In Situ Observation of Domain Structure in Monolayers of Tetraphenylporphyrin Derivatives Containing Four Fluorocarbon Chains by Brewster Angle Microscope

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The morphologies in monolayers of tetraphenylporphyrin derivatives with four fluorocarbon chains have been observed *in situ* on the water surface by a Brewster angle microscope (BAM). It has been suggested that the homogeneity of the monolayers depends upon the chain length of substituents for the porphyrin derivatives and in the case of the shorter chain the nucleation and the process of growing crystallines in the monolayers can be clearly observed at zero surface pressure or on compression.

Recently, a Brewster angle microscope (BAM) with a high sensitivity has been applied to provide a new method for obtaining structural informations on monolayers[1,2] at the air-water interface. BAM has its own particular advantages in directly studying the dynamic process during the compression and the phase transition without introducing any probe molecule into the monolayer.[3,4] On the other hand, a two-dimensional nucleation/growth model has been described theoretically the constant-pressure monolayer relaxation on the basis of nucleation and subsequent growth of the nuclei taking account of the overlap of the growing nuclei.[5-7] BAM studies on the monolayer structure have been focused on the common film-forming substance such as fatty acids and phospholipids.[8] Recently, the self-organization of amphiphilic porphyrins with alkyl chains at the air-water interface has been studied by BAM.[9] LB films containing fluorocarbon chains have received much attention because of characteristic properties such as low friction, excellent insulation, remarkable durability and so on.[10] In this letter, the morphology change of monolayers of tetraphenylporphyrin derivatives with four fluorocarbon substituents has been monitored by visualization with a BAM to obtain informations for nucleation and growth of two-dimensional crystallites *in situ*.

The tetraphenylporphyrin derivatives containing four fluorocarbon substituents (TFPP) with different chain lengthes used in this work, are shown in the inside of Figure 1. These compounds were synthesized by Lindsey's method[11] and the monolayers were spread from both chloroform and toluene solutions in concentration of 10^{-5} M onto the twice distilled water surface. A PTFE coated rectangle stainless steel trough with total surface area of 3.5 x 100 cm^2 was used. It was equipped with a Wilhelmy balance and the surface temperature of the subphase could be controlled by a water circulation system. The morphology of monolayers on the water surface was observed with a Brewster angle microscope (BAM1, Nanofilm Technologie GmbH, Germany) through p-polarized irradiation and detection. The monolayer compression rate was in a range of 1-3 cm/min. For the molecular area of 418 $Å^2$/molecule, the surface pressure was held at zero mN/m for 3-4 h. The morphology changes after spreading the monolayer and during the process of compression from zero to five mN/m for TFPP-1 were observed with a BAM and recorded on a videotape.

Figure 1 shows the surface pressure-area isotherms at 20 °C of the tetraphenylporphyrin derivatives measured by a Lauda film balance. TFPP-2 and 3 exhibit transition from the liquid-expanded to condensed states, whereas TFPP-1 gives a stable condensed monolayer without any transition. Figure 2 shows the BAM images for TFPP-1, TFPP-2 and TFPP-3 monolayers at zero mN/m. It is considered that the bright parts are due to crystalline states and the lower reflectance implies amorphous or thinner monolayers. More homogeneous domains regularly formed in the condensed phase with some ordered "dots"(highly reflective parts) were observed in the monolayer of TFPP-1

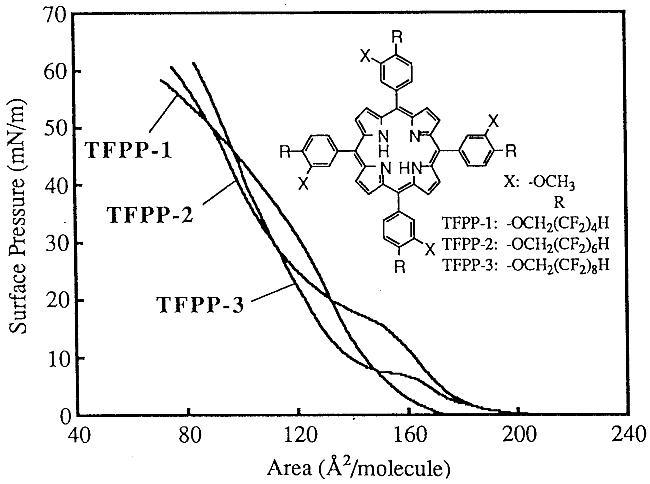

Figure 1. π -A isotherms ofTFPP monolayers at 20 °C.

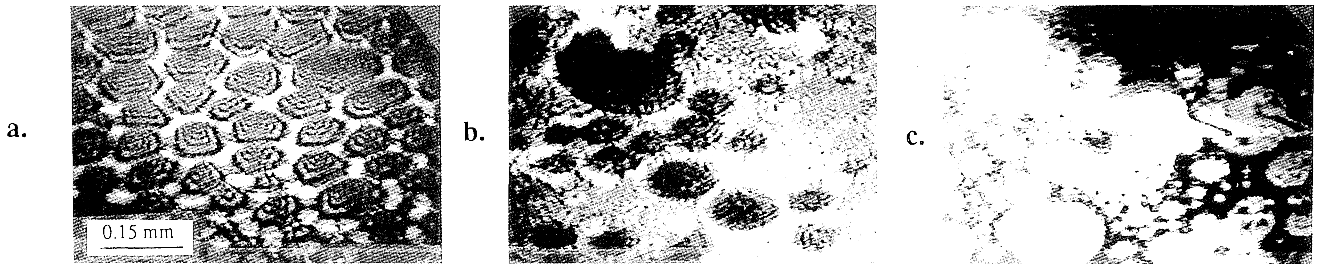

Figure 2. BAM images at π = 0 mN/m, T = 20 °C for a) TFPP-1, b) TFPP-2 and c) TFPP-3.

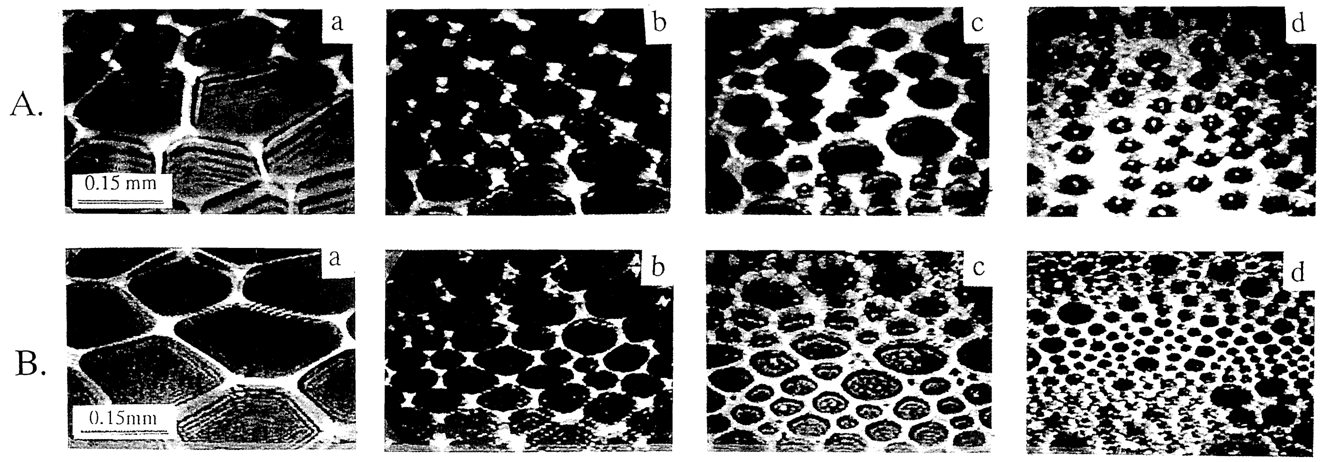

Figure 3. Nucleation process of TFPP-1 monolayer spreading from chloroform (A) and toluene solution (B) at π = 0 mN/m, T = 20 °C: (a) after spreading (t) = 0 and after (b) t = 60 min.; (c) t = 120 min.; (d) t = 180 min.

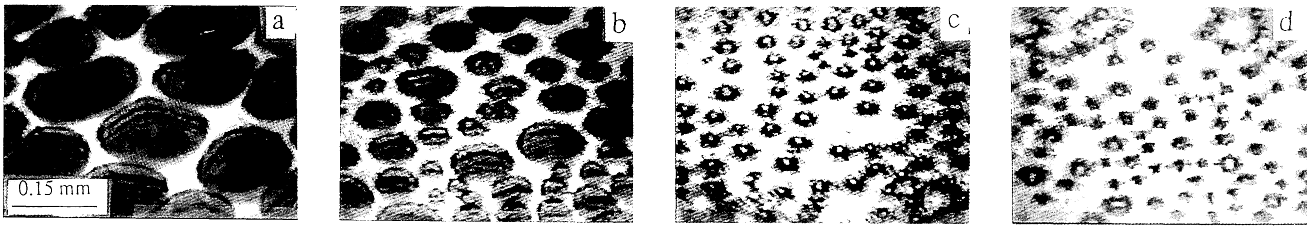

Figure 4. Nucleation process of TFPP-1 for compression from 0-5 mN/m (a-d).

(shown in Figure 2-a), as compared with those of the TFPP-2 and TFPP-3 (Figures 2-b and c) in which the heterogeneous domain structures were formed immediately after spreading. The highly crystalline states seem to be due to stronger interactions between the fluorocarbon chains existed in TFPP-2 and TFPP-3 comparing with those in TFPP-1, which is unfavorable to obtain a monodispersed monolayer. It has been clearly demonstrated that the homogeneity of the TFPP monolayers depends on the substituent chain length. A similar behavior was found for the monolayers at 2 mN/m. Figure 3 shows BAM images during the nucleation process of the TFPP-1 at zero mN/m spreading from both chloroform (Figure.3-A) and toluene solutions (Figure.3-B). In the primary stage, ripple structures were observed, which seem to be due to crystallization on the solvent evaporation. Some "dots" in the domain of the TFPP-1 monolayer as spread at zero pressure, grow for one h to form a fine order structure and nucleation proceeds for 3 h to the brightened monolayer. Essentially the similar results were observed for the TFPP-1 monolayer spread from the toluene solution (Figure 3-B). Since the evaporation rate of toluene is slower than that of chloroform and there is difference in polarity of these sovents, a relatively slower appearance of nuclei was observed in the early step for the TFPP-1 monolayer spread from the toluene solution. And further, this nucleation growing process was promoted by compression up to 5 mN/m for the TFPP-1 monolayer spread from the chloroform solution. Figure 4 shows the compressing process of the TFPP-1 monolyer from zero to five mN/m within 30 min., in which a close packing of the ordered structure can be formed. However, heterogeneous monolayers were only formed for TFPP-2 and TFPP-3 and any nucleation or growing process of crystallites could not be observed at both zero and five mN/m.

In conclusion, we have demonstrated the successful application of a Brewster angle microscope to visualize the nucleation and growing processes of monolayers of the porphyrin derivative with fluorocarbon chains at zero surface pressure and through the compression of the monolayer. In comparison with TFPP-2 and TFPP-3, TFPP-1 exhibits a more homogeneous monolayer at the surface pressures of both zero and a few mN/m. For tetraphenylporphyrin derivatives, the homogeneity of the monolayers depends significantly on the substituent chain length. Furthermore, the nucleation growing process was promoted by compression of the monolayer.

References

1 S. Henon and J. Meuniep, *Rev. Sci. Instrum.*, **62**, 936 (1991).
2 D. Honig and D. Möbius, *J. Phys. Chem.*, **95**, 1991, 4590.
3 Z.H. Lu and H. Nakahara, *Chem. Lett.*, **1994**, 2005.
4 Z.H. Lu and H. Nakahara, *Chem. Lett.*, **1995**, 117.
5 D. Vollhardt and U.Retter, *J. Phys. Chem.*, **95**, 3723 (1991).
6 D. Vollhardt, U. Retter and S. Siegel, *Thin Solid Films*, **199**, 189 (1991).
7 D. Vollhardt and U. Retter, *Langmuir*, **8**, 309 (1992).
8 D. Honig and D. Möbius, *J. Phys. Chem.*, **96**, 8157 (1992).
9 K. Kobayashi, M. Takasago, Y. Taru and K. Takaoka, *Thin Solid Films*, **247**, 248-251 (1994).
10 J.M. Kroon, E.J.R. Sudholter, A.P.H.J. Schenning, and R.J.M. Nolte, *Langmuir*, **11**, 214-220 (1995).
11 J.S. Lindsey, and R.W. Wagner, *J. Org. Chem.*, **54**, 828 (1989).