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A. Bhattacharyya [a] & K. A. Suresh [a]

[a] Raman Research Institute, Bangalore, 560080, INDIA

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PHASE DIAGRAM OF A LIQUID CRYSTAL SILOXANE POLYMER AT AIR WATER INTERFACE

A. BHATTACHARYYA AND K. A. SURESH
Raman Research Institute, Bangalore 560080, INDIA

Abstract We have carried out surface manometry and epifluorescence microscopic studies on a polymeric liquid crystal, siloxane polymer of 1-methyl propyl 4 (4′-hexyloxy benzoyloxy) benzoate, n ∼ 40 at the air water interface. At room temperature, on compression, the usual liquid-expanded (LE) phase transforms to a different structure consisting of small bright domains. On further compression, these join to form striations which in turn change to a melted stripe structure. At 35°C, on compression, the LE phase changes to a new structure which appears as large irregularly shaped bright domains. On cooling, these domains change to the melted stripe structure.

INTRODUCTION

Amphiphillic molecules spread spontaneously at the air-water interface to form stable two-dimensional (2D) Langmuir monolayers[1]. Some liquid crystal polymers are also known to form monolayers[2-4]. One can expect the monolayers of these polymers to exhibit some interesting structures. In the case of a siloxane side-chain polymer[4], the surface pressure (π) - area (A) isotherms show a number of steps, which the authors attribute to conformational changes. Such steps have also been seen in monomers[5,6]. These have been attributed to multilayer formation by roll over mechanism. We have studied the structural changes in the monolayer of a related side-chain polymer by surface manometry and epifluorescence microscopy. We find the formation of some new structures on compressing the monolayer. Our studies show that the occurence of these structures depends strongly on temperature. We find that the π-A isotherms of the polymer monolayer are very different from those of the corresponding monomer[5,6]. Also, we do not find any evidence of multilayer formation.

EXPERIMENTAL

Our studies were carried out on monolayers of a polymeric liquid crystal, siloxane polymer of 1-methyl propyl 4 (4′-hexyloxy benzoyloxy) benzoate, chain length n ∼

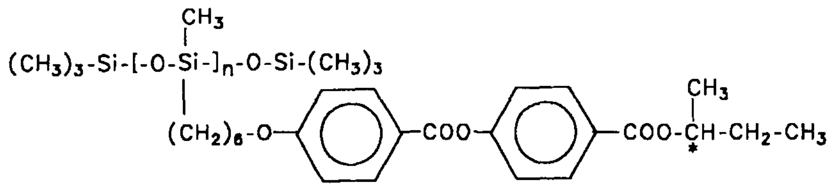


FIGURE 1 Molecular Structure of the polymer LCP1.

40 (LCP1), [Figure 1.]. The material was obtained from Merck and used as received. The monolayer was formed by depositing 25μL of dilute (milli-molar) LCP1 solution (in chloroform) using a micro-syringe on Millipore water in a teflon trough (35cm × 10cm). The trough was equipped with an electric heater to control the sub-phase temperature. The monolayer was compressed by a teflon barrier driven by a computer controlled DC motor. Phase transition points were located by surface manometry. The surface pressure was measured by the Wilhelmy plate method[7] with a platinum blade.

We employed epifluorescence microscopy[8] to characterise the phases indicated by π- A studies. A dye 4-(hexadecylamino)-7-nitrobenz- 2 oxa-1,3 diazole (Molecular Probes, USA) was added to the LCP1 solution to get 1% molar concentration of the dye. The monolayer was directly observed under a Leitz Metallux 3 microscope. The preferential solubility of the dye in the LE phase made this phase appear bright compared to the dark gas phase. The images were obtained using a photon intensified CCD camera (Model P 46036A/V22, EEV). We investigated the surface topography of the domains by reflection microscopy, using a reflection mode adapter on the same microscope.

RESULTS AND DISCUSSIONS

The π-A isotherms are shown in Figure 2. At room temperature, the isotherm showed four steeply increasing regions separated by plateaus indicating delicate

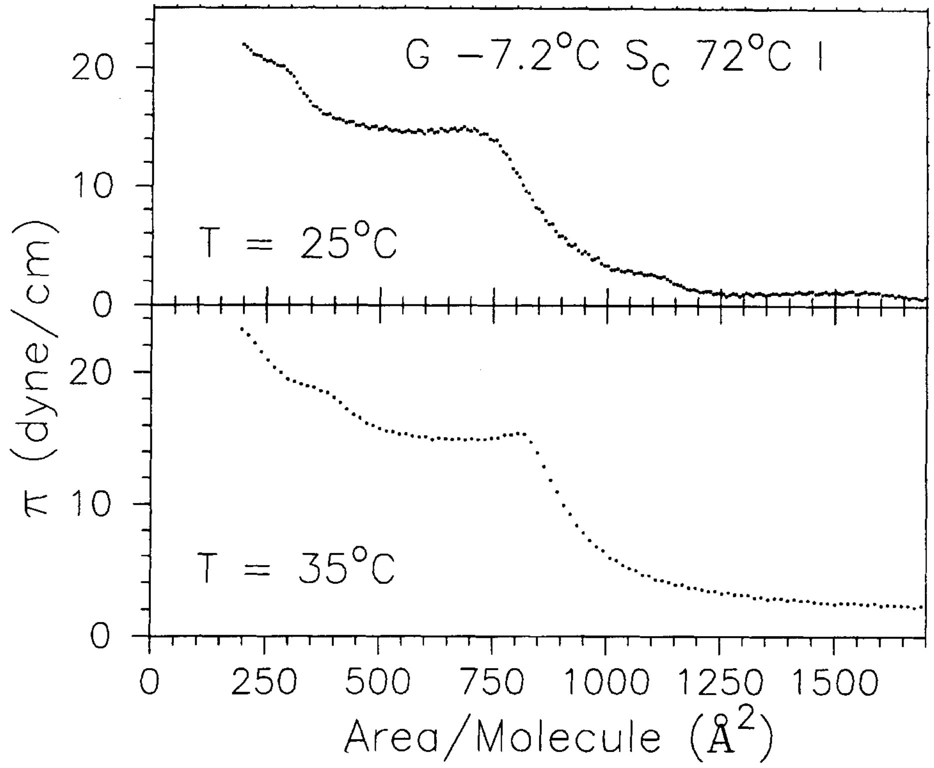
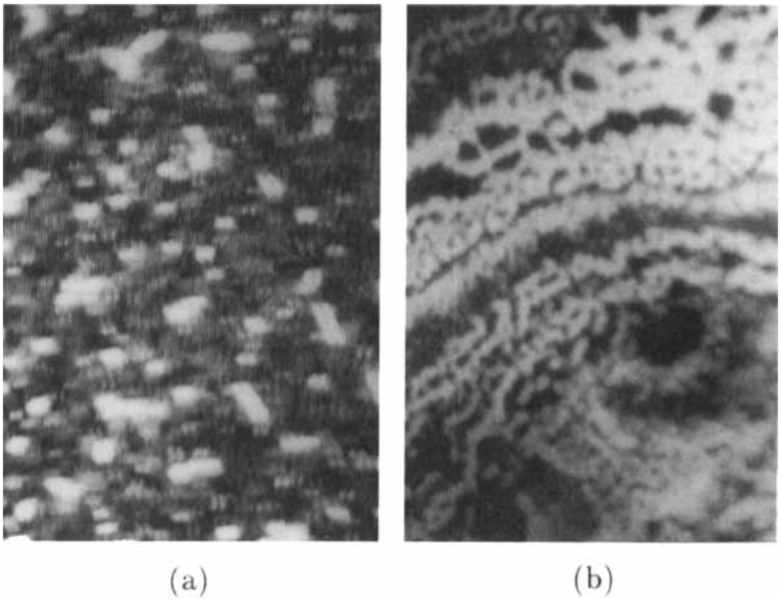


FIGURE 2 Surface pressure (π) - area/molecule isotherms of LCP1 monolayer at two different temperatures. The compression rate was 18.4 Å^2/molecule/sec. The transition temperatures of LCP1 are also shown [Glassy state (G); Chiral smectic C (S_C); Isotropic (I)].

structural changes in the monolayer. Interestingly, at 35°C, the small plateau with Area/Molecule (A/M) between 1000 and 1250 Å^2 was supressed and we found only three plateaus.

Fluorescence studies indicated that the plateau for A/M greater than 1400 Å^2 represented the gas and liquid expanded (LE) two phase region. The intensity contrast between the gas and the LE phases was very poor at room temperature. On compression, the whole field of view became bright (1000 Å^2 A/M) showing the onset of the LE phase corresponding to the steeply increasing π region. On further compression, small bright domains (D_1) started appearing around 800 Å^2 A/M [Figure 3(a)]. As the compression continued, more and more of these domains appeared. The co-existence of the LE phase with these domains gave the large plateau (800 - 350 Å^2 A/M). Finally, around 300 Å^2, these domains started coalescing to form



(a) (b)

FIGURE 3 Fluorescence Images at room temperature. (a) Small bright domains appearing in the LE phase (700 Å^2 A/M). Scale of the image: 200 μm × 300 μm. (b) The small bright domains joining together into striations (300 Å^2 A/M). Scale of the image: 200 μm × 300 μm.

striations [Figure 3(b)] which changed to a melted stripe (MS) structure [Figure 4(a), (b)] around 250 Å^2 A/M. A similar structure has been observed by Seul and Sammon[9] in a phospholipid - cholesterol mixed monolayer. The MS structure coexisted with the LE phase and the striations in the plateau region (250 - 200 Å^2 A/M). From fluorescence studies, we could not detect any changes corresponding to the small plateau seen around 1100 Å^2 A/M, which might be due to some structural adjustments in the LE phase.

On expanding from A/M less than 250 Å^2 at room temperature, the remaining LE phase first changed to the gas phase. After this the MS structure started giving rise to a foam like structure [Figure 4(c)]. As the expansion continued, the foam structure started breaking, resulting in a structure resembling the MS structure but with much less bright domains.

At 35°C, the gas to LE intensity contrast was better. Here on compressing from the LE phase we observed the formation of extremely bright domains (800 Å^2 A/M) of irregular shape (D_2) [Figure 5(a), (b)]. On cooling to room temperature, these domains slowly changed to the MS structure. Seul and Sammon[9] have observed a

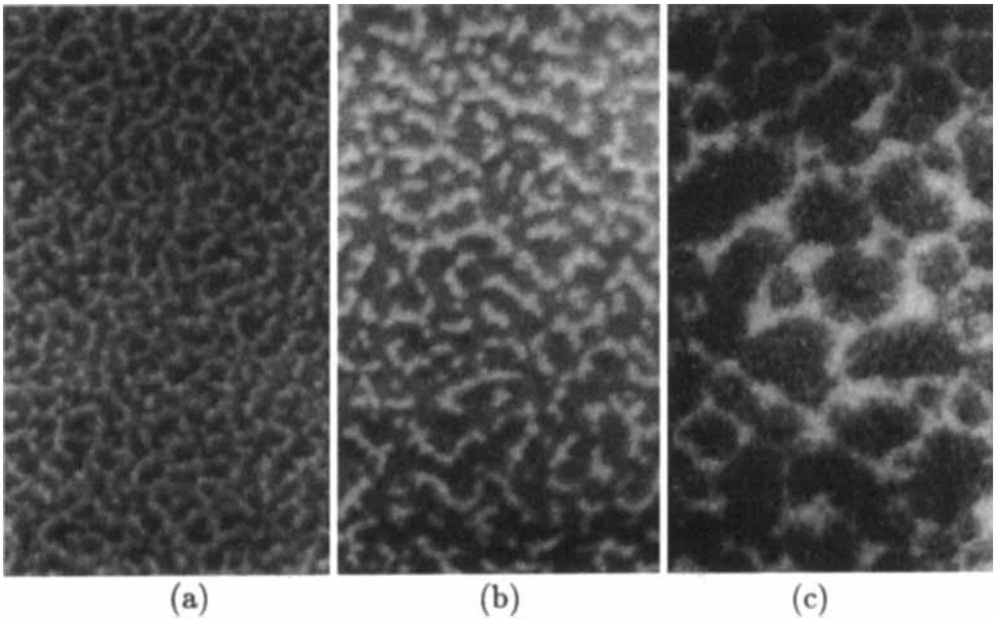


FIGURE 4 Fluorescence Images at room temperature. (a) Melted stripe structure at 200 Å^2 A/M. Scale of the image: 175 μm × 300 μm. (b) The melted stripe structure at slightly higher A/M (250 Å^2). Scale of the image: 175 μm × 300 μm. (c) The foam structure formed on expanding from the melted stripe structure. (600 Å^2). Scale of the image: 175 μm × 300 μm.

similar transition on compression which they attribute to a branching instability.The reverse transition from the MS to irregular domains was observed on heating.

Our surface manometry results on the polymer were very different from those on the corresponding monomer by Diep-Quang and Ueberreiter[5,6] who found many steps interspaced by plateaus. They attributed these steps to multilayer formation. In the case of another polymeric liquid crystal (an azo-siloxane side-chain polymer), the isotherms exhibited somewhat similar steps[4] which were attributed to changes in molecular conformation. In both these cases, the interpretation was based on surface manometry studies.

We studied the surface topography of the bright (D_1, MS and D_2) domains by reflection microscopy. The D_1 domains were visible under reflection indicating that they were thick. Also, not much variation was seen in their colours indicating somewhat uniform thickness. This was also true for the MS structure. On the other hand, the D_3 domains showed varying colours indicating a non-uniformity in thickness. In addition, some D_3 domains exhibited concentric interference rings, indicating a convex lens-like shape.

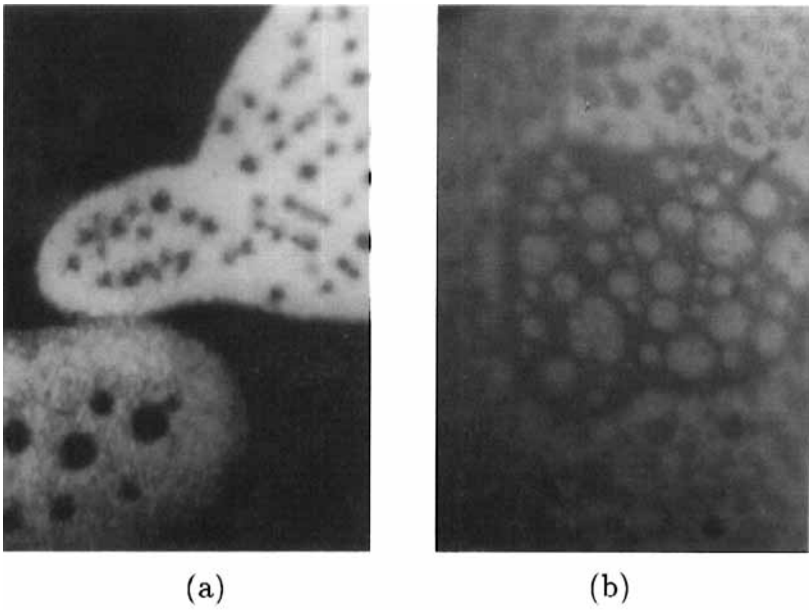

(a) (b)

FIGURE 5 Images of the monolayer at 35°C. (a) Fluorescence image of two irregular shaped domains (750 Å^2 A/M). Scale of the image: 200 μm × 300 μm. (b) Reflection Image of an irregular shaped domain (750 Å^2 A/M), taken with an ordinary still camera. Scale of the image: 200 μm × 300 μm.

In conclusion, the LCP1 monolayer goes into some new structures on compression. The formation of these structures depends strongly on temperature.

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