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## Formation and Properties of Langmuir–Blodgett Films Prepared from Diacetylene-containing Compounds

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**Abstract**—The properties of films based on new amphiphilic derivatives of diacetylene alcohols and acids were studied by using compression isotherms, ellipsometry, atomic-force microscopy, and ultraviolet and visible spectroscopies. It was shown that the location of diacetylene groups in the vicinity of the polar heads of amphiphilic molecules does not preclude the production of solid-state monolayers at the water surface and the formation of multilayer structures on solid supports. Upon irradiation with ultraviolet light, multilayer Langmuir–Blodgett films prepared from a diacetylene derivative of *m*-benzoic acid polymerized into a polydiacetylene with the absorption maximum at 650 nm, as distinct from polymeric films based on diacetylene alcohols, which exhibited the absorption maximum at about 590 nm.

Polydiacetylenes (PDA) are promising compounds for the production of materials for nonlinear optics [1], photoresistors [2], chemical sensors [3, 4], etc. One advantage of PDA is its thermal stability in aggressive solvents at temperatures as high as 200°C [5]. The properties of PDA are largely determined by the presence of polyene chains, which can only be prepared by topochemical polymerization of regularly located diacetylene groups. The use of the Langmuir–Blodgett (LB) method makes it possible to produce highly organized quasicrystal films in which molecules are arranged so that the distances between the diacetylene links of neighboring molecules are no more than 4 Å [6, 7].

The structure of the diacetylene (DA) molecule, polymerization conditions, and structures of the side radicals of the resulting polymeric chain (ene-yne) have a great effect on the properties of the resultant PDA. In particular, LB films prepared from diacetylene-containing higher fatty acids turn light blue during exposure to ultraviolet light and then, upon prolonged irradiation, orange-red [8]. In many cases, color changes in PDA are reversible. At present, thermochromism [9], mechanochromism [10], and biochromism [11] of PDA films are well documented; however, all the details of the mechanism of color changes in PDA are yet unknown. The authors of [12] believe that these changes are due to the existence of two resonance structures in the polyacetylene chain, the transition between which is determined by the orientation of the substituents in the chain. The best-studied diacetylene monomers suitable for the formation LB

films are diacetylene analogues of fatty acids of general formula  $\text{CH}_3(\text{CH}_2)_m\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_n\text{COOH}$ . The hydrocarbon tails are closely packed in a film, when the diacetylene group is located in the middle of the linear chain, for example, at  $n, m = 8, 10$  [13]. In this case, a polyene chain is surrounded by a dielectric interlayer containing hydrocarbon substituents. In this regard, an urgent problem is to find new amphiphilic diacetylene structures in which the acetylene links are located close to the polar head of a molecule. In this case, the polyene chain can directly contact the solid surface.

The purpose of this work is to study the relation between the structure of a diacetylene compound with a terminal diacetylene fragment and the properties of monolayer and multilayer films prepared from it.

### EXPERIMENTAL

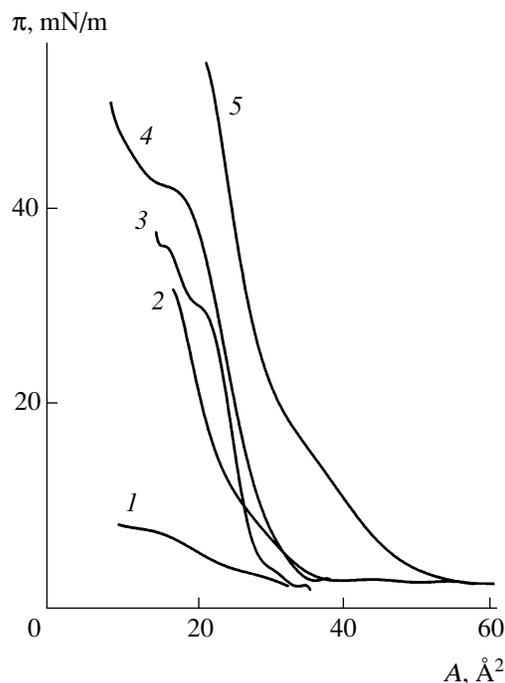
The amphiphilic diacetylene-containing acids and alcohols (Table 1) were synthesized as described in [14]. The structures and physicochemical characteristics of these compounds were established by using NMR, IR, and UV spectroscopies. Diacetylene alcohols (DAA1, DAA2, and DAA3) are rather reactive: with time, their color change from white to light blue. Therefore, before experiments aimed at studying the surface properties of the alcohols, they were additionally purified on a column packed with silica (the eluent was chloroform). Diacetylene acid (DAAc2), which turned rose with time, was purified by recrystallization from ethanol in the red light.

The surface properties of the diacetylene alcohols and acids at the water surface were examined by using surface pressure–area per molecule ( $\pi$ – $A$ ) isotherms [15]. Monolayers at the water surface were formed by applying DA solutions in chloroform  $[(0.5\text{--}0.7) \times 10^{-3} \text{ M}]$ . The rate of monolayer contraction was  $15 \text{ \AA}^2/(\text{molecule min})$ .

The monolayers were deposited on quartz plates by the Langmuir–Blodgett vertical technique [16] and on the mica by the horizontal deposition (HD) procedure [17, 18]. The latter method allows one to obtain much more homogeneous films. Y-type films (1 cycle) were formed by the vertical method at a surface pressure of  $30 \text{ mN/m}$  and a support transport velocity of  $1 \text{ cm/min}$ . Monolayer structures of Z type were produced by the HD method at a velocity of water surface lowering of  $0.5\text{--}0.6 \text{ ml/min}$  [18]. Immediately before applying a monolayer, the mica surface was purified by tearing off the upper layer with a sticky tape.

The diacetylene films were polymerized under the action of radiation from a DRSh-500 mercury lamp equipped with a water filter;  $254\text{-nm}$  radiation was isolated with a MUM monochromator. The supported films were irradiated at  $20^\circ\text{C}$  in a flow nitrogen atmosphere. The absorption spectra of the DAs under study and the DA films were recorded on a KSVU-23 spectrometer.

The thickness of the films was measured by reflection ellipsometry [19] on an LEF-3M ellipsometer ( $\lambda_{\text{inc}} = 6328 \text{ \AA}$ ). The refractive index and the film thickness were calculated by the Monte Carlo method with multidimensional grids and by the Newton–Raffson method (IBM PC-AT) as applied to the ideal optical

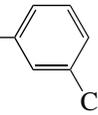


**Fig. 1.** Compression isotherms of the derivatives of diacetylene acids and alcohols at the water surface: (1) DAAc1, (2) DAA1, (3) DAAc2, (4) DAA2, (5) DAA3;  $A$  is the surface area per molecule.

multilayer system model medium– $n$ -layer film–support [15, 19].

We studied the morphology of the surface of monomolecular films isolated at various pressures by atomic-force microscopy (AFM) with a Nanoscope-IIIa microscope (Digital Instruments) equipped with standard cantilevers of length  $100$  and  $200 \text{ }\mu\text{m}$  with a

**Table 1.** Surface-active properties of diacetylene alcohols and acids ( $s_{\text{min}}$  is the minimum area occupied by a molecule in a monolayer,  $\pi_c$  is the pressure of collapse)

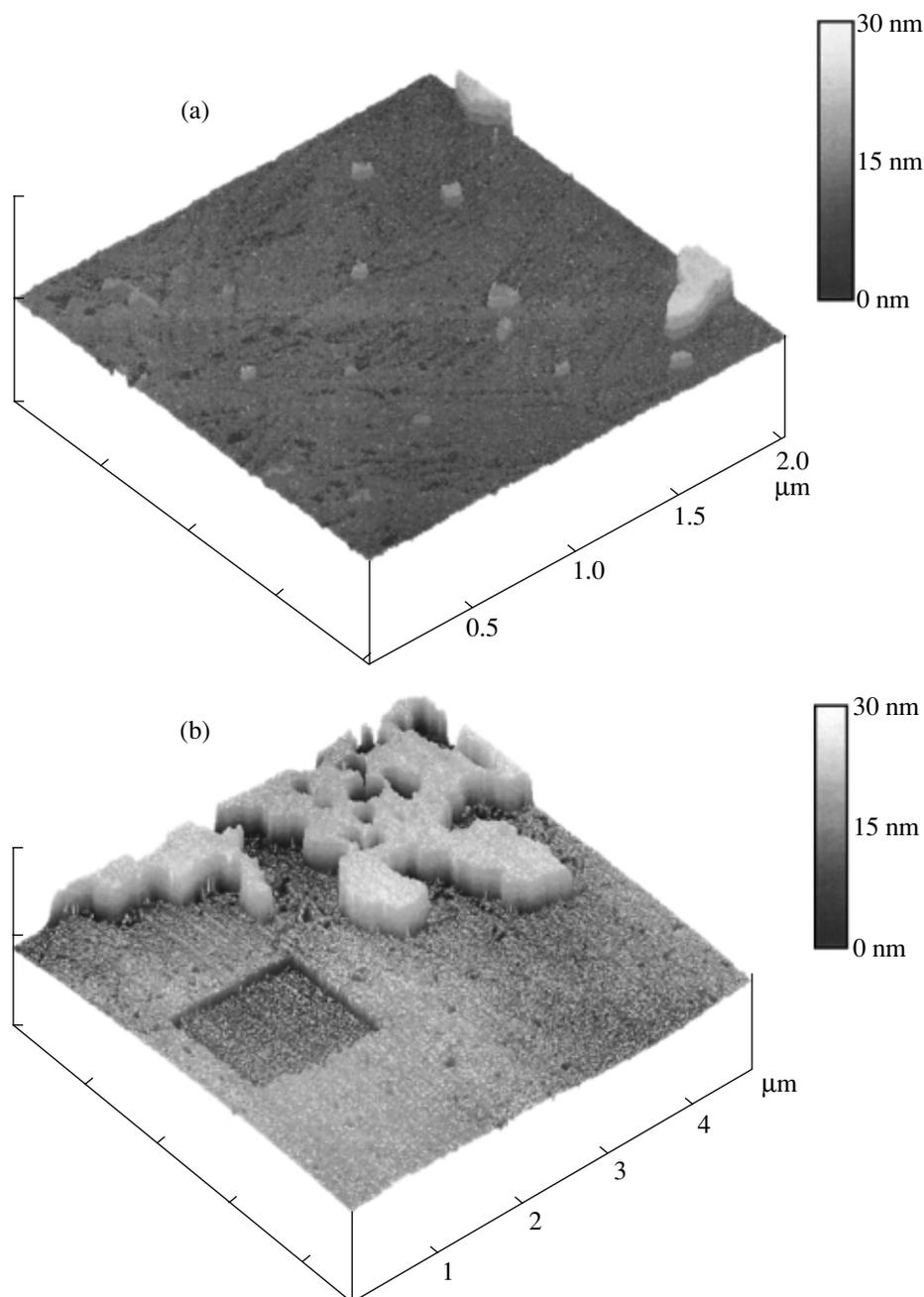
Compound	$s_{\text{min}}, \text{nm}^2$		$\pi_c, \text{mN/m}$
	calculation	experiment	
$\text{C}_{16}\text{H}_{33}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CH}_2\text{OH}$ (DAA1)	$0.295 \pm 0.01$	$0.25 \pm 0.04$	30
$\text{C}_{16}\text{H}_{33}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_2\text{OH}$ (DAA2)	$0.323 \pm 0.01$	$0.30 \pm 0.03$	45
$\text{C}_{16}\text{H}_{33}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_3\text{OH}$ (DAA3)	$0.351 \pm 0.01$	$0.30 \pm 0.04$	42
$\text{C}_8\text{H}_{17}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}$ -  (DAAc1)	–	$0.28 \pm 0.03$	7
$\text{C}_{16}\text{H}_{33}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}$ -  (DAAc)	$0.340 \pm 0.04$	$0.34 \pm 0.02$	48

$\text{Si}_3\text{N}_4$  needle and with elasticity moduli of 0.06, 0.12, and 0.36 N/m (Nanoprobes, Digital Instruments) [18]. The rate of scanning was varied within 1–12 Hz, the efficiency in scanning ranged from units to tens and hundreds nN, and the information density was  $512 \times 512$  points.

## RESULTS AND DISCUSSION

The length of the hydrocarbon tail of a molecule is shown to have a profound effect on the surface-active

properties of diacetylene monomers and on the strength of monomolecular films. For example, diacetylene alcohols with  $\text{R}=\text{C}_{16}\text{H}_{33}$ , form strong solid films at the water surface (Fig. 1). The surface area occupied by a diacetylene alcohol molecule in a monomolecular film increases with the number of  $\text{CH}_2$  groups located between the diacetylene and alcohol groups in the molecule (Table 1). In this case, a correlation between the experimental and calculated data is observed. The latter were obtained as follows. After optimizing the geometry of the molecule



**Fig. 2.** AFM image of a fragment of the a DAA1 monomolecular film isolated by the horizontal deposition method from the water surface onto a mica support at surface pressures of (a) 15 and (b) 30 mN/m.

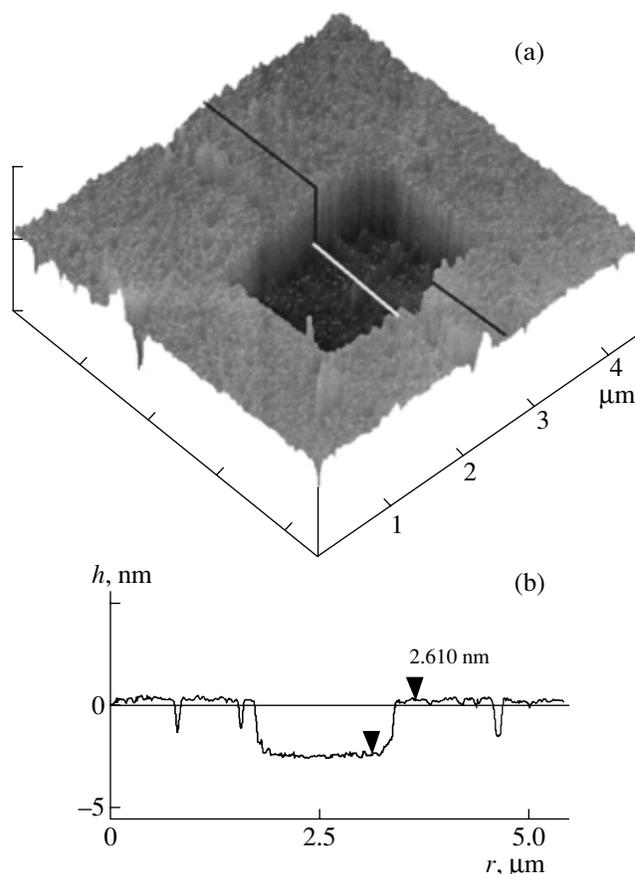
according to the Alchemy-II program, we calculated the projection of the molecule on the surface by using a specially developed program.<sup>1</sup> It is believed that for all the compounds under study, the diacetylene group remains at the water–air interface during the formation of a monomolecular film. Otherwise, the surface area occupied by a molecule would not depend on the number of CH<sub>2</sub> groups and a more pronounced bend would be observed in the compression isotherm in the region of the L–S (liquid–solid) phase transition.

When a film is transferred onto a solid surface (silicon, quartz), its thickness strongly depends on the surface pressure applied. For example, at a pressure of 30 mN/m, the thickness of the DAA1-based film is several times larger than at pressure of 15 mN/m; at either pressure, the thickness of the films increases regularly with the number of transfer cycles (Table 2). It is reasonable to suggest that a multimolecular structure is formed at the water surface when the pressure applied to a monolayer approached that of collapse of the film.

AFM measurements were performed with films prepared by the HD method in order to prevent the structure from distorting during isolation (for example, from crystallizing at the meniscus of the liquid). In this case, homogeneous monomolecular films are formed at a pressure of 15 mN/m, an insignificant extrusion of the film material into the second layer being observed (Fig. 2a). The monolayer thickness determined from the relief depth of the artificially formed defect is ~2.5 nm (Fig. 3). This value agrees satisfactorily with the calculated length of the molecule in the maximum-extension conformation (~2.7 nm). At the same time, a greater number of multimolecular structures is observed at the film surface at a pressure of ~30 mN/m (Fig. 2b); as this takes place, the height of the step in such structures is a multiple of the monolayer thickness. The shapes of the multilayer structures obtained suggest that an ordered multilayer films with a rigid fixation of the linearly extended DA molecules in the monolayers are formed.

After photopolymerization, the diacetylene alcohol films under study turned red, with the absorption peak being located at 580 nm. Note that the initial monomeric films do not absorb in this spectral region. For comparison with diacetylene alcohols, we studied the surface-active and film-forming properties of diacetylene-substituted *m*-benzoic acids (Table 1). The obtained data show that the strength of the monomolecular film grows substantially with increasing length of the hydrocarbon tail of the acid molecule. DAAc1 with a C<sub>8</sub> hydrocarbon tail yields only a liquid spread film ( $\pi \approx 7$  mN/m), whereas

<sup>1</sup> We thank V.N. Staroverov for developing the program.



**Fig. 3.** AFM image (a) of the surface fragment of a DAA1 monomolecular film with the artificially formed defect and (b) of the profile of the film; the film was isolated by using the horizontal deposition method from the water surface onto a mica support at a surface pressure of 15 mN/m.

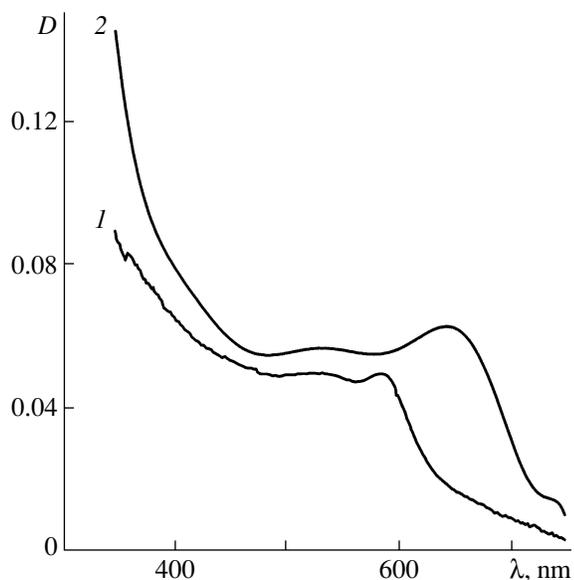
DAAc2 yields a solid film, which can be readily transferred onto a support (Fig. 1).

Among the structural peculiarities of DAAc2 films, we can note the high homogeneity of the films and the presence of islet domains. The latter fact appears to be associated with a partial polymerization of the acid during the formation of the film.

When exposed to 254-nm ultraviolet light, multimolecular LB film prepared from DAAc2 (amphiphilic

**Table 2.** Relationship between the film thickness (nm) and the number of cycles (*n*) of isolation of the DAA1 monolayers from the water surface at surface pressures of 30 and 15 mN/m

<i>n</i>	30	15	<i>n</i>	30	15
1	4.0	2.3	5	33.0	16.0
2	9.0	5.0	7	55.0	20.0
3	21.0	7.2	10	70.0	25.0



**Fig. 4.** Absorption spectra of multimolecular (~50 bilayers) (1) DAA2 and (2) DAAc2 films after their irradiation with monochromatic light from a DRSh-500 lamp at 254 nm for 45 min.

diacetylene derivative of *m*-benzoic acid) polymerizes into the blue form of PDA (the absorption peak is at about 680 nm). By contrast, red PDA films are formed from diacetylene alcohol films (Fig. 4). The marked distinction between the absorption spectra of the irradiated PDA films based on the diacetylene alcohols and the *m*-benzoic acid derivative can be explained as follows. The initial diacetylene alcohol-based film shows a greater extent of disordering owing to a substantial disorientation of the hydrocarbon tails of the molecules compared to a more ordered structure of the acid-based film, in which the allene resonance structure of PDA is formed upon irradiation [13].

PDA blue films prepared from the derivative of *m*-benzoic acid may be promising for developing systems in which reversible photochromic transitions typical of PDA occur and for forming conducting layers on metallic electrodes.

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