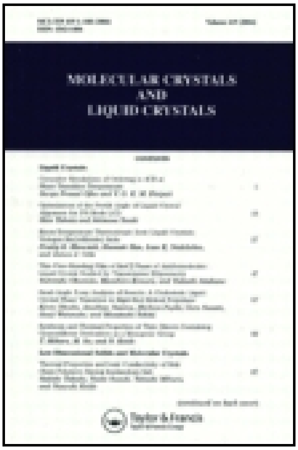

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Layered Structure of Some Mesogenic Monomers and Polymers in Thin Films and Bulk Samples

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Layered Structure of Some Mesogenic Monomers and Polymers in Thin Films and Bulk Samples

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X-ray diffraction and structural simulation were performed to elucidate the structure of Langmuir-Blodgett (LB) films fabricated from monomeric and polymeric monolayers of some mesogenic compounds and corresponding bulk samples. The multilayer structure of LB films of nematic-forming compounds (parasubstituted dibenzo-18-crown-6) was shown to be not quasi-two-dimensional. It is unstable and displays a tendency for the transformation into a three-dimensional crystalline structure. LB films of smectic-forming monomers and polymers (parasubstituted biphenyl and phenylbenzoate) have quasi-two-dimensional multilayer structure, which differs in many aspects from layered structures of bulk smectic and crystalline phases.

Keywords: mesogenic compounds; LB films; structure

INTRODUCTION

In search of new materials for molecular electronics, necessary for construction of thin film functional units, the main attention is given to creation of molecular structures having desirable array of properties. Langmuir-Blodgett (LB) technology basically allows to make quasi-two-dimensional (2D) multilayer structures with required properties. These structures, however, in many cases show unstable behaviour, which manifests itself in the loss of the film layer regularity. Thus the transition of 2D layer structure to more energetically favorable three-dimensional (3D) structure is accompanied by cracking of the film. The problem of stability and structural homogeneity of LB films is especially important for electronic units, and the absence of due attention to it has resulted in relative slippage of this area comparably, in comparison for example, with the area of development of thin film sensors.

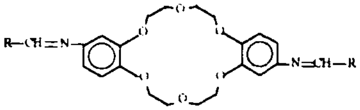
To obtain the stable 2D film structures on solid substrate we can use organic molecules, which are able to form thermodynamically stable layered structures, for example, smectic layers. In this case the layer structure fabricated by LB technology will be similar to the structure of the bulk phase. Another way to create stable film structures - to use the polymeric monolayers or polymerize the monomeric LB films [1-2]. The usage of mesogenic molecules seems to be advantageous in this case too.

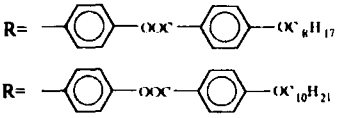
The polymeric monolayers can be formed from polymeric molecules or can be obtained by UV polymerization of monomeric layers directly on a water surface. In the first case the molecules with enough flexible polymeric chains (polysiloxanes) are required to fabricate the dense, smooth LB films, but such flexible chain does not interfere with a crystallization [3]. The molecules with acrylate or methacrylate polymeric chains do not form smooth homogeneous monolayers. In this case to form regular multilayer structure the additional spacer layers from classical amphiphilic molecules is required [4]. The UV polymerization of monomeric layers on a water surface seems more perspective than UV polymerization of multilayer LB film on a solid substrate, because in the latter case the film can crystallize before transformation to a polymeric state. In both cases the successful formation of polymeric layers without destruction of layer structure will depend on ability of initial structure to adopt polymerization. In the ideal case the initial monomeric and finite polymeric structure are identical. From this point of view the best choice will be to use the mesogenic molecules which under polymerization form comb-shaped polymers with the smectic structure.

EXPERIMENTAL

In present work were have studied the thin films fabricated by means of LB technology on a basis of the number of mesogenic molecules - crown-ethers, biphenyls and phenylbenzoates. The films were investigated before and after UV polymerization. In parallel way the structure of the corresponding balk samples have been studied.

The 8th (Cr-6-8) и 10th (Cr-6-10) homologues of 4,5'-bis(4-alkyloxybenzoiloxybenzilideneamino) dibenzo-18-crown-6





were synthesized in Ivanovo State University by Dr. O.B. Akopova [5].

Mesogenic acrylates on a basis of parasubstituted chiral biphenyl
$CH_2{=}CH\text{-}CO\text{-}O\text{-}CH_2\text{-}CH^*(CH_3)\text{-}(CH_2)_2\text{-}CO\text{-}O\text{-}(C_6H_4)_2\text{-}O\text{-}CO\text{-}C_7H_{15}$ - M2
and achiral phenylbenzoates
$CH_2{=}CH\text{-}CO\text{-}O\text{-}(CH_2)_6\text{-}O\text{-}C_6H_4\text{-}CO\text{-}O\text{-}C_6H_4\text{-}O\text{-}C_6H_{13}$ - M3,
$CH_2{=}CH\text{-}CO\text{-}O\text{-}(CH_2)_6\text{-}O\text{-}C_6H_4\text{-}CO\text{-}O\text{-}C_6H_4\text{-}O\text{-}CO\text{-}C_7H_{15}$ - M4
were synthesized in Topchiev Institute of Petrochemical Synthesis by Dr. I.I. Konstantinov.

Molecular monolayers on water surface were formed with the help of LB instrument. Molecules were dispersed on a surface of water subphase (bidistillate) from a solution in chloroform or benzene (concentration from 0.1 up to 0.5 mg/ml). The monomeric monolayers formed on water subphase also were used to obtain the polymeric monolayers by means of UV polymerization. The deposition of monolayers on solid substrate (silicon) was carried out by Schaefer method (horizontal lifting).

Structure investigations of LB films were carried out using X-ray small-angle diffractometer with linear position-sensitive detector for data collecting. Diffraction patterns were registered from crystalline and liquid crystalline samples on flat-plate photographs. Cu K_α radiation (Ni filter) was used in both experiments. X-ray powder patterns were indexed by Ito's method [6]. The structure and molecular simulations were used to interpret of small-angle X-ray data. For this purposes we have used the *Hyper Chem* and *OUP* software. The diffraction from LB film structure models was calculated in following way: molecular model → molecular packing model of a layer → layer form-factor → diffraction from multilayer structure [7]. In our calculation the geometry, absorption, polarization and mosaic (Lorentz's factor) factors were taken into account.

RESULTS AND DISCUSSION

1. Parasubstituted dibenso-18-crown-6

The length (l) and width (w) of the Cr-6-8 and Cr-6-10 molecules were determined from the *Hyper Chem* (calculation of power fields by MM' method and geometrical optimization). These parameters depend on molecular conformation and may be estimated as : $l = 63 \div 64$ Å and $68 \div 69$ Å, $w = 8.5 \div 9$ Å and $4.5 \div 5$ Å respectively. It is necessary to note, that different conformation states are very close in their energies. In some states the molecules have a chair-like conformation of their central part in others - the conformation is more or less plane. More information about preferable molecular conformation may be obtained from powder diffraction data.

X-ray patterns of polycrystalline samples of Cr-6-8 and Cr-6-10 display nearly the same positions in arrangement and intensity ratio of the small- and wide-angle circular reflexes. The radial cross-section of the X-ray powder pattern for Cr-6-10 compound is shown in Fig. 1. The results of indexing for the Cr-6-8 compound is presented in Table 1.

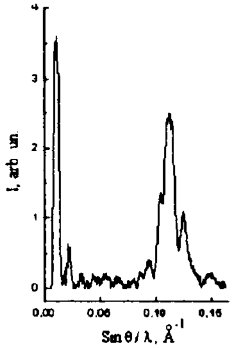


FIGURE 1 The radial cross-section of the X-ray powder pattern for Cr-6-10 compound

TABLE 1 Indexing of the X-ray data for polycrystalline Cr-6-8 compound

N reflect.	*I*, a.u	$d_{exp.}$, Å	*HKL*	$d_{calc.}$, Å
1	100	39.6	100	40.02
2	18	20.0	200	20.01
3	8	13.3	300	13.34
4		8.55	010, 2-10	8.55
5		7.20	4-10	7.21
6		6.57	310, 5-10	6.65
7		5.96	410	5.97
8		5.22	7-10	5.23
9		4.87	001, 101	4.85
10		4.52	301	4.57
11		4.26	011, 020, 1-11, 2-11	4.25
12		4.13	111, 120, 3-11	4.15
13		3.79	411	3.77
14		3.59	511	3.60
15		3.24	021, 1-21,2-21	3.21
16		2.68	330	2.69
17		2.07	222, 240, 322	2.08

Here I - intensity of reflections, $d_{exp.}$ and $d_{calc.}$ - experimental and calculated Bragg's periods, *HKL* - diffraction indexes

The results of indexing are following. The lattice of Cr-6-8 is monoclinic with parameters: a = 40.8 Å, b = 8.71 Å, c = 4.87 Å and γ = 101°. For monoclinic lattice of Cr-6-10: a = 43.4 Å, b = 8.50 Å, c = 4.83 Å and γ = 99°. Both structures are similar with elementary cells containing one molecule. The space group P2. The difference in values of the parameter a is determined by different length of side substitutes. In the structures of both homologues there are small regular shifts (on an edge) of central parts of the molecules and overlap of aliphatic tails with phenylbenzoate fragments (*ab* plane). This structure is typical for nematic-forming compounds. The molecular packing of Cr-6-10 is shown in Fig. 2. A conformation of the central part of the molecules is plane and the symmetry of the lattice does not assume shift of the molecules in *ac* plane (a chair-like conformation and compact packing inevitably would result in regular shift of molecules in this plane). The alternative lattices, which result in the indexing, have smaller (on 16-17 %) density of molecular packing. For main variant the densities are equal 1.031 g/cm^3 (Cr-6-8) and 1.003 g/cm^3 (Cr-6-10).

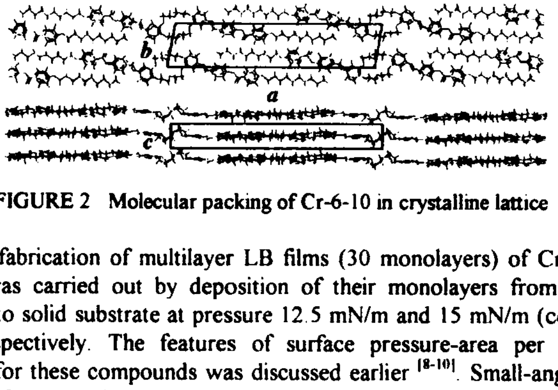


FIGURE 2 Molecular packing of Cr-6-10 in crystalline lattice

The fabrication of multilayer LB films (30 monolayers) of Cr-6-8 and Cr-6-10 was carried out by deposition of their monolayers from a water surface onto solid substrate at pressure 12.5 mN/m and 15 mN/m (condensed phase) respectively. The features of surface pressure-area per molecule isotherms for these compounds was discussed earlier [8-10]. Small-angle X-ray diffraction from LB films of Cr-6-8 and Cr-6-10 compounds show the same number of visible reflections and similar intensity ratios. Some structural parameters of these LB films are presented in Tabl. 2.

In simulation of the structure of LB film the thickness of the layers was made equal to the period calculated from the diffraction peaks positions. The adjustment of models was made on the basis of comparison of intensity ratios of diffraction peaks with the ratios calculated from models of multilayer structure. It was shown, that the use of the molecular tilt in the layers as an only adjustable parameter of the model is inadequate and it is essential to introduce the additional parameter - overlap of end groups in adjacent layers.

The introduction of this overlap indicates that the structure of the LB films of both homologues cannot be considered as quasi-two-dimensional. This is the main difference of our basic model from a model offered earlier [8,9].

TABLE 2 Structure parameters of LB films of Cr-6-8 and Cr-6-10

	N refl.	$d_{exp.}$, Å	$I_{exp.}$, a.u.	$I_{calc.}$, a.u.	Tilt, degr.	Overlap, Å
	1	40.2	100	100		
Cr-6-8	2	20.1	20	26	45	8
	3	13.4	10	9		
	1	45.5	100	100		
Cr-6-10	2	22.7	9	12	45	8
	3	15.1	2	3		

The structure of these LB films has the same type of molecular packing (tilt and overlap) as the structure of bulk crystalline phase, Fig. 3 and Fig. 2 (*ab* section). Apparently the transformation of layer structure of LB film into the structure with bulk structural elements begins already on the stages of the film fabrication.

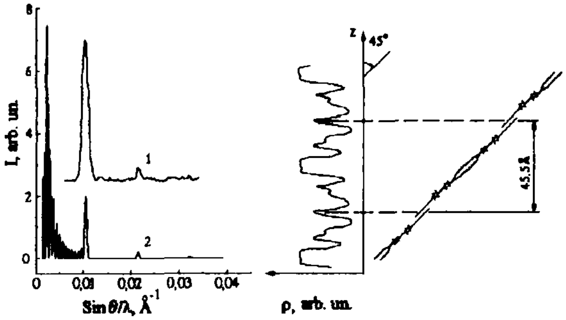


FIGURE 3 Molecular packing, electron density $\rho(z)$, experimental (1) and calculated (2) diffraction from multilayer structure for LB film of Cr-6-10

2. Parasubstituted biphenyls and phenylbenzoates

The monolayer of M3 compound strongly differs from monolayers of M2 and M4 compounds by greater square per a molecule in a condensed phase, lower pressure of a collapse and noticeable decrease of its stability under UV irradiation, fig. 4. For M2 compound the monolayer stability under UV polymerization remains unchanged while for M4 compounds it increases essentially. More details concerning monolayer behaviour of these compounds are presented in [11].

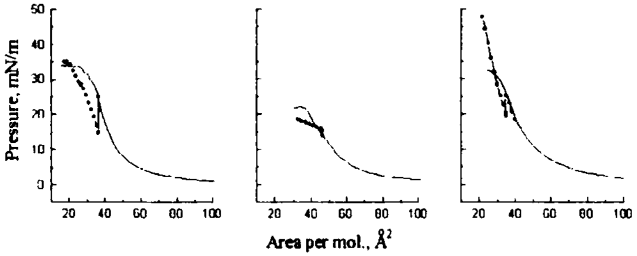


FIGURE 4 *P-A* isotherms of the monomers M2, M3 and M4 before (—) and after (•-•-) UV irradiation

Small-angle X-ray diffraction patterns of multilayer LB films fabricated from the monomeric monolayers display maxima the positions of which correspond to smaller periodicity than the molecular length, Table 3. This allow us to interpret the layer structure as tilted. However these diffraction curves differ in the number of reflexes and intensity distribution, that is indicative of specific differences in multilayer structure of LB films. The simulation with given molecular tilt in layers and overlap of the end groups into adjacent layers together with the adjustment of calculated diffraction to experimental data allowed us to determine the structural parameters of LB films.

TABLE 3 Structural parameters of LB films of M2, M3 and M4 compounds

			I		II		III	
	P, mN/m	*N* refl.	*I*, a.u.	*d*, Å	*I*, a.u.	*d*, Å	*I*, a.u.	*d*, Å
M2	25	1	100	26,6	100	27	100	30
M3	12.3	1	100	33				
		2	18	16.5				
	14	1	100	28	100	28		
		2	170	14	146	14		
M4	25	1	100	33.6	100	33.6	100	36
		2	21.5	16.8	29.5	16.8		

Here I - monomeric LB film, II - LB film after UV irradiation, III - LB film fabricated from UV polymerized monolayers, *I* - intensity, *d* - Bragg's period

LB film of M2 compound fabricated from monolayers with pressure 25 mN/m displays small-angle diffraction pattern with one peak corresponding to interlayer period of 26.6 Å (molecular length of M2 is equal to 34.5 Å). From the layer structure simulations we found that such type of diffraction corresponds to LB film of X-type (polar structure) with molecular tilt 37° and slight overlap of the end groups of the molecules in adjacent layers on 1.6 Å. The calculated intensity of the second maximum is twenty times less than the first. This explains its absence on the diffraction pattern, Fig. 5. The layer structure of the LB film of M2 compound is similar to the structure of the crystalline phase of M2, which polar structure is characterized by monoclinic lattice (γ =125.7°, that corresponds to molecular tilt 35.7°) and antiparallel longitudinal packing of the molecules (space group $P2_1$) [12]. The only difference is that in the layers of the LB film the molecules are parallel to each other.

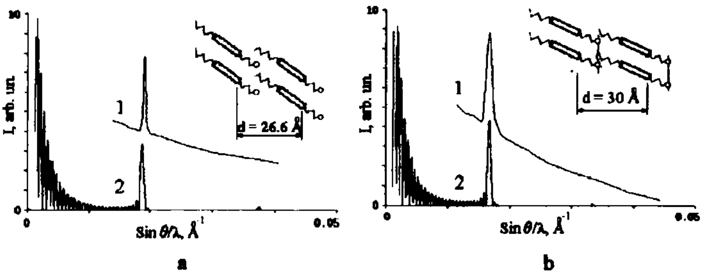


FIGURE 5 Structural models, experimental (1) and calculated (2) diffraction for LB films: monomeric (a) and fabricated from UV polymerized monolayers M2 (b)

The deposition of monolayers of M3 compounds to fabricate the multilayer LB films was made at pressure 12.3 mN/m and 14 mN/m. The corresponding X-ray diffraction profiles show two maxima, essentially differing in intensity ratios and positions, Table 3. In the first case (the first reflex is stronger than the second reflex and interlayer period is equal to 33 Å) the comparison of calculated intensity to experimental gives a model with an overlap of the end groups in adjacent layers on 1.8 Å and the absence of molecular tilt the layer, Fig. 6-a. In the second case (the second reflex is stronger than the first reflex and interlayer period is equal to 28 Å) the optimal model shows an overlap of the end groups on 4.6 Å with 20° tilt of molecules in the layers, Fig. 6-b. The deviation of calculated intensity from experimental does not exceed 1%.

The LB film structures of M3 compound have the interlayer periods similar to the smectic (32.3 Å) and crystalline phase (d_{100} = 26.3 Å), but these LB film structures differ from the bulk structures by the parallel packing of molecules in the layers (polar structures of X-type). The crystalline structure of M3 is monoclinic (a = 33.4 Å, b = 10.62 Å, c = 5.20 Å, β = 128°, 2 molecules in elementary cell) and with polar (space group $P2_1$) lateral packing of the molecules. The smectic structure of M3 is of the A-type. These bulk structures have no overlap of the molecules in adjacent layers.

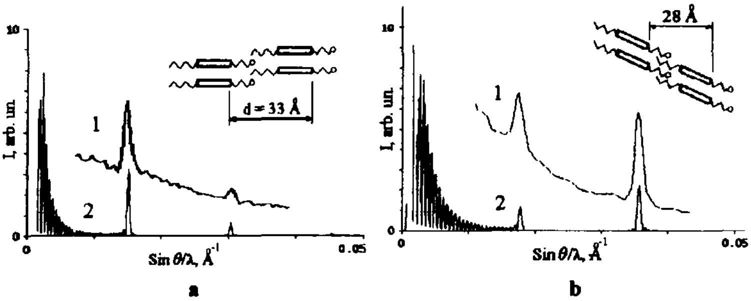


FIGURE 6 Structural models, experimental (1) and calculated (2) diffraction for LB films of M3, formed at pressure 12.3 mN/m (a) and 14 mN/m (b)

Multilayer LB film of M4 compounds was fabricated on the basis of monolayers at the pressure 25 mN/m. The film shows small-angle diffraction pattern with two maxima which have intensity ratios and the periods nearly the same as in the LB films of M3 compound, fabricated at pressure 12.3 mN/m (smectic-like structure), Table 3. However the longer tail of M4 compound and the presence of carbohylic group modifies the distribution of electron density in the layer. As a result the modeling shows molecular tilt of the order of 10° and increasing of the overlap of the end groups up to 2.8 Å, Fig. 7. This multilayer structure is of the X-type and similar to bulk crystalline structure of M4 in the values of interlayer period 33.6 Å and d_{100} = 34.3 Å respectively. The monoclinic structure of M4 compound in bulk crystalline phases (a = 37.2 Å, b = 4.96 Å, c = 16.0 Å, β = 113°, space group P2, 4 molecules in elementary cell) has twice as much molecular tilt (23°) and antiparallel packing of the molecules.

It should be noted that the appreciable overlap of the molecules in the polar LB film structures of M3 and M4 compounds shields the molecular fragment with C=C bond thus preventing UV polymerization.

The deposition of UV polymerized monolayers of M2 compound on the solid substrate was carried out at the pressure 25 mN/m. Small-angle X-ray diffraction from such multilayer LB film displays only one reflex which corresponds to larger interlayer distance (30 Å) than in the case of monomeric LB films of the same compound, Table 3. The simulation gives the layer structure of essentially smaller molecular tilt in a layer (25°) and overlap of the end groups in adjacent layers at a previous level (1.5 Å), fig. 5-b. The polar structure of the X-type markedly differs from the comb-shaped structure of the polymer based on M2 (PM2) compound in a bulk, Table 4. In a glassy state PM2 has smectic structure with a bilayer period 54.5 Å (similar to Y-type structure in LB films) and with twice as less period corresponding to thickness of sublayers. The tilt of parallel packed side groups in sublayers of PM2 appears larger (30°), than in the LB film structure based on polymerized monolayers of M2.

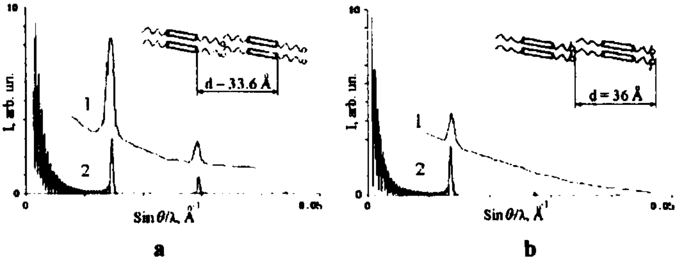


FIGURE 7 Structural models, experimental (1) and calculated (2) diffraction for LB films: monomeric (a) and fabricated from UV polymerized monolayers M4 (b)

TABLE 4 Diffraction and structure parameters of the polymers in a glassy state

20° C	*N* refl.	*I* arb.un.	*d* Å	Half-width radn.	Distortion parameter g_l
PM2	M1	100	54.5	0.00762	0.024
	M2	59	27.3	0.00772	
	M3	11	7.82		
	E		4.52	0.01715	0.073
PM3	M1	100	59.0	0.00889	0.054
	M2	22	29.9	0.01051	
	E		4.49	0.06318	0.151
PM4	M1	100	52.4		
	M2	23	25.7	0.00976	0.014
	M3	4	16.8	0.00984	
	E		4.40	0.01851	0.074

Our attempts to fabricate the regular multilayer LB films based on the UV irradiated monolayers of M3 compounds were unsuccessful. This was indicated by the absence of interlayer diffraction from these films in small-angle X-ray experiment. Such behaviour is associated with essential heterogeneity and roughness of the UV irradiated monolayers, that prevents the formation of regular multilayer structures on a solid substrate.

The LB films formed from UV polymerized monolayers of M4 compound at pressure 25 mN/m contrary to the monomeric LB films, display small-angle X-ray diffraction with only one reflex corresponding to period 36 Å, which is a little larger, than the period defining layers thickness for the multilayer monomeric film, Table 3. The model of the LB layer structure based on the UV polymerized monolayers of M4 compound (X-type structure) provides 15° tilt and the absence of an overlap of side groups of the polymeric molecules in adjacent layers, Fig. 7-b. The structure of such polymeric films markedly differs from a bulk structure of the polymer based on M4 (PM4) compound, Table 4. PM4 transforms into a glassy state from smectic phase with tilted bilayer structure, which is characterized by the period 52.4 Å and the tilt of side groups on 42°.

UV irradiation of multilayer monomeric films of M3 (formed with the pressure 14 mN/m) and M4 compounds, as it was supposed, has not resulted in their polymerization because of the shielding of the molecular fragment with C=C bond by the tails of molecules in adjacent layers. X-ray diffraction from the multilayer films after UV irradiation corresponds to the same structural model, as before their irradiation. The small changes in intensity ratios of the diffraction maxima may be explained by the subtle distortions in molecular packing due to the disturbing effect of UV irradiation, Table 3. The influence of UV irradiation on the structure of LB film of M2 monomer is very subtle and corresponds to small shift in the position of small-angle X-ray diffraction peak.

CONCLUSION

In summary, our X-ray diffraction studies have shown, that the structure of LB films based on nematic-forming compounds (parasubstituted crown-ethers) cannot be considered as having quasi-two-dimensional layering. These films have the same structural feature (appreciable overlap of molecular fragments) as in corresponding balk crystalline samples. Such film structure is not stable and starts to transform to crystalline types of ordering already at the stages of the film fabrication.

Contrary to the LB films on the basis of the crown-ethers, the LB films of smectic-forming monomers (biphenyl and phenylbenzoate) have structural elements (polar longitudinal molecular packing and an overlap of molecular tails in adjacent layers) which are absent in corresponding bulk crystalline structures. The polar film structures are originated from the method of a film fabrication (X-type films) while the overlap of molecular fragments should be considered as some type of defect, which formation depends on molecular structure (length of hydrophobic fragments and their branching).

In the LB films formed by UV polymerized monolayers the presence of a main chain results in increasing of interlayer period. The film structure based on polymerized monolayers is more stable than its monomeric analogue due to a rigidity and extended length of a main chain. Such LB films may be considered as new polymeric smectic structures of the polar type, which are not formed by these compounds in a bulk state.

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