

STRUCTURE OF MATTER AND QUANTUM CHEMISTRY

The Structure and Properties of Monomolecular Films Based on *N*-Octadecyl-3,4:9,10-Perylene-bis(Dicarboxydiimide)

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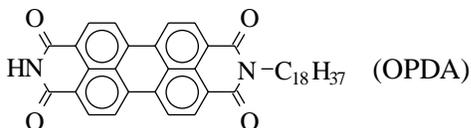
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Abstract—Atomic force microscopy, ellipsometry, and piezoquartz microweighing techniques were used to study the characteristics of *N*-octadecyl-3,4:9,10-perylene-bis(dicarboxydiimide) monomolecular layers depending on the conditions of isolation and the nature of the substrate. The Langmuir–Blodgett film of the compound was found to have an aggregation structure; film quality characteristics (uniformity, absence of defects) were highest when monolayers were formed by X-type deposition on a hydrophilic surface. It was shown that atomic force microscopy thickness measurements for monomolecular layers of perylenetetracarboxylic acid derivatives should be performed taking into account film elastic deformations under the action of the probe of the microscope during scanning.

In the past two decades, considerable attention has been given to studies of the structure and properties of thin films based on perylenetetracarboxylic acid (PTA) dianhydride derivatives having nonlinear optical properties and exhibiting high optical and thermal stability [1]. These films are used in such advanced fields as the production of solar cells [2] and superfast optical switches and optical memory elements [3].

Microminiaturization of electronic devices and the search for more effective thin-film systems based on PTA derivatives impose the requirement of controlling the structure of films at the molecular level. The Langmuir–Blodgett procedure [4] is a unique method for preparing ultrathin ordered layers whose structure and properties can easily be controlled during film formation by changing the structure of chemical compounds and conditions of their isolation.

Earlier, we studied Langmuir films based on *N,N'*-dioctadecyl-3,4:9,10-perylene-bis(dicarboxydiimide) (DOPDA) [5]. The purpose of this work was to study the structure of Langmuir–Blodgett films based on the monosubstituted diimide of perylenetetracarboxylic acid



and the influence of the conditions of film formation on film quality.

The topology of the surface of OPDA monolayers was determined by atomic force microscopy, which, in recent years, became a powerful tool for studying the surface of solids and, in particular, Langmuir–Blodgett films [6].

EXPERIMENTAL

OPDA was synthesized from dianhydride of 3,4:9,10-perylenetetracarboxylic acid and octadecylamine under reflux in dioxane as recommended in [7]. The structure of the compound was checked by elemental analysis and NMR and IR measurements.

The surface-active properties of OPDA were studied by measuring surface pressure–area per molecule (π – A) isotherms, as in [8]. A monolayer of OPDA was prepared by depositing it from a solution in chloroform (1×10^{-3} M) onto the surface of distilled water. The rate of monolayer compression was varied from 2 to 30 $\text{\AA}^2/(\text{molecule min})$. Langmuir–Blodgett films were separated by X-, Z-, and Y-type deposition with the use of the vertical method [4] at surface pressure $\pi = 20$ mN/m and a 1 cm/min velocity of substrate movement. Plates of silicon (100), fused quartz, and mica were used as substrates. Before separation, the silicon and quartz substrates were purified by boiling in toluene with subsequent hydrophobization [9] (to separate the Y- and X-type films) or hydrophilization [10] (to separate the X-, Y-, and Z-type films). To obtain a pure, atomically smooth mica surface (hydrophilic substrate), the upper layer of mica was removed by adhesive tape.

The coefficient of film compressibility (k_s) was calculated by the formula [11]

$$k_s^{-1} = -A_0(d\pi/dA),$$

where A_0 is the limiting molecular area obtained by extrapolating the straight-line portion of the condensed film isotherm to its intersection with the abscissa axis ($\pi = 0$).

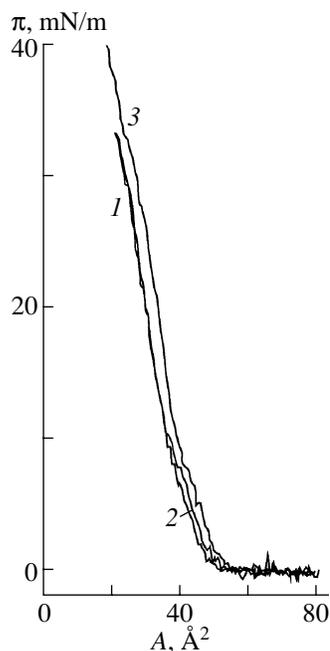


Fig. 1. Surface pressure (π)–area (A) isotherms for a monolayer of OPDA on a water surface at compression rates of (1) 2, (2) 4, and (3) 28 $\text{\AA}^2/(\text{molecule min})$.

Film surface images were obtained with the use of a Nanoscope-IIIa (Digital Instruments) microscope, standard cantilevers 100 and 200 μm long with elasticity constants 0.06, 0.12, 0.38, and 0.58 N/m, and a Si_3N_4 needle (Nanoprobes, Digital Instruments). The rate of scanning was 2–12 Hz, and the density of information was 512×512 dots per frame. Force of probe action on the sample during scanning was minimized to 10^{-9} N. Film thicknesses were determined by atomic force microscopy from the depth of the relief of film defects formed as a result of preliminary scanning of some surface region under an increased microscope needle load of $(0.5\text{--}1.0) \times 10^{-7}$ N at a slow (1 Hz) scanning rate.

The parameters of Langmuir–Blodgett films on hydrophilic silicon were determined by reflective ellipsometry [12] on a standard LEF-3M ellipsometer ($\lambda_{\text{inc}} = 6328 \text{ \AA}$). Complex refractive index ($n - ik$) and film thickness (d) were calculated by the Monte Carlo method on multidimensional nets and the Newton–Rafson method (IBM PC-AT) with the use of the model of an ideal optical multilayer medium–film (N layers)–substrate system (number of layers $N < 10$). The n , k , and d values for the organic film on hydrophilic silicon were determined from independent measurements taking into account the presence of the transition SiO_2 layer as recommended in [13].

Quantitative data on transfer of monomolecular layers from the surface of water onto solid substrates were obtained by quartz microweighing. The mass (Δm_f) of

the Langmuir–Blodgett film deposited on the resonator was calculated by the formula [14]

$$\Delta m_f = (\Delta f N_f \rho_q s) / f_0^2,$$

where f_0 is the nominal quartz resonator frequency, Δf is the change in resonator frequency as a result of film deposition, N_f is the frequency constant ($N_f = 1.67 \times 10^{-5} \text{ Hz cm}$), ρ_q is the quartz density ($\rho_q = 2.648 \text{ g/cm}^3$), and s is the surface area of the resonator.

The absorption spectra of films and solutions were recorded on a KSWU-23 single-beam spectrometer.

RESULTS AND DISCUSSION

OPDA was found to form strong solid monolayers on the surface of water; the layers withstood surface pressures up to 40 mN/m (Fig. 1). The limiting area per OPDA molecule in the closely packed layer equaled 42 \AA^2 at a 2–4 $\text{\AA}^2/(\text{molecule min})$ rate of compression and somewhat increased (to 47 \AA^2) at a 28 $\text{\AA}^2/(\text{molecule min})$ rate (Fig. 1). It follows that, under slow compression, OPDA molecules form closer packings. The compressibility coefficient of monomolecular OPDA films is somewhat larger than that of DOPDA [5] and amounts to $1.4 \times 10^{-2} \text{ m/mN}$, which is evidence of elasticity of OPDA films. The obtained limiting area values are substantially lower than the calculated area of the perylene fragment, $A = 75 \text{ \AA}^2$ [15]. At the same time, the area of the projection of this fragment onto the surface when the fragment stands on its shortest face normally to the surface equals 29 \AA^2 [16]. We can therefore suggest that OPDA molecules in a monolayer are oriented predominantly vertically, and the angle between the normal to the substrate and the longer axis of the molecule is small (this suggestion is justified on the condition that three-dimensional aggregation films are not formed).

Atomic force microscopy measurements showed (Fig. 2) that transfer of a monolayer onto the surface of mica results in the formation of a uniform monomolecular film with a small number of defects (holes) in the structure. This result is typical of Langmuir–Blodgett films deposited on the surface by the vertical method [17]. In the center of the photograph (Fig. 2), the region of preliminary scanning ($400 \times 400 \text{ nm}$, increased force of probe action on the sample $1 \times 10^{-7} \text{ N}$) is clearly seen; preliminary scanning removed film material from this region. On the whole, the film was fairly uniform, which facilitates interpretation of the results obtained by other physicochemical methods.

According to the ellipsometry and quartz microweighing data, transfer of OPDA films onto solid substrates is accompanied by linear growth of film thickness and mass, which is evidence that the transfer process is reversible. The largest increase in film mass and thickness was observed when the film was transferred by X-type deposition (table). The thicknesses of X- and Z-type films per monolayer determined ellipsometri-

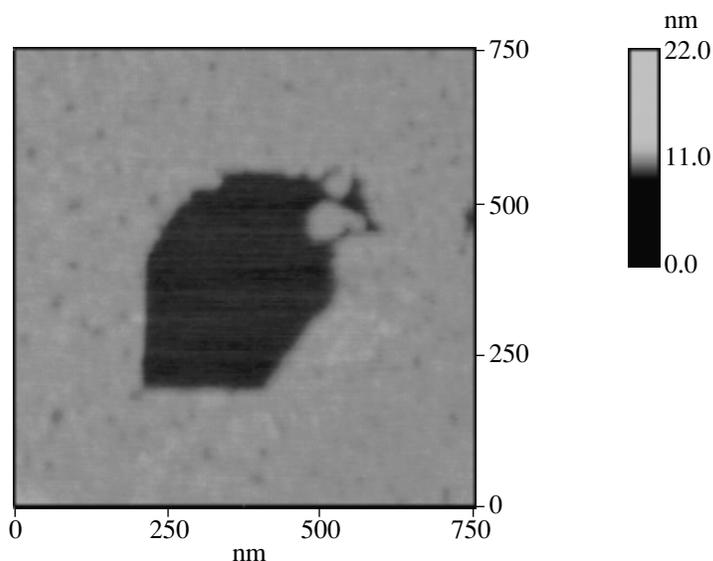


Fig. 2. Atom-force microscopy image of the surface of an X-type monolayer transferred onto mica under a 20 mN/m surface pressure. Shown in the center is the region destroyed by the microscope probe during preliminary scanning with an increased force of action (1×10^{-7} N).

cally were 24 and 22 Å, respectively (table), which is somewhat smaller than the maximum length of OPDA molecules (~ 29 Å) estimated by molecular mechanics calculations (Alchemy-II) for the longest possible conformation. This substantiates the conclusion that OPDA molecules are oriented in films at a small angle with respect to the normal to the surface.

Transfer of Y-type films onto a substrate should occur during both substrate immersion into and removal from water. The mass of Y-type layer was, however, even smaller than that of X-type monolayers (table). This observation can be explained by the destruction of the already formed X-type film while the substrate moves upward through the monolayer. It follows that OPDA monomolecular films are fairly plastic, labile, and prone to structural rearrangements.

A comparison of the cross sections of surface reliefs of films formed on different surfaces (Fig. 3) lends support to this conclusion. Indeed, X- and Y-type films formed on a hydrophilic surface are fairly uniform and stable (Figs. 3a, 3b), whereas, on the surface of hydrophobic silicon, islet aggregation films are formed (Fig. 3c). The profiles of the window of film scanning by a microscope needle under increased load are also shown in Figs. 3a and 3b; the height of the profiles can be used to determine film thicknesses [18]. The absence of film material at window edges (Fig. 2) removed from the region of preliminary scanning by the increased force of probe action can be related to adsorption of this material on the probe. Deviations of the shape of the scanning window from quadratic (Fig. 2) substantiate the conclusion of plastic behavior of the material and lability of OPDA molecules.

We also found that the thickness of the OPDA layer determined by atomic force microscopy (table) was smaller by 25–30% than that measured ellipsometrically. It appears that microscopic measurements underestimate film thicknesses, which also follows from the actual length of molecules and the data of π -A isotherm measurements, according to which amphiphilic molecules are oriented almost vertically. Thickness underestimation may be caused by material deformation under the action of the probe needle. Although the force of this action during scanning was minimized to 10^{-9} N, pressure at contact points might be substantial because of the small (~ 10 nm) radius of curvature of the pointed end of the probe. Indeed, calculations of elastic mechanical deformation of amphiphilic molecules in layers related to changes in the tilt of molecules and their conformational rearrangements [19] show that a decrease in layer thickness during scanning can be as large as 25% at standard parameters.

It appears that interactions between perylene fragment planes are fairly strong. Indeed, the absorption spectrum of the Langmuir–Blodgett OPDA film only contains a

Comparison of the parameters of the OPDA films deposited on hydrophilic silicon

Film type	$\Delta m_f \times 10^{-7}$, g	d_1 , Å	d_2 , Å
Y	1.66	31	15
X	2.0	24	18
Z	1.43	22	15

Notation: Δm_f is the mass of the film; d_1 and d_2 are film thicknesses per deposition cycle determined by ellipsometry and atom-force microscopy, respectively (for the Y-type film, d_2 refers to the film deposited on mica).

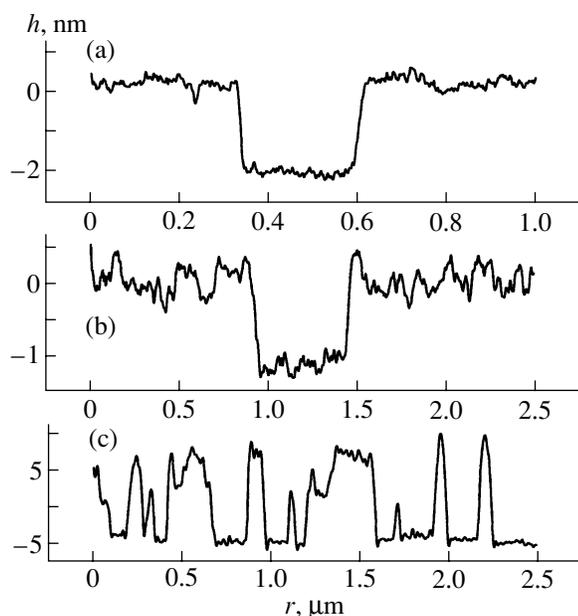


Fig. 3. Cross-section profiles of the surface of OPDA films deposited on (a, b) hydrophilic and (c) hydrophobic silicon; (a) and (b, c) are X- and Y-type films, respectively (h is the profile height, and r is the cross section length).

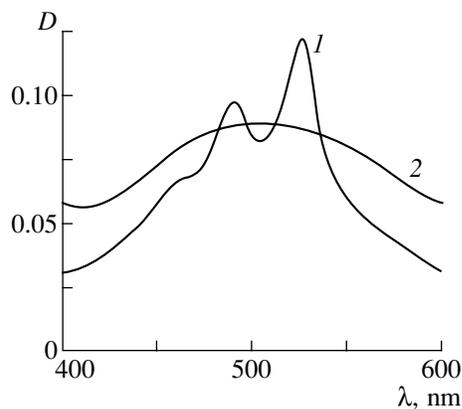


Fig. 4. Absorption spectra of (1) a solution of OPDA in chloroform and (2) a Langmuir-Blodgett OPDA film formed by 10 Y-type layers.

broad band, whereas a solution of OPDA gives three well-defined maxima at 457, 490, and 525 nm (Fig. 4) characteristic of perylenetetracarboxylic acid derivatives in the molecularly dispersed state [20]. In films, the formation of associates of molecules linked by intermolecular H-bonds between amide hydrogens of one molecule and carbonyl groups of another is quite possible [21].

To summarize, OPDA forms strong condensed monolayers on the surface of water. Films of the high-

est quality are obtained by X-type transfer of these monolayers onto a hydrophilic surface.

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