Preparation and Characterization of Langmuir Blodgett film of Poly (acrylamide-co-acrylic acid)

Ramesh S. Bhande, Vinay A. Juvekar*

Abstract— The Langmuir film of poly (acrylamide-co-acrylic acid) has been prepared on two different substrates viz. pure water and 1 mM NaOH solution. The film is organized by repeated compression and expansion. The influence of the subphase on the behavior of π–Γ isotherm of the organized film of poly (AAm-co-AAc) is studied. There is a considerable difference in the behavior of the films prepared on water from those prepared on NaOH solution. The films on the water subphase are unique. They have the same isotherm after organization irrespective of the initial amount of the polymer loaded in the film. On the other hand films on the NaOH subphase are not well organized. They however exhibit higher surface pressures due to electrostatic repulsion among the chains.

Index Terms— AFM, Langmuir monolayer, NaOH, Poly (acrylamide-co-acrylic acid), Subphase.

I. INTRODUCTION

The Langmuir–Blodgett (LB) technique is the one of promising methods for fabricating ordered ultrathin films on solid substrates at the molecular level by transferring monolayers from the water surface. LB films have been characterized by using various techniques. [3] They also provide information on the arrangement and orientation of molecule as well as transition, and conformational changes. [1, 2] LB technique is useful for studying the basic properties of functionalized and amphiphilic diblock at interface. Poly (acrylamide-co-acrylic acid) is designated as poly (AAm-co-AAc). Song et al. studied the response of adsorbed of hydrophobically modified poly (AAm-co-AAc) layers to selective solvents. [5] The aim of the present work is to investigate the effect of the subphase on organization of the Langmuir film of poly (AAm-co-AAc). Two subphase used here are pure water and 1 mM NaOH solution. The organization of molecules in the film is quantified in terms of surface pressure π (mN.m^{-1}) and the surface concentration is represented by surface density Γ (mg.m^{-2}).

R. S. Bhande is with Department of Chemical Engineering, IIT Bombay, Powai, Mumbai- 400076, India (e-mail: bhanderamesh@iitb.ac.in)

V. A. Juvekar is with Department of Chemical Engineering, IIT Bombay, Powai, Mumbai- 400076, India (e-mail: vaj@che.iitb.ac.in) (phone: +91-22-2576 7236; fax: + 91-22-2572 6895)

II. EXPERIMENTAL

A. Materials

Poly(acrylamide-co-acrylic acid) (MW = 200 kDa) was purchased from Sigma-Aldrich Ltd., (US) and was used without any further purification. Aqueous solution of the polymer having concentration of 500 mg.L^{-1} was spread on the subphase to form the film in all experiments. Two subphases were used viz. Milli-Q water and 1 mM solution of NaOH.

B. Isotherm Measurement

Surface pressure measurements were accomplished by the use of a Langmuir mini-trough system (KSV instruments Ltd., Finland) having trough size 324mm x 75mm. The precision in the surface pressure measurements was ± 0.02 mN.m^{-1}. Milli-Q water (resistivity >18.2 MΩ.cm at 25 ^{0}C) was used as the subphase. The surface pressure was measured using the Wilhelmy plate method. The measurements were performed at 25^{0}C by using a constant temperature bath (PolyScience Digital Controller, US). The Langmuir balance was enclosed in a box of glass in order to minimize air turbulence as well as the fallout of dust particles. Appropriate amount of the solution was spread on the water surface, and allowed to equilibrate for 20 min before starting compression. Isotherms were recorded at a compression speed of 10 mm.min^{-1}. The π-A curves were recorded for different loadings of diblock and during repeated compression and expansion.

III. RESULTS AND DISCUSSION

A. Behavior of the polymer film on repeated compression - expansion

The surface pressure of the Langmuir film increases when the film is compressed. The highest pressure is reached when the barriers are at the closest attainable distance (40 mm). When the spread film is subjected to repeated compression-expansion sequence, the highest pressure increases after each cycle. Fig.-1 shows the highest film pressure attained during a cycle as a function of the number of cycles. Here water is used as the subphase.
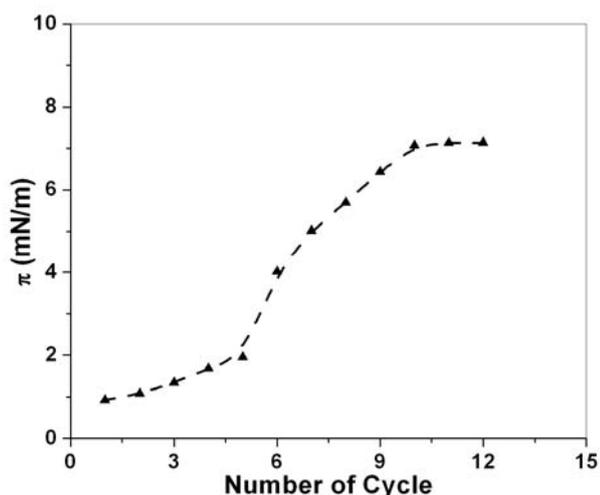
Fig. 1 Surface Pressure (π) vs. number of cycles. (Subphase= Water, Amount loaded = 200 μg of PAAm-co-AAc)

It is seen that initially the maximum pressure varies linearly with number of cycles. This is the dewatering phase where the film shades water. After certain number of cycles, the pressure increases more rapidly. Here chain begins to interact strongly and get organized. This is followed by a plateau when the organization of the chains is complete. We only studied the behavior of the films which were fully organized. In most cases, 10-12 cycles of repeated compression-expansion were needed to reach the organized state.

Fig.-2 shows the similar plot when the subphase is 1 mM solution of NaOH.
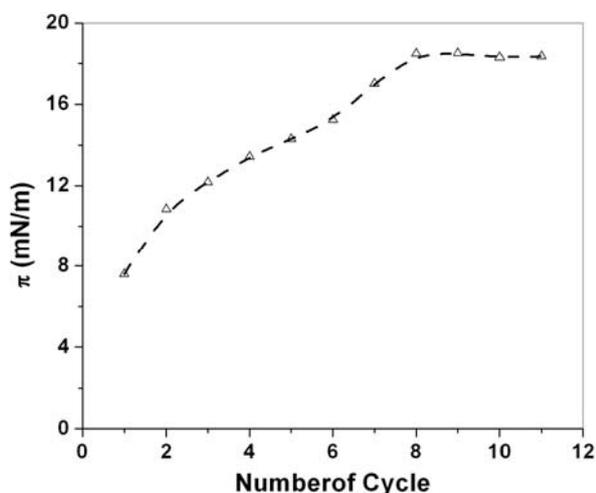

Fig. 2 Highest Surface Pressure vs. number of cycles. (Subphase= 1mM NaOH solution, Amount of poly (PAAm-co-AAc) loaded = 200 μg)

In behavior of this plot is very different from that shown in Figure-1. There is initial sharp rise followed by linear rise and then a plateau. Also, the surface pressures are much higher in this case. In NaOH solution, polyacrylic acid is partially converted into sodium salt. Negative charges are developed on the polymer chains. The repulsion among these charges give rise to higher surface pressure. When dewatering occurs during the initial phase of cycling, the interchain distances decrease and hence the repulsion increases rapidly. This is the reason why there is rapid rise in

the film pressure. The acrylate anions have strong tendency to hydration and hence it retains a considerably amount of water. Such chains do not come close to each other due to electrostatic repulsion and hence do not exhibit the chain organization phase.

Fig.-3 shows the surface pressure vs. surface area isotherm of organized films containing three different amounts of poly (PAAm-co-AAc) on water subphase. There is only a small variation in the three isotherms, but no trend is observed
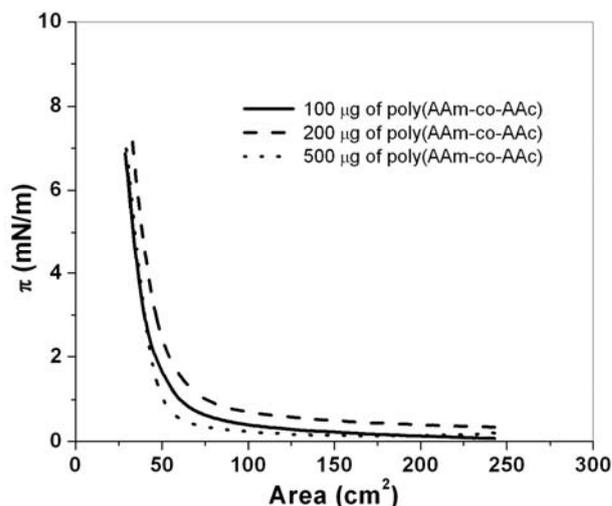

Fig. 3 Surface Pressure (π) vs. area plot for 200 kDa molecular weights of poly (acrylamide-co-acrylic acid) on water subphase; (Amount loaded = 100, 200, 500 μg of poly (PAAm-co-AAc)

This indicates that a part of the polymer is lost during the compression-expansion process and only a fixed amount of the polymer is retained in the film at the end. This means that the organized film has a well defined structure having a specific chain density. We now consider the effect of polymer loading on π–A isotherm for a organized film of the polymer on 1 mM NaOH subphase. This is shown in Fig.-3. It is now seen that the surface pressure at 100 μg of loading is significantly lower that at 200 μg loading. This indicates that two films have different structure and chain density. This behavior is opposite of the film on water, which has a unique structure irrespective of the initial loading.
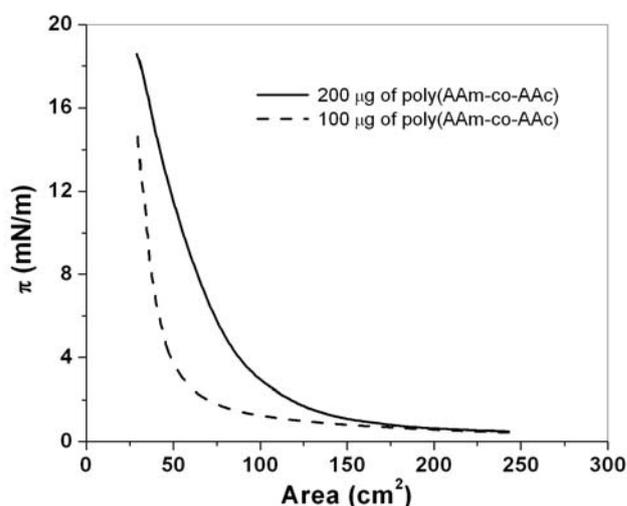
Fig. 4 Surface Pressure (π) vs. area plot for 200 kDa molecular weights of poly (acrylamide-co-acrylic acid) on water subphase; (Amount loaded = 100, 200 μg of poly (PAAm-co-AAc)

B. Effect of change of subphase on π-A isotherm

The final $\pi - \Gamma$ isotherm is compared with the isotherm of poly(PAAm-co-AAc) in the absence of NaOH in subphase as shown in Fig.5. A significant increase in the surface pressure of the film, in presence of NaOH in subphase, is observed. It is also seen that in the presence of NaOH in subphase, the behavior $\pi - \Gamma$ isotherm is changed. A rapid rise in the surface pressure was observed for 200 μg of poly (PAAm-co-AAc). With change in subphase for the same amount of loading, we get the maximum surface pressure ~ 18.5 mN.m^{-1} after repeated compression-expansion
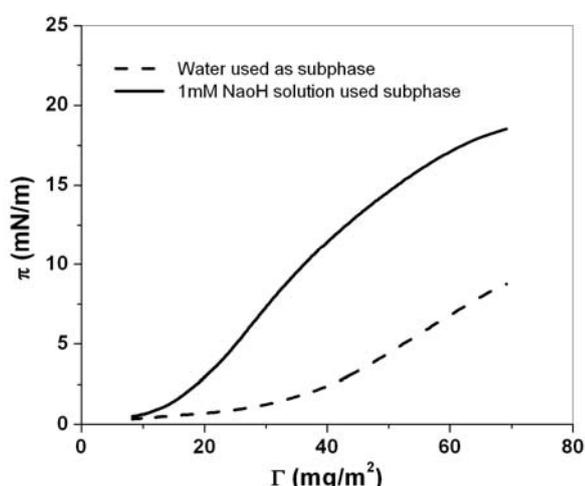

Fig.5 Surface Pressure (π) - Surface Concentration (Γ) plot for 200 kDa molecular weights of poly (acrylamide-co-acrylic acid) for two different subphases; (Amount loaded = 200 μg of poly(PAAm-co-AAc))

C. Static Dilatational Modulus (E)

An important parameter for characterization of monolayer at air-water interface is their Gibbs elasticity, defined as the resulting change in surface pressure (dπ) caused by a change of the surface area (A), expressed as the relative area variation, dA/A.[3]

$$ E = A\left(\frac{d\gamma}{dA}\right) = \frac{d\gamma}{d\ln A} = -\frac{d\pi}{d\ln A} \qquad (1) $$

In case of Langmuir monolayer i.e. spread film of composed insoluble molecules at air-water interface; the surface dilatational modulus is also called static dilatational modulus. It is calculated as the derivative of the π- ln Γ isotherms; Gibbs elasticity (E) is defined as

$$ E = \left(\frac{d\pi}{d\ln\Gamma}\right) \qquad (2) $$

Where π surface pressure, A is mean molecular area and Γ

surface concentration of polymer molecules at air-water interface. By compressing barrier available areas per polymer molecule get reduced. Due to compression lateral pressures of film get increased and polymer chains are goes through different physical states and molecular orientation. Fig. 6 shows Static dilatational modulus as a function of surface pressure (E-π curves). It is found that modulus increases with surface pressure. The static dilatational modulus for film is found 14.5 mN/m.
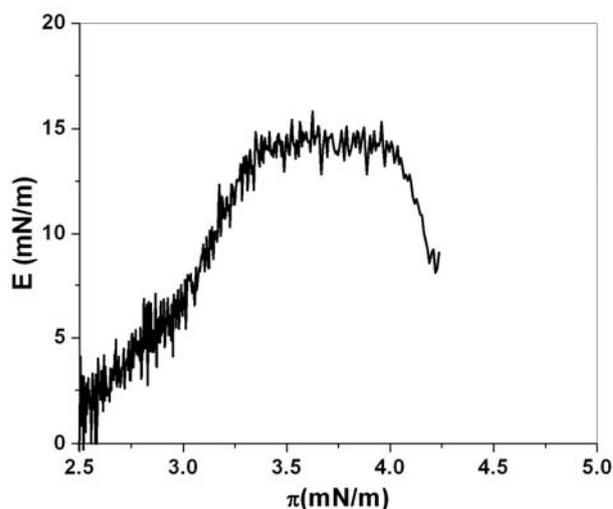

Fig. 6 Static dilatational modulus of poly(PAAm-co-AAc) spread film, as calculated from surface pressure-area isotherms obtained by compression in a Langmuir trough. (Amount loaded = 200 μg of poly (PAAm-co-AAc))

D. Atomic Force Microscopy (AFM) Measurements

The surface morphology of the LB film of PEO was characterized with AFM. (NanoScope IV, Veeco Metrology Group Inc, Santa Barbara, CA, USA.) AFM was used to get an idea of monolayer deposition on quartz substrate along with uniform area coverage of crystal surface. The images were scanned in tapping mode in air. The speared film is transfer at constant surface Pressure at 15 mN.m^{-1}.
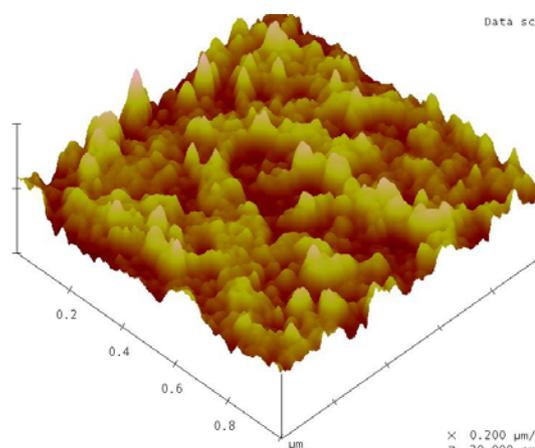

Fig.7 AFM images of PAAm-co-AAc (MW=200kDa) with monolayer (Quartz crystal gold coated) (Amount loaded = 200 μg of poly(PAAm-co-AAc))

IV. CONCLUSION

Using the technique of repeated compression-expansion, it is possible to prepare highly elastic Langmuir films of PAAm-co-AAc at the air-water interface. There is a considerable difference in the behavior of the films prepared on water from those prepared on NaOH solution. The films on the water subphase are unique. They have the same isotherm after organization irrespective of the initial amount of the polymer loaded in the film. On the other hand films on the NaOH subphase are not well organized. They however exhibit higher surface pressures due to electrostatic repulsion among the chains.

REFERENCES

[1] K.B.Blodgett, I. Langmuir (1937). Built-Up Films of Barium Stearate and Their Optical Properties. Phys. Rev. 51. pp. 964 - 982.
[2] P. Lavigne, P. Tancrede, F.Lamarche, JJ. Max. (1992). Packing of Hydrophobic Alpha-Helices - a Study at the Air-Water-Interface. Langmuir 8(8). pp. 1988-1993.
[3] J.Lucassen, M. Van Den Tempel. (1972). Longitudinal waves on visco-elastic surfaces Journal of Colloid and Interface Science 41(3). pp. 491-498.
[4] V. C. Petty, Langmuir–Blodgett Films: An Introduction. Cambridge Univ. Press, Cambridge. 1996, ch. 2,3.
[5] X.Y.Song, M.W. Cao, Y.C. Han, Y. L.Wang, JCT. Kwak. (2007). Adsorption of hydrophobically modified poly(acrylamide)-co-(acrylic acid) on an amino-functionalized surface and its response to the external solvent environment. Langmuir 23(8). pp. 4279-4285.