Relationship between Morphology and Na^+ Content of Langmuir-Blodgett Mesoscopic Tapes Induced by a Change in pH

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Langmuir-Blodgett (LB) films of a short chain carboxyazobenzene derivative on mica exhibit nearly straight tape structures 1 nm thick, 80 nm wide, and over several μm long at pH 7.0. Lowering pH causes the tapes to be wavy and irregular without coagulation. The fraction of straight tapes at a constant salt concentration increases smoothly till pH 7, then drops sharply. Above 8, no transfer occurs. The fraction of Na per molecule in the film also increases with pH and becomes 0.5 at pH 7. The wavy tapes are found to become straight even with a slight ionization. An importance of the charge distribution rather than the total charge density is suggested.

A short chain amphiphile, 4-heptoxy-4'-carboxyazobenzene (C7) gives the mesoscopic tapes as a Langmuir-Blodgett film on mica.[1] At pH 7.0, C7 produces the nearly straight tapes that are monolayer thick, 80 nm wide, and can be as long as 0.1 mm. The film possesses a number of unique properties. The film on water develops no surface pressure. It is spontaneously formed on the water surface as long as the concentration at which the spreading solvent evaporates exceeds the critical aggregation concentration of 8 nm^2/molecule at 20 °C. Morphologically, each tape appears to consist of small clusters having diameters in a few tens of nm.

Neither a spread monolayer[2-4] nor a two dimensional (2D) crystal[5,6] explains these characteristics fully. Instead, these properties are similar to those of micelles and colloidal particles in 3D solution.[7] In this case, the tape can be thought of an associated assembly of small 2D clusters, which in turn are crystalline aggregates of molecules.[1] As an initial stage of studying this *weakly self-organizing system*, the effects of the subphase pH is investigated.

The compound C7 was synthesized as reported earlier.[8] The subphase pH was adjusted to below 6.0 by HCl and above 6.0 by $NaHCO_3$. The Na^+ concentration was maintained at 0.5 mM by NaCl. The compound dissolved in chloroform was spread on water at 20 °C so that the molecular area became 2.5 nm^2/molecule. After aged for 15 min, the film was compressed to 0.5 nm^2/molecule. A single up-stroke transfer was made on muscovite mica without moving the barrier. The film was examined by atomic force microscopy (AFM) operating in a non-contact mode in ambient conditions.

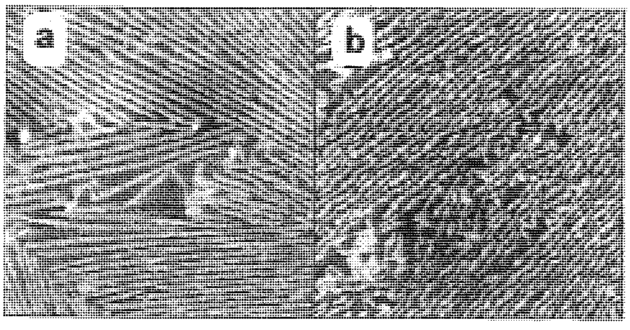

Figure 1. AFM images of mesoscopic tapes transferred at pH of 6.0, showing (a) straight and (b) wavy tapes. The tape height is approximately 1 nm and the scan range is 2500 nm.

Two AFM images shown in Figure 1 were obtained from different places on the same sample surface prepared at pH 6.0. Figure 1(a) shows the relatively straight tapes, whereas Figure 1(b) exhibits the wavy tapes among naturally occurring defects (flocculated patches at the lower left corner). Lowering pH makes more wavy and irregularly shaped tapes to appear. To see the effect more quantitatively, the fraction of straight tapes is measured at various pH. We classify a tape to be straight if a line drawn at the middle width of the tape is straight over a distance of about 1 μm. The averaged straight tape fractions are plotted against the subphase pH in Figure 2. At pH 3.0, all tapes are irregular. As pH increases, the straight tape fraction increases smoothly to 7.0. Then, it drops abruptly and becomes zero at 8.0. Because of the presence of defects, the high fraction at 7.0 means that almost all tapes are straight.

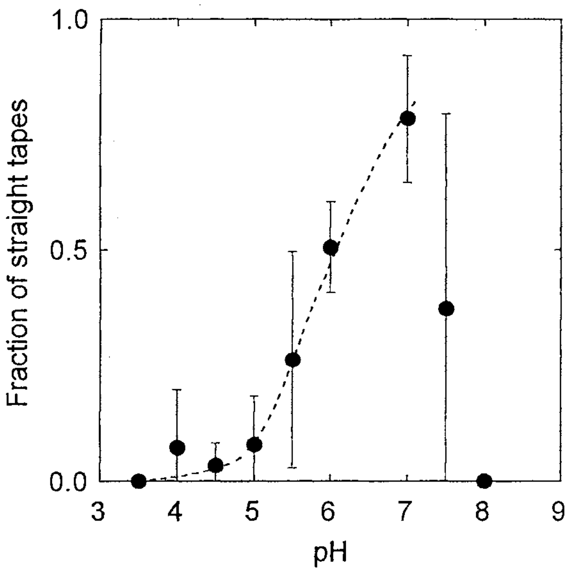

Figure 2. A plot of the fraction of the straight tape area over the total film area as a function of the subphase pH. A dotted line is drawn to show the average behavior. The point at pH 8.0 is zero because of no LB transfer.

The UV-vis reflection spectra was found to be independent of molecular areas and pH below 8.0. All spectra have two peaks at 250 and 305 nm, a characteristic of H-like aggregates of the azobenzene chromophore.[9] At 8.0, no peak including one at

250 nm was observed. Also, the mica surface lifted from pH 8.0 showed no presence of any film by AFM and X-ray photoelectron spectroscopy (XPS). These results indicate that the compound is heavily hydrated and randomly oriented near the air-water interface at 8.0. Thus, the sharp decrease of the straight tape fraction above 7.0 is due to poor LB transfer.

In order to estimate the fraction of carboxylates, the atomic concentration ratio of Na to N was measured at various pH by XPS. The ratio of C or N to Al (from mica) was also monitored to make sure that each sample had the same surface coverage. The atomic sensitivity was calibrated with a cast film of 100% Na salt of C7. The resulting data set gave the Na fraction of 0.13 for all low pH samples, which was taken as the freely adsorbed Na and was subtracted from all samples. The fraction of Na per molecule in LB films is displayed in Figure 3.

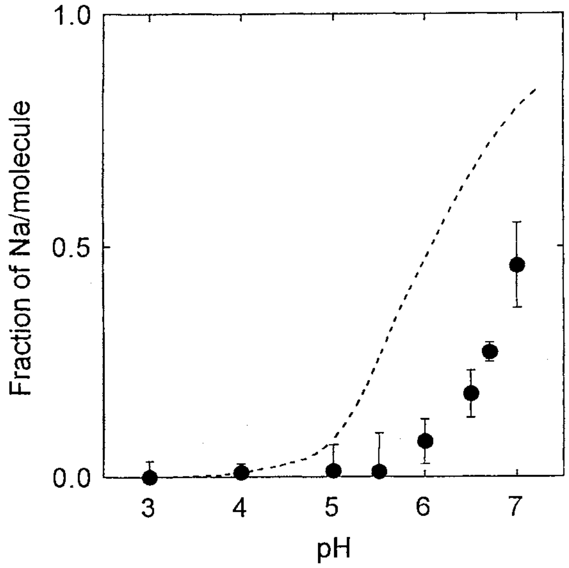

Figure 3. A plot of the fraction of Na per molecule in the films at various subphase pH. A dotted line is the average fraction of straight tapes shown in Figure 2.

It was not possible to make measurements above 7.0 by the above reason. Even then, we see that the ratio of Na per molecule reaches 0.5 approximately at pH 7. The literature values of pK_a of carboxylic acid monolayers depend heavily on the presence of salts and varies anywhere from an "intrinsic" value of 5.6[10] to 8.[11-17] A similar azobenzene compound with an alkyl spacer as a barium salt monolayer has pK_a of 6.2.[18] Thus, in the present case of the LB film on mica, the measured Na fraction closely parallels the degree of ionization on mica.

Figure 4 compares the straight tape fraction with the Na fraction by plotting the values obtained from the smooth lines connecting the average points of Figures 2 and 3. It is clear that only small degree of ionization is necessary to make the tapes straight. This implies that, even though a large fraction of molecules may be hydrogen bonded, the electrostatic interactions supplied by a small fraction of carboxylates are enough to shape the tape straight. Also, the plot indicates that once the tape becomes straight, it is no longer sensitive to the change of carboxylates. Thus, the charge distribution rather than the total charge density in a cluster is important for the present mesoscopic self-organization.

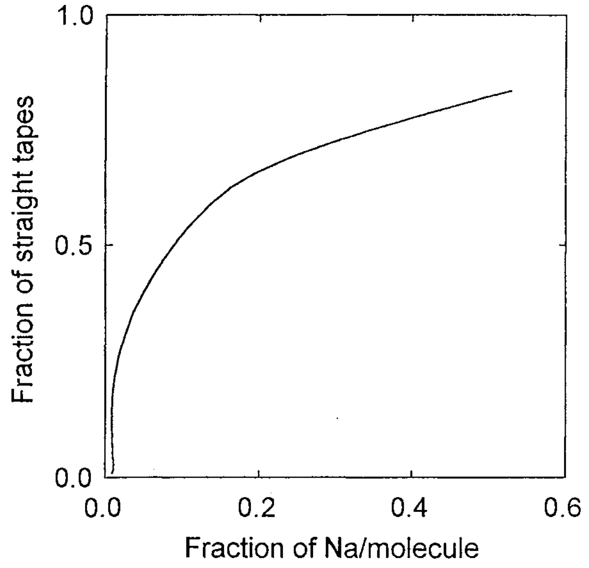

Figure 4. A plot of the fraction of straight tapes against the fraction of Na/molecule. The values are taken from the lines connecting the average points of the plots in Figures 2 and 3.

References and Notes

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