NOVEL MATERIALS FOR MOLECULAR ELECTRONICS AND THEIR CHARACTERIZATION

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Summary Defect-free diacetylene (DA) Langmuir-Blodgett films polymerized on a air/water interface have various applications in biosensors, membrane physics or low-dimensional physics. Polymerization of DA monolayers is in general way characterized by optical spectroscopy. In this study for evaluation of photopolymerization process for the first time the Maxwell displacement current (MDC) measuring technique was used. In experiment MDC flows through the metal electrode/air gap/Langmuir monolayer/water surface structure. The effect of polymerization as well as the phase transition of polymerized DA was observed. Moreover PDA domain creation and homogenization was registered.

1. INTRODUCTION

The study of 3-dimensional crystalline polymers of diacetylene (DA) had already made substantial progress even before the attention was turned to Langmuir-Blodgett films formed of these materials. The polymers of diacetylene derivatives have some interesting properties such as non-linear optical properties, anisotropic electric conductivity [1]. Also the patterning of polymerized diacetylene (PDA) monolayers is a feasible approach for various components, where functional molecules can be integrated into a membrane with well-defined spatial arrangement [2] for preparing a biosensor with molecular recognition [3]. It was found that the Langmuir technique, in which dissolved monomers are spread onto a water surface, subsequently compressed, and then polymerized prior to deposition onto a substrate (LB film), are extremely effective in producing well-controlled and highly organized ultrathin PDA films [4].

A lot of studies have been reported on the photochemical reactions of diacetylene monolayers and LB films of DA, mostly focused on the colour change observed by optical spectroscopy [5]. The so-called "blue" and "red" phases have been extensively investigated. The names are derived from absorption bands of the LB fims at 643 and 588 nm (blue phase) and 540 and 500 nm (red phase). However, the nature of the process is still not clear.

The photopolymerization process in DA is rather rapid under irradiation by the light having the wavelength of approx. 300 nm, but also a slow process passes under irradiation by the light having longer wavelengths. Usually the polymerization is investigated by watching the phase transition from the red phase to the blue one. A subsequent annealing of the LB film (50-70°C) induces an irreversible color change from red to blue [6]. On the other hand, in the Langmuir film it is possible to initiate a reversible phase transition from blue to red by increasing the surface pressure [5].

After spreading DA molecules at the air/water interface a spontaneous domain formation can be observed, each domain having its own uniform molecular tilt [7]. The domain size after LB deposition is in the range of 1-100µm depending on external conditions (e.g. pH of the subphase).

2. THERMAL STABILITY

One of the most severe drawbacks in large-scale commercial use of organics resides in their low mechanical and thermal stability [8]. The increase in the stability in some cases can be achieved by subsequent technological treatment. The most effective procedure in this trial is polymerization. As an evidence of this phenomenon we arranged a relatively simple electrical test. A schematic drawing of the apparatus is shown in Fig 1.

The substrate used in the measurements was spectroscopic quartz, cleaned by heating at 90°C in H_2SO_4/H_2O_2 mixture (1:3 v/v), washed in water (bidistilled deionized, 15MΩ/cm), and dried in N_2 atmosphere. The contacts for the electrical test were made by thermal evaporation of Al. The thin film was deposited onto the substrate using the Langmuir-Blodgett method on the equipment obtained from Nima Technology Ltd. (England). The number of monomolecular layers deposited was 50 for each sample, which corresponds to the thickness of 135 nm. The deposition allowed two samples to be prepared during one technological cycle simultaneously, one of them subsequently exposed to UV radiation and polymerized. Both samples were then subjected to the measurement of transverse electrical resistance in dependence on elevating temperature at a linear rate of 5°C. The top electrode was a needle with a rounded tip (the radius approx. 0.5 mm) pressed against the sample surface with a force of approx.1N. The total resistance was measured by a Keithley electrometer 617 in the I/V mode (the test voltage was set to 1 V). For experimental details see [9].
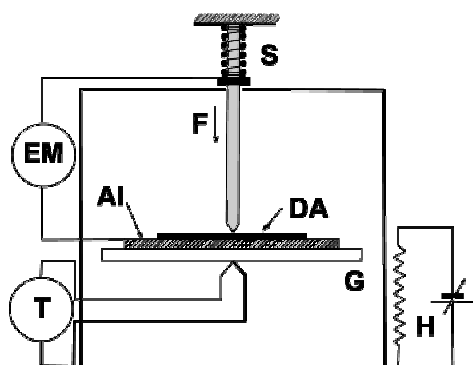
Fig.1: Schematic view on the thermal stability measurement. Needle (S) press with the constant force (F) on the diacetylene layer (DA) deposited on the aluminium (Al) substrate. Disruption of the insulating layer is recorded by the sensitive electrometer (EM) Thermal stability is provided by heating (H) and controlled by the thermometer (T).

Typical results as measured on a pair of samples (monomer – polymer) are presented in Fig. 2. After a gradual slow decrease of the resistance, there is an abrupt drop at T_1 in the monomeric DA phase and at T_2 in the polymeric phase. All the measurements revealed the tendency $T_2 > T_1$, the difference being about 60 °C for all pairs of samples tested. The systematic approx. twofold increase in absolute resistance after the polymerization was observed. The sudden drop of the transverse resistance is associated with the mechanical destruction of the sample initiated by the increased temperature when the top electrode penetrates into the organic thin layer short-circuiting the structure.
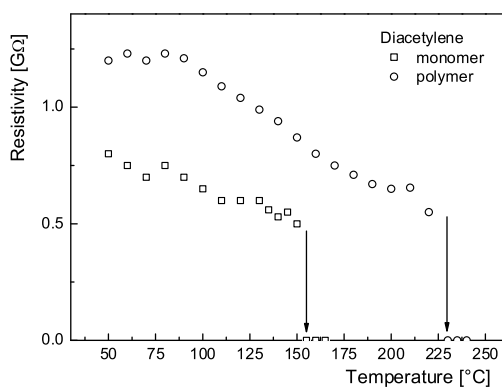

Fig. 2: Thermal stability of monomer and polymer diacetylene LB film.

3. MDC EXPERIMENT

For a displacement current measurement a monomer of tricosa-10, 12-diynic acid molecules (Dojindo Laboratories, Japan) was spread on the subphase from a chloroform solution and allowed 15 min before compression for solvent evaporation. The water subphase was thermostated to the temperature of 17°C. The film was compressed at a rate of

0.07nm^2/min per molecule. The monolayer was polymerized by the exposure to UV light at constant surface pressure (15mN/m) for 60 min. The obtained surface pressure-area isotherms are shown in Fig.3.
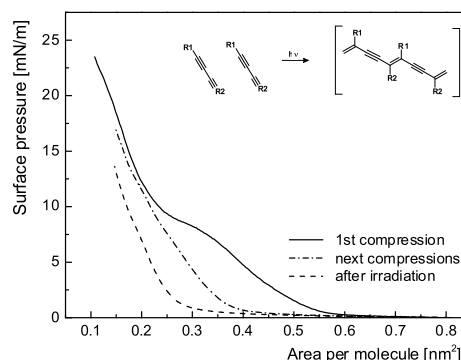

Fig. 3: Surface pressure-area isotherm of the diacetylene monolayer before and after polymerization process. In the insert is shown the effect of polymerization on the chemical structure of diacetylene.

Polymerization of the monolayer was also investigated by Maxwell's displacement current (MDC) technique [10, 11]. The displacement electric current I flows through a short-circuited capacitor being formed by two parallel plates, the one in air above the monolayer detached at a certain spacing (1.3 mm in our case), the other immersed in the water subphase below the organic monomolecular layer, Fig.4.
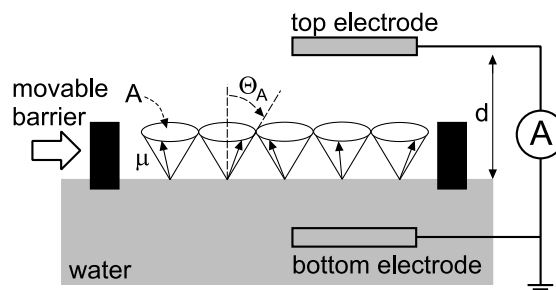

Fig 4: Sketch of the experimental setup for MDC measurement. Diacetylene molecules execute precessional motion at the air/water interface with maximal tilt angle Θ_A, which is determined by the barrier. Electrical shielding of the top electrode is not drawn.

Compression of the monolayer, carried out by a movable barrier, results in the change of the number of molecules under electrode N as well as in the mean orientational change of the direction of molecular electric dipoles $\langle \cos \Theta \rangle$. The change of projection of the orientational polarization vector to the normal μ_z can be associated with Maxwell's displacement current flowing through the monolayer [11]:

$$\mu_z = \mu \langle \cos \Theta \rangle = \frac{1}{GN} \int I dt, \qquad (1)$$

where G is the geometrical factor of the experimental arrangement. The measured displacement currents as well as the calculated dipole moment projections are presented in Fig. 5.
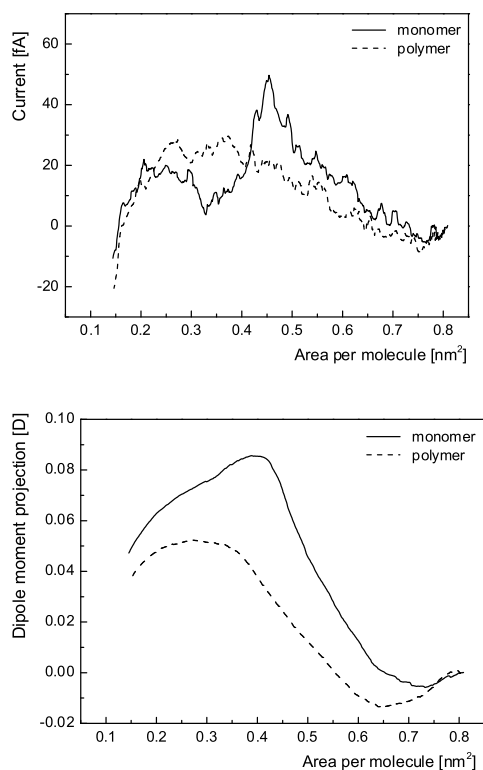

Fig. 5: (up) MDC signals obtained on monomeric DA and polymeric DA monolayers. (down) Calculations of the dipole moment projections of DA molecules before and after photopolymerization.

Because the dipole moment projection μ_z is a product of the dipole moment orientation and its magnitude, MDC technique can provide different profits. The dipole moment projection – area isotherm for monomers characterizes the orientational changes of the molecules, i.e. we assume a constant value of the dipole moment. However, after photopolymerization of diacetylene monolayer the molecular tilt is conserved and the MDC signal is generated by the change of the dipole moment magnitude. Therefore, the dipole moment projection of polymerized DA reflects blue to red phase transition.

The signals for as measured first three compressions in series after UV polymerization are shown in Fig. 6. The amplitude of the signal was changed, however the total induced charge (the area under the current-time, or current-area isotherm for constant compression rate) is conserved. Stabilization of the signal, formation of the monolayer, is therefore caused by the homogenization of material distribution, not by a destructive process. This result is in accordance with spontaneous domain creation in PDA [7].
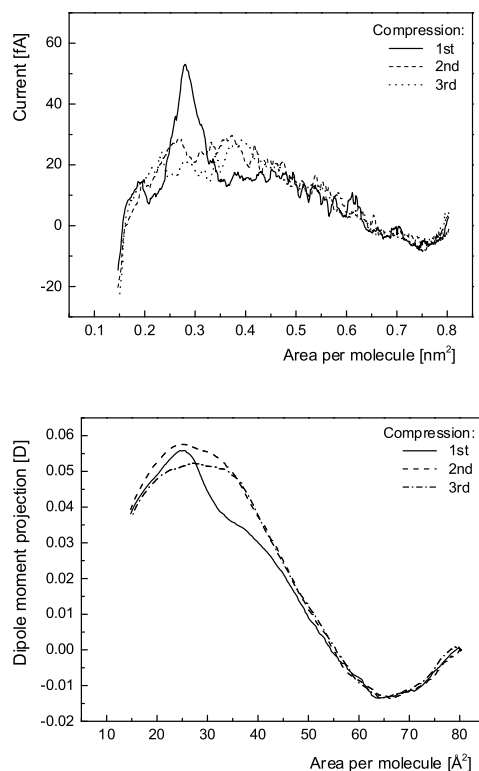

Fig 6: (up) MDC signals obtained on polymerized DA monolayer in course of first three compressions. (down) Calculations of the dipole moment projections of polymerized DA monolayer.

4. CONCLUSION

The MDC method was used for studying monolayer polymerization for the first time. It was shown, that its application is highly effective and significantly complement optical measurements (absorption spectroscopy). The experiment performed on the DA monomolecular film situated on the water surface revealed the effect of polymerization on the π-A as well as I – A isotherms and, thus, the changes of the molecular dipole moment could be calculated in the course of polymerization. Moreover, the experiment is sensitive to domain creation and their spatial distribution.
Further systematic measurements of the polymerization process in diacetylene monolayers are in progress.

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