

Reorganization of Langmuir monolayers on solid surfaces

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Abstract

Langmuir–Blodgett (LB) monolayers of behenic acid, beeswax and long-chain amphiphilic amides were prepared on graphite and mica surfaces by the horizontal precipitation method. The monolayer films and products of their reorganization were studied with atomic force microscopy. LB films of amphiphilic amides were found to self-organize into superstructures with a hexagonal arrangement of hydrocarbon tails. Repeatedly observed supramolecular formations suggest that reorganization is a common phenomenon in monolayers on substrates. It is suggested that the driving force for the molecular reorganization is the surface tension gradient arising from the change in type of hydrocarbon tails packing. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Uncontrolled reorganization of Langmuir–Blodgett (LB) monolayers [1–6] transferred to a solid surface remains one of the main barriers to their application. The phenomenon has been observed in behenic acid layers on silicon dioxide [7], LB films of fatty acid salts stored under water [1–3], and phospholipid films kept in a humid environment [5]. The causes of the monolayer destruction are poorly understood to the extent that the process remains largely unpredictable.

In practice, manifestations of the inherent instability of monolayers may be difficult to distinguish from structural defects originating during the film preparation [5,8]. Indeed, even the perfected vertical deposition method [9] is often complicated by molecular disordering, aggregation in the meniscus, and blocking by certain ions. We showed earlier [10,11] using atomic force microscopy (AFM) that in those cases where the film could not be successfully transferred to a substrate by the vertical deposition technique, high-quality monolayers on hydrophilic (mica) and hydrophobic (graphite) substrates could be prepared by the ‘horizontal precipitation’ (HP) method. We also studied the morphology of

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monolayer films formed by the HP method from amphiphilic compounds (acids, alcohols, amides, etc.) and found that their reorganization on a solid surface is a common phenomenon. In a number of cases, initially homogeneous films were found to reorganize on a substrate within 1–3 months; some molecules desorbed from the surface and formed multilayer structures without any external influence. The effect of a substrate was clearly observed for reorganization of composite monolayer film from behenic acid molecules and CdTe nanoparticles. The most interesting behavior during storage was exhibited by monolayer films of amphiphilic amide derivatives. In this report, we present more conclusive results of a subnanoscale AFM study of molecular reorganization in these systems.

2. Experimental

2.1. Materials

The films were prepared from behenic acid (Aldrich), purified beeswax (natural, m.p. 55–60 °C), amino-substituted β -ketoamide and β -diamides (the structures of the amides are shown in Table 2).

Beeswax (a mixture of fatty acid esters [12]) was purified by recrystallization from chloroform. β -Ketoamide: (1) *N*-hexadecyl-3-oxobutanamide; and β -diamides: (2) *N*-hexadecyl-*N'*-(2-naphthyl)propanediamide; (3) *N,N'*-dihexadecyl-; and (4) *N,N'*-dioctadecylpropanediamide were synthesized by the method described in Ref. [13]. *N*-Hexadecyl-3-oxobutanamide was prepared by condensation of equimolar amounts of ethyl acetoacetate with cetylamine in boiling *p*-xylene. Propanediamide (2) was synthesized by condensation of fivefold excess of diethyl malonate with cetylamine followed by the reaction of purified ethyl 3-(hexadecylamino)-3-oxopropanoate with 2-naphthylamine. Symmetric *N,N'*-dialkylpropanediamides (3) and (4) were synthesized from diethyl malonate and excess of cetylamine or octadecylamine in boiling *p*-xy-

lene. The products were purified in a liquid chromatography column using chloroform as the eluent.

2.2. Sample preparation

Monolayers were prepared by spreading 0.5–0.8 mM chloroform solutions of the film-forming compounds on the surface of bidistilled water (pH 5.5). Compression was started after the solvent had completely evaporated and the film attained sufficient stability (ca. 10 min). Z-type monolayers were transferred by the HP method onto freshly cleaved atomically flat surfaces of mica (muscovite) or highly oriented pyrolytic graphite (HOPG). The HP method included the following steps:

- the substrate was placed inside the trough and the trough was filled with water;
- the monolayer was formed on the aqueous surface by spreading the solution of the film-forming compound and then compressed to the 'solid' state;
- after the monolayer was transferred onto the substrate, the water was allowed to slip off slowly (0.5–0.6 ml min⁻¹), leaving a homogeneous monolayer film deposited on the surface. The surface pressure during the deposition was kept at 20 or 30 mN m⁻¹ with deviations of less than 2–3 mN m⁻¹.

2.3. Instrumentation

The computer-controlled Langmuir trough was used for film depositions and 'surface pressure–area per molecule' (π -*A*) isotherm measurements. The isotherms were recorded with compression speed of 0.2–0.3 Å² molecule⁻¹ min⁻¹). The temperature of the subphase was maintained at 290 K.

AFM images were obtained using Nanoscope IIIa (Digital Instruments, USA) device operated in a constant force mode (1.5–5 nN) in the open air. Nanoprobe 100 and 200 μ m cantilevers (spring constants of 0.06 and 0.12 N m⁻¹) with oxide-sharpened Si₃N₄ integral tips were used. The device was equipped with a 'D' scanner calibrated using the manufacturer's grating. The

applied force during image recording was minimized to a few nN. The scanning frequency ranged from 5 to 60 Hz. The thermal drift error estimated by measuring lattice parameters of mica and graphite did not exceed 2–3% under these conditions. The best subnanometer resolution was achieved using a high scanning frequency (60 Hz) for friction force images. Values of AFM-measured lattice parameters averaged over several dozen images are summarized in Tables 1 and 2.

3. Results and discussion

3.1. Films of fatty acid derivatives

In the vertical deposition method, films of fatty acid derivatives are formed in the salt form on an ionic subphase. The HP method, however, allows the deposition to be carried out on a subphase free from counter-ions. Advantages of the HP method are apparent from the AFM images of

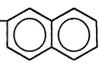
Table 1

Lattice parameters of LB films of long-chain fatty acid derivatives (theoretical values predicted by Kitaigorodsky [14] are also shown)

#	Material	Substrate	Sample description	a (nm)	b (nm)	Molecular area (nm ²)	
						AFM	π -A isotherm
1	Behenic acid	Mica	Monolayer from water	0.53 ± 0.03	0.77 ± 0.04	0.203 ± 0.007	0.20 ± 0.005
3	Beeswax	HOPG	Monolayer from water	0.50 ± 0.04	0.79 ± 0.07	0.195 ± 0.015	–
4	Kitaigorodsky, R[0, ± 1] cell		Theory	0.496	0.785	0.195	–
5	Kitaigorodsky, H[0, 0] cell		Theory	0.48	–	0.196	–

Table 2

Lattice parameters of LB films of various amide derivatives on mica

#	Material	Type of unit cell	a (nm)	b (nm)	Molecular area (nm ²)	
					AFM	π -A isotherm
1.	$C_{16}H_{33}NH-C(=O)-CH_2-C(=O)-CH_3$	Hexagonal ^{**})	0.476 ±0.018		0.196 ±0.008	0.27±0.005
2.	$C_{16}H_{33}-NH-C(=O)-CH_2-C(=O)-NH-$ 	Rectangular [*])	0.566 ±0.015	0.80 ±0.03	0.227 ±0.011	0.325±0.007
3.	$C_{16}H_{33}NH-C(=O)-CH_2-C(=O)-NH-C_{16}H_{33}$	Hexagonal ^{**})	0.477 ±0.011		0.197 ±0.006	0.529±0.006
4.	$C_{18}H_{37}NH-C(=O)-CH_2-C(=O)-NH-C_{18}H_{37}$	Hexagonal ^{**})	0.477 ±0.014		0.197 ±0.007	0.528±0.006

*, on the monolayer film.

**, on the top of multilayer structure.

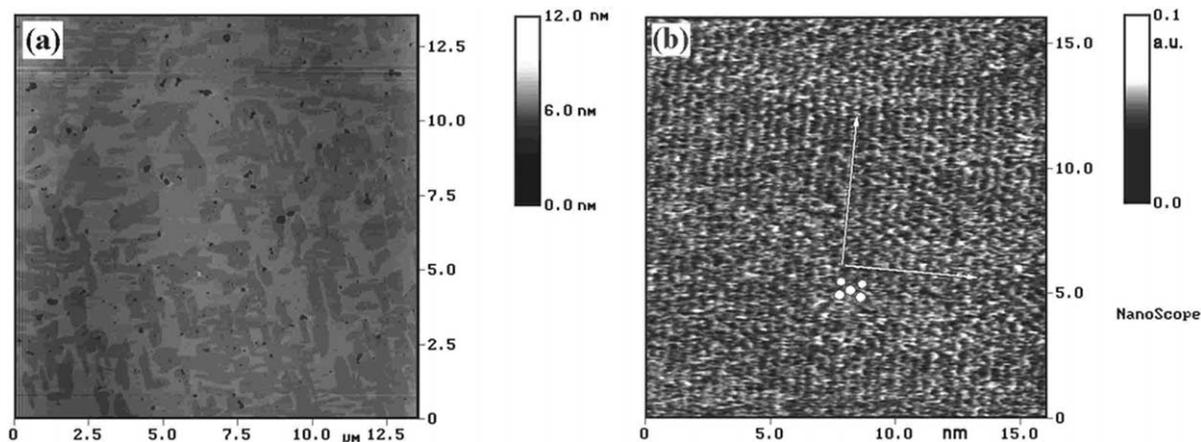


Fig. 1. Unprocessed AFM images of behenic acid films on mica. The films were formed at a surface pressure of 20 mN m^{-1} and transferred by the HP method: (a) large scale; (b) high-resolution.

behenic acid layers on mica shown in Fig. 1. The films prepared by HP method allow to see the coexistence of two phases—solid (the brighter regions) and liquid-condensed (the darker regions). A monolayer of a comparable constitution can hardly be prepared by the vertical deposition method.

As evidenced by molecular resolution AFM data (Table 1), beeswax forms arrays of rectangular face-centered cells (two molecules per cell) on graphite. The surface area (ca. 0.195 nm^2) per molecule in the beeswax monolayer is extremely close to the limiting surface area of behenic acid molecules (Table 1). We assume the hydrocarbon tails of beeswax molecules form a closest-packed layer. Estimates of the unit cell parameters are in a nearly perfect agreement (see Table 1) with the theoretical values of Kitaigorodsky [14] calculated using the closest packing principle. Hence we conclude that graphite does not significantly affect the structure of beeswax monolayers.

AFM data for the surface area per molecule in behenic acid films on mica agree well with the value of the limiting area derived from the π - A isotherm (Table 1). However, the measured parameter 'a' is 0.53 nm , whereas typical values fall in the range from 0.48 to 0.50 nm [15]. We believe that this discrepancy is due to the disordering influence of mica substrate.

3.2. Reorganization of monolayers

3.2.1. The influence of the substrate

The influence of the substrate on the film structure was studied by the example of composite films of behenic acid and CdTe nanoparticles which undergo most drastic changes during storage. The samples were formed on the interface of a 0.01 mM CdTe dispersion [16] and transferred onto mica and graphite. Composite films spontaneously crystallized on graphite (see Fig. 2(a)) but not on mica. Fig. 2(a) suggests that crystallites tend to be oriented along the crystallographic directions of HOPG.

This was confirmed by inspecting the AFM images of a small region of the film in the vicinity of an artificial defect. The defect was created in the monolayer by applying an AFM tip pressure of about 100 nN at a slow scan speed (ca. 3 Hz). Fig. 2(b) and (c) shows arrangements with a marked distribution of angles between the crystallites themselves and between the crystallites and the crystallographic axes of HOPG.

3.2.2. Arrangement of alkyl tails in monolayers of amide derivatives

Representative π - A isotherms for amide derivatives are shown in Fig. 3. The monolayers were transferred onto mica by the HP procedure. It was established that the morphology of the

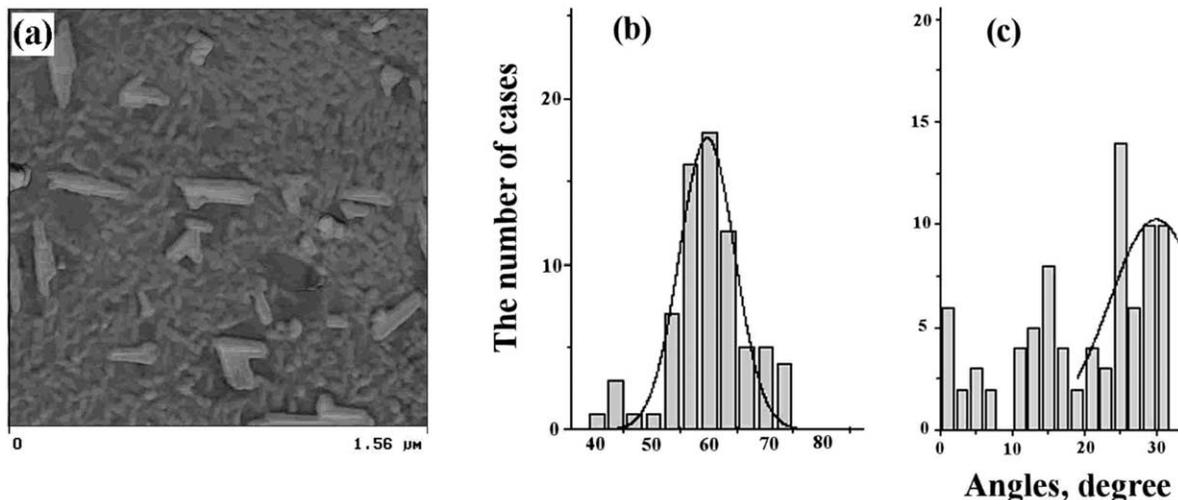


Fig. 2. (a) AFM image of composite film of behenic acid and CdTe nanoparticles on HOPG surface. Distribution of angles: (b) between the long axis of lamella crystals on the surface of HOPG; and (c) between the lamella and the crystallographic axis of HOPG.

initially homogeneous amide films undergoes drastic changes with time. Initial stages of reorganization include the formation of microscopic crystallites from nearby molecules. The redistribution of molecules produces spots visible around crystallites (Fig. 4(a)). AFM section analysis of such areas (Fig. 4(b)) suggested that typical crystalline structure is, in fact, a three-layer assembly. This conclusion agrees with the observations of Riegler and Spratte [17] for lipid films [17]. The height of the monolayer (about 2 nm) indicates the vertical orientation of both alkyl tails in the monolayer, as shown in Fig. 5(a). After the initial stage, monomolecular layers of various amide derivatives regroup into multilayer structures (for example, see Fig. 4(c)) within 1–3 months.

Based on molecular resolution AFM images, we found that films of amide derivative (2) form rectangular face-centered unit cells (Table 2). Although we did not succeed in obtaining comparable AFM images for the monolayers of amides (1), (3) and (4), we did achieve molecular resolution for their multilayer structures (Table 2). Fourier analysis of the images showed that: (i) the amides (1), (3) and (4) form highly symmetric hexagonal arrays (see Table 2); (ii) the area occupied by unit cell of hexagonal lattice (~ 0.195

nm^2) is very close to the cross-section of a hydrocarbon tail. Crystallographic parameters of a hexagonal unit cell (Table 2) are almost identical (deviations of less than 1%) with the translation parameters $H[0, 0]$ of the unit cell of hydrocarbon chains in the ‘gaseous crystalline phase’ model of Kitaigorodsky [14] (Table 1).

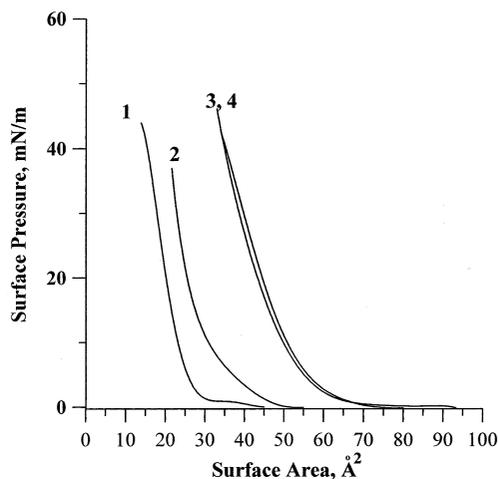


Fig. 3. Compression isotherms of monolayers of amphiphilic amides recorded on water interface at 290 K (the numbers correspond to the structures in Table 2).

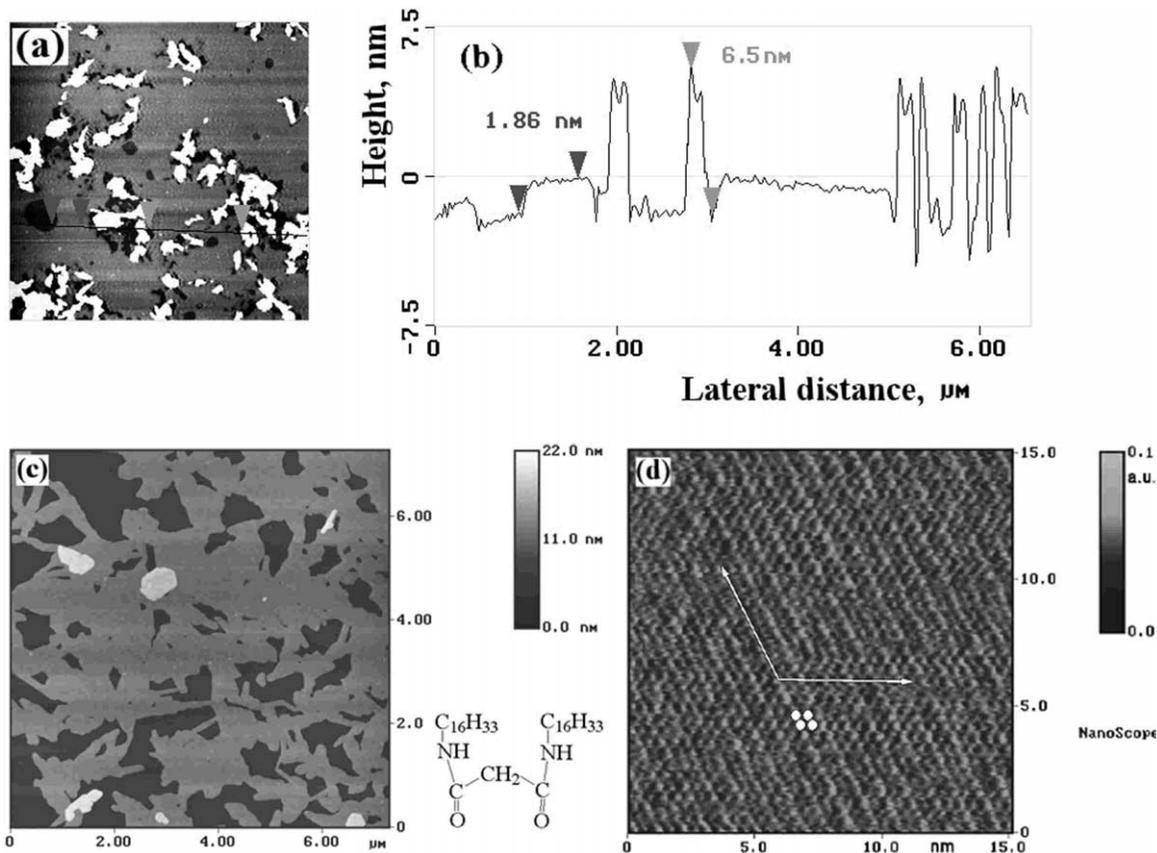


Fig. 4. (a) AFM images of the initial stage of *N,N'*-dihexadecylpropanediamide monolayer crystallization. The monolayer was transferred from aqueous interface onto mica at 30 mN m^{-1} by the HP method. (b) AFM section analysis of a film fragment. (c) AFM image of the final stage of reorganization of amphiphilic amide monolayer into three-layer aggregates. (d) AFM image of the molecular packing in the top layer of the aggregates.

It should be emphasized that the limiting area obtained from the π - A isotherms is considerably greater than the value determined with AFM from reorganized structures (Table 2). The decrease of the area per molecule during transition to superstructures indicates that polar molecular fragments also change their orientation. The cohesion of hydrophobic zones may also have played a role in the reassembly of molecules into supramolecular structures. We believe that the structure of molecules determines the process of film reorganization, in a whole, and the shape of reorganized structures, in particular. Indeed, in some cases we observed three-layered needle-shaped crystals (unpublished results), in others we

detected a growth of crystals in the direction perpendicular to the surface of the substrate. As a rule, amide derivatives form plateaus of three-layered aggregations whose shape is far from the shape of perfect crystals. This suggests that molecular structure is the controlling factor in the reorganization of monolayer films on the substrate. At the same time, the mobility of the molecules is determined by the interplay between long-range intermolecular van der Waals forces and film adhesion to the substrate [18].

In order to explain the hexagonal packing of molecules in a monolayer, one has to assume that the polar fragments do not disturb the pattern set by hydrocarbon tails. We considered the possibil-

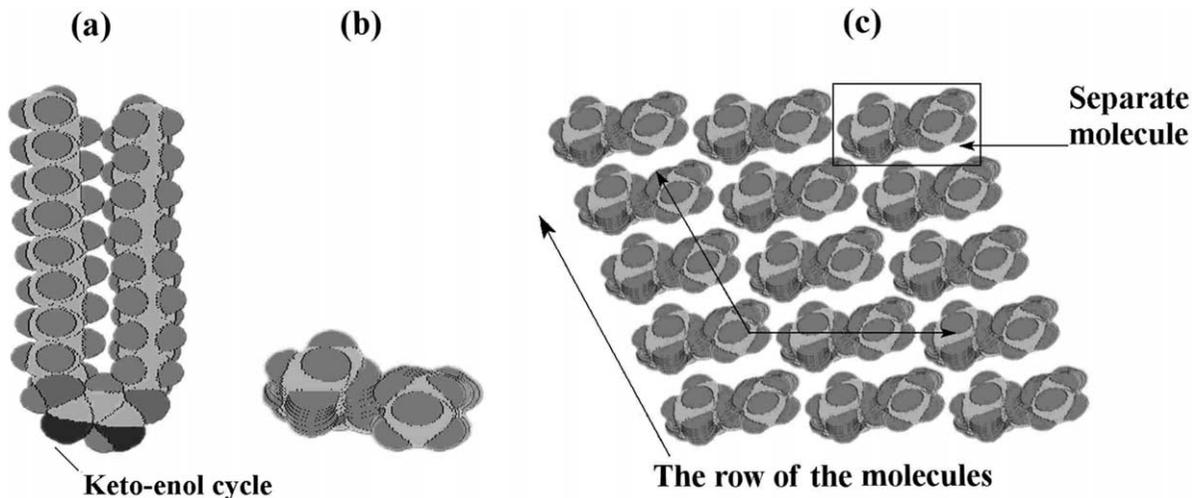


Fig. 5. (a, b) Schematic representation of the structure of *N,N'*-dihexadecylpropanediamide: (a) side view; (b) top view; (c) hypothetical scheme of molecular packing in the superstructure in Fig. 4(d).

ity of six-member cyclic enol structures [13] formed by polar heads of amide derivatives. Such rigid cycles would not impede the hexagonal packing of hydrocarbon tails, yet allow them to have a certain degree of freedom characteristic of the 'rotary-crystalline phase'. Based on these assumptions, we attempted to rationalize the AFM image appearing in Fig. 4(d). In accordance with the proposed model (Fig. 5) molecules are packed in rows extending in the direction of the ridges. The molecules in adjacent rows are shifted relatively to each other to form the hexagonal packing of hydrocarbon tails. The enol cycles are located parallel to each other and perpendicularly to the substrate. Each peak along the ridge corresponds to one tail of a molecule, while the second tail lies underneath.

The principal driving force for the reorganization is probably the surface tension gradient arising from non-uniformities of molecular packing. A much more detailed understanding of the mechanism would be required, however, to explain the influence of the substrate, the adsorbed water, the role of the molecular structure, and other effects.

4. Conclusions

The horizontal precipitation method is a convenient procedure for the preparation of LB mono-

layers. Reorganization of monolayers of amphiphilic organic molecules appears to be a rather common phenomenon. The process can be influenced by a number of external and internal factors, such as the nature of the substrate, cohesion between hydrophobic zones of the molecules, the tendency to form densely packed structures. Considering the ease of spontaneous reorganization, it is imperative to ensure the stability of LB films for their applications.

References

- [1] J.A. Spink, *J. Colloid Interface Sci.* 23 (1967) 9.
- [2] D.K. Schwartz, J. Garnaes, R. Viswanathan, J.A.N. Zasadzinski, *Science* 257 (1992) 508.
- [3] D.K. Schwartz, J. Garnaes, R. Viswanathan, J.A.N. Zasadzinski, *J. Phys. Chem.* 96 (1992) 10444.
- [4] L. Bourdieu, O. Ronsin, D. Chatenay, *Science* 259 (1993) 798.
- [5] J.M. Mikrut, P. Dutta, J.B. Ketterson, R.C. MacDonald, *Phys. Rev. B* 48 (1993) 14479.
- [6] H.D. Sikes, J.T. Woodward, D.K. Schwartz, *J. Phys. Chem.* 100 (1996) 9093.
- [7] A. Asmussen, H. Riegler, *J. Chem. Phys.* 104 (1996) 8151.
- [8] J. Fang, C.M. Knobler, *J. Phys. Chem.* 99 (1995) 10425.
- [9] K.B. Blodgett, I. Langmuir, *Phys. Rev.* 51 (1937) 964.
- [10] V.E. Agabekov, G.K. Zhavnerko, V.S. Staroverov, G. Bar, H.-J. Cantow, *Acta Phys. Pol. A* 93 (1998) 383.

- [11] G.K. Zhavnerko, V.E. Agavekov, I.V. Yaminsky, in: V.E. Borisenko, A.B. Filonov, S.V. Gaponenko, V.S. Gurin (Eds.), *Physics, Chemistry and Application of Nanostructures, Reviews and Short Notes to Nanomeeting 99*, World Scientific, Singapore, 1999, p. 218.
- [12] *Wachs-enzyklopädie* von L. Ivanovszky in zwei Bänden, Die Wachse und ihre wichtigsten Eigenschaften, Augsburg, Verlag für chemische Industrie H. Zialkowsky K.G., 1954.
- [13] S.K. Phadtare, S.K. Kamat, G.T. Panse, *Indian J. Chem.* 22B (1983) 493.
- [14] A.I. Kitaigorodsky, *Organic Chemical Crystallography*, Consultants Bureau, New York, 1961.
- [15] J.A. Zasadzinski, R. Viswanathan, D.K. Schwartz, J. Garnaes, L. Madsen, S. Chiruvolu, J.T. Woodward, M.L. Longo, *Colloids Surf. A* 93 (1994) 305.
- [16] G.K. Zhavnerko, V.S. Gurin, A.L. Rogach, M.O. Gallyomov, I.V. Yaminsky, *J. Inclusion Phenomena Macrocycl. Chem.* 35 (1999) 157.
- [17] H. Riegler, K. Spratte, *Thin Solid Films* 210/211 (1992) 9.
- [18] F.R. Rana, S. Widayati, B.W. Gregory, R.A. Dluny, *Appl. Spectrosc.* 48 (1994) 1196.