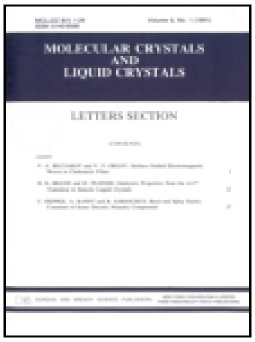

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Spectroscopic and microscopic study of aggregate formation in the nano-dimensional Langmuir-Blodgett films of perylene with a fatty acid/polymer

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ABSTRACT
Perylene (PYL) mixed with Behenic acid (BA) and Polymethyl methacrylate (PMMA) separately have been incorporated in the Langmuir-Blodgett film. The surface pressure versus area per molecule area isotherms are measured at various molar ratios. Stability of the mixed monolayer of PYL and BA/PMMA and their collapse pressure are much higher than that of pure PYL. Negligible amount of hysteresis observed in the compression-decompression isotherms indicate the formation of stable monolayer. Miscibility of the mixed systems is found to vary with the film composition. The formation of PYL aggregates in the mixed films is investigated using UV-Vis absorption spectroscopy, emission spectroscopy and atomic force microscopy (AFM).

KEYWORDS
Perylene (PYL); monolayer; Langmuir-Blodgett (LB) film; Hysteresis; AFM.

PACS NUMBERS
68.37.-d; 68.18.-g; 68.47.Pe

Introduction

Langmuir-Blodgett (LB) technique is widely used for the fabrication of ordered ultrathin films of a wide variety of advanced materials for application in nanotechnology based optoelectronic, photonic devices [1], non-linear optical devices [2], bioelectronic devices [3], biosensors [4], and also in molecular electronics [5]. Condensed ring polyaromatic hydrocarbons (PAHs) are one such material that has attracted considerable interest in recent years as these molecules are deemed to be the active ingredients for future generation superfast biocomputers [6]. PAH dyes molecules are used to fabricate LB film based light emitting diodes (LEDs), optical switches, sensors [7]. Interest in an important PAH namely, perylene stems from the fact that it has interesting photophysical characteristics like intense fluorescence, high molar absorptivity, high solubility in organic solvents, tremendous propensity to aggregate into highly ordered molecular assemblies and its vast use in thin film p-n heterojunctions, rectifiers, molecular switches, liquid crystal displays (LCDs), organic light emitting diodes (OLEDs), organic solar cells and xerographic devices [8-10]. Despite such interesting properties and application of perylene, little effort has been made in studying perylene in the restricted geometry of Langmuir-Blodgett films. Since LB films closely mimic biomembranes and represent restricted geometry, it was felt that incorporating perylene molecules in such

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films may provide information on the less understood role of the microenvironment and their spectroscopic properties. Although, LB films of perylene and its derivatives were studied be several authors [11-14], miscibility and molecular interactions between the components of the mixed monolayer film were never studied. The study of film in-homogeneity and miscibility behavior is very important for optimization of their macroscopic properties. In the present paper, we have investigated the mixing behavior and morphology of the mixed LB film of perylene (PYL) with two different supporting matrixes such as behenic acid (BA) and polymethyl methacrylate (PMMA) on the basis of surface pressure and atomic force microscopy. Spectroscopic characterization of such films was also carried out using UV-Vis absorption and emission spectroscopy.

2. Experimental

The sample perylene (PYL) whose molecular structure is shown in the inset of the Figure 1a was obtained from Aldrich Chemical Company (USA). Purity of the PYL sample was checked by absorption and emission spectroscopy. Polymethyl methacrylate (PMMA) and behenic acid (BA) procured from Sigma (USA) were used without further purification. The solvent chloroform (SRL, India) used was of spectral grade and its emission spectrum was checked before use.

The study of surface pressure versus area per molecule isotherm and also deposition of LB films were carried out by a commercially available Langmuir-Blodgett (LB) film deposition instrument (Apex Instruments Co., India, Model 2007 DC). A filter paper Wilhelmy plate was used for determining the surface pressure at the air-water interface with an accuracy of ±0.1 mN/m.

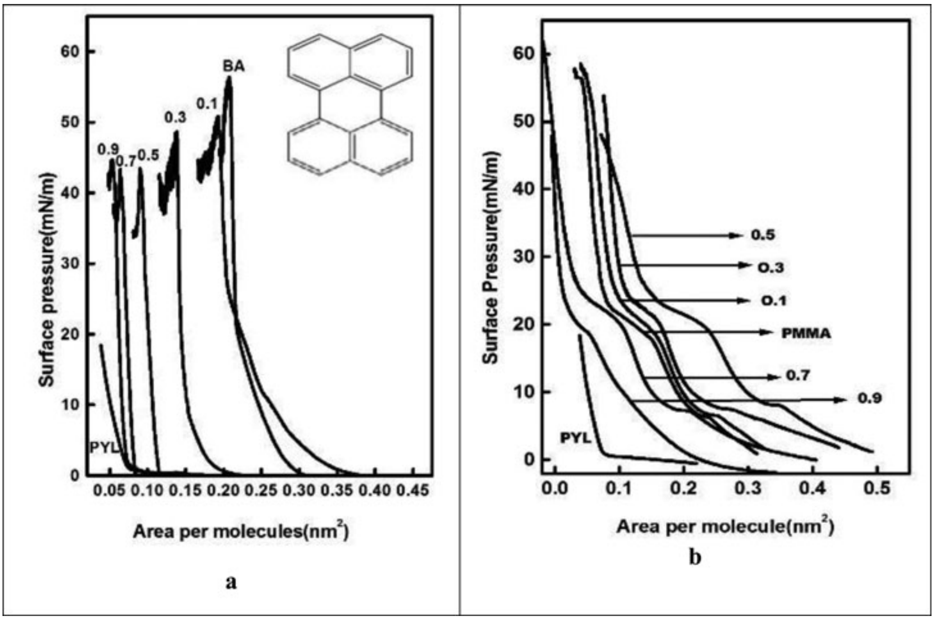

Figure 1. (a) Surface pressure (π) versus area per molecule (A) isotherms of Perylene (PYL) in BA matrix at different mole fractions of PYL. The numbers denote corresponding mole fractions of PYL in BA. The inset of Figure 1a represents the molecular structure of PYL. (b) Surface pressure (π) versus area per molecule (A) isotherms of PYL in PMMA matrix at different mole fractions of PYL. The numbers denote corresponding mole fractions of PYL in PMMA.

Quartz slides was cleaned by leaving them overnight in chromic acid, subsequently boiled in concentrated nitric acid to remove all the traces of organic material and then washed with deionized water, dried.

Monolayers at the air-water interface were prepared in a conventional manner by spreading the mixture of PYL and BA at the air-water interface and compressing the barrier at a low speed of compression speed $5\times\mathbf{10^{-3}}$ nm mol^{-1} s^{-1} after allowing 10-15 min for the volatile solvents to evaporate. An identical method was used for the mixed film of PYL-PMMA. Y-type deposition of mono-or multilayers on quartz substrates was achieved by dipping the substrate vertically through the monolayer. The dipping and withdrawal speed were kept at 5mm/min. Sufficient waiting time (5-10 min) was given between dips to dry up the pre-deposited films. The transfer ratio for the mixed films deposited onto solid substrate was calculated from the ratio of decrease in the monolayer area at the air-water interface to the actual surface area of the substrate and was evaluated to be 0.98 ± 0.01.

Microcrystal film of PYL was prepared by spreading a few drops of PYL solution onto a quartz substrate by a micro-syringe and allowing them to spread uniformly throughout the substrate. After the evaporation of the solvents, a cast film was formed which actually confined the micro-crystals of PYL.

The UV-VIS absorption spectra of solution, mixed LB film and microcrystal were recorded using a Perkin Elmer Lambda 25 spectrophotometer (USA) and their emission spectra were recorded on Shimadzu RF-5000 Spectrofluorometer. The surface morphologies of the mixed LB monolayer films of PYL/BA and PYL/PMMA transferred onto silicon wafer were determined by Innova, Broker Inc, USA atomic force microscope (AFM). All the images were obtained in tapping mode under ambient atmosphere.

3. Results and discussion

3.1. *Surface pressure-area per molecule (π-A) isotherms*

The surface pressure versus area per molecule isotherm could measure the ability of a molecule to form a monolayer and also indicate the orientation of molecules on the air-water interface. To study the monolayer behavior of pure PYL at the air-water interface, a solution of pure PYL in chloroform (1×10^{-3}M)was spread at the A-W interface and after evaporate the solvent, the barrier moved slowly. It is observed that surface pressure did not rise significantly. Addition of large amount of PYL solution to the water surface leads to the formation of crystalline domains which was clearly visible under naked eye. Therefore, pure PYL molecules were failed to form stable floating monolayer at the A-W interface. In order to obtain a stable film that could be transferred onto a solid substrate, PYL was mixed with the supporting matrix such as BA or PMMA and then spread over water surface. On compression, a highly stable monolayer was obtained. The molar mixing ratio of PYL to BA/PMMA was varied and a series of isotherms were obtained as shown in the Figures 1a and 1b.

The area per molecule of pure BA is about 0.22 nm^2 at a surface pressure of 15 mN/m, which is in good agreement with the result reported in the literature [15]. However, the area per molecule of pure PMMA is 0.12 nm^2 at a surface pressure of 15 mN/m and the pure PMMA shows an inflection point at about 20 mN/m. The behavior of PMMA is also consistent with the result published previously [15]. The area per molecule of the mixed film of PYL and BA decreases with increasing mole fraction of PYL in BA matrix (Figure 1a). The interesting feature of PYL/PMMA mixed film isotherm (Figure 2b) is that the area per molecule of the mixed film initially increases, reaches maximum, and then decreases. This feature is

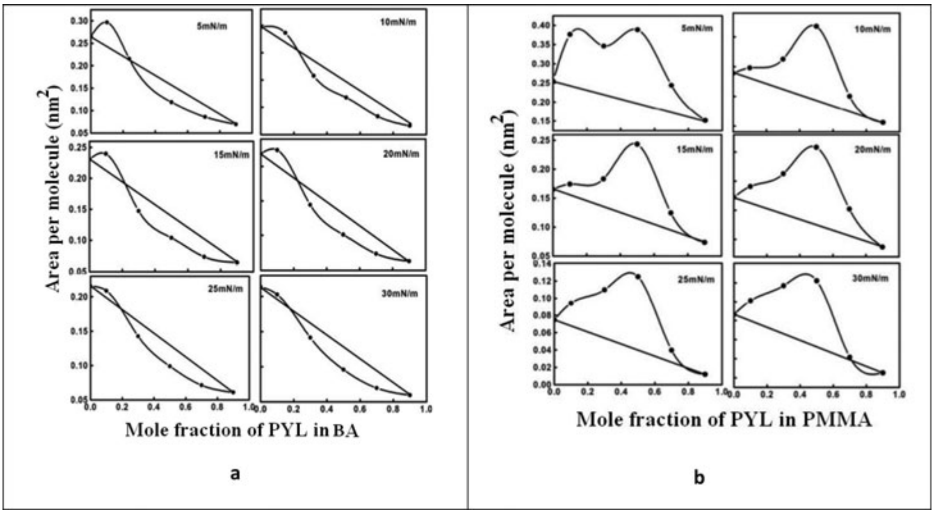

Figure 2. (a) Plot of area/ molecule versus mole fraction for mixed PYL/BA monolayers on water subphase at various surface pressures. (b) Plot of area/ molecule versus mole fraction for mixed PYL/PMMA monolayers on water subphase at various surface pressures.

also evident from the Figure 2b, discussed later. One possible explanation seems to be that at lower concentrations of PYL, the PYL moieties find BA matrix an excellent microphase in which they are readily accommodated. However, at higher concentrations of PYL in PMMA matrix and at all mole fractions of PYL in BA matrix, phase separation between the PYL and PMMA/BA moieties occurs that originates from the immiscibility of the components owing to their differences in molecular structure and physical and chemical properties, which generate aggregates. The formation of aggregates at the air-water interface is manifested as a decrease in the average area per molecule. However, other explanations are also plausible. While one possibility could be that the PYL moieties sandwiched between the PMMA/BA chains and squeezed into the PMMA/BA matrix and out on the air-water interface, an alternative possibility could be the loss of PYL molecules through precipitation into the water subphase.

To confirm whether or not the PYL molecules at the (A-W) interface were lost through precipitation in the bulk of subphase, small amount of water from just below the (A-W) interface were sucked out by a bent pipe and the fluorescence of water sample was checked. It was confirmed from the failure to detect any fluorescence that PYL molecules were not lost through submerging below the (A-W) interface. Therefore, the most plausible explanation may be that the PYL molecules are pushed up in between PMMA/BA chains in such a way that very small area of PYL molecule occupy at the (A-W) interface. These results support the fact that very likely the PYL aggregates were forced out of the air-water interface and remain ledged in between the PMMA/BA chains partially and also partially squeezed out on the surface of layer. In this context, it may be mentioned that AFM and SEM images of the surfaces of the mixed monolayer films of other non-amphiphilic organic molecules and fatty acid/polymer [16, 17] provided the evidence of crystallites indicating squeezing out of non-amphiphilic organic molecules out of the floating layers.

To have more information about the mixed monolayer at the air-water interface, the apparent compressibility (C) of the monolayer films was calculated according to the equation [18, 19] and listed in Table 1.

$$C = -\frac{1}{a_1}\frac{a_2 - a_1}{\pi_2 - \pi_1}$$

Table 1. Monolayer characteristics taken from the π-A isotherms. Mean molecular area or limiting area (A_0) occupied per repeating unit in the monolayer is estimated by extrapolating the constant slope region of the isotherm to zero surface pressure.

Mole fraction of PYL in PMMA/BA	A_0 in BA (nm^2)	A_0 in PMMA (nm^2)	C in BA (mN^{-1})	C in PMMA (mN^{-1})
0	0.243	0.121	6.67	32.37
0.1	0.226	0.143	11.42	29.18
0.3	0.163	0.159	3.63	27.28
0.5	0.110	0.180	5.07	29.42
0.7	0.078	0.087	4.91	42.48
0.9	0.068	0.076	5.10	46.57
1	0.059	0.059	18.92	18.92

where a_1 and a_2 are the area per molecules at surface pressures π_1 and π_2 respectively. In the present case π_1 and π_2 are chosen as 10 and 30 mN/m.

Figure 1(a) (b) show that pure PYL isotherm did not rise beyond 18 mN/m. So the area per molecule of pure PYL monolayer at 30mN/m is estimated by extrapolating the pure PYL isotherm. The compressibility of pure PYL and PMMA were found to be 18.92 mN^{-1} and 32.37mN^{-1} respectively. The monolayers with high compressibility values possesses different phases and in some cases platue like regions and they are found to unstable, hence these high values of C in pure PYL and PMMA monolayer are consistent. With the increase in mole fraction of PYL in PMMA matrix C value decreases upto 0.5 and remains almost same. But at higher concentration of PYL i.e 0.7-0.9M of PYL-PMMA mixed films show higher C values. Therefore incorporation of PYL in the mixture makes the PYL-PMMA films less rigid, i.e. more expanded which may be the characteristic of the sample.

On the other hand, compressibility (C) of pure BA film is 6.67 mN^{-1}. This value is reasonable as the long chain fatty acid monolayer on the water surface stand vertically and has closest molecular packing [20]. With the inclusion of PYL in the PYL-BA mixed monolayers C values were found to be lower than pure PYL and closer to the BA film. This is clear indication that PYL-BA mixed monolayers becomes more rigid, incompressible and harder to form self supporting stable films at the air-water interface.

3.2. *Miscibility study*

The miscibility behavior in the mixed monolayer system is very much important for optimization of its macroscopic properties. Here, we have studied the mixing behavior of PYL-BA and PYL-PMMA using additivity and surface phase rule [21, 22]. Information about the miscibility of the two components in mixed monolayer can be obtained from the surface pressure-Area isotherms for various mole fractions. For a non-interacting two-component system, the average area/molecule according to additivity rule [21] is given by

$$A_{12}= N_1A_1+N_2A_2 \qquad (1)$$

where A_1 and A_2 are the monomer areas occupied by pure components, and N_1 and N_2 are the mole fractions of the pure components in the mixed monolayer.

Figures 2(a) and 2(b) show the plots of the data of area per molecule versus mole fraction of PYL in BA/PMMA matrixes at various fixed surface pressures namely 5, 10, 15, 20, 25, 30mN/m. The dotted lines in both the figures represent the ideal curve for non interacting two component systems calculated by the Equation (1). The use of additivity rule here is purely statistical and this rule predicts the molecular area in an ideal binary mixture, assuming no chemical or physical interaction between the components in the mixture. The PYL/BA mixed monolayer shows negative deviation from the ideality except a small exception at very low mole fraction, which is an indication of attractive type of interaction between PYL and BA molecules. The lower molecular areas compared with the statistical calculation using the Equation 1, most likely originate from the formation of multilayer structure/aggregates. However, positive deviation is observed in case of PYL/PMMA monolayer system at all compositions indicating repulsive type of interaction is operative between the component molecules. The area occupied by the (PYL-PMMA) mixed monolayer at a particular surface pressure is greater than the area occupied by the same amount of the pure components indicating existence of repulsive interaction between the PMMA and PYL molecules. The cohesive forces between like molecules (PYL – PYL and PMMA-PMMA) may dominate in the mixed films with respect to the adhesive force between the unlike components (PYL-PMMA) resulting to a partial or total phase separation and the formation of clusters or microcrystalline aggregates of PYL in the two mixed films. In fact similar repulsive interaction has been reported for other non-amphipilic molecules like bathophenanthroline and p-Quaterphenyl mixed with fatty acid/PMMA [16, 23].

To further illuminate the mixing behavior of the mixed monolayers, we have used the Gibb's surface phase rule described by Gaines and Petty [21,22]. In monolayer experiment, the degrees of freedom are temperature, external pressure, monolayer surface pressure, and film composition. When the temperature and external pressure are kept fixed, the number of degrees of freedom for a monolayer system is expressed by the equation:

$$F = C^b + C^s + P^b - (q - 1) \tag{2}$$

Where, F, C, and P indicate the number of degrees of freedom, components, and phases that are in equilibrium in the bulk (b) and surface (s) phases, respectively. Here, q is the number of monolayer phases present in equilibrium with one another. For a two components monolayer system at the air-water interface, $C^b = 2$, $C^s = 2$ and $P^b = 2$. So, Equation 2 simplifies to

$$F = 3 - q \tag{3}$$

Here, we have applied the phase rule to collapse pressures of mixed monolayers. If the film components are miscible, two homogeneous phases will be present at equilibrium with each other and so $q = 2$ and hence the system will have one degree of freedom. Therefore, collapse pressures will show variation as a function of film composition. On the other hand, in a two component, mixed monolayer system in which the film components are immiscible, there are three equilibrium surface phases and so $q = 3$ and thus the system will have zero degree of freedom. This means that collapse pressure will be independent of composition.

Figures 3a and b describe the variation of the collapse pressures of the PYL-BA and PYL-PMMA mixed systems as a function of PYL mole fraction. Here, in the PYL-BA mixed system, the collapse pressure is found to be independent of concentration of the PYL, which clearly reveals that phase separation occurs in the mixed monolayers. This phase separation leads to the formation of aggregates in the mixed monolayers. However, the collapse pressure is dependent on the concentration of PYL in the PYL-PMMA mixed system, indicating a certain level of miscibility between the film components.

3.3. *Hysteresis study*

To evaluate how well the monolayer materials can retain its configuration during compression and expansion, we have investigated the hysteresis study of PYL-BA mixed monolayer.

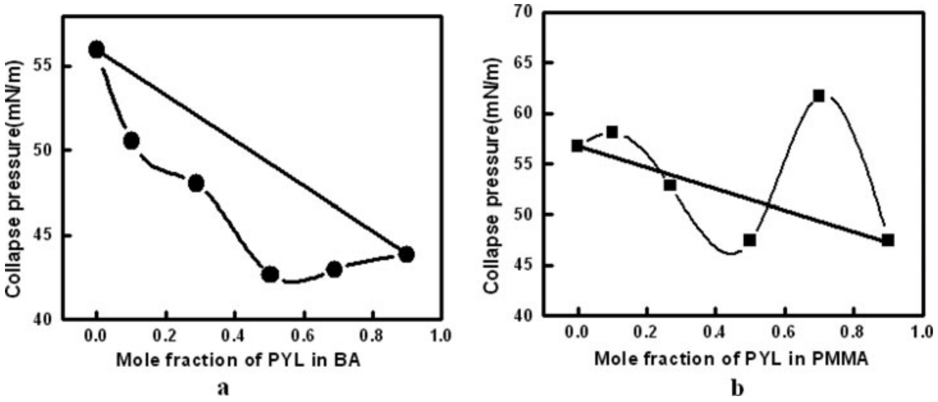

Figure 3. (a) Plot of collapse pressure versus mole fraction for mixed PYL/BA monolayer (b) Plot of collapse pressure versus mole fraction for mixed PYL/PMMA monolayer.

For this purpose, monolayer is first compressed to a predetermined pressure and then decompressed. The compression and decompression cycles of the monolayer film were recorded for pressures below the collapsing point by moving barrier on the water surface with a speed of 3 nm^2 mol^{-1} s^{-1}. Successive compression-expansion cycles for the mixed monolayer system shown in the Figure 4 reveals a good reproducibility, indicating the formation of a stable monolayer. The superimposition of the cycles ruled out the possibility of significant amount

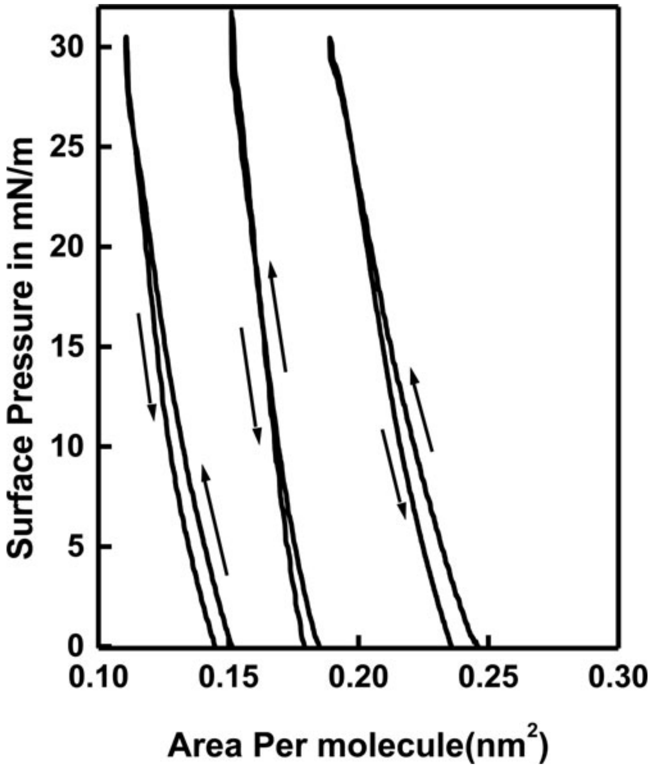

Figure 4. Compression-decompression isotherms of PYL-BA mixed monolayers at different molar ratios. Molecular area presented in the figure does not indicate the actual molecular area. Arrows represent the corresponding compression and decompression cycles.

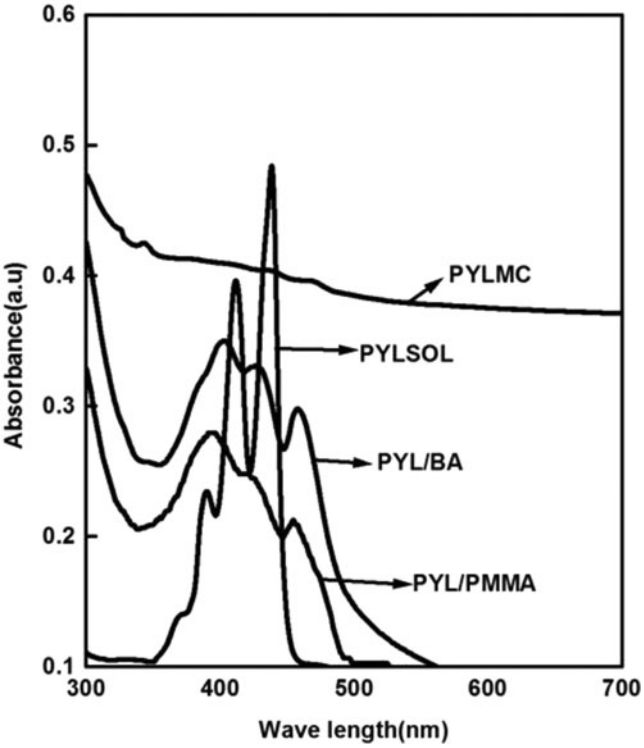

Figure 5. UV-VIS absorption spectra of PYL in chloroform solution (PYLSOL), microcrystal (PYLMC) and mixed LB films of PYL in BA and PMMA matrixes at a mole fraction of 0.5.

of material dissolution into subphase. The negligible amount of hysteresis observed between the compressions-decompression isotherms may possibly due to the difference in the organization and de-organization process of the sample molecules on the water surface during compression and extension respectively.

3.4. *UV-Vis absorption spectroscopic study of (PYL-BA) and (PYL-PMMA) mixed LB films*

The UV-Vis absorption spectra of mixed LB films of PYL in BA and PMMA matrixes along with PYL spectrum in chloroform solution are presented in Figure 5. The microcrystal spectrum of pure PYL is also included in the same graph for comparison. At 10^{-4}M concentration, the absorption spectrum of PYL in chloroform solution is structured in nature and is typical of the monomer. It consists of distinct bands in the 350-500 nm region having vibronic transitions appeared at 440 nm (0-0 transition), 411 nm (0-1 transition), 390 nm (0-2 transition) and 367 nm (0-3 transition). These characteristics of PYL solution spectrum are consistent with the result reported by Feguson [24]. The microcrystal spectrum and LB films absorption spectra of PYL in both the matrices shows almost identical band position and much broader than that of the solution spectrum. It is interesting to note that for the mole fraction of PYL in both the matrices the 0-0 band and 0-1 band are visible at 459 nm and 427 nm, shift of 19 nm and 17 nm respectively. Another transition 0-2 and 0-3 merge to form a new band at 403 which also most intense prominent peak. Moreover all the absorption bands in LB films and microcrystal are red shifted along with extensive broadening may be due to aggregation.

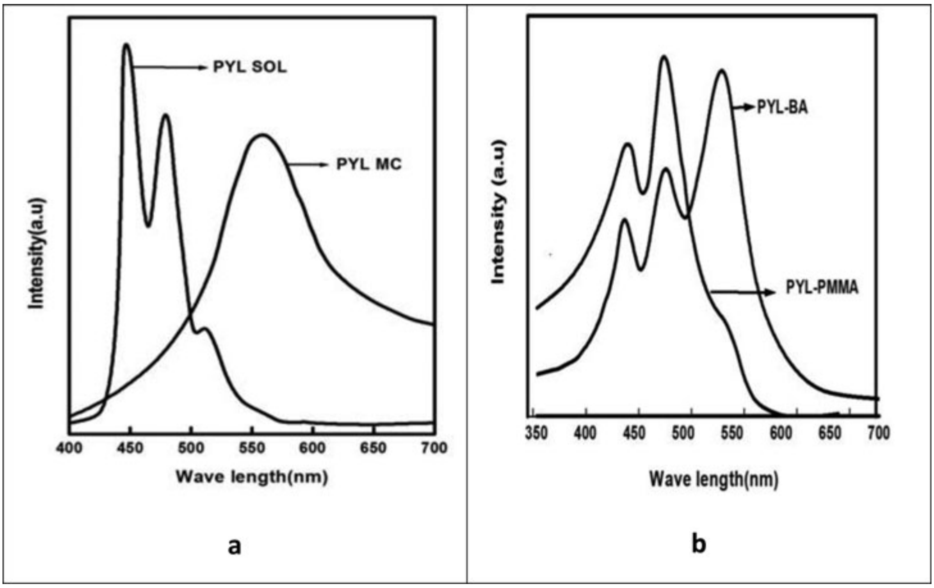

Figure 6. (a) Emission spectrum of PYL in chloroform solution (PYLSOL), microcrystal (PYLMC) (b) Emission spectra of mixed LB films of PYL in BA and PMMA matrixes at a mole fraction of 0.5.

According to the exciton model of McRae and Kasha [17], dipole – dipole interaction results band shift and splitting the energy level of the excited state with raising and lowering of the exciton band to a position either energetically higher or lower than the monomeric band. Such a change in energy is given by the relation:

$$\Delta E = \frac{2\mu^2(1 - 3Cos^2\,\theta)}{r^3} \tag{4}$$

where μ is the dipole moment of the molecules. θ is the angle between the dipole moment of the molecule and r, the line joins the centers of two dipoles. When $0° < \theta < 54.7°$, the exciton band is energetically located below the monomeric band that causes a red shift and the corresponding are referred to as the J-aggregates[18] while for $54.7° < \theta < 90°$ the exciton band is located energetically above the monomeric band that causes a blue shift and the corresponding are referred to as the H-aggregates[18].Corresponding to the magic angle $\theta = 54.7°$, no significant shift in the absorption spectrum is observed and the corresponding aggregates are referred to as I-aggregates[19].

In the present investigation, for both the matrices the broadening of the absorption band profile accompanied with the red shift in the mixed LB films of PYL identified as J-aggregates. Our AFM study also provides visual evidence of aggregate formation in the mixed LB films of PYL.

3.5. *Fluorescence study*

Figure 6a represents the emission spectrum of PYL in solution and microcrystal. The emission band at446 nm correspond to $0 \leftarrow 0$ transition, the band at 479 nm to $0 \leftarrow 1$ and the weak band at 507 nm corresponds to $0 \leftarrow 2$ transition. The microcrystal spectrum shows an unstructured band at about 558nm situated at lower energy. Both the emission spectra of LB films in PMMA and BA matrix shown in the Figure 6b are red shifted with respect to the PYL

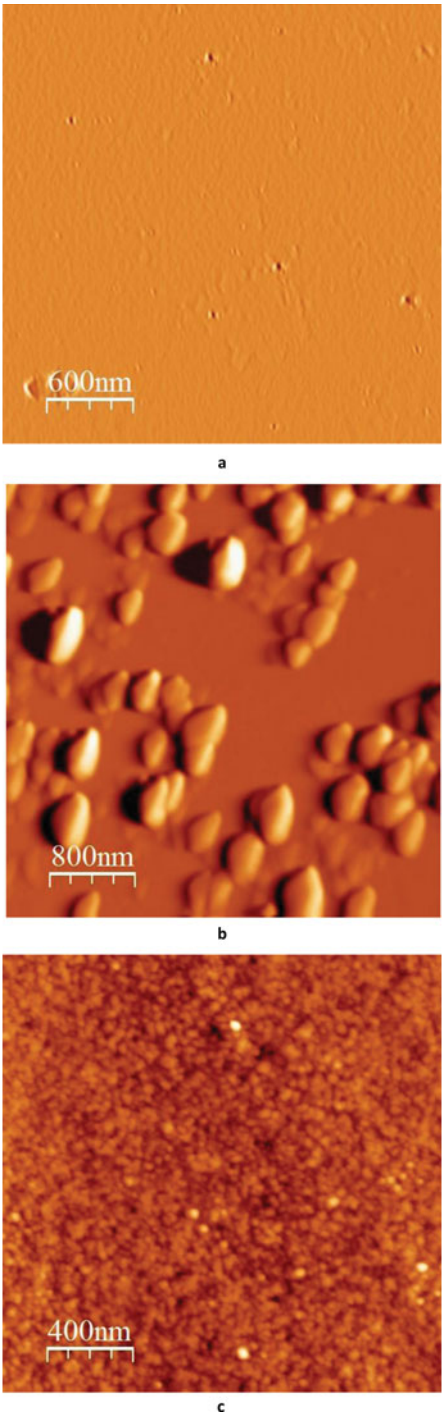

Figure 7. a: AFM of bare silicon wafer, b: one layered PYL-BA mixed LB film and c: one layered PYL-PMMA mixed LB film at a mole fraction of 0.5.

solution spectrum, the shift is more in case of BA matrix. Such behavior of PYL in LB films is an indication of dimer formation and is consistent with the results reported elsewhere [25].

3.6. *Study of surface morphology of mixed LB film*

To explore the morphological features of the mixed LB films deposited on silicon wafers and confirm the presence of PYL aggregates squeezed out of the BA and PMMA matrixes onto the monolayer film surface, the surface textures of these films were examined by AFM. AFM is a very powerful tool for obtaining information on surface morphology, particularly for the finer structure of LB monolayers. The AFM image of the bare silicon wafer is presented in Figure 7a for comparison with the mixed monolayer films. Figures 7b and c represent the AFM images of the mixed monolayer LB film of PYL/BA and PYL/PMMA which clearly indicate grainy morphology. In case of PYL-BA film, large aggregates of nanometer scale are observed at the upper surface of the monolayer films. In PYL-PMMA mixed film, the coverage surface area is more than 90%. These aggregates are believed to be the aggregates of PYL molecules, which form due to squeezing out of PYL molecules on the floating monolayers.

4. Conclusions

The present study shows that pure perylene (PYL) molecules can be easily incorporated in Langmuir and Langmuir-Blodgett films when mixed with a long chain fatty acid (behenic acid) or an inert polymer matrix PMMA. The surface pressure versus area per molecule isotherm and area versus mole fraction curves indicate a attractive type interaction between PYL and BA molecules in the PYL/BA mixed system, whereas repulsive type interaction play dominant role in PYL/PMMA mixed system with a little exception. The compressibility of PYL-PMMA mixed films were observed to be higher than the PYL-BA mixed films. A comparison of the mixed LB films and solution absorption spectra shows broadening along with shifting indicating the formation of organized aggregates in the both mixed film systems. The analysis of emission spectra of LB films compliments these results by exhibiting the red shift with respect to the solution. AFM images revealing heterogeneous grainy morphology confirms the formation of aggregates in the mixed LB films.

Acknowledgments

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