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Fabrication of PMMA / arachidic acid LB films

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Fabrication of the polymethyl methacrylate (PMMA) molecules onto solid substrates in order to form Langmuir-Blodgett (LB) thin films have been studied in this paper. As a first step to determine the optimum conditions for the deposition isotherm graphs of PMMA molecules have been recorded which showed that PMMA molecules can easily be organised on the water surface. Mean value of the area per molecule of the selected PMMA molecules have been calculated between 2000 and 3500 nm^2. Alternate layer (AL) type LB thin films of PMMA molecules have been fabricated using arachidic acid as a promoter. Mixed monolayers of PMMA and arachidic acid could also form stable monolayers and thin films up to 2 layers.

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1. Introduction

In the last two decades the nanoorganic thin films have attracted great interest due to a number of applications in the field of molecular electronics [1-4]. Poly (methyl methacrylate) (PMMA) is one of the frequently used materials in this field [5-7]. A number of methods such as spin coating [8] and self assembly [9] have been used to fabricate thin films of PMMA and additionally Langmuir-Blodgett (LB) Thin Film Fabrication method is desired to be used because of its low cost and high quality with a very well ordered structure [10].

Therefore the fabrication conditions of PMMA thin films using LB thin film fabrication method is investigated. The isotherm graphs of the PMMA molecules have been recorded to investigate their behavior at the air-water interface. Arachidic acid has been used as a promoter during the fabrication of the AL type thin films of PMMA and arachidic acid. Mixed monolayer of PMMA and arachidic acid molecules has also been investigated to fabricate the nanoorganic thin films where only a bilayer of thickness was possible.

2. Materials and methods

PMMA molecules were synthesized using emulsifier-free emulsion polymerization method and chemical properties of these materials have been investigated and the chemical structure can be found elsewhere [9, 11]. 5 different kinds of PMMA have been used to investigate surface properties coded as P15, P16, P17, P18, P19 having different molecular weights 830, 1100, 1200, 810 and 680 kg/mol respectively. Arachidic acid were purchased from NIMA technology and used without further purification.

A computer controlled NIMA 622 alternate layer type through (Coventry, England) has been employed to record isotherm graphs and to fabricate the LB thin films. Solutions of PMMA molecules in the range 0.6 and 0.7 mg.ml^{-1} have been prepared using chloroform as a solvent. The isotherms have been recorded with a compression speed of 30 cm.min^{-1} by spreading 30 μl solution on the water surface using a Hamilton microsyringe and standing for 15 minutes for the solvent to evaporate. The surface pressure of the floating monolayers for the thin film fabrication was 25 mN.m^{-1} for PMMA and 20 mN.m^{-1} for the arachidic acid layer. The downstroke and upstroke deposition velocity of the substrates were between 10 and 20 mm.min^{-1}.

3. Result and discussion

Isotherms of PMMA molecules with different molecular weights have been investigated. Fig. 1 shows the surface pressure versus area per molecule for 5 different kinds of PMMA molecules (P15 – P19) for water subphase pH value 5.8. Area enclosed by the barriers per molecule on the water subphase are 2750, 2250, 3200, 2150, 1750 nm^2 for P15 – P19 respectively. These values are determined by extrapolating the linear region of 15 – 20 mN.m^{-1} surface pressure value in the isotherms to the zero surface pressure. The minimum area per molecule has been recorded for P19 material which has the minimum molecular weight and therefore has the minimum chain length. Similarly the maximum area per molecule has been recorded for P17 which has the maximum molecular weight. Isotherms for pH values 12, 9 and 2,8 have been investigated but not given in the text because of their similarity with the isotherm given in Fig. 1 for pH 5.8 which means the isotherm graphs are independent of pH value of the water subphase [12]. In those graphs the area per molecule for P19 material also has the minimum value and for P17 has the maximum value. Furthermore the isotherm graphs of the same polymer material for different pH subphase values were similar indicating the pH independency of the floating monolayers on the air-water interface.

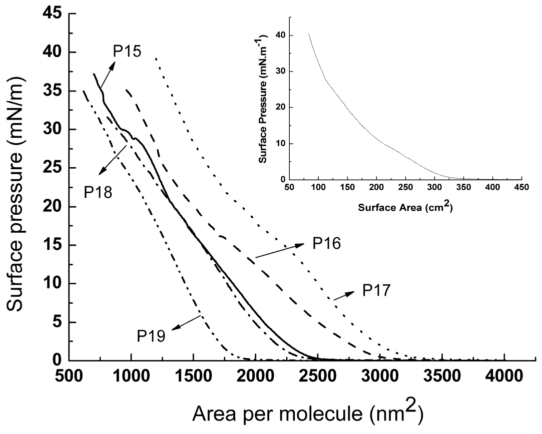
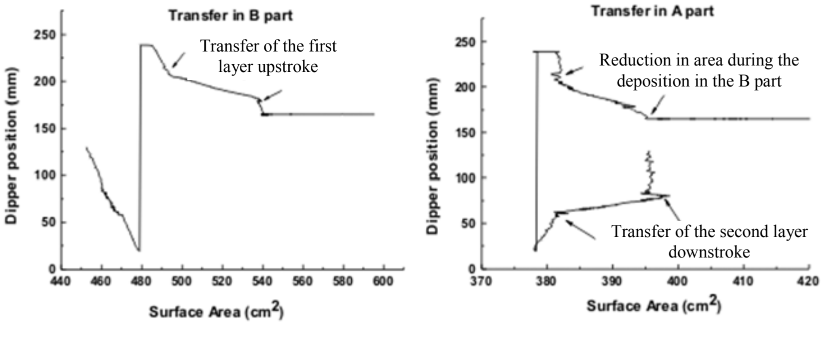


Fig. 1. Surface pressure-area isotherms of PMMA series at pH 5.8 water subphase. Isotherm graph of mixed monolayer of PMMA molecule and arachidic acid with a ratio of 1:1 (Inset).

For the fabrication of the LB thin layers the solid phase surface pressure value has been determined between 15-25 mN.m^{-1} using the isotherm graphs. Vertical dipping method has been used to obtain the LB thin films of PMMA molecule. Alternate layer LB through has been used to obtain symmetric structure. P19 polymer has been selected to start with the experiments because of its lowest molecular weight thus shortest chain length and simplest molecular structure. Adequate amounts of P19 molecule has been spread onto the water surface and the thin film fabrication surface pressure of 25 mN.m^{-1} has been supplied by compressing the barriers with a withdrawal speed of 20 mm.min^{-1}. The transfer graph which gives a first impression on the fabrication of the thin film using the reduction in the surface area versus dipper position is given in Fig. 2 for this deposition in both B and A parts of the LB through. As seen in Fig. 2 in this first test, in part B the first P19 layer has been transferred upstroke but the second layer which has been attempted to be deposited by the downstroke deposition of P19 layer was not successful. Moreover the expansion of the barriers resulting with an increase in the surface area means that the deposited first layer set itself back onto the water surface.



(a) (b)

Fig. 2. Transfer graphs of the P19 polymer in a) A part and b) B part of the LB through.

To avoid such a problem Arachidic acid has been used as a transfer promoter to deposit PMMA molecules onto the solid substrates [13-18]. After a number of experiments to obtain the optimum conditions for the thin film deposition the best films were fabricated by spreading arahidic acid to A part and PMMA polymer to B part of the LB through, the first layer were fabricated by the downstroke deposition of arachidic acid as first layer and the second layer were fabricated by the upstroke deposition of the PMMA molecule. For multilayer fabrication this process has been repeated. The surface pressure for the deposition of arachidic acid monolayer was 25 mN.m^{-1} where this value was set to 15 mN.m^{-1} for the PMMA monolayer. The vertical deposition speed for both upstroke and downstroke were 10 mm.min^{-1}. In Fig. 3 the transfer graphs for 16 layers of AL type LB film using arachidic acid and P19 polymer are given for both A and B parts of the LB through. Using the same procedure multilayered LB thin films of polymer P18 and P15 have also been fabricated with 14 and 18 layers respectively. LB thin film fabrication attempt using PMMA molecules coded as P16 and P17 has resulted with failure which is believed to be a result of their high molecular weight with respect to P19, P18 and P15.

Mixed monolayer of P19 molecule and arachidic acid in 1:1 ratio has been examined as a floating layer and isotherm graph of the monolayer has been recorded and given in Fig. 1 in the inset. The isotherm graph has indicated that a monolayer is formed on the air-water interface. A surface pressure value of 20 mN.m^{-1} is predicted as the solid phase pressure value and deposition of this monolayer onto solid substrate has been made at this individual surface pressure value. The transfer graphs for this thin film has been given in Fig. 4 where the mixed monolayer were spread on both A and B parts of the through. Starting with an upstroke deposition in A part followed by a downstroke deposition in part B only first 2 layers were successfully deposited. Following layers could not be deposited in any attempt therefore only bilayered thin films of the mixed monolayer could be fabricated using this method.

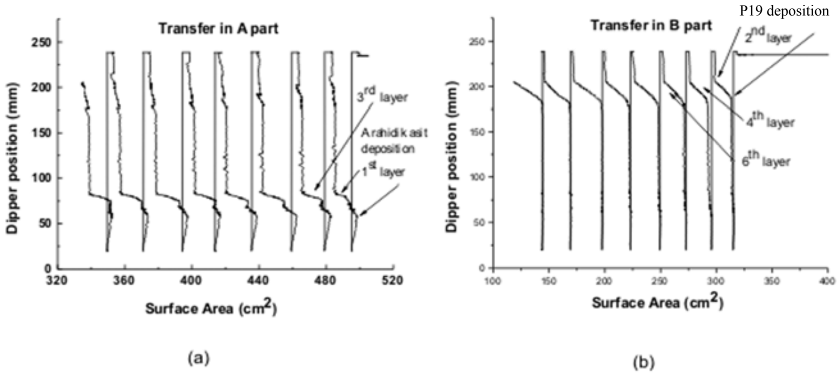


Fig. 3. Transfer graphs for 16 layers of AL type LB film using arachidic acid and P19 polymer (a) for A part and (b) for B part of the LB through.

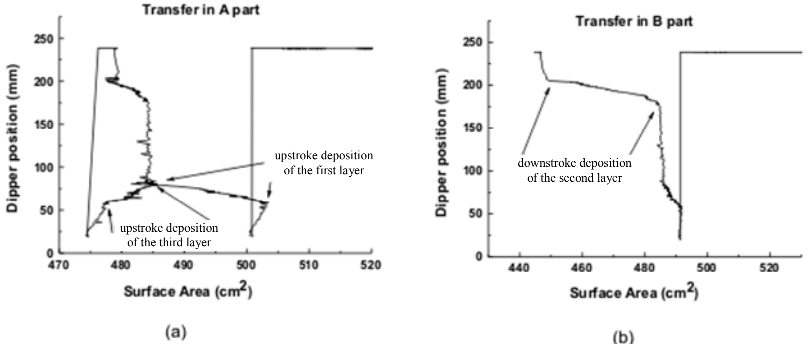


Fig. 4. Transfer graphs for LB film using a mixed monolayer of P19 and arachidic acid in 1:1 ratio (a) for A part and (b) for B part of the LB through.

4. Conclusion

In this work the Langmuir Blodgett thin film fabrication conditions of PMMA molecules onto solid substrates have been examined in detail. Fabrication of multilayered LB thin films of PMMA molecules were possible only in the case of AL type thin films using arachidic acid as a promoter. Mixed monolayers of PMMA and Arachidic acid were transfered onto solid substrates to form LB thin films up to a bilayer.

References

[1] T. H. Richardson, Functional organic and polymeric materials, John Wiley, 2000.
[2] D. Vuillaume, CR Phys. **9**, 78 (2008).
[3] L. Fu, L. Cao, Y. Liu, D. Zhu, Adv. Colloid Interfac. **111**, 133 (2004).
[4] C. J. F. Dupraz, P. Nickels, U. Beierlein, W. U. Huynh, F. C. Simmel, Superlattices Microst. **33**, 369 (2003).
[5] E. Kapetanakis, A. M. Douvas, D. Velessiotis, E. Makarona, P. Argitis, N. Glezos, P. Normand, Org. Electron. **10**, 711 (2009).
[6] G. Chaidogiannos, D. Velessiotis, P. Argitis, P. Koutsolelos, C. D. Diakoumakos, D. Tsamakis, N. Glezos, Microelectron. Eng. **73–74**, 746 (2004).
[7] Q. D. Ling, D. J. Liaw, C. Zhu, D. S. H. Chan, E. T. Kang, K. G. Neoh, Prog. Polym. Sci. **33**, 917 (2008).
[8] N. G. Semaltianos, Microelectron. J. **38**, 754 (2007).
[9] İ. Çapan, Ç. Tarimci, T. Tanrisever, Sensor Lett. **5**, 533 (2007).
[10] A. Ulman, An Introduction to Ultrathin Organic Films from Langmuir–Blodgett to Self-assembly, Academic Press, San Diego, 1991.
[11] T. Tanrisever, O. Okay, I. Ç. Sonmezoglu, J. Appl. Polym. Sci. **61,** 485 (1996).
[12] F. Petriat, E. Roux, J. C. Leroux, S. Giasson, Langmuir, **20**, 1393 (2004).
[13] I. L. Emelianov, V. V. Khatko, Sensor Actuat. B-Chem. **60**, 221 (1999).
[14] L. Xu, X. Hu, Y. T. Lim, V. S. Subramanian, Thin Solid Films **41**, 790 (2002).
[15] Z. Chen, Ng. Siu-choon, S. F. Y. Li, L. Zhong, L. Xu, H. S. O. Chan, Synthetic Met. **87**, 201 (1997).
[16] S. Zhang, Z. K. Chen, G. W. Bao, F. Sam, Y. Li, Talanta **45**, 727 (1998).
[17] R. Rella, P. Siciliano, G. Toscano, L. Valli, L. Schenetti, A. Mucci, D. Iarossi, Sensor Actuat. B-Chem. **57**, 125 (1999).
[18] F. Babudria, G. M. Farinola, S. Giancane, F. Naso, R. Rella, A. Scarpa, L. Valli, Mat. Sci. Eng. C-Bio S **22**, 445 (2002).

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