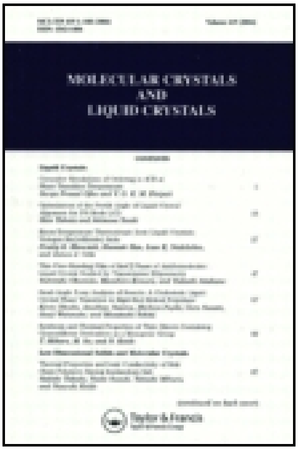

Molecular Crystals and Liquid Crystals

Unusual Features in the Surface Pressure - Area Isotherms in the Langmuir Monolayer of a Siloxane Polymer

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UNUSUAL FEATURES IN THE SURFACE PRESSURE – AREA ISOTHERMS IN THE LANGMUIR MONOLAYER OF A SILOXANE POLYMER

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Here we report some interesting features seen in the surface pressure (π) – area isotherms of the Langmuir monolayer of a liquid crystalline polymer LCP1. Our studies on the compression – expansion hysteresis in the π – area isotherms indicate some unusual features. Usually, in the compression cycle, one obtains a steep increase in π corresponding to the liquid expanded (LE) phase and then a plateau. However, for LCP1, at room temperature, the LE region terminated with an unusual decrease in π. After this there was a plateau and then a rise. The expansion cycle carried out from this point showed a sharp fall in π and then a slight increase, followed by a plateau. This increase was of the order of 0.5 to 0.7 mN/m, much higher than the instrumental resolution. On increasing the temperature, the behaviour of the expansion cycle was somewhat different. Our epifluorescence microscopic studies revealed some new phases. We have correlated the unusual features of the isotherm with the formation of these phases.

INTRODUCTION

It is known that many polymeric materials form stable Langmuir monolayers at the air-water interface [1–5]. However, the monolayer properties of these materials are not well understood. For example Reda *et al.* [1] report some deviations in the behaviour of a poly (L-glutamic acid) monolayer as compared to the monolayer of a small molecule. We have studied the monolayer of a side chain liquid crystalline siloxane polymer. Our studies indicate some surprising features. The surface pressure (π) – Area per Molecule (A_m) isotherms of the polymer monolayer at 25°C, at large A_m exhibited the usual plateau corresponding to the co-existence of the gas and the liquid expanded (LE) phases. On compression, the

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co-existing phases changed to the pure LE phase, which corresponded to a steep rise in π. After this rise, there was an unusual decrease in π. After this there was a large plateau. On further compression, there was an increase in π. At this stage, on expanding the monolayer, there was a sharp decrease in π. Interestingly, after this fall, there was a slight increase in π. This was followed by a plateau. We checked that the increase in π was reproducible and much higher than the instrumental resolution.

From epifluorescence studies, we found that the large plateau in the compression isotherm corresponded to the formation of a structure that resembled small bright spots (BS). On compression, the BS domains joined to form striations, which finally changed to melted stripe (MS) domains [5,6]. These domains co-existed with the LE phase. On expansion, the LE phase changed rapidly to gas phase. After this the MS domains started melting gradually.

For higher temperatures, the behaviour was somewhat different. For example, at 35°C, the compression cycle was similar to that at lower temperatures, but on expansion there was a sharp drop in π, followed by a plateau. There was no subsequent increase in π after the drop, as seen at lower temperatures. Under epifluorescence, we saw the appearance of BS domains on compressing the LE phase, which changed to irregular shaped (IS) domains instead of the MS domains.

EXPERIMENTAL

The experiments were carried out on a siloxane polymer of 1-methyl propyl 4 (4′-hexyloxy benzoyloxy) benzoate (LCP1), with a degree of polymerisation n $\approx$ 40. The molecular structure is shown in Figure 1. The material was obtained from Merck and used as received. The experiments were carried out in a Teflon trough of size 35 cm × 10 cm. The trough was cleaned by leaving it overnight with chromo-sulfuric acid and rinsed repeatedly with Millipore-Milli Q water (pH 2, resistivity greater than 18 mΩm). It was considered properly clean when Millipore water completely dewetted the surface on emptying. The trough was heating using a built in nichrome heater and the temperature measured by a platinum resistance thermometer. The whole setup was enclosed in a box to eliminate contami-

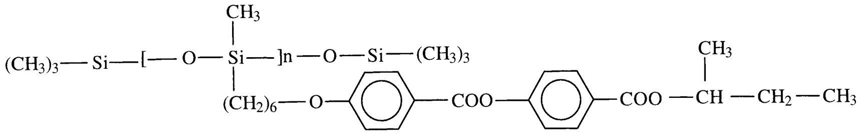

FIGURE 1 Molecular structure of the polymer LCP1.

nation and air currents. The monolayer was formed by depositing 25 μL of dilute (milli-molar) LCP1 solution (in chloroform) using a micro-syringe on Millipore Milli Q water in the trough. The monolayer was allowed to stabilise for at least 15 minutes. The monolayer was compressed by a Teflon barrier moved by a computer controlled DC motor. The experiments were also repeated with a stabilising time of 1 hour.

Surface pressure was measured by Wilhelmy plate technique using a platinum blade attached to a Nima tensiometer. The instrument was capable of measuring π to accuracy better than ± 0.1 milli Newton/m (mN/m). The hysteresis curves were studied by compressing and then expanding the monolayer at the same rate after an interval of 1 minute.

For epifluorescence studies, we doped the monolayer with 1% of a dye 4-(hexadecyl amino)-7-nitrobenz-2 oxa-1,3 diazole (Molecular Probes, USA). The monolayer was directly observed under the microscope (Leitz, Metallux 3). We used a reflection mode adapter on the same microscope for reflection studies to probe the surface topography of the thick domains. These techniques are described in details elsewhere [5].

RESULTS

The π – Am isotherms for the LCP1 monolayer at 25°C are shown in Figure 2 for three different compression rates. The isotherms did not depend on the stabilising time elapsed between the spreading of the monolayer and the starting of the experiment, indicating that LCP1 did not dissolve in water. The compression cycle of the isotherms showed a plateau for A_m greater than 1000 Å^2. On compression, there was a steep rise in π. This was followed by a slight decrease at 750 $\text{Å}^2 A_m$ and a plateau, after which there was another rise at 200 $\text{Å}^2 A_m$. The decrease in π (indicated by a downward pointing arrow in Figure 2) was greater than the instrumental resolution. It was more pronounced for slow compression, as can be seen in Figure 2(c). The expansion cycle showed a sharp drop in π at 180 Å^2 A_m and then a slight increase (indicated by an upward pointing arrow). This increase was of the order of 0.5 to 0.7 mN/m, much higher than the instrumental resolution of 0.1 mN/m. We confirmed by repeated experiments that this feature was reproducible and occurred at the same value of A_m. This increase was followed by a plateau. The value of π dropped to much lower values for fast compression, as shown in Figure 2(a), and the subsequent rise was more pronounced.

From epifluorescence microscopic studies, we found that the plateau at A_m greater than 1000 Å^2 corresponded to the usual gas – LE co-existence region. The region with the steep rise in π around 900 Å^2 A_m corresponded to the LE phase. After this, we found a new structure that appeared like

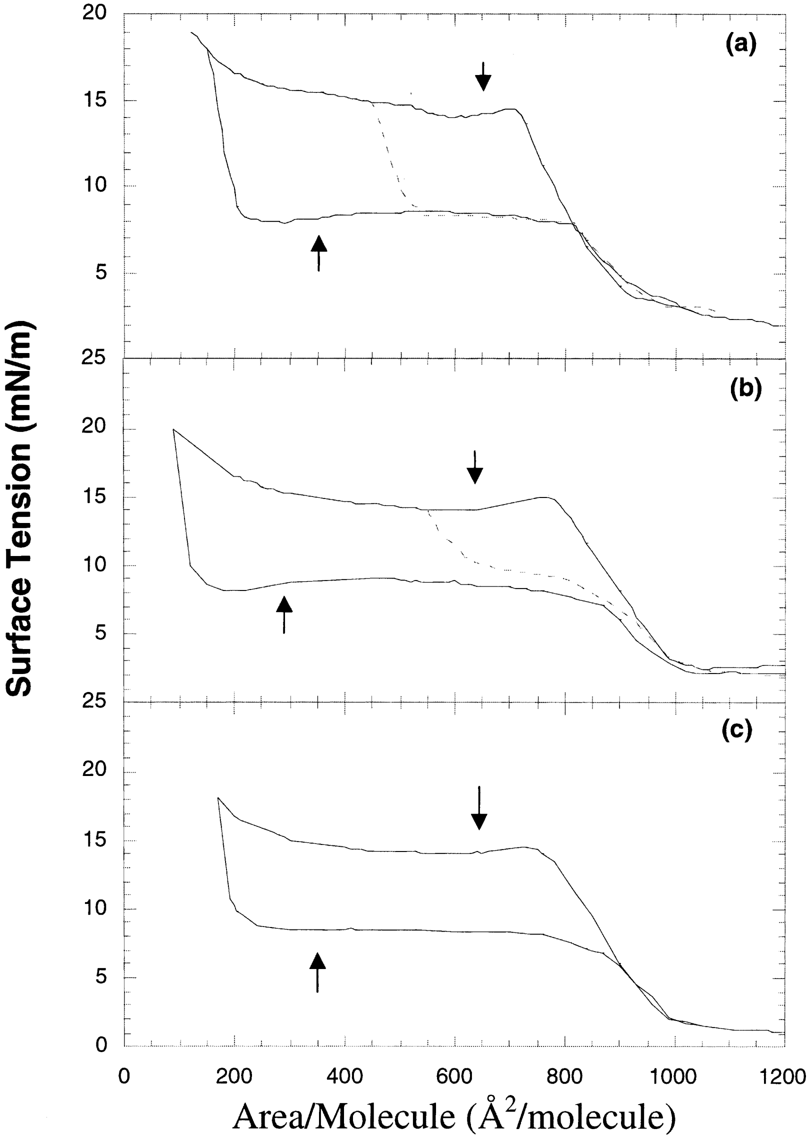

FIGURE 2 Surface pressure (π) – Area per molecule (A_m) isotherms for the LCP1 monolayer at 25°C for different compression/expansion rates. (a) 9 Å^2/molecule/second, (b) 6 Å^2/molecule/second and (c) 4.5 Å^2/molecule/second. The dashed lines indicate expansion from within the LE – BS co-existence region. The downward pointing arrow indicates the decrease in π in the compression cycle and the upward arrow indicates the decrease in π in the expansion cycle.

bright spots (BS). This corresponded to the decrease in π around 750 Å^2 A_m. The BS domains co-existed with the LE phase and their number increased on further compression. This corresponded to the large plateau between 600 and 300 Å^2 A_m. On stopping the compression at this point, π decreased slowly and stabilised at 8 mN/m. Around 300 Å^2 A_m, the BS domains started combining to form striations which ultimately changed to a melted stripe (MS) structure around 200 Å^2 A_m, as depicted in Figure 3(a). The rise in π at 200 Å^2 A_m corresponded to the formation of the MS structure. These domains co-existed with the LE phase and the striations. The striations and the MS domains were visible under reflection, indicating a thickness of at least a fraction of a micrometre (μm) [7]. They showed somewhat uniform colours, indicating uniform thickness.

On expanding from this point, the LE phase alone rapidly changed to the gas phase. This corresponded to the sharp decrease in π around 180 Å^2 A_m. On further expansion, after the LE phase changed to the gas phase, the MS domains started melting very slowly into a foamlike structure [Fig. 3(b)]. Interestingly, an unusual increase in π was observed at this point. On expanding the monolayer from a point within the LE – BS co-existence plateau (600–300 Å^2 A_m), there was a sudden decrease in π, but no subsequent increase. This is shown in Figure 2 (a) and (b) as dashed curves. Under the epifluorescence microscope, it appeared that the BS domains melted faster than the MS domains. On expanding from a point with A_m greater than 800 Å^2 *i.e.* before the plateau is reached, there was no hysteresis.

On heating, the behaviour of the monolayer changed to some extent. We report our studies carried out at 35°C. The $\pi - A_m$ isotherm is shown in Figure 4. The compression cycle was similar to that for 25°C except that the decrease in π at 750 Å^2 A_m after the steep rise was smaller and independent of the compression rate. The expansion cycle showed a sharp decrease in π at 350 Å^2 A_m, followed by a gradual decrease. Unlike at 25°C, there was no rise in the value of π after the sharp drop, even for fast compression rates.

Under the epifluorescence microscope, the structures obtained at 35°C were different. Here again the BS domains appeared on compressing the monolayer in the LE phase. On further compression, the BS domains grew in size to form large irregular shaped (IS) domains, instead of increasing in number as seen at 25°C. This corresponded to the plateau for A_m between 800 and 300 Å^2. The IS domains co-existed with the LE phase. Under reflection microscope, the IS domains showed patches of different colours, indicating non-uniformity in thickness [7]. The IS domains are shown in Figure 5. On expansion, the LE phase changed into gas phase. This corresponded to the fall in π at 300 Å^2 A_m. On further expansion, the IS domains started melting till they turned into the BS domains that were seen earlier. After this the BS domains gradually changed to the gas phase.

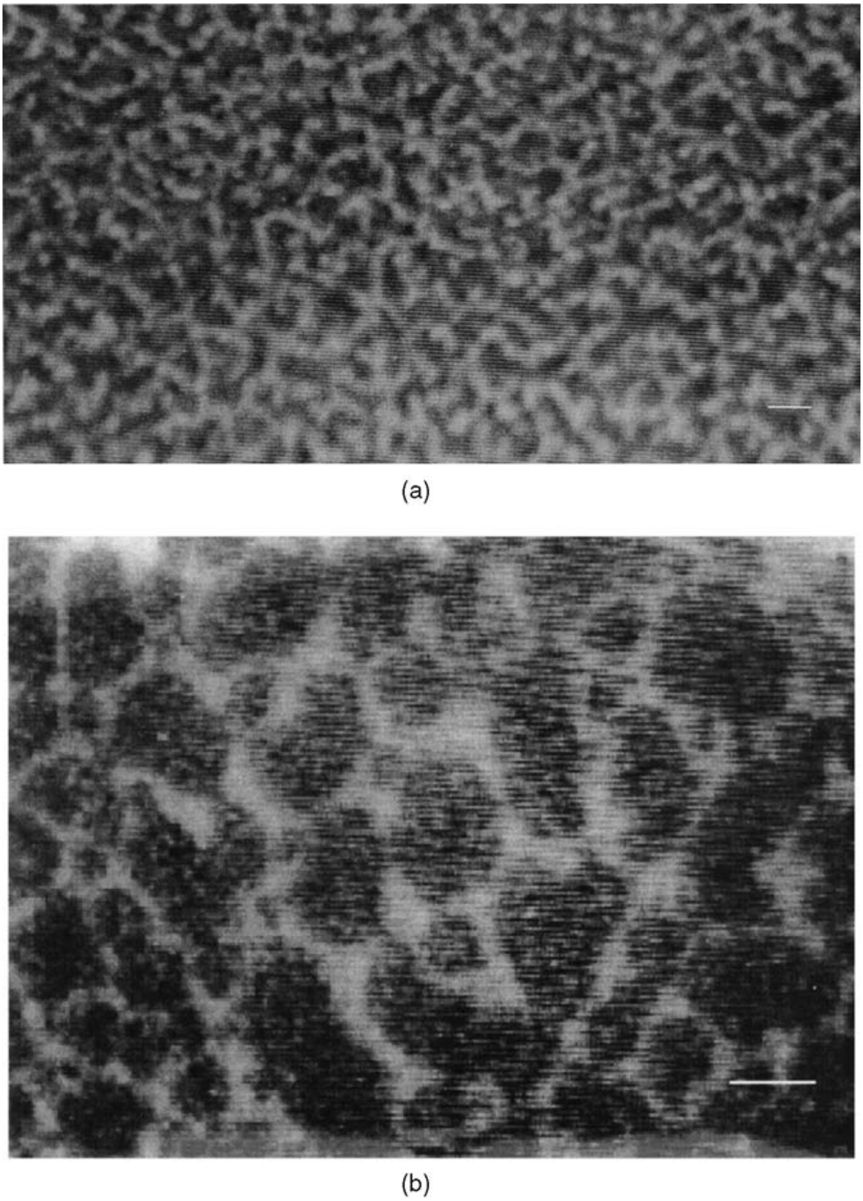

FIGURE 3 Epifluorescence images of LCP1 monolayer at 25°C. (a) Melted stripe domains at 200 Å^2 A_m. (b) Foam structure obtained on expanding the MS domains to 500 Å^2 A_m. The white line represents 50 µm.

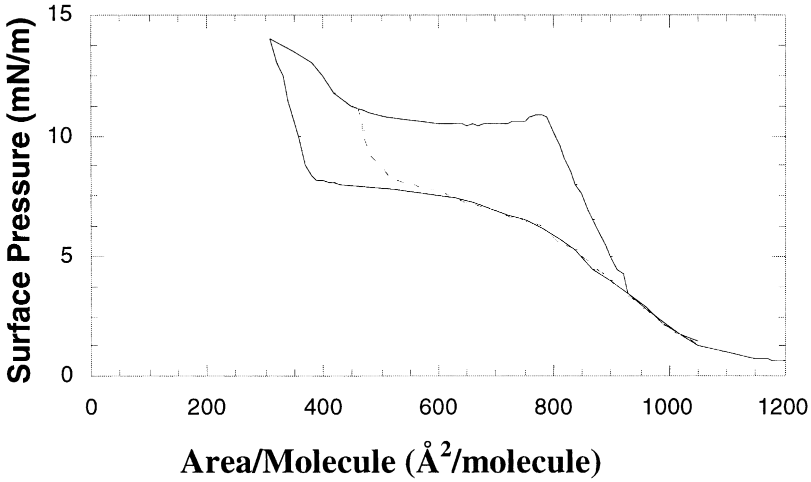

FIGURE 4 The $\pi - A_m$ isotherms for the LCP1 monolayer at 35°C at a compression rate of 6 Å^2/molecule/second.

We also studied the structural changes with change in temperature. We found that the MS domains changed gradually to the IS domains on heating to 35°C. This transition was not sharp and occurred in the range of about

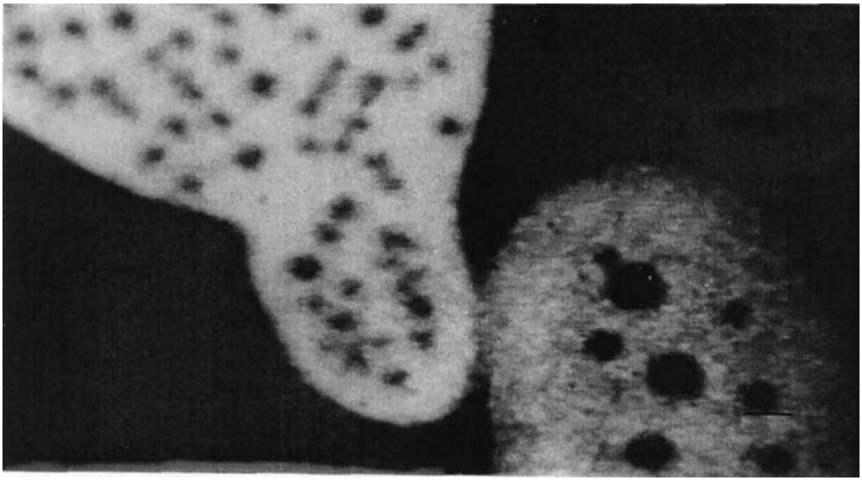

FIGURE 5 Reflection image of irregular shaped domains of LCP1 monolayer at 35°C and 500 Å^2 A_m. The different shades indicate that the domains are of different thicknesses. The white line represents 50 μm.

28–32°C. The reverse transition occurred on cooling. These transitions were slow and took a few hours to complete.

DISCUSSIONS

An interesting result from our studies is the decrease in π in the compression cycle of the isotherm. We suggest that the formation of the BS domains required a threshold value of surface molecular density. Once the nucleation started, the growth continued on its own. As a result there was a depletion of molecules in the LE phase and the π value dropped. In the literature, we do not find a report of such a decrease in π in a polymer monolayer. However, such a decrease has been reported [8] for a monolayer of NBD-stearic acid. There is also a similar dependence on compression rate. The authors attribute this behaviour to a nucleation barrier in the formation of the condensed phase.

The LCP1 monolayer exhibits prominent compression – expansion hysteresis. Hysteresis has been reported in some other polymers [1–4]. Chen *et al.* [2] suggest that on compressing the monolayer, the side chains of the polymer tilt away from the water and pack tightly to form dense crystallites. On expanding, these crystallites tend to remain as islands, without contributing to the surface molecular density. The authors attribute this to the sharp decrease in π. On the other hand, Reda *et al.* [1] observe the formation of thick domains on compressing the monolayer of a polymer. These domains melt very slowly on expansion, resulting in a depletion of molecules in the monolayer. This is attributed to the sharp decrease in π on expansion. Our epifluorescence results show that the LE phase changes to gas phase on expansion. This indicates that the slow melting of the thicker domains like BS, MS and IS is not comparable to the rate of compression. This results in a depletion of molecules in the monolayer and gives rise to the decrease in π. The process is very similar to that reported by Reda *et al.* [1]. The hysteresis indicates that the high density phases BS, MS and IS are more stable compared to the LE phase.

A very interesting result, which is not reported in the literature to our knowledge, is the increase in π on expanding the monolayer. This increase occurred only if MS domains were present in the monolayer. We attribute this effect to a delayed melting of the MS domains. We observed that for faster expansion, π dropped to even lower values and the subsequent rise was more pronounced. For fast expansion, there was a longer time delay between the LE – gas transition and the melting of the MS domains. This lead to a sharper decrease in π. After this, when the MS domains started melting, more molecules were released to the interface, which contributed to the increase in π.

Another observation is that of a gradual transition between the MS and IS structures on changing the temperature. Seul and Sammon [6] have reported a similar transition on compressing a phospholipid – cholesterol mixed monolayer. They attribute it to branching instabilities in the monolayer.

Hysteresis has also been reported for the monolayers of some small molecules, for example in NBD—stearic acid [8] monolayer. The authors also determine the equilibrium curve by stopping the compression at different values of A_m and allowing π to equilibrate. The equilibrium curve does not show hysteresis. This indicates that hysteresis is a non-equilibrium phenomenon. Diep-Quang and Uberreiter [9] report some hysteresis in the compression – expansion cycles of the monolayer of a compound which resembles the side chain of LCP1. They attribute the hysteresis to relaxation effects and multilayer formation.

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