

Stress-strain relation in the collapse of Langmuir monolayer of a dimer of disk shaped moiety

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Langmuir monolayer of a novel molecule containing dimer of disk shaped moiety, viz., terephthalic acid bis-[6-(3,6,7,10,11-pentahydroxy-triphenylene-2-yloxy)-hexyl] ester (tp-dimer), was studied at air-water interface. The monolayer of the tp-dimer at air-water interface exhibited the coexistence of condensed and gas phases at large area per molecule which on compression transformed to a uniform condensed phase at lower area per molecule (1.80 nm^2) and then collapsed at 1.67 nm^2 . The monolayer film transferred by Langmuir-Blodgett technique onto a hydrophilic silicon substrate was studied using an atomic force microscope. The topography image showed the film to be of height of about 1.5 nm corresponding to the edge-on configuration of the triphenylene moieties. We have studied the collapse of monolayer at air-water interface as a function of compression rate and temperature. We find that the collapse pressure increased with increase in the compression rate. The surface pressure of the monolayer is considered as stress and compression as strain. The strain rate is related to the collapse pressure by a power law similar to that found in the dendrimers. Our studies on the effect of temperature on the collapse pressure of tp-dimer monolayer showed that the collapse pressure decreased with increase in temperature. We have considered the Arrhenius temperature dependence of the strain rate and calculated the activation energy for the collapse of monolayer. Our analysis of the relative area loss as a function of time in the collapse region suggests that the monolayer collapses by the formation of nuclei of three-dimensional crystallites. © 2010 American Institute of Physics. [doi:10.1063/1.3465575]

I. INTRODUCTION

Amphiphilic molecules spread at air-water interface can form insoluble monolayer called Langmuir monolayer. They provide an ideal model system for studying phase transitions in two-dimensional (2D) systems. Langmuir monolayer at air-water interface can be compressed from a uniform condensed phase to a collapsed state wherein the molecules go into the third dimension. The mechanism of the collapse depends on factors such as monolayer phase, pH, and ions present in the subphase.^{1,2} It is known that the condensed monolayer can collapse by forming three-dimensional (3D) crystallites or by forming multilayers.³ Although the physical properties of a material in 2D system can be different from the bulk, the concepts developed to describe the bulk materials can be extended to describe the properties of 2D systems. For example, in the study of monolayer rheology, the bulk continuum concepts has been applied to monolayers.⁴ Similarly, using constitutive equations based on the stress-strain models of bulk solids, Kampf *et al.*⁵ related the experimental parameters of an insoluble monolayer in the collapse regime.

We have studied the monolayer of a novel dimer of disk shaped triphenylene moiety, terephthalic acid bis-[6-(3,6,7,10,11-pentahydroxy-triphenylene-2-yloxy)-hexyl] ester (tp-dimer) at air-water interface. It is known that the molecules with such moieties can take either face-on or edge-on

configuration at an air-water interface depending on the area per molecule and surface pressure.^{6,7} In the edge-on configuration, the molecules can assemble into columns with column axis parallel to the interface. Such films transferred onto the solid substrates are of importance as they have high degree of anisotropy in conductance and can behave like one-dimensional conductors with potential applications.^{8,9} Hence, understanding the stability of the film under different conditions of temperature and strain is important.

We have studied the collapse of the tp-dimer Langmuir monolayer at an air-water interface as a function of compression rate and temperature. We find that the collapse pressure increases with increase in compression rate. We consider the surface pressure of monolayer as stress and compression of the monolayer as strain.⁵ The strain rate is calculated from the compression rate. For metals and polymers, it has been reported that the strain rate has Arrhenius temperature dependence and the yield stress is related to the strain rate by a power law.^{10,11} It has been shown that for the Langmuir monolayers of dendrimer⁵ and alkanethiol,¹² a power law relates the strain rate and collapse pressure in the plastic flow region. Our analysis also shows that for the monolayer of tp-dimer, the strain rate is related to the collapse pressure by a power law, but in the absence of plastic flow region. Our studies on the effect of temperature on the collapse pressure showed that the collapse pressure decreases with increase in temperature. Assuming the Arrhenius temperature dependence of the strain rate, we have calculated the activation

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energy for collapse of the monolayer. The surface pressure—area per molecule isotherm indicates that the tp-dimer monolayer exhibits slow collapse. We have studied the collapse mechanism by measuring the monolayer area loss as a function of time at a constant surface pressure. A model considering the nucleation of 3D crystallites and their subsequent growth was proposed by Smith *et al.*¹³ to understand the slow collapse mechanism. Weis¹⁴ has further given the thermodynamic description of the rate constants involved in the kinetics of slow collapse process. Our analysis of the monolayer area loss as a function of time for the tp-dimer monolayer suggested that the collapse mechanism can be attributed to the formation of nuclei of 3D crystallites.

II. EXPERIMENTAL

The material tp-dimer was synthesized in our laboratory. The purity of the material was found to be better than 99% by NMR, IR, and elemental analysis techniques. The Langmuir monolayer of the material tp-dimer was studied by surface manometry and Brewster angle microscopy (BAM) techniques. The solution of tp-dimer was prepared in high performance liquid chromatography (HPLC) grade chloroform with a concentration of about 0.1 mg/ml. Surface manometry studies were carried out using a Nima trough (model: 611M). Ultrapure de-ionized water (MilliQ) of resistivity 18 M Ω and pH of 5.7 was used as subphase. The freshly made solution was spread using a microsyringe on the subphase. The solvent was allowed to evaporate for 15 min before compressing the monolayer between two moving barriers. To study the effect of compression rate on the collapse pressure of monolayer, the speed of the barriers was varied at 7–100 cm² min⁻¹. This corresponds to a compression rate of the monolayer in the range of 0.10–1.50 nm² molecule⁻¹ min⁻¹. The temperature of the subphase was controlled by circulating water through the trough using a temperature controller (model: F25, Julabo). The monolayer was studied for different temperatures in the range of 15–32 °C. The BAM studies were carried out using MiniBAM (NFT, Nanotech) and the images were obtained using a frame grabber.

The Langmuir–Blodgett (LB) film of tp-dimer was prepared on a hydrophilic substrate. The double-side polished silicon wafers were used as hydrophilic substrates. The film was transferred at a target pressure of 5 mN/m and a dipping speed of 3 mm² min⁻¹. One layer of the film gets coated during one dipping cycle. The atomic force microscope (AFM) (model: Picoplus, Molecular Imaging) studies were carried out to characterize the LB film of tp-dimer. The sample was scanned in the tapping mode using a cantilever of average spring constant of 30 N/m and resonance frequency of 175 kHz.

III. RESULTS AND DISCUSSION

A. Surface manometry and Brewster angle microscopy

Surface manometry studies showed that the material tp-dimer forms a monolayer at air-water interface. The surface pressure (π)—area per molecule (A_m) isotherm obtained by compressing the monolayer at a rate of

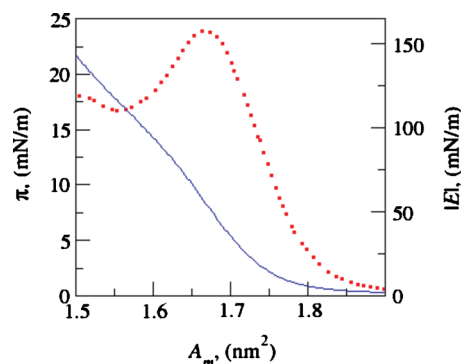


FIG. 1. Surface pressure (π) and compressional modulus $|E|$ as a function of area per molecule A_m for the tp-dimer monolayer at 15 °C. Solid line represents the surface pressure and dotted line represents the compressional modulus. The monolayer was compressed with a compression rate of 0.10 nm² molecule⁻¹ min⁻¹.

0.10 nm² molecule⁻¹ min⁻¹ and at a temperature of 15 °C is shown in Fig. 1. At large A_m , the isotherm shows zero surface pressure. The π starts increasing around the A_m of 1.80 nm². After the sharp rise in π , a kink is observed in the isotherm at an A_m of 1.67 nm², suggesting a phase transition. Below this area per molecule, the surface pressure of the monolayer held at constant A_m decreases sharply with time. This indicates the collapse of monolayer. The limiting area A_0 was 1.75 nm². The BAM images at A_m greater than 1.80 nm² showed the coexistence of dark and gray regions [Fig. 2(a)]. The gray domains exhibited a variation in intensity. This variation could be partially due to orientation of the molecules and partially due to variation in thickness. In our BAM setup, the incident laser light is linearly polarized. Also we had an analyzer in the path of the reflected light. The image in Fig. 2(a) was taken with a crossed analyzer. To check the contrast in the domain intensity, we rotated the crossed analyzer. We observed a variation in the domain intensity which can be attributed to the variation in the orientation of molecules. On compression, a uniform phase was observed between the A_m of 1.80 and 1.67 nm² [Fig. 2(b)]. At 1.67 nm², bright 3D crystallites start appearing from the uniform gray phase [Fig. 2(c)], which continued to grow with further increase in π . This indicated a phase transition from the uniform phase to the collapsed state, wherein the uniform monolayer breaks down to form 3D crystallites. The phase exhibited by the monolayer in the uniform gray region can be characterized by the compressional modulus $|E|$ of the monolayer. The $|E|$ value can be calculated from the π - A_m isotherm using the equation,

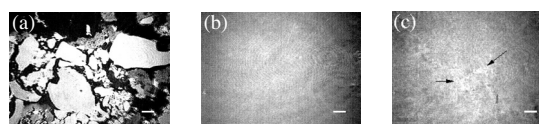


FIG. 2. BAM images of the tp-dimer monolayer at different area per molecule. (a) shows coexistence of gas and liquid condensed phase at A_m of 3.00 nm². (b) shows uniform phase at A_m of 1.70 nm². (c) shows the collapsed state of the monolayer. The arrows indicate the onset of 3D crystallites. The scale bar in each image represents 500 μ m.

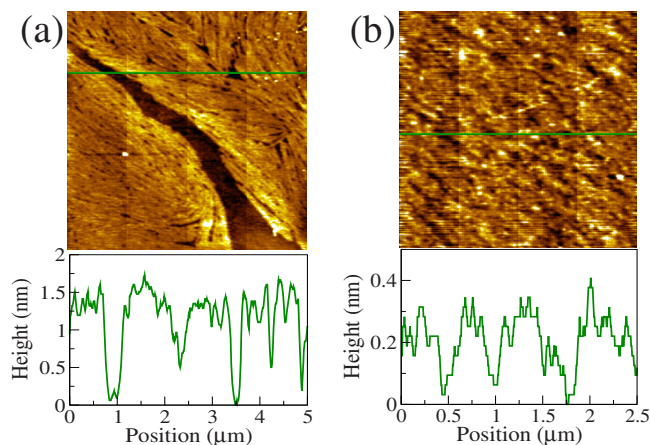


FIG. 3. (a) AFM image of the LB film of tp-dimer on a hydrophilic silicon substrate. Here, the condensed monolayer film was transferred at a target pressure of 5 mN/m. The line profile yields an average thickness of the film to be 1.5 nm. (b) AFM image of a bare hydrophilic silicon substrate. The line profile yields the rms roughness less than 0.4 nm.

$$|E| = A_m \left(\frac{d\pi}{dA_m} \right). \quad (1)$$

Here, $d\pi/dA_m$ is the change in surface pressure with area per molecule. In monolayers, the liquid expanded phase will have an $|E|$ value in the range of 12.5–50 mN/m and the condensed phase will have an $|E|$ value in the range of 100–250 mN/m.^{15,16} Figure 1 shows the plot of $|E|$ as a function of A_m for the tp-dimer monolayer. Here $|E|$ exhibits a maximum value of 157 mN/m at A_m of 1.67 nm². This value of $|E|$ indicates that the monolayer of tp-dimer corresponds to the condensed phase. From the π - A_m isotherm, BAM and $|E|$ value, we infer that the monolayer exhibited coexistence of gas and condensed phase at large value of A_m . Below an A_m of 1.80 nm², the monolayer exhibited uniform condensed phase and collapsed at an A_m of 1.67 nm².

The estimated length of the molecules (using CHEMDRAW) was found to be about 5 nm. If the molecules are stacked into columns due to Π - Π interaction between the triphenylene moieties, the intermolecular distance in a column will be about 0.34 nm. Thus, the estimated molecular area will be about 1.7 nm². Comparing this value with the A_o value of 1.75 nm², we infer the molecules to be in the edge-on configuration. Similar configuration of the molecules has been reported in the discotic triple molecules.¹⁷

B. Atomic force microscopy

The LB film transferred onto a hydrophilic silicon substrate was studied using an AFM. The transfer ratio of the film was about 90%. Figure 3(a) shows the AFM topography image of the monolayer film transferred onto a hydrophilic silicon substrate at a target pressure of 5 mN/m. The film exhibited needlelike features with some voids. The formation of needlelike features of uniform width can be attributed to the Π - Π stacking of the triphenylene moieties. The average thickness of the film calculated from the line profile drawn over a void was 1.5 nm. The rms roughness of the bare silicon substrate obtained from the line profile was less than 0.4 nm [Fig. 3(b)]. The estimated diameter of the triphenylene moiety (using CHEMDRAW) was 1.6 nm. Hence the height obtained from the AFM topography image of the monolayer film suggests that the triphenylene moieties of the tp-dimer molecules are in the edge-on configuration and the hydrophilic ester groups are anchored to the silicon substrate. Figure 4(a) shows the molecular structure of tp-dimer and Fig. 4(b) shows a schematic diagram of the organization of molecules. The limiting area obtained from the π - A_m isotherm indicates similar configuration of the molecules at air-water interface. This configuration is favored as it maximizes the Π - Π interaction between the triphenylene moieties.

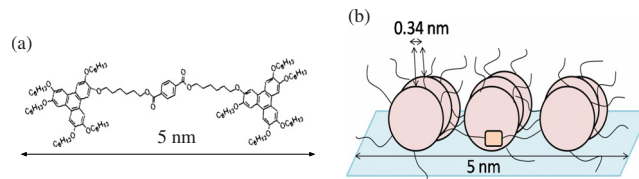


FIG. 4. (a) Molecular structure of tp-dimer with approximate length of the molecule according to standard bond lengths and angles. (b) Schematic diagram showing the organization of the tp-dimer molecules with the triphenylene moieties in the edge-on configuration. The estimated molecular area for this configuration is about 1.7 nm² which is close to the limiting area calculated from the π - A_m isotherm.

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C. Effect of compression rate on the collapse of Langmuir monolayer

We have studied the effect of compression rate on the collapse of tp-dimer Langmuir monolayer. The monolayer was compressed at various rates from an A_m corresponding to the coexistence of gas and condensed phase. We find that with the increase in compression rate, the collapse pressure (π_c) increases. Similar behavior has been reported for the monolayers of dicarboxylic acids.¹⁸ The dependence of the collapse pressure on compression rate indicates that the monolayer is in a metastable state. The π - A_m isotherm and the corresponding $|E|$ value also varied as a function of compression rate. Below the collapse pressure, the slope of the isotherm slightly increased. However, the change in surface pressure and $|E|$ value was negligible. On the other hand, in the collapsed region, the π - A_m isotherm and the corresponding $|E|$ value showed prominent change. We observed that both surface pressure and $|E|$ value considerably increased with the compression rate. However, we do not attach much importance to the $|E|$ value for the monolayer in the collapsed state. In our case, during the collapse, the monolayer breaks down to form 3D crystallites. We find that on expansion, the collapsed state was not reversible to the monolayer state. Hence, the transformation of the monolayer in the condensed phase to the three-dimensional crystallites during the collapse is similar to the transformation from elastic region to the plastic region in the bulk materials.¹² With this analogy, the surface pressure can be identified as the monolayer stress.⁵ The molecular area in the monolayer can be related to the monolayer strain (α) by the expression, $\alpha = 1 - (A/A_i)$, where A is the molecular area at time t and A_i is the initial molecular area. The strain rate (α_t) obtained from the above expression is given by the relation,

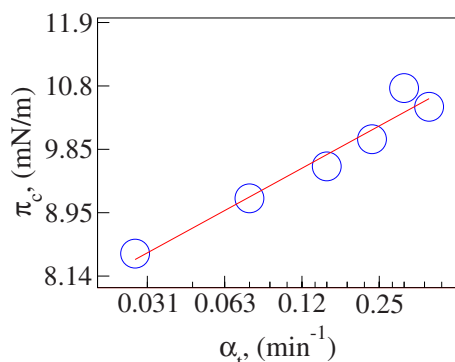


FIG. 5. Variation of collapse pressure (π_c) as a function of strain rate (α_t) for tp-dimer monolayer at 25 °C. The open circles represent the experimental data and the solid line represents the power law fit ($\pi_c = C_1 \alpha_t^{1/n}$) to the data points. The fit parameter yields the value of n to be 11.14.

$$\alpha_t = -\frac{1}{A_i} \frac{dA}{dt}. \quad (2)$$

Here $(dA)/(dt)$ is the compression rate. The strain rate can be calculated from the compression rate using Eq. (2). The A_i value is obtained from the lift off area (i.e., onset of the uniform condensed phase) in the π - A_m isotherm. Figure 5 shows the variation of collapse pressure as a function of strain rate at a temperature of 25 °C. Our data can be fitted with a power law relation similar to that given for dendrimer,⁵

$$\pi_c = C_1 \alpha_t^{1/n}. \quad (3)$$

Here, C_1 is constant at a given absolute temperature T .

The value of n calculated from the fit was 11.14. In our system, the monolayer does not exhibit a plastic flow region (a plateau region after the monolayer collapse in the π - A_m isotherm). The power law relation between the collapse pressure and strain rate has been reported in the Langmuir monolayers of dendrimer⁵ and alkanethiol¹² which exhibit the plastic flow region. We find that the value of n obtained for tp-dimer is of the same order as that reported for the dendrimer and alkanethiol monolayers ($n \approx 13$). In bulk, similar power law relation between strain rate and shear stress has been reported for polymers,^{11,19} where the constant C_1 is called the consistency and n is called power-law index. The deformation mechanism for linear polymers in the plastic flow region is known and the power law relation can be attributed to the nature of deformation mechanism. The insufficient experimental evidence to determine the nature of collapse in the monolayer makes it difficult to understand the power law relation between the strain rate and collapse pressure for the case of Langmuir monolayer.⁵ Hence, our study of power law relation in the absence of plastic flow region is important.

D. Effect of temperature on the collapse of Langmuir monolayer

The effect of temperature on the collapse of the Langmuir monolayer was studied from the π - A_m isotherms. The π - A_m isotherms were obtained for various temperatures with a constant compression rate. We find that with an increase in

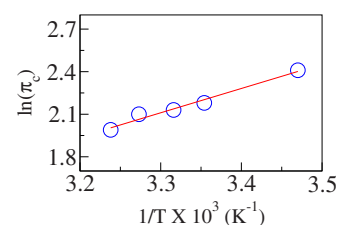


FIG. 6. Variation of $\ln(\pi_c)$ as a function of $1/T$ for the monolayer of tp-dimer. The monolayer was compressed at a rate of $0.10 \text{ nm}^2 \text{ molecule}^{-1} \text{ min}^{-1}$. Solid line represents the straight line fit to the data points (open circles). The slope of the line (ε/nR), yields a value of 1.71×10^3 .

temperature of monolayer, the collapse pressure decreases. Similar behavior has been reported in the Langmuir monolayers of other systems such as oligomers²⁰ and fluoroalkanes.¹⁶ For the monolayers of dendrimers⁵ and alkanethiol¹² molecules, it has been reported that the strain rate shows an Arrhenius temperature dependence. We have analyzed our experimental data by considering the strain rate to have Arrhenius temperature dependence¹² of the form $\alpha_t \propto \exp\{-\varepsilon/(RT)\}$ where, ε is the activation energy for the collapse of the monolayer and R is the universal gas constant. Rearranging Eq. (3) and by adding the temperature dependence of the strain rate, we get the following:

$$\alpha_t = C_2 \pi_c^n \exp\left(-\frac{\varepsilon}{RT}\right). \quad (4)$$

Here, C_2 is a constant. In order to obtain the value of ε , Eq. (4) is linearized and rearranged,

$$\ln(\pi_c) = \frac{1}{n} \ln(C' \alpha_t) + \frac{\varepsilon}{nRT}. \quad (5)$$

Here, C' is a constant. The plot of $\ln(\pi_c)$ versus $1/T$ yields a straight line. From the slope ε/nR , we can obtain the activation energy for the collapse of monolayer. Figure 6 shows the variation of the $\ln(\pi_c)$ as a function of $1/T$. The data points are fitted to a straight line. Activation energy (ε) obtained from the slope of the straight line was equal to 158.6 kJ/mol. The activation energy is the measure of energy required for the molecules in 2D monolayer to escape into the third dimension. The ε value reported for the monolayer of dendrimer⁵ was 596 kJ/mol and for that of alkanethiol¹² was 108 kJ/mol. The ε value depends on many factors such as interaction between the amphiphilic molecules, their interaction with the subphase and the mechanism of collapse.

Studies on the alkanethiol monolayer at air-water interface showed Arrhenius temperature dependence of strain rate only at high temperatures.¹² In our system, the Arrhenius temperature dependence was found throughout the temperature range studied.

E. Collapse mechanism

The π - A_m isotherm shows that the tp-dimer monolayer does not collapse catastrophically but undergoes a slow collapse mechanism. Slow collapse occurs at low surface pressures and the collapse of the monolayer can be realized through microscopic observations.¹⁴ Smith and Berg¹³ pro-

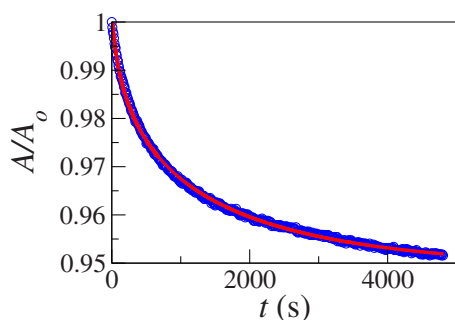


FIG. 7. Variation of A/A_0 as a function of time (t) for the monolayer of tp-dimer. The monolayer area was monitored with t at a constant surface pressure of 12 mN/m in the collapsed state. Solid line represents the fit to the data points (open circles).

posed the idea of modeling the monolayer collapse by homogeneous nucleation of the bulk phase and subsequent growth of the nuclei. They showed that the collapse mechanism can be understood by obtaining the collapse rate. The collapse rate can be conveniently obtained from the variation of monolayer area as a function of time at a constant surface pressure. We have obtained the relative area loss of the monolayer as a function of time at constant surface pressure in the collapsed region. The monolayer was compressed to a target surface pressure of 12 mN/m (above the collapse pressure) at a rate of $0.10 \text{ nm}^2 \text{ molecule}^{-1} \text{ min}^{-1}$. Then the monolayer area was varied to maintain the target surface pressure. Figure 7 shows the variation of A/A_0 as a function of time t . Here, A is the monolayer area at t and A_0 is the monolayer area at $t=0$. The experimental data can be fitted to the equation,

$$A/A_0 = a \exp(-k_1 t) + b \exp(-k_2 t^{1/2}), \quad (6)$$

where a , b , k_1 , and k_2 are constants. The first term in the Eq. (6) has been attributed to the collapse mechanism by the formation of the critical nuclei.^{13,14} The second term can be attributed¹³ to the area loss due to the diffusion process at large values of time. Weis¹⁴ has carried out systematic studies on the area loss-time isobaric dependencies at various temperatures and isothermal dependencies at various pressures for the stearic acid monolayer. He showed that the area loss was due to the processes of homogenous nucleation and growth of the 3D crystallites. Vollhardt *et al.*²¹ have studied the collapse mechanism of the Langmuir monolayers of fatty acids and showed that the nucleation theory introduced for apparent area relaxation of insoluble monolayers at constant surface pressure can be characterized by two main features: (i) the overall rate of the process described by convolution of the nucleation rate and growth rate and (ii) the overlap of the growing centers. In our case, the variation of A/A_0 as a function of t had nonzero initial slope which suggest that the growth of the nuclei does not contribute to the monolayer area loss. The area loss is mainly due to the formation of the nuclei of 3D crystallites.

IV. CONCLUSIONS

The molecule containing a dimer of disk shaped triphenylene moiety (tp-dimer) forms a monolayer at air-water interface. It exhibits a coexistence of gas and uniform condensed phase, a uniform condensed phase and a collapsed state on decreasing the area per molecule. For the uniform condensed phase, the limiting area obtained from the isotherm suggests that the triphenylene moieties in the molecule are in the edge-on configuration at air-water interface. The AFM studies on the LB monolayer film on a hydrophilic silicon substrate also indicate that the triphenylene moieties in the molecule are in the edge-on configuration. We have studied the effect of compression rate and temperature on the collapse of the monolayer. The surface pressure is considered as the monolayer stress and the compression is considered as the monolayer strain. In our system, we obtain a power law relation between the strain rate and collapse pressure of the monolayer in the absence of plastic flow region. Our studies on the effect of temperature on collapse showed that the collapse pressure decreases with increase in temperature. We have analyzed the data by using the bulk constitutive equations and considering the Arrhenius temperature dependence of the strain rate. Our analysis yielded an activation energy of 158.6 kJ/mol for the collapse of the monolayer. Our studies on the collapse mechanism indicated that the collapse of the tp-dimer monolayer is through the formation of nuclei of 3D crystallites.

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