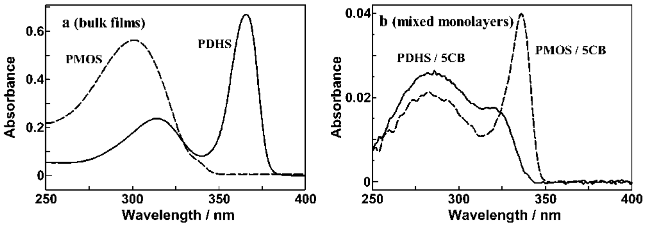

Figure 1. UV−visible absorption spectra of the thick polysilane films (thickness = ca. 50 nm) (a) and polysilane/5CB hybrid monolayers on water (b). In the hybrid monolayer, the molar ratios (*R*) of Si unit per 5CB were 1.5 and 3.0 for PDHS and PMOS, respectively.

Figure 1b shows the UV−visible absorption spectra of PDHS and PMOS in the monolayer state formed on the 5CB monolayer prepared by the cospreading method at the air/water interface.[12b] The hybrid PDHS/5CB monolayer gave a completely different spectrum characterized by two absorption peaks around 280 and 320 nm. The band around 320 nm is attributed to the *helical-gauche* conformation of PDHS as stated above, and the major band around 280 nm stems from the $\pi-\pi^*$ transition of 5CB. It is stressed that the monolayer exhibited no trace of absorption ascribed to the *all-trans-zigzag* conformation around 370 nm. When the hybrid film was collapsed upon further compression, an abrupt growth of the higher energy band around 370 nm was observed. This fact should indicate a 3D structure formation after the collapse as will be stated later. In the case of the PMOS/5CB monolayer, a sharp narrow absorption band peaking at 336 nm was observed, indicative of the pseudo-trans conformation of the PMOS backbone.[14] By subtracting the contribution of the absorption of 5CB, it was shown that the PMOS backbone almost fully adopts the pseudo *trans-zigzag* conformer in the monolayer state. In the above manner, the obvious conformational transitions occur when the polymers adopt the monolayer state, and quite interestingly the transitions proceed just in the reverse manner for the two polysilanes. The rheological nature in the monolayer state could be visualized by Brewster angle microscopy.[14]

The hybrid monolayer of the two polysilanes could be transferred onto a solid substrate. The deposited monolayers on mica exhibited a molecularly flat surface having undulations within 0.5 nm as observed by AFM,[14] indicating that these films were transferred uniformly with retention of the monolayer state. No pinhole defects were observed. The multiple layer-by-layer transfer was successful only for the hydrophobic substrate. Interestingly, the 5CB molecule

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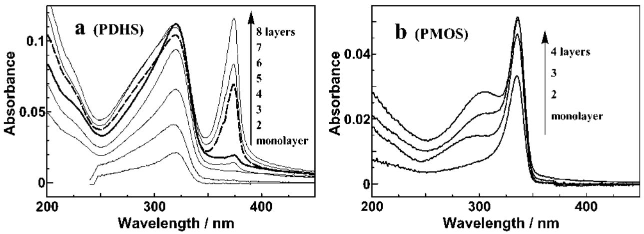

Figure 2. UV−visible absorption spectra of PDHS (a) and PMOS (b) films on a hydrophobilized surface as a function of layer number. The transfer was performed at 8 mN m^{-1} for both monolayers. 5CB molecules were expelled from the film in the transfer process and pure polysilane films were deposited on the substrate (see text).

was fully excluded during the transfer when a hydrophobic surface was employed, and LB films composed of the pure polysilane were formed.[14] In this way, 5CB behaves as a molecular mediator that conveys the polymer from the water surface to the solid substrate.

Figure 2 depicts UV−visible absorption spectra of pure PDHS (a) and pure PMOS (b) multilayers deposited on the hydrophobic substrate. The layer-by-layer transfer was achieved from 1 to 8 layers for PDHS (a). The absorption band around 320 nm corresponding to the *helical-gauche* conformation increased in conformity with the deposition numbers up to 5 layers. Thus, the PDHS backbone in each layer retained in the gauche conformation as on water within the 5-layer thickness. In sharp contrast, the absorption peak at 374 nm abruptly enhanced at the sixth layer. Above this critical layer number, absorbance and features of the band at 320 nm stayed essentially unchanged, and only the sharp peak at 374 nm increased. These results indicate that the *all-trans-zigzag* conformation of PDHS corresponding to the bulk state suddenly starts to grow above 6 layers. Since the thickness per layer estimated by AFM was 1.4 nm,[15] almost in accord with the rod diameter of PDHS, the thickness of the 6 layers corresponds to ca. 8 nm. Annealing the 8-layered film at ca. 40 °C resulted in a complete loss of the *all-trans-zigzag* conformation; however, essentially the same absorption spectrum as shown in Figure 2a was recovered after successive cooling to room temperature. Thus, the thickness profile involving the double structure of the *helical-gauche* and *all-trans-zigzag* conformations in the lower and upper layers, respectively, is retained after this moderate heating and cooling.

PMOS behaved in a quite different manner as shown in Figure 2b. For the first layer, the backbone adopted only the pseudo *trans-zigzag* conformation. In the second layer, a broad absorption band around 300 nm attributable to the disordered gauche conformation appeared, and the sharp peak at 336 nm showed a minor enhancement in consideration of the spectral overlap. Above 3 layers, the absorbance at 336 nm due to the *trans-zigzag* conformer of the polymer backbone showed little increase. Thus, the conformational population above the second layer is mostly inclined to the gauche state corresponding to the bulk state.

The above results clearly provide answers to important questions as to at which thickness and how sharp the characters from the 2D-constrained state to the bulk occur. Despotopoulou et al. demonstrated that the crystallinity in the PDHS spincast films decreases significantly below 50 nm thickness, and the *all-trans-zigzag* state finally diminishes below 10 nm thickness.[7] In our bottom-up approach, the thickness control is attained in a 1.4 nm precision starting from the surface, and the conformational transition is observed at ca. 8 nm thickness. Thus, judging from the experimental accuracy, a satisfactory coincidence is obtained in the two research approaches. Below this criterion thickness, the intrinsic aggregation of polymer chains is strongly suppressed by the unfavored chain packing owing to the 2D geometrical confinement.[7] When PDHS chains are placed at distances of 8 nm away from the surface, the polymer segments can freely aggregate according to its intrinsic thermodynamical requirement. PMOS adopts the pseudo *trans-zigzag* conformation only for the monolayer in direct contact with the surface. The *trans-zigzag* conformation in the first layer is probably attained as the stretched contact of the octyl substituent with the hydrophobic surface. This will force the zigzag conformation of the backbone. Above the second layer, the gauche-containing segments of PMOS as in the bulk are mainly involved. In this case, the influence of the surface ranged mostly in the level of monolayer (ca. 1.5 nm as estimated by AFM). The difference of the transition thickness observed for the two polysilanes can be ascribed to the differed packing cooperativity. PDHS has a mesophasic liquid crystalline character in the *helical-gauche* state,[16] and this can be the origin of the longer range structural correlation.

In conclusion, the build-up LB manipulation of fully hydrophobic polymers was successfully performed for the first time via 5CB-assisted spreading on water. We anticipate that the present method is applicable to other types of hydrophobic polymers including π-conjugated soluble polymers and dielectric polymers composed of pure hydrocarbons. This may provide new opportunities for polymer nanoscience and technologies.

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Supporting Information Available: Experimental details and an AFM image of PDHS/5CB (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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(14) Supporting Information.

(15) The thickness of a single layer of spread PDHS ranged from 0.9 to 1.5 as estimated by AFM,[12b] which is in good agreement with the interchain spacing evaluated by X-ray analysis (1.35 nm).[9c,d] We adopt a figure of 1.4 nm for the thickness per PDHS layer as the most plausible average value.

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