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The behaviour of bis-(*p*-toluene sulphonate) of 2,4-hexadiyne-1,6-diol as a spread film on a water surface

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The characteristic surface pressure–area compression isotherm and surface pressure–surface potential curves are reported for bis-(*p*-toluene sulphonate) of 2,4-hexadiyne-1,6-diol (TS) spread on a water surface. The elasticity of the TS film as a function of surface pressure is measured by means of a dynamic method. The polymerization of the TS film on the water surface was initiated by u.v. irradiation and the reaction was found to be instantaneous without any induction period. The reaction is thus much more rapid in comparison with the solid-state polymerization of TS in its crystalline state.

1. Introduction

The Langmuir–Blodgett (LB) technique provides a competitive way to produce artificial molecular architectures. The LB films prepared by this technique have highly ordered structure, they are ideally ultrathin and molecularly smooth. Molecular mono- and multilayer films are predicted to become important in many high technology applications, especially in molecular electronics, nonlinear optics and chemical/biological sensors [1].

One of the restrictions of the LB technique is that the film-forming substance should be bifunctional. The constituent hydrophobic and hydrophilic residues must be effectively separated to the ends of the molecule in order to be able to form a monomolecular film at the liquid–gas interface. As a consequence, a number of organic compounds with interesting electronic and optical properties unfortunately cannot be applied in LB technology due to their lack of bifunctionality. Recently, however, some efforts have been made to produce LB films from such compounds [2, 3].

Bis-(*p*-toluene sulfonate) of 2,4-hexadiyne-1,6-diol (TS) and its polymer PTS are able to form large macroscopic single crystals (on the 10^{-1} m scale), which has attracted extensive investigations of their properties [4, 5]. They exhibit semiconductivity at room temperature [6] and a high second-order optical nonlinearity [7]. In order to probe their nonlinear optical properties in an unambiguous way, it is necessary to prepare a sample of a very small thickness and with a very smooth surface. Thakur *et al.* [8] devised a new technique to prepare an optically active thin laminate of TS. McCaffrey *et al.* [3] tried to prepare thin films made of TS by a modified LB technique. We [9] have also obtained LB-deposited TS thin films with a highly ordered structure. The aim of this study is to characterize the behaviour of spread TS films. The elasticity of a TS film spread on a water surface has been measured by a dynamic oscillation method, and the resulting elastic modulus for the film is reported for the first time. The polymerization of spread TS films was monitored under the influence of u.v. irradiation at a constant surface pressure.

2. Experimental procedure

2.1. Synthesis and spreading of TS

The film substance of bis-(*p*-toluene sulphonate) of 2,4-hexadiyne-1,6-diol (TS) was synthesized by the method reported by Wegner [10]. Pure TS was recrystallized three times from acetone and dissolved in xylene to form a solution with a concentration of about 4.2 mg ml^{-1}. The solution was protected against light and stored in a refrigerator prior to the spreading.

A KSV LB-5000 Langmuir trough system (KSV-Instruments, Finland) equipped with a Wilhelmy balance for the surface pressure detection and a teflon trough of size $47.5 \times 15 = 712.4$ cm^2 was used in the experiments. The TS film was obtained by spreading the solution on a subphase of pure water. The water was purified with a Milli-Q filtration system to give water resistances as high as 18 MΩcm. The film was compressed with a barrier speed of 20 mm min^{-1}. All the measurements were performed at a constant temperature of 20 ± 0.3 °C if not specified otherwise.

2.2. Polymerization

The spread TS film was irradiated at a constant surface pressure using a 30 W low pressure mercury

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lamp mounted 15 cm above the film. The Langmuir trough was protected against natural u.v. light with a yellow semitransparent plastic shield. Under the influence of u.v. irradiation the mean molecular area changes as a result of intermolecular reactions which induce a reorganization of the molecules within the film. The changes in the molecular area may then be related to the geometrical changes in the film structure. The reaction kinetics were monitored by recording the change of the barrier speed during irradiation. When reaching the predetermined surface pressure, even in the absence of u.v. irradiation, some molecular self- or reorganization takes place in the film, which causes some fluctuations in molecular area. Thence, a stabilization period of about 15 min is needed in order to minimize the barrier fluctuation prior to u.v. treatment.

2.3. Elasticity measurements

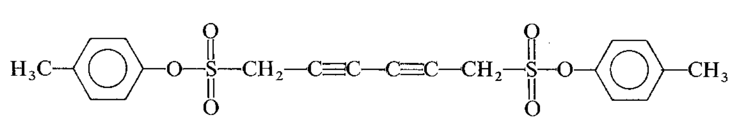
The elasticity measurements were performed with a KSV-5000 Langmuir trough system using the specially designed program made available to generate sinusoidal barrier vibrations with a pre-determined frequency and amplitude. The compression speed was chosen to be 20 mm min^{-1} and the compression was started about 10 min after the spreading, in order to enable the solvent to evaporate totally. As soon as the surface pressure reached the pre-set value, the periodic compression–expansion cycles with a given frequency and amplitude were automatically activated. Both the barrier oscillation and the corresponding change of the surface pressure were recorded.

The following constraints of the elasticity measurements may be worth noting. The amplitude of the barrier oscillation can be adjusted from 0.1 mm to principally any value. However, too large amplitudes may induce incorrect results, especially if phase transitions (change of monolayer state) take place. An amplitude of 1–2 mm was found to be suitable for most experiments. The oscillation frequency can be varied between 0.1 mHz and 150 mHz. Frequencies lower than 20 mHz could not be used due to instability of the monolayer, whereas the use of very high frequencies was made inaccessible by the heavy and thus mechanically slow barrier. Hence, a frequency of 40 mHz was used.

3. Results and Discussion

3.1. Behaviour of TS spread film

TS may be considered to be a kind of diacetylene with the following symmetric structure:



$$H_3C-C_6H_4-O-\overset{O}{\underset{O}{S}}-CH_2-C\equiv C-C\equiv C-CH_2-\overset{O}{\underset{O}{S}}-O-C_6H_4-CH_3$$

As shown, no separated hydrophobic and hydrophilic groups can be found. Therefore, when spread, the molecules strongly adhere to the water and will simply float horizontally, instead of rising to a vertical orientation on the water surface. On the other hand, TS is a highly crystalline compound and its macroscopic

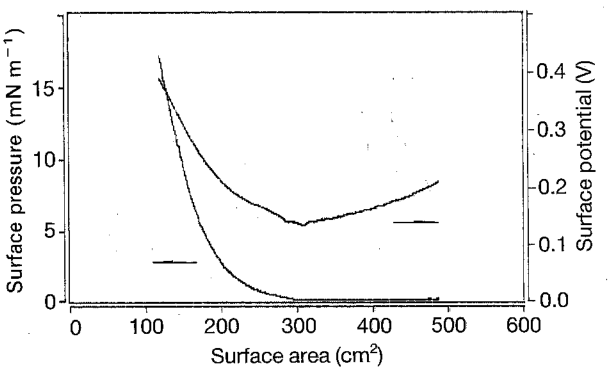


Figure 1 The surface pressure (left scale) and surface potential (right scale) curves as a function of trough area for a TS film spread on a water surface.

single crystal may be prepared by means of solvent evaporation. Young *et. al.* [11] have, for example, prepared TS thin laminates on a water surface by toluene evaporation. TEM results confirmed that the crystal laminates deposited on glass slides had an excellent ordered structure. This suggests that TS molecules are arranged regularly also on the water surface and that this tendency is reinforced by applying a constant surface pressure on the film. This is reflected in the pressure–area isotherm obtained for a spread TS film [9] under compression. The film is transferable onto a solid substrate to form a structure with the same regular molecular arrangement [3, 9].

Instead of the spreading procedure that Young has used, we have applied the Langmuir method to obtain the floating film. Although we obtained the isotherm for a spread TS film on a water surface as shown in Fig. 1, the spead film was never uniformly distributed over the water subphase, in contradiction to the above-mentioned results. Fortunately, the TS monomer is very sensitive to the u.v. irradiation and will change its colour from colourless to dark blue due to polymerization, which offers a visible means to observe the TS distribution on the water surface. Several domains with different degrees of colour can be observed to float as a homogeneous continuous matrix layer over the trough surface.

The amount of TS spread on the water surface exceeds the amount required to form a single monolayer by isotherm compression. The trough area available for the spread film was 675 cm^2. The mass spread on the water surface of the trough is 0.42 mg which, assuming a flat orientation of the TS molecules (0.71 nm^2 molecule^{-1}) would cover a 0.43 m^2 surface. This is consequently over six times the amount theoretically required to form a monolayer over the available surface area. The physical "state" of a spread TS film should thus correspond to a continuous TS multilayer with some thicker "islands" on it. These islands seem not to affect the nature of the matrix layers, since the isotherm response is similar to the homogeneous monolayer. In order to reduce the possible effect of multilayer spreading a TS concentration of 0.042 mg ml^{-1} was used, which was less than the estimated minimum quantity to form a condensed monolayer. Some multilayer domains could, however, still be observed after u.v. irradiation, which renders the parameters such as the surface area available per monomer molecule (such as estimated in [3]) meaningless. This is why we present our data in relation to the trough area instead of the mean molecular area. An excess amount of TS was spread on the water surface in order to reach a surface pressure rising over trough areas large enough to further enable a larger dynamic range for the kinetic studies.

There are two simultaneous processes taking place during the spreading of the TS solution. One is the spreading of the mixture of TS molecules and the xylene solvent. After solvent evaporation the TS molecules try to occupy an area which is as large as possible. On the other hand, the TS molecules will associate, forming crystals. Thus, there exist some crystal laminates which become visible when u.v. irradiated.

The surface pressure–trough area isotherm of a spread TS film is shown in Fig. 1. Although some excess amount of TS was used in the experiment, the surface pressure started to rise at an area of 300 cm^2, which is considerably smaller than the area occupied by a float monolayer (4300 cm^2). Simple calculation shows that the condensed TS film should consist of 14 layers of TS molecules. Until 12 mN m^{-1}, the compression of the spread TS film is homogeneous and the isotherm is smooth. The interesting point is that although no collapse can be observed in the isotherm, at least within the range of surface pressure detected, a very light yellow collapsed film becomes visible in the neighbourhood of the barrier at $\pi > 12$ mN m^{-1}. The reason is probably that the local density of TS molecules is high enough to initiate the macroscopic crystallization process.

The surface potential–trough area curve for the spread film is also shown in Fig. 1. The surface potential reaches a minimum value at a trough area of ≈ 300 cm^2, below which a rising surface potential could be detected. A change in the surface potential is interpreted in terms of molecular orientation or a change in the state of the molecule (or both). The sulfonate groups $-SO_2-$, with their large dipole moments, as well as the aryl- and $-c=c-$ groups are all components in the TS molecule that contribute to the surface potential. It is thus difficult to determine which group is the primary contributor to the change in the surface potential below and above the area ≈ 300 cm^2.

3.2. Elasticity of TS Spread films

The elasticity E of a monolayer on the subphase surface is defined as $E = d\pi/(dA/A)$, where A is the surface area occupied by the spread film [12]. The method of changing the surface area (dA) and concomitantly the surface pressure ($d\pi$) by generating a sinusoidal vibration on the barrier has been reported elsewhere [13]. The dynamic oscillation method is especially accurate when the sinusoidal compression–expansion cycles of the barrier have small frequency and amplitude. Blank *et al.* [14] have used the dynamic method to measure the elasticity of protein monolayers.

The experimental response of the surface pressure oscillation of a spread TS film on a water surface caused by a periodic compression–expansion cycle with a frequency of 40 mHz and an amplitude of 1.5 mm and at a surface pressure of 3 mN m^{-1} is shown in Fig. 2. As shown, the response curve of the Wilhelmy plate is in phase with the barrier oscillation which indicates, at least with the used oscillation frequency, a negligible contribution from the viscosity. The spread TS film was, however, not stable during the compression–expansion cycles. The surface pressure decreased quickly with increasing number of oscillation cycles. However, the elasticity of the film can still be estimated from the surface pressure response corresponding to the first barrier oscillation cycle. Fig. 3 shows the elasticity of the spread TS film on a water surface at 20 °C as a function of the surface pressure.

The elasticity of the spread TS film increases from 34 mN m^{-1} to 66 mN m^{-1} when the surface pressure is increased from 2 mN m^{-1} to 7 mN m^{-1}. Assuming a molecular thickness of 0.5 nm one obtains a "bulk" surface elasticity of 70–130 N mm^{-2} for a monolayer film. To our knowledge, there is no previous data about the elasticity of spread TS films on water surfaces in the literature. As a reference, the Young's modulus of a TS polymer single crystal has been measured by a standard stress–strain experiment to be 4.4×10^4 N mm^{-2} along the molecular chain direction [11]. It is generally thought that the interaction along the molecular chain direction is 100 times larger than that in the direction perpendicular to the molecular chain. Thus the modulus of a PTS single crystal perpendicular to the chain direction can be estimated to be about 400 N mm^{-2}. The compression isotherm shows that the spread TS film at a surface pressure of 8 mN m^{-1} does not correspond to a solid-like state. This may explain the findings of an elastic modulus that is lower than that reported for a bulk polymer PTS crystal. The increase of elasticity with increasing surface pressure is in agreement with the surface pressure–area isotherm. Actually, the elasticity–surface pressure curve is the differential form of the compression isotherm and seems to respond very well

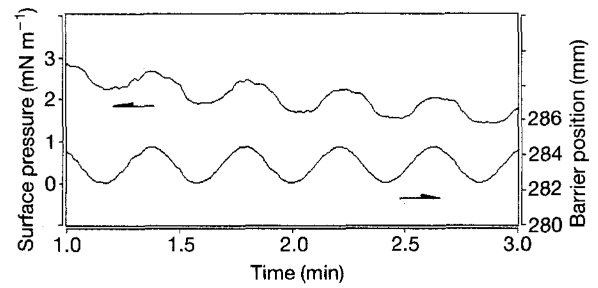


Figure 2 The barrier-generated oscillation and the Wilhelmy plate response at a constant surface pressure of a TS film spread on a water surface.

to the surface state of the spread film. The linearity of the elasticity–surface pressure curve indicates that no phase transitions take place during the film compression within the measured surface pressure range.

3.3. Polymerization of a TS film spread on a water surface

TS is a diacetylene derivative which can be polymerized only in the solid state or in the "ordered state". The polymerization of TS monomer single crystals by heating or u.v. irradiation has been studied extensively [4, 5].

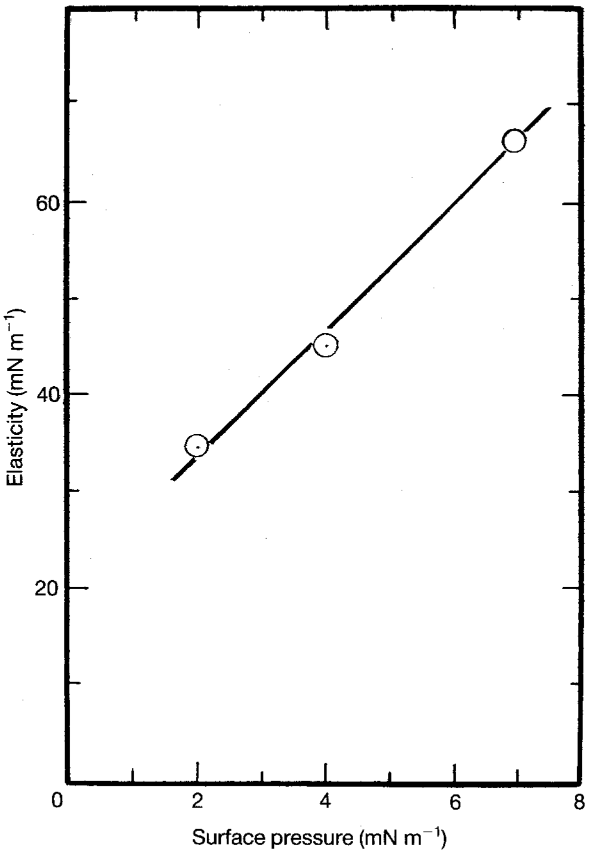


Figure 3 The elasticity as a function of surface pressure for a TS film spread on a water surface.

For any material the polymerization is a process in which the monomer molecules which are at a van der Waals' distance (0.3–0.5 nm) become interconnected by chemical bonds (0.15 nm). This leads to a (bulk) volume or an area (surface) contraction during polymerization. The surface contraction can be monitored by the change of the barrier location when the surface pressure is adjusted to be constant. Consequently, this gives an opportunity to measure the polymerization kinetics of spread TS films on a water surface.

Fig. 4 shows the change in the parameters recorded when irradiating a spread TS film on a water surface with u.v. light at a constant surface pressure of $2\,\mathrm{mN\,m^{-1}}$ and at 20 °C. The u.v. irradiation was started after a 15 min stabilization period, which was enough to minimize the influence of the barrier movement on the surface pressure. The polymerization reaction started immediately the u.v. light was switched on. As visualized in Fig. 4, the area covered by TS molecules contracted so rapidly that the barrier could initially not keep the surface pressure constant. The surface pressure fell instantly and the barrier speed "jumped up". Less than 1 min of u.v. irradiation was enough to complete the polymerization reaction and the barrier speed reduced to its original average value. The colour of the film changed from colourless to dark blue. By sweeping the surface carefully, a dark purple solid residue with more or less metallic lustre was obtained. The insolubility of the residue (reacted product) in acetone indicated that the TS monomer had been completely converted to its polymer PTS, because the TS monomer is easily dissolved in acetone. The experiment was repeated for constant surface pressures of 4, 6 and $8\,\mathrm{mN\,m^{-1}}$. u.v. Irradiation produced the same overall changes in the film, although the reaction time was slightly reduced at a higher surface pressure. This is apparent from Fig. 5.

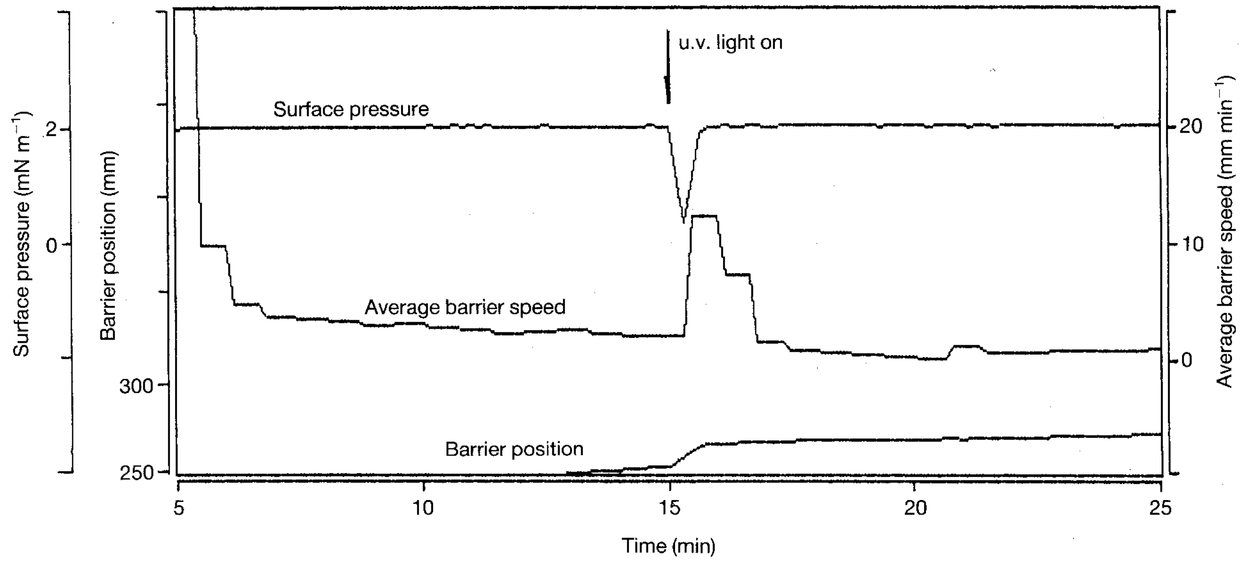


Figure 4 The experimental response curves of spread TS film polymerized under u.v. irradiation at a constant surface pressure of $2\mathrm{mN\ m^{-1}}$ and 20 °C.

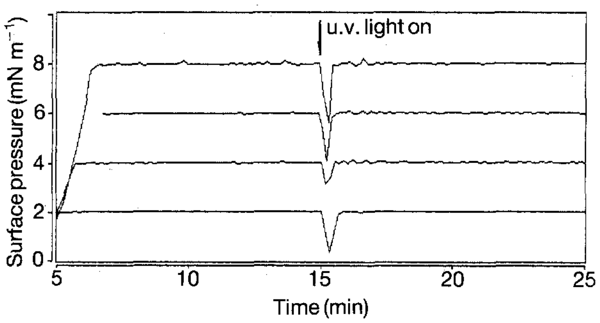


Figure 5 The adjustment of surface pressure needed due to the polymerization of a spread TS film under u.v. irradiation at four different constant surface pressures.

The polymerization of a TS monomer in the solid state has an induction period of several hours for either heat-polymerization or photo-polymerization in bulk [15]. The polymerization will be completed in 72 h for an annealed TS single crystal at 60 °C [16]. Obviously, there exists a very big difference between the polymerization rate of a TS single crystal and a film spread on a water surface. The solid-state polymerization is lattice controlled, it takes place only if the lattice distances are comparable with the bond distance in the polymer chain [17]. When the monomer molecules are spread on a water surface and compressed to a condensed-like state, a system is created resembling that of biological membranes. Due to the enforced molecular alignment and the liquidized state the molecules have more degrees of freedom to orient themselves into optimal positions for polymerization to take place.

The polymerization of diacetylene occurs by a carbene mechanism [18]. The conjugated triple bond is excited by u.v. light which produces a carbene as the reactive species. This reacts with its neighbouring carbene to form a dimer. The mixture of other excited monomers and the dimers leads to the formation of a macromolecule. This is not a radical polymerization but a step polymerization and depends on the amount of excited carbene.

4. Conclusions

TS has been successfully spread on a water surface. However, the film was never homogeneous, but corresponded to a continuous TS multilayer film probably having some thicker "islands" on it. The polymerization of the film under u.v. irradiation at a constant surface pressure is instantaneous, without any induction period. This is totally different from the process observed for a bulk TS crystal. This indicates that the spread film is only a few TS molecules thick, which allows the u.v. light to be absorbed simultaneously by all the TS molecules. Since the molecules in the liquid state are effectively oriented but maintain a considerable flexibility, the conditions for an instantaneous and quick reaction are generated. The measurements thence show that the Langmuir method can be used to produce and to characterize not only monolayers but also inhomogeneously spread surfactant films. More specifically, the polymerization kinetics as well as the elastic modulus for a spread TS film are reported here for the first time.

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