Chapter 5

UNUSUAL FEATURES OF THE SURFACE PRESSURE ISOTHERMS OF A POLYMER MONOLAYER

5.1   Introduction

So far we considered the monolayers of amphiphilic molecules of low molecular weight (monomers) which exhibit liquid crystallinity in bulk. It is natural to next study monolayers of polymeric mesogens which are amphiphilic in nature. Katz and Samuel [1] were the first to study the monolayers of synthetic polymers, namely poly vinyl acetate and poly methyl acrelate. In recent times, there has been a lot of work on Langmuir monolayers and LB films of polymers [2, 3]. This interest is partly due to the increased mechanical and thermal stability provided by the LB films of polymers.

The structural requirements for monolayer formation appear to be less stringent for polymers and a wide range of materials have been studied [3]. To form a stable monolayer, it is important that the polymer have a main chain with hydrophilic groups distributed regularly at short intervals. The hydrophobic tail groups of the polymer influence the monolayer properties. However, unlike in the case of monomers, the formation of a monolayer does not depend crucially on the structure of the tail groups. For example, polymers with small hydrophobic tail groups can form insoluble monolayers, due to the inherent insolubility of
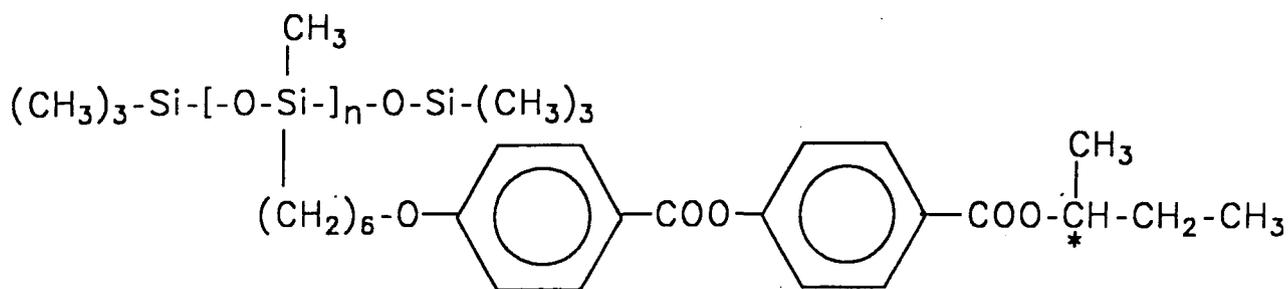
Figure 5.1 The molecular structure of the polymer LCP1. Degree of polymerisation n ∼ 40.

polymers.

The study of monolayers of polymeric liquid crystals has gained a lot of importance in recent times [3, 4]. The study of polypeptides at interfaces is useful in view of medical implications *e.g.* the importance of salmon calcitonin in the treatment of osteopathies [5] or the understanding of the role of the protein SP − B in the functioning of lung surfactant [6].

In this Chapter we describe our studies on the monolayer of a liquid crystal side chain siloxane polymer. The material chosen was a side chain siloxane polymer of 1 - methyl propyl 4 (4′ - hexyloxy benzoyloxy) benzoate with a degree of polymerisation n ∼ 40 (LCP1). The molecular structure of the compound is shown in Fig 5.1. In bulk, it shows the following phase sequence.

$$Glass \xrightarrow{7.2°C} Smectic\ C \xrightarrow{72°C} Isotropic.$$

We investigated the LCP1 monolayer using surface manometry, fluorescence and reflection microscopy. We also studied the compression expansion hysteresis of the monolayer.

5.2 **Experimental Techniques**

To study the monolayer of the polymer, we employed the techniques of surface manometry, fluorescence and reflection microscopy. The $\pi - A$, isotherms were plotted using the same setup, already described in Chapter 2. For our fluorescence studies, we used around 2% molar concentration of the dye NBD HDA. The higher concentration of the dye was chosen to compensate for the very large size of the LCPl molecules, as could be seen from the A, values in the isotherms. The surface topography of the multilayer domains formed on compressing the monolayer were investigated using reflection microscopy. The photographs in reflection microscopy were taken using a still camera as the film was sufficiently stiff. The film was immobile in the range of tens of seconds.

The spreading solution was made in chloroform. The solution was allowed to remain for about 30 minutes to make sure that the entire quantity of LCPl dissolved in it. This was necessary since LCPl did not dissolve in chloroform as rapidly as the other samples. The solution was added dropwise on the water surface using a microsyringe. The monolayer was allowed to stabilise for about 15 minutes.

To obtain the hysteresis curves, the monolayer was compressed to the desired point. It was kept in this condition for one minute and then it was expanded. The compression and expansion rates were always kept the same.

5.3 Results

The $\pi - A$, curves obtained from surface manometry are shown in Figs 5.2 and 5.3. Unlike for the monolayers described earlier, the compression and expansion curves for LCPl were very different, suggesting a strong hysteresis. As can be seen in Fig 5.2, the curves at 25°C depended on the compression rate. The isotherms were independent of the time elapsed between the spreading of the monolayer and the starting of the experiment. The compression curve showed
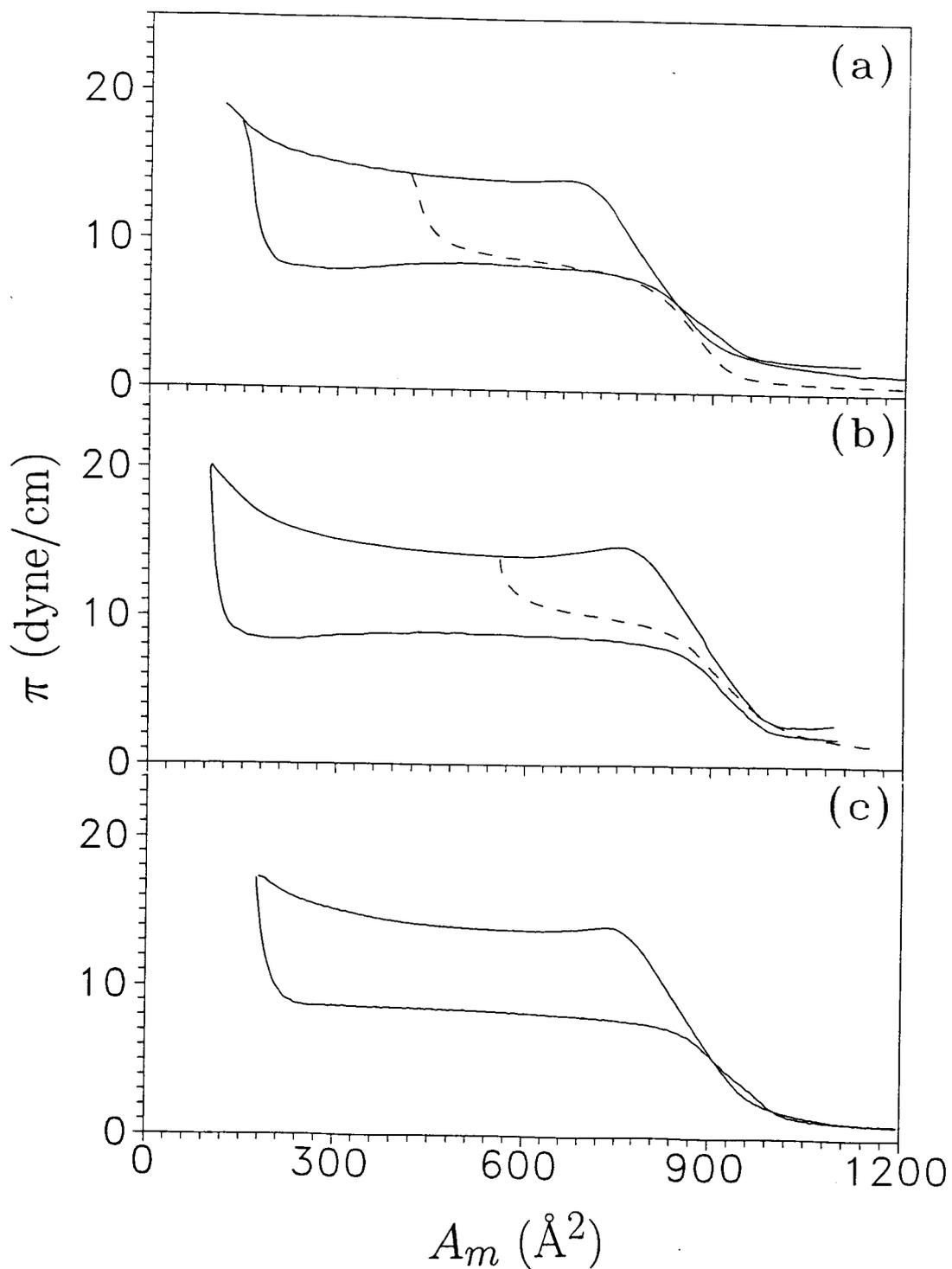
Figure 5.2 Compression expansion isotherms for the LCP1 monolayer at 25°C for different compression rates. (a) 9 A^2/molecule/second, (b) 6A^2/molecule/second, (c) 4.5A^2/molecule/second. The dashed lines indicate expansion cycle from within the LE – BS co-existence region.
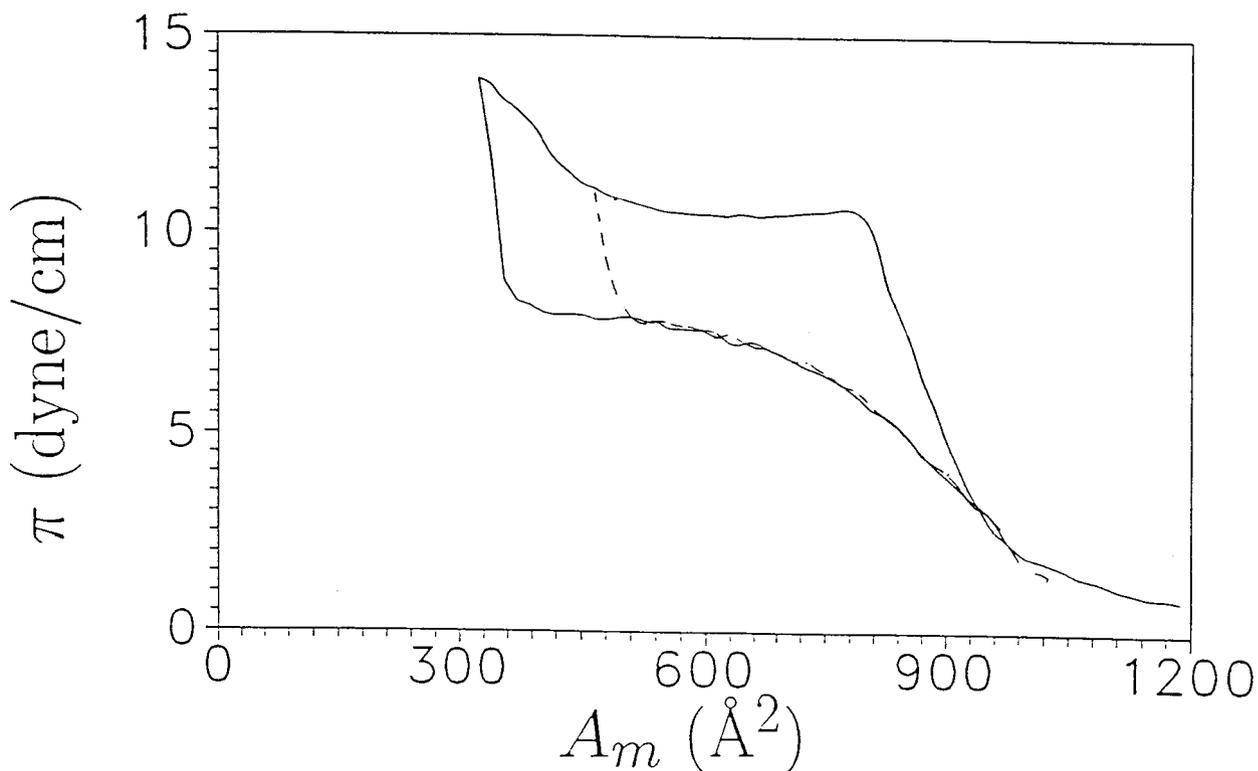
Figure 5.3 Compression expansion isotherm for LCP1 monolayer at 35°C. The compression rate is 6 Å²/molecule/second. The dashed curve indicates the expansion plot from within the LE – BS co-existence region.

steeply increasing regions, separated by plateaus. Also, at the starting point of the large plateau $(A, \sim 750$ Å²$)$ there was a decrease in π. The extent of this decrease depended on the compression rate and was more for slow compression. The expansion cycle from the final plateau showed a sharp fall in π. This was followed by an increase in π, in the range 0.5 to 0.7 dyne/cm. The resolution of our instrument was $\pm$ 0.1 dyne/cm. After this there was a large plateau. The expansion cycle almost retraced the compression cycle beyond this plateau. The magnitude of the rise after the first drop was dependent on the expansion rate, and ranged between 0.5 and 0.7 dyne/cm, which was larger than the instrumental resolution of 0.1 dyne/cm. For faster expansion, π dropped to even lower values and the subsequent rise was larger.

If the monolayer were expanded from within the large plateau, as shown in Fig 5.2, (b and c, dashed curves), there was a sharp drop in π. This drop was followed by a plateau. There was no subsequent increase in π. The drop in the isotherm here was comparatively less sharp than what is described earlier.

The hysteresis curve for 35°C is shown in Fig 5.3. Here again the compression
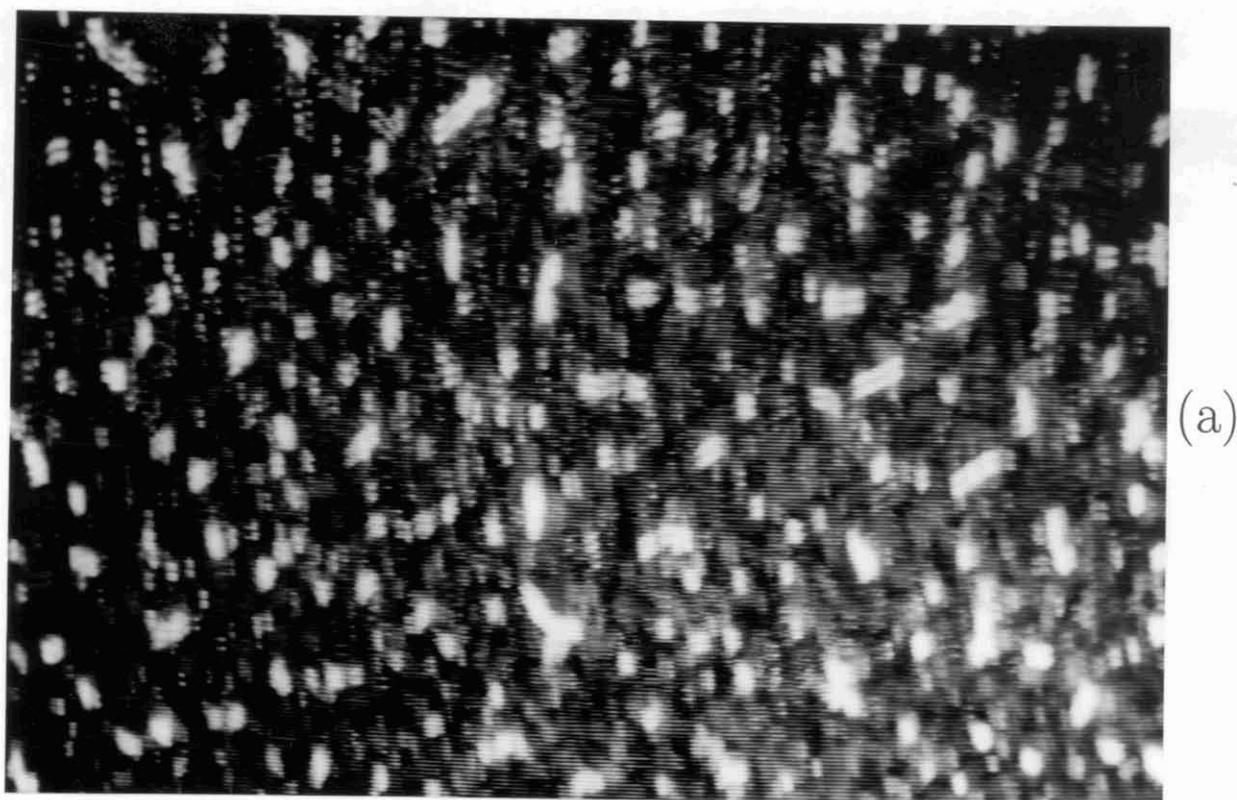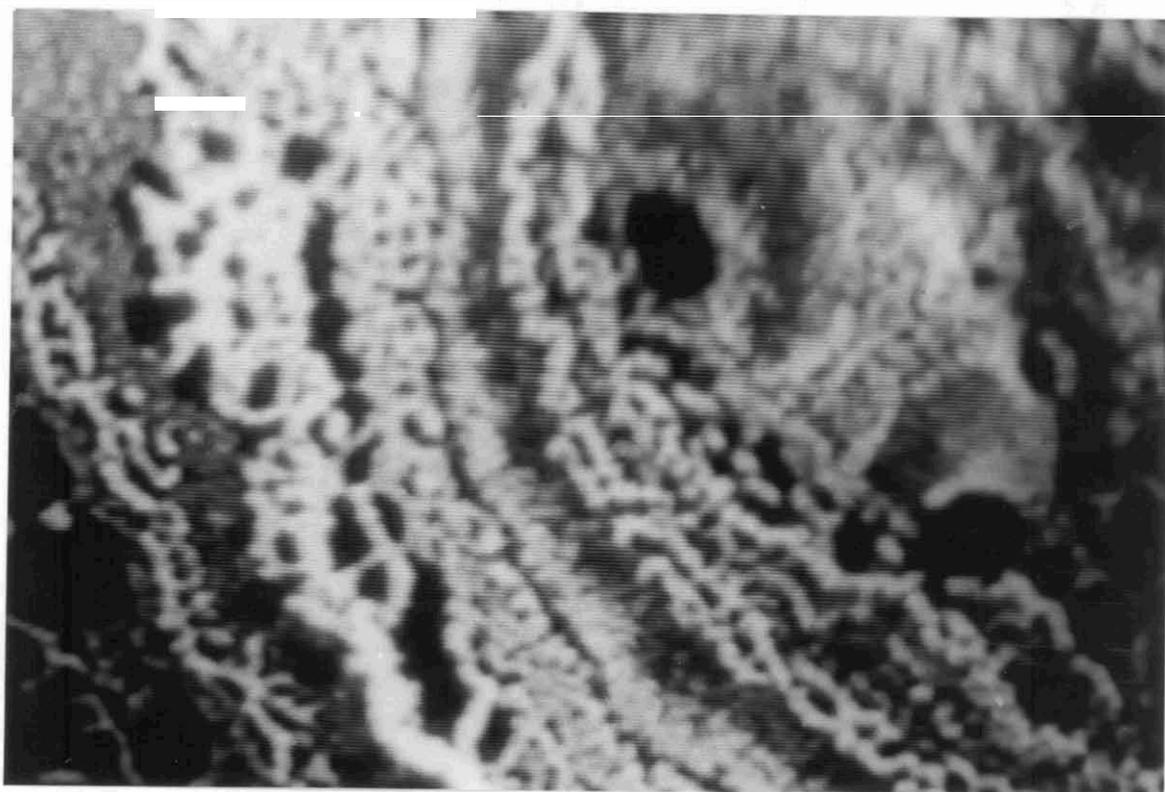
Figure 5.4 Fluorescence images of LCP1 monolayer at 25°C. **(a)** Bright spot (BS) domains co-existing with the LE phase at 700 $Å^2 A_m$, and (b) The BS domains joining together to form striations at 300 $Å^2 A_m$. Scale of the images: $300 \mu m$ x $200 \mu m$.

cycle exhibited three regions with steeply increasing π, which were interspaced by plateaus. The expansion cycle showed a sharp decrease in π, which was followed by a plateau. The drop in π was not as sharp as at 25°C, also there was no subsequent increase in π. The entire isotherm at 35°C was independent of compression or expansion rate.

From fluorescence microscopy we found that the large plateau for $A > 1000$ Å^2 corresponded to the usual gas and LE co-existence region. The contrast between gas and LE phases was very poor. This could be due to the fact that the structure of NBD HDA did not match that of LCP1. Hence it did not dissolve readily in the monolayer. It might also be due to the presence of very small number of NBD-HDA molecules in the field of view, due to the large size of the LCP1 molecules. This can be seen from the values of A (1000 Å^2) corresponding to the rise in π. The gas phase disappeared at 1000 Å^2 A, and the whole field of view became uniformly bright, indicating the onset of the LE phase. The LE phase corresponded to the region with steeply increasing π in the isotherm. On further compression, very small bright domains, looking like bright spots (BS) started appearing around 800Å^2 A, as seen in Fig 5.4(a). The appearance of these domains was marked by a decrease in π. As the compression continued, more and more BS domains appeared, but they did not grow in size. The large plateau in the isotherm (800 - 350 Å^2 A,) corresponded to the co-existence of BS domains with the LE phase. Around 300Å^2 the BS domains started coalescing to form striations, shown in Fig 5.4 (b). The striations ultimately changed to a melted stripe (MS) structure, as seen in Fig 5.5. This change corresponded to the final rise in the isotherm. The BS and MS domains always co-existed with the LE phase.

The striations, BS and MS domains were visible under reflection. This indicates that their thickness was at least a fraction of 1μm, as implied by Equation 2.5, Chapter 2. The thickness of the BS domains was uniform, as we did not see much variation in their colours. This was also true for the MS domains and the striations.
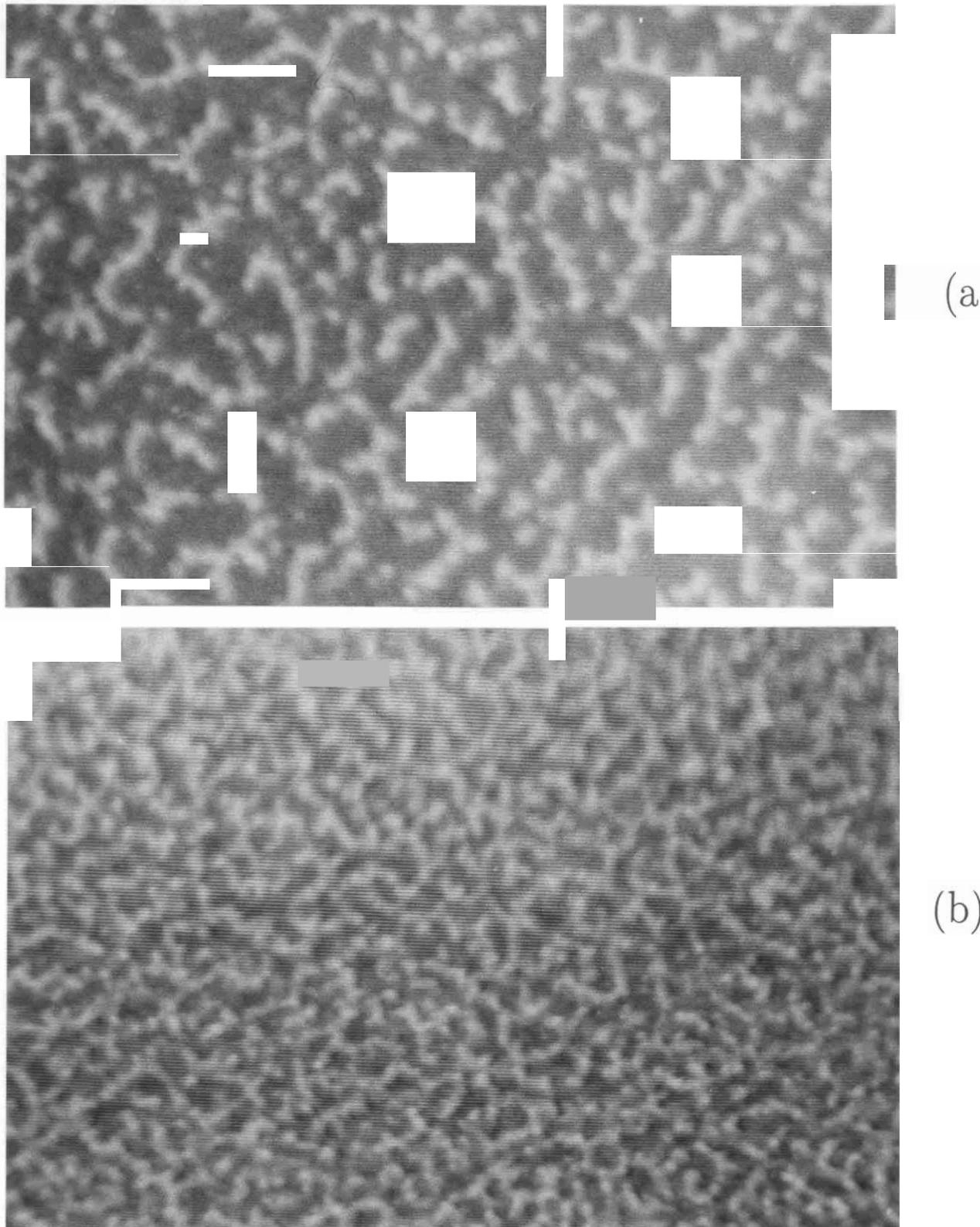
Figure 5.5 (a) Fluorescence image of melted stripe (MS) domain in the LCP1 monolayer at $25°C$, 250 $Å^2 A_m$. (b) The MS domain on compressing to 200 $Å^2 A_m$. Scale of the images: 300 μm x 200 pm.

On expanding the monolayer from this point, the LE phase in co-existence with the MS domains changed to gas phase. The monolayer become somewhat more mobile at this stage. This corresponded to the sharp drop in π in the isotherm (see Fig 5.2). On further expansion, after the entire LE phase had transformed to the gas phase, the MS domains started melting into a foamlike structure, as depicted in Fig 5.6. Interestingly, at this point there was an unusual increase in n. For faster compressions, π dropped to lower values and the subsequent increase was more pronounced. On further expansion, the foam structure broke up to give a structure that resembled bright wormlike domains in the dark background of the gas phase. These domains were very bright and were distributed all over the monolayer. After this, the domains started shrinking in size till they changed to the BS domains seen earlier. On further expansion, the BS domains started reducing in number.

If the monolayer were expanded from the LE – BS co-existence region, there was a sharp drop in π, but no subsequent increase (see Fig 5.2, dashed curves). Under the fluorescence microscope, we found that the LE phase in co-existence with the BS domains transformed to the gas phase. After this, the BS domains kept decreasing in number and the field of view showed more and more of the gas phase. It appeared that the BS domains melted faster than the MS domains.

If the monolayer were expanded from a point before the onset of the LE - BS co-existence region, there was no hysteresis. The expansion cycle of the isotherm retraced the compression cycle. Here, we saw the LE phase change to the gas phase.

The behaviour of the monolayer at higher temperatures was different. At 35°C, there was the gas – LE co-existence, with a somewhat better contrast. The gas phase disappeared at $A, \sim 1000\text{Å}^2$, giving an all LE monolayer. This corresponded to the sharply increasing region of the isotherm. On compressing from here, the BS domains appeared. This was accompanied by a slight decrease in n in the isotherm. This decrease was independent of the compression rate. Unlike at 25°C, here the BS domains started growing in size on compression,
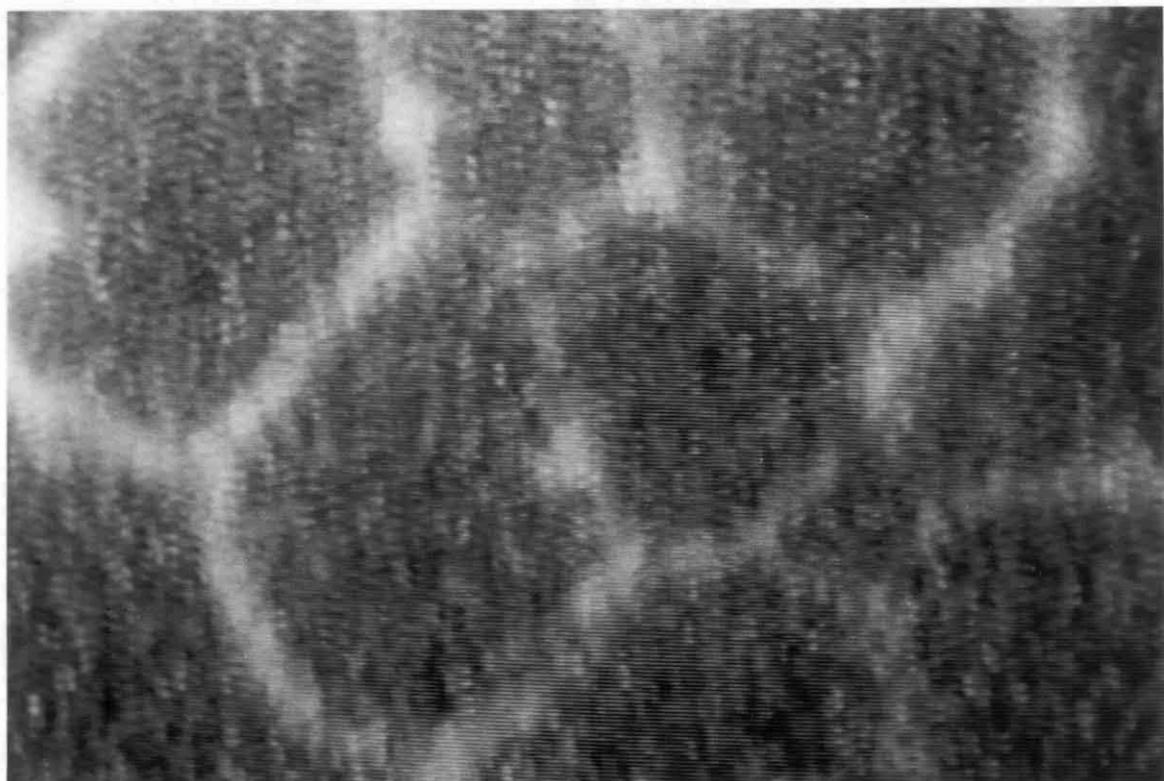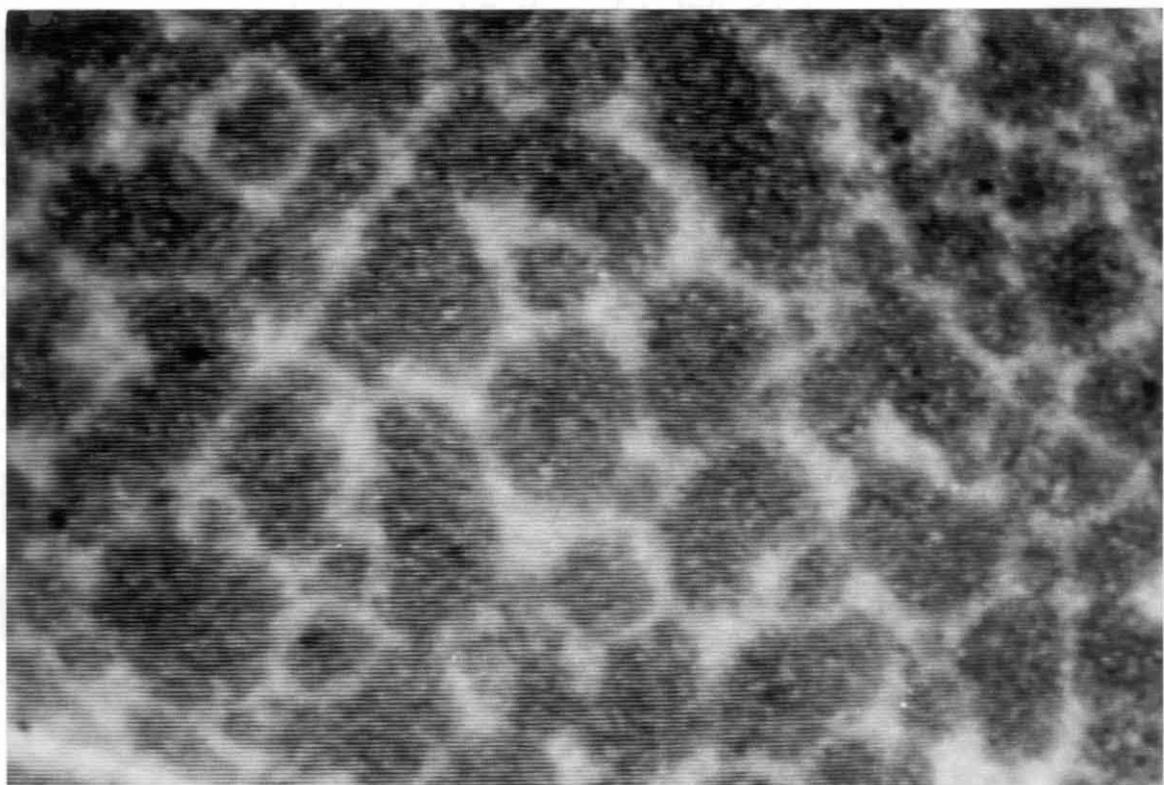
Figure 5.6 (a) Fluorescence images of foam structure obtained on expanding the monolayer from the region corresponding to the MS domains to 600 $\mathring{A}^2 A_m$. (b) Another image of the foam structure, at 500 $\mathring{A}^2 A_m$. Scale of the images: 300 μm x 200 pm.
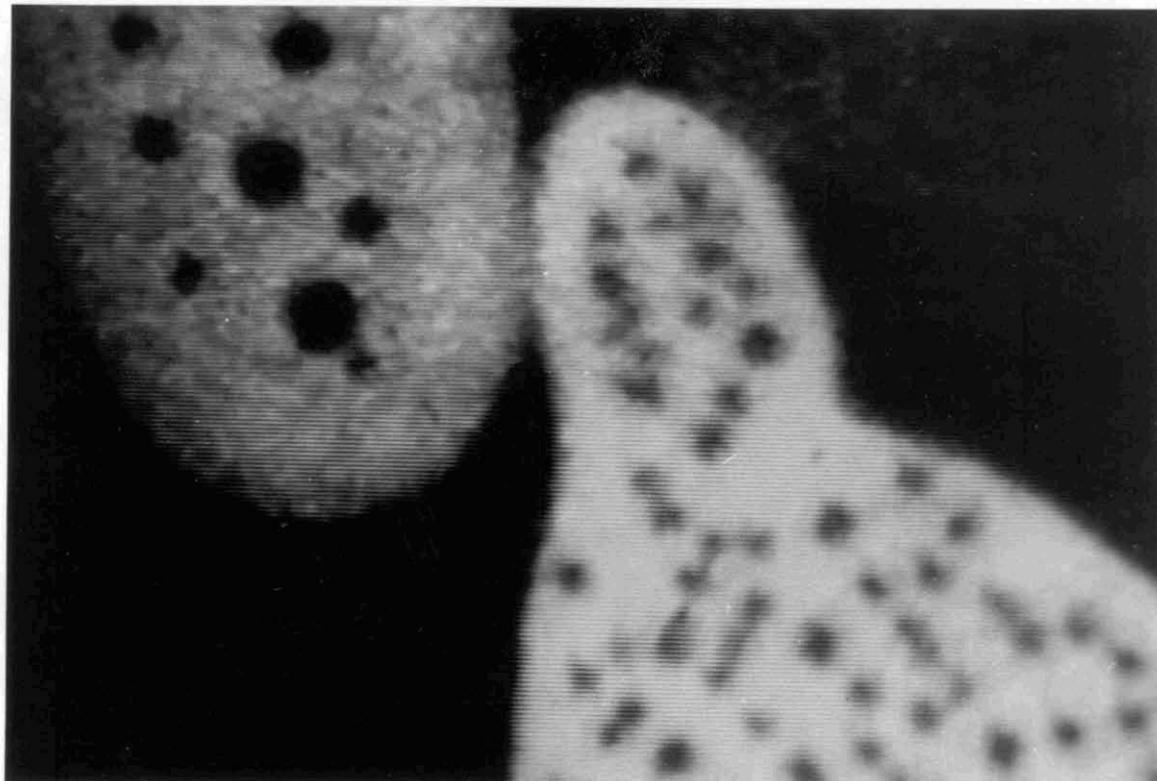
Figure 5.7 Fluorescence image of irregular shaped (IS) domains formed at 35°C at 400 $\text{Å}^2 A_m$. The dark background is the LE phase. Scale of the image: 300μm $\times$ 200 μm.

ultimately $(A, \sim 450\text{Å}^2)$ giving rise to very large bright irregular shaped domains (IS) (Fig 5.7). The IS domains were seen in co-existence with the LE phase. The IS domains were visible under reflection (Fig 5.8), indicating a thickness of at least a fraction of a micron. The domains showed patches of different colours which suggests non-uniform thicknesses.

The expansion cycle at 35°C exhibited a drop in **a**, followed by a plateau. The drop was not as sharp as at 25°C. Also, there was no subsequent rise in **a.** Under fluorescence, we observed the LE phase co-existing with the IS domains change to gas phase. This corresponded to the fall in **a.** After this the IS domains started melting till they turned into BS domains. The melting of the IS domains seemed to be faster than that of the MS domains. On further expansion, the BS domains started decreasing in number and there was more gas phase in the field of view.

On expanding the monolayer from the LE – BS co-existence region, the LE phase changed to gas. This corresponded to the decrease in a (Fig 5.3, dashed curve). After this the BS domains started decreasing in number.
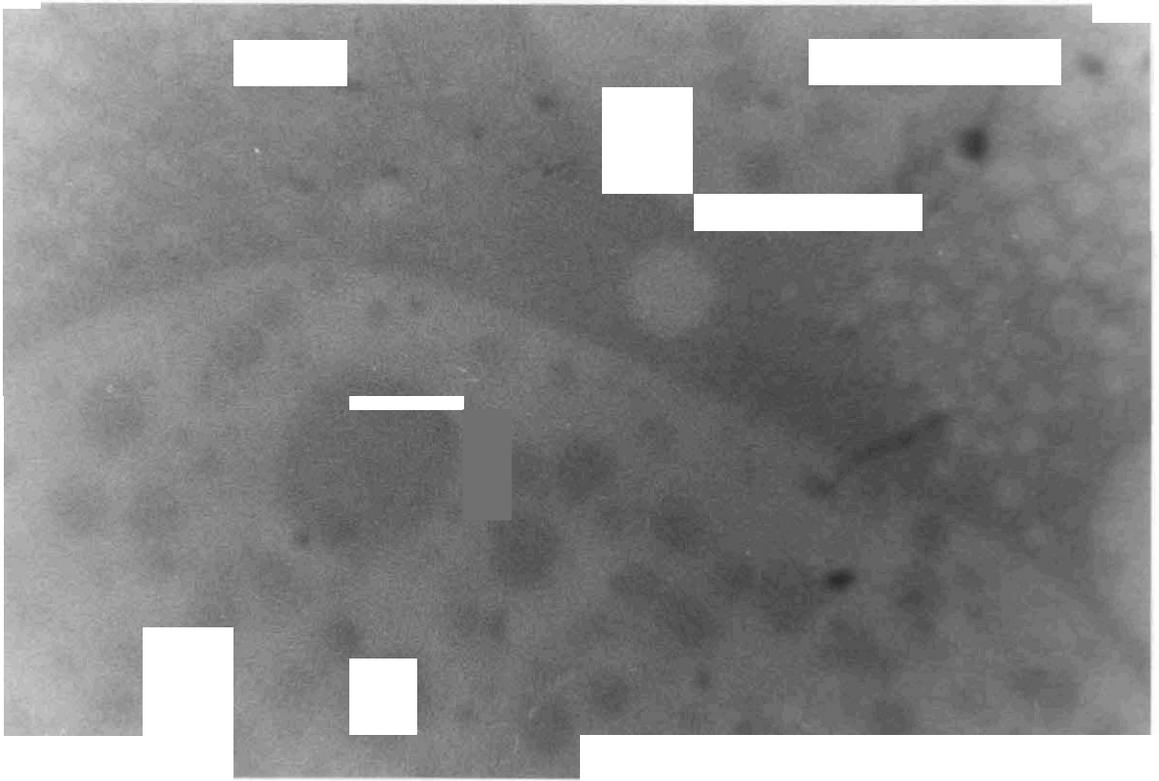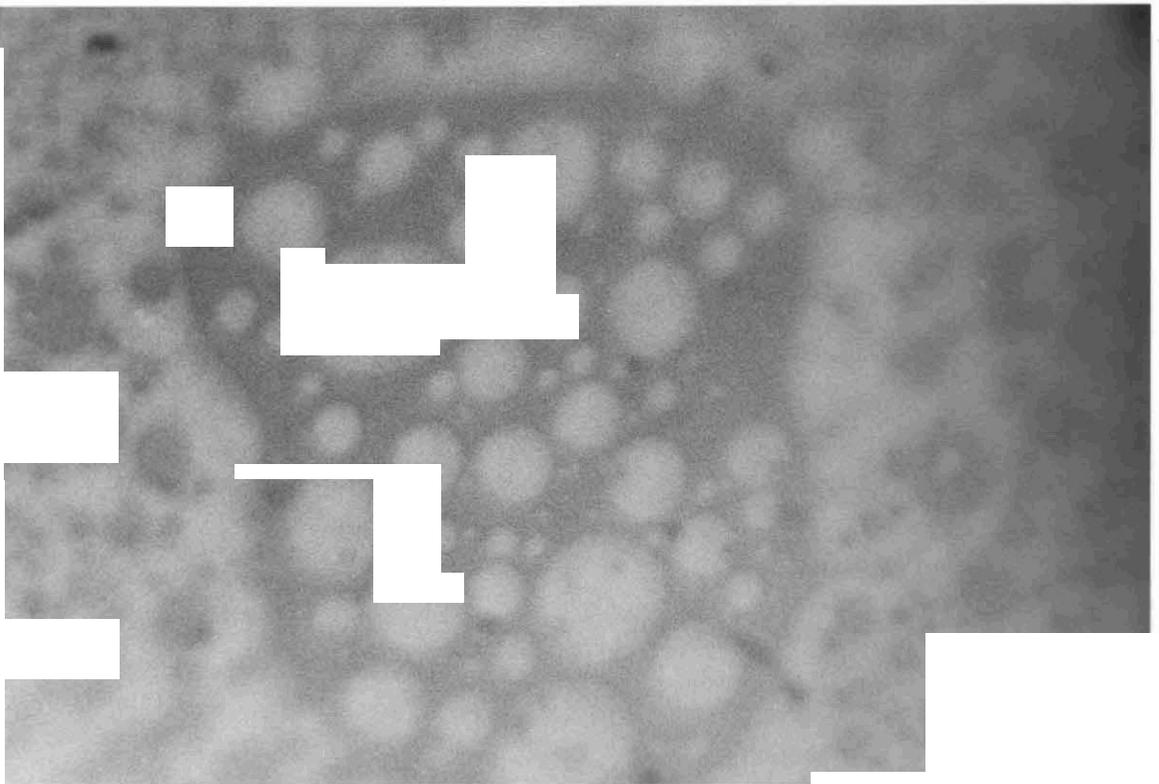
Figure 5.8 Reflection images of IS domains at $35°C$, 450 $Å^2 A_m$. (a) The bright domains are the IS domains, while the dark background is the LE phase. (b) **A** similar image. Scale of the images: 300 μm × 200 pm.

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On expanding from a point before the LE – BS co-existence region, there was no hysteresis. Here, the LE phase changed to the gas phase.

The IS domains transformed into MS domains slowly on cooling to 25°C. The reverse transition from MS to IS occurred on heating to 35°C. These transitions were very slow and took a very long time ($\sim$ 1 to 2 hours) to complete.

5.4   Discussions

Our studies show a very pronounced hysteresis in the compression – expansion cycles of the isotherm. On expanding the monolayer in the MS – LE co-existence region, there is a very sharp drop in π. There is a drop even on expanding from the LE – BS co-existence region, but this drop is not so sharp. Under the fluorescence microscope, we see that this drop in π corresponds to the co-existing LE phase transforming to the gas phase. The gas phase is identified by the fact that the monolayer'becomes more mobile after the transition. This indicates a greater stability of the high density phases like BS, MS or IS compared to the low density LE phase. Hysteresis occurs for the monolayers of some other polymers [5, 6, 7, 8, 9] and some smaller molecules [10, 11].

Hysteresis has been reported for the monolayer of the compound resembling one side chain of LCP1 [10], though it is less prominent. The authors attribute the hysteresis to *(a)* loss of monolayer film substance by crystallisation at low temperature and (b) a relaxation effect at higher temperatures.

Reda *et.al.* [8] report a similar hysteresis in a polymer monolayer. Using Brewster angle microscopy, they observe the formation of thick domains on compressing the monolayer. On expanding, these domains rupture in the direction of the moving barrier. This suggests that the thick domains are energetically stable and do not melt on expansion. This leads to a depletion of molecules at the interface which causes the decrease in π. Our observation of the LE phase transforming to the gas phase supports this explanation.

Alternatively, it is suggested [9] that on spreading the monolayer, the molecules

spread uniformly with the polymer backbones at the interface and the side chains tilted towards the air. On compressing, the side chains tilt further away from the water and aggregate to form crystallites. The crystallites remain as such on expanding and do not spread again. This reduces the number of molecules in the monolayer, causing a drop in π.

Bercegol *et. al.* [11] report hysteresis in the isotherms of NBD - stearic acid. They also determine the equilibrium curve, by stopping compression at different values of A, and waiting for π to equilibriate. The equilibrium isotherms do not show any hysteresis, thereby indicating that hysteresis is a non-equilibrium phenomenon.

An interesting feature of the polymer is a decrease in π in the compression cycle of the isotherm at the point where the BS domains appear. This decrease is more pronounced for slow rate of compression. The monolayer appears to exhibit a negative compressibility at this point. We suggest that the formation of the BS domains requires a minimum threshold value of surface molecular density. Till this value is reached, the monolayer remains in the LE phase. As a result, π keeps on increasing. Once the nucleation of the BS domains starts, the growth continues on its own. This takes away molecules from the LE phase, hence there is a drop in π. This is further confirmed by the fact that on stopping the compression, π continues to fall till it reaches 8 dyne/cm. In case of slow compression, the drop is more pronounced as the compression of the monolayer cannot compensate for the molecules being taken away by the formation of BS domains. A similar drop in π on compression, of a similar magnitude, has been reported by Bercegol *et. al.* [11] in the monolayer of NBD-stearic acid. There is a similar de'pendence on compression rate. The authors attribute this drop in π to a nucleation barrier for the formation of the condensed phase. Sethson and Aberg [12] propose the formation of a 3D phase through a two phase co-existence similar to the LE − LC phase transition. The LE − BS transition is very similar to that.

It may be noted that LCP1 does not dissolve in water. Otherwise, the isotherms plotted after a long time delay would show a shift towards lower A,.

A very unusual result is the increase in π of the isotherm following the sharp decrease in the expansion cycle. This increase is of the order of 0.5 to 0.7 dyne/cm, much greater than the experimental resolution of 0.1 dyne/cm. Such an increase is not reported in the literature to our knowledge. This effect can be attributed to a delayed melting of the MS structure. As the monolayer is expanded, the LE phase changes to the gas phase, thereby reducing n. When the whole of the LE phase has transformed to gas phase, there is a depletion of molecules in the monolayer, with a majority of them forming the MS domains. The delay of melting of the MS domains causes a further decrease in n. The decrease in π stops only when molecules are released to the monolayer by the melting of the MS structure. Hence, there is a drop in π to even lower values for fast expansions. The subsequent rise in π seems to indicate that the release of molecules to the monolayer from the MS domains is more than the expansion rate. This release soon balances off, giving rise to the plateau. Also, if the monolayer is expanded from the LE – BS co-existence region, there is a drop in π, but no subsequent increase. This indicates that the BS domains do not exhibit delayed melting, confirming the fluorescence observation that they melt fast.

The monolayer exhibits many interesting phases at low $A_{,}$. The MS and the IS domains occur at the same $A_{,,}$ at different temperatures. They transform smoothly from one to the other on changing the temperature. This transformation is very slow. This can be attributed to a decrease in line tension in the IS domains on decreasing the temperature. Alternatively, an increase in electrostatic repulsion between the molecules in the IS domains can also bring about this transition. A similar transformation has been reported by Seul and Sammon [13] in a phospholipid cholesterol mixed monolayer. Here the transformation occurs on varying $A_{,}$. According to Seul [14], this phenomenon raises the possibility that topologically metastable states may appear whenever quenched connectivity accompanies a phase transition.

The expansion isotherm at **35°C** also shows hysteresis, but the fall here is less sharp as compared to **25°C.** Also there is no subsequent increase in n. This

indicates that delayed melting is a characteristic of the MS domains alone, and is not exhibited by the IS or BS domains.

Diep-Quang and Ueberreiter [10] have studied a compound with a structure resembling the side chain of LCP1 using surface manometry. They report a number of steps in the compression cycle of the isotherm interspaced by plateaus. They attribute these steps to multilayer formation. They report the formation of **2, 3** and 4 molecule thick films, based on the comparison of the molecular surface area at the points where the steps occur. On expanding, there is a **stepwise** reduction in the multilayers.

5.5   Conclusions

The polymer LCP1 spreads at the air-water interface to form stable monolayers. The compression and expansion isotherms of the monolayer show very marked hysteresis. This hysteresis appears to be due to the greater stability of the high density phases compared to the low density LE phase.

There is a decrease in π in the compression isotherm, which is followed by a large plateau. We attribute this decrease to the presence of a nucleation threshold for the formation of the BS domains.

Interestingly, there is a very unusual increase in π in the expansion isotherm, which is much larger than the instrumental resolution. This expansion is present only if the monolayer is expanded from the MS – LE co-existence region. Such an increase in π has not been reported in the literature to our knowledge. We attribute this increase to a delayed melting of the MS structure.

The monolayer exhibits the usual gas and LE phases, alongwith some unusual structures like BS, striations, MS, IS and foam. The later ones are identified as 3D structures, since they are visible under reflection.

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