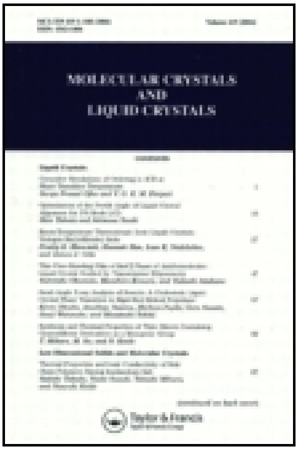

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 04 Oct 2006.

To cite this article: Yu. M. Lvov, V. I. Troitsky & L. A. Feigin (1989): Structure Analysis of Langmuir-Blodgett Films with Alternating Bilayers by Means of Small-Angle X-ray Scattering and Electron Diffraction, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 172:1, 89-97

To link to this article: http://dx.doi.org/10.1080/00268948908042154

Mol. Cryst. Liq. Cryst., 1989, Vol. 172, pp. 89–97
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Printed in the United States of America

Structure Analysis of Langmuir-Blodgett Films with Alternating Bilayers by Means of Small-Angle X-ray Scattering and Electron Diffraction

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(*Received December 19, 1988*)

Langmuir-Blodgett films containing alternating bilayers of 4-*n*-octadecylphenol (ODPh) and Ba behenate (L-B superlattices) were prepared and studied by means of small-angle X-ray scattering and electron diffraction analysis. The spacing of the L-B superlattice is 109 Å, the unit cell contains one bilayer of ODPh molecules and one bilayer of Ba behenate molecules.

The structural changes which occur in these L-B superlattices during the process of cross polymerization of the ODPh in layers by electron irradiation were investigated too, and show that discrete doses of radiation can cause crosslinking of the ODPh in layers without causing substantive destruction of the Ba behenate layers.

Keywords: Langmuir-Blodgett films

INTRODUCTION

The Langmuir-Blodgett (L-B) method[1] of pre-assembling a molecular layer at the air/water interface and transferring one monolayer at a time to a solid substrate is one of the most popular methods of preparing films of amphiphilic molecules. This method makes it possible to construct organic films of complicated composition—that is films with alternating molecular layers of different molecules (superlattices). In this work we prepared L-B films with alternating bilayers of 4-*n*-octadecylphenol (ODPh) and Ba behenate and studied these using small-angle X-ray analysis and electron diffraction. The structural changes which occur in these films when cross-linking of the ODPh in layers was induced by irradiation with electrons were investigated as well.

MATERIALS AND METHODS

L-B films were deposited on silicon substrates for X-ray analysis and on the special networks cowered by nitrocellulose for electron diffraction experiments. In the X-ray experiments we used samples which contained 40 monolayers (ODPh bilayer + behenate Ba bilayer)$_{10}$ and for electron diffraction 20 monolayers (ODPh bilayer + behenate Ba bilayer)$_5$. Using a buffered water subphase at pH 7.4 containing 10^{-4} mole/l of Ba acetate, alternate bilayer structures were prepared on a substrate using ODPh and Ba behenate monolayers maintained at a surface pressure of 30 mN m^{-1} and 27 mN m^{-1} respectively. After transferring each bilayer, the surface of water was cleaned after which a droplet of the next substance was added. In addition to superlattices, L-B films with 20 and 100 monolayers of ODPh and Ba behenate (separately) were prepared.

A small-angle X-ray diffractometer using Cu K_α radiation with a position sensitive detector[2] was used to obtain diffraction patterns. This diffractometer allows the measurement of the intensities of X-ray scattering simultaneously in 1000 channels with angle resolution 0.01°. The path of the incident beam and the scattered beam was under vacuum. Samples were scanned on an axis perpendicular to the direction of primary beam.

Electron diffraction experiments were performed on JEM-100 C (Japan) electron microscope.

RESULTS

X-ray analysis

Analysis of the meridional X-ray patterns from the L-B superlattice gives us the Bragg-spacing of $D = 109 \pm 0.5$ Å in the direction perpendicular to the surface of the substrate in which 14 orders of reflections were measured (Figure 1). The Bragg-spacings obtained for a monocomponent L-B film of ODPh molecules (50 monolayers) is 49.5 ± 0.5 Å and for monocomponent L-B film of Ba behenate (50 monolayers) is 58.3 ± 0.5 Å. In both cases 10 orders of reflections were measured. The additivity of thicknesses of layers of the two different molecules forming the L-B superlattice is $49.5 + 58.3 = 107.8 \pm 1.0$ Å, it is close to 109 Å.

From the width of the reflections it is possible to calculate a parameter of long range ordering in the packing of molecular layers (L).[3] Widths of reflections for all types of the L-B films were found to be approximately the same having a value $L = 1100 \pm 100$ Å. This value is approximately equal to the thickness of the L-B films studied, suggesting that we succeeded in forming a film from alternating molecular layers of two different types with the packing of the layers essentially the same as they are packed in monocomponent L-B film.

An electron density profile of the L-B film superlattice with alternating bilayers of ODPh and Ba behenate including the positions of the molecules in the unit cell is presented in Figure 2. Calculations were based on Fourier transformation of 14 scattering amplitudes. The intensities of reflections were normalized by multiplication by the number of reflections. The phases of reflections were determined with the help of a molecular refinement procedure.[4,5] The greatest maximum of electron density on the profile is due to the position of Ba atoms followed by a section showing (at 8 Å resolution) electron density obtained from a crystalline

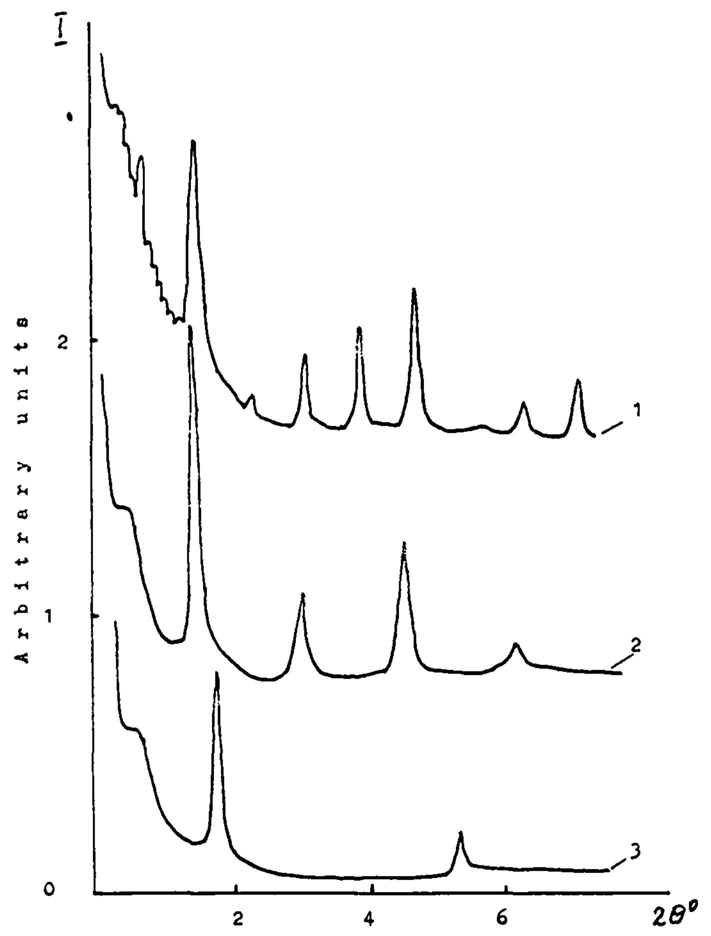

FIGURE 1 The curves of intensities of small-angle X-ray scattering I (2θ): 1 = of the L-B superlattice (bilayer ODPh + bilayer of Ba behenate)$_{10}$. The subsidiary maxima of the Laue-function due to the small number of unit cells in the film are visible in the inner part of the curve. 2 = curve of the monocomponent Ba behenate L-B-film, 3 = of the monocomponent ODPh L-B film.

packing of hydrocarbon chains. There is then a density minimum caused by tips of chains touching one another, followed by a section of electron density corresponding to the hydrocarbon chains of ODPh molecules. These are shorter than chains of Ba behenate and give a smooth maximum in the density profile where the phenyl rings of ODPh molecules are present.

Electronography

A detailed description of sample preparation is presented in Reference 6. An analysis of electron diffraction patterns shows that the packing of hydrocarbon chains in layers of the L-B films of Ba behenate and of ODPh are the same as in the superlattice with alternation of these molecular layers (Figure 3a). In particular, for bilayers of Ba behenate there is a hexagonal two-dimensional lattice ($a = 4.8 \pm 0.05$ Å). Rectangular units ($a = 8.25 \pm 0.05$ Å, $b = 5.35 \pm 0.02$ Å) of ODPh bilayers contain 4 molecules with possible group of symmetry P 1 a/2 1 or P 1 a/2 1_1.[6] Epitaxial growth in L-B films with alternating bilayers is absent, which differs from multilayers of monocomponent L-B films. But each previously suspended bilayer influences the orientation of growth on the two-dimensional crystallites of the second type of molecules. It displays small arcs on electron diffraction reflections from ODPh bilayers which correspond to the hexagonal symmetry of molecular packing in bilayers of Ba behenate. This phenomena was absent on electron diffraction patterns from monocomponent ODPh L-B films.

Polymerization of L-B superlattices in bulk

Earlier[7] it was shown that when an L-B film is irradiated by electrons crosslinking of ODPh molecules occurs in the region of the phenyl rings in a single monolayer. After intensive irradiation, L-B films of ODPh became amorphous. However, Ba behenate films don't polymerize under such conditions. By forming L-B films from alternating layers of two types of molecules, one of which may be polymerized, we propose to change the mechanical and other properties of such a superlattice using electron beam polymerization.

In our initial experiments, films with alternating molecular layers were irradiated by electrons with 3 keV energy. When the dose of irradiation was $q = 0.75 \cdot 10^{-3}$ cl/cm^2, the spacing was found to decrease from 109 Å to 102 Å as calculated from X-ray diffraction data. The diffraction field decreases too, showing only 4 orders of reflections instead of 14 as for the basic superlattice.

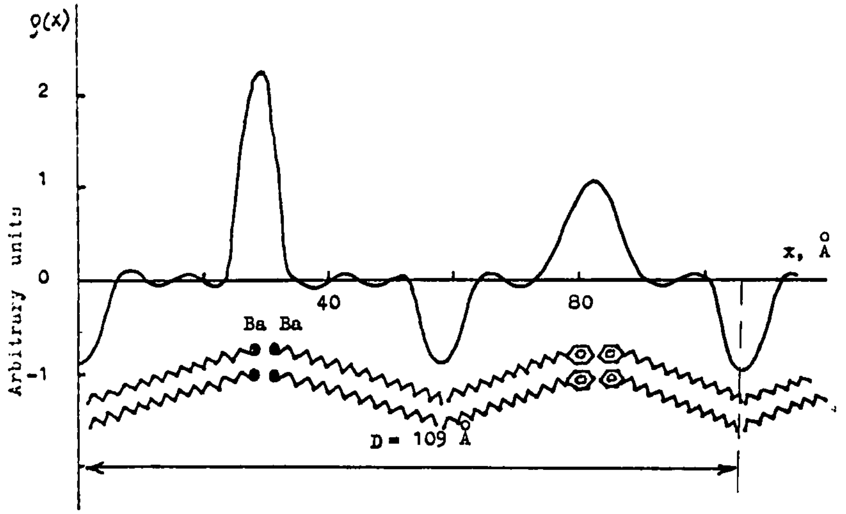

FIGURE 2 An electron density profile δ(n) across an L-B film superlattice (bilayer ODPh + bilayer Ba behenate) and positions of Ba behenate and ODPh molecules in a unit cell (OH = group in ODPh is not drawn). The Bragg-spacing is 109 Å.

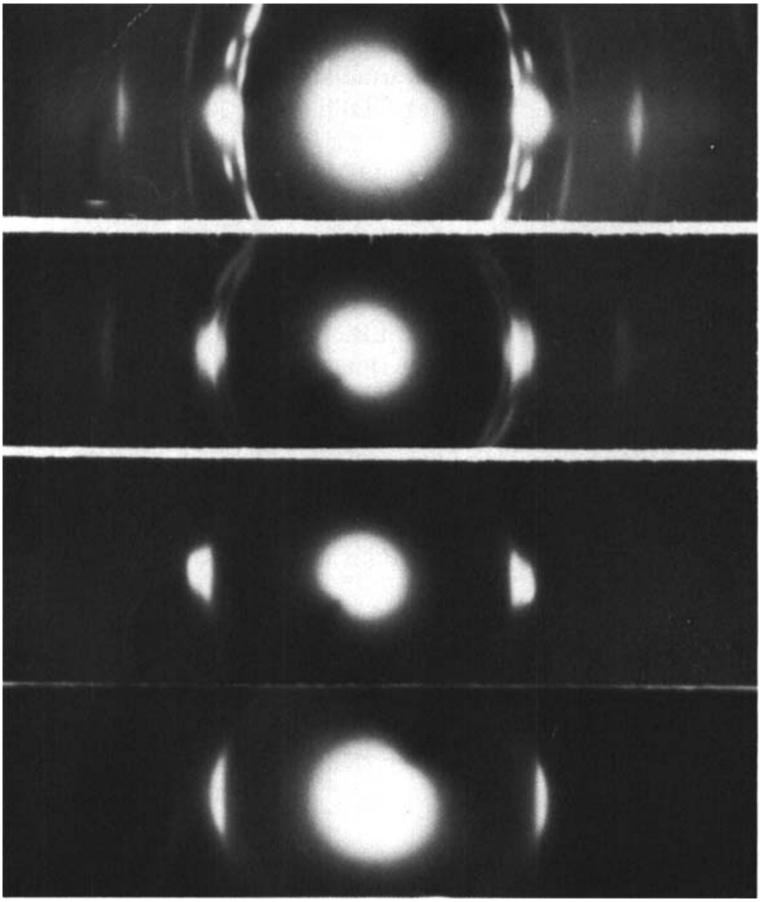

FIGURE 3 Electron diffraction patterns of L-B superlattice in dependence on doses of irradiation by electrons with 100 eV energy, *a* – $q = 0$, *b* – $q = 0.28 \cdot 10^{-3}$ cl/cm^2, *c* – $q = 0.42 \cdot 10^{-3}$ cl/cm^2, *d* – $q = 0.8 \cdot 10^{-3}$ cl/cm^2. Tilt of the samples is 50°.

Increasing the electron irradiation up to $q = 3 \cdot 10^{-3}$ cl/cm^2 results in the disappearance X-ray reflections, it shows that the long range order in periodicity due to the stacking of molecular layers is destroyed. It was also noted from changes in the interference colors that the optical thickness of the films was decreasing.

After additional doses of irradiation the interference color remains constant suggesting that there are no further changes in the optical thickness of the films. Electron diffraction data on the samples irradiated up to $q = 6 \cdot 10^{-3}$ cl/cm^2 shows that the hydrocarbon chains of Ba behenate generally remain vertical in the L-B film.

Changes in a structure of L-B films under electron irradiation

To try to understand the lack of long range ordering in irradiated superlattices with alternating molecular bilayers of ODPh and Ba behenate, we investigated the influence of electron irradiation on monocomponent L-B films of ODPh and Ba behenate. Figures 4 and 5 show dependences of X-ray diffraction patterns and spacings in these L-B films on doses of irradiation by electrons with 3 keV energy. The changes of thickness of bilayer for ODPh are far less than for Ba behenate at the same doses of irradiation.

It should be noted that L-B films of ODPh lose solubility in organic solvents when irradiated by a dose of about $0.8 \cdot 10^{-3}$ cl/cm^2 (suggesting that polymerization occurs) and at doses of more than $3 \cdot 10^{-3}$ cl/cm^2, the films become amorphous.

In L-B films of Ba behenate drastic disturbances in a structure begin at $q = 0.1 \cdot 10^{-3}$ cl/cm^2 (Figure 4). The final stage of destruction of L-B films of Ba behenate may result from a separation of atoms of Ba from the molecules. This assumption is a consequence of our previous experiments with destruction of L-B films of thallium behenate in the process of electron irradiation. The changes in the spacings for L-B films of behenates Ba and Tl are the same and the limits of these changes are close. For Tl behenate L-B films after very large doses of irradiation, the electron diffraction patterns show reflections from small crystals of metallic Tl. But reflections from metallic Ba for Ba behanate after irradiation were not detected, possibly because the metallic phase of Ba is amorphous.

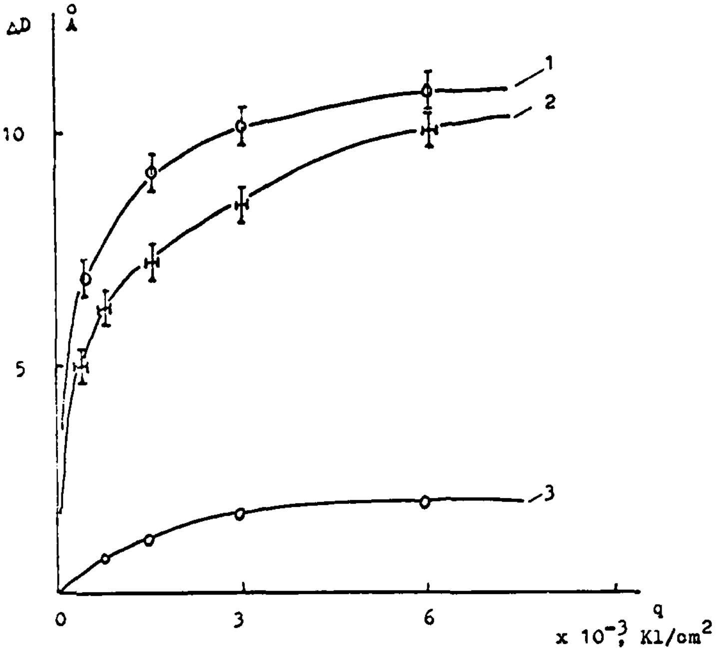

FIGURE 4 Decreasing of spacings ΔD in monocomponent L-B films in dependence on doses of irradiation in bulk by electrons with 3 keV energy; 1 = electron diffraction data for Ba behenate films, 2 = X-ray data for Ba behenate films, 3 = an optical interferometry data for ODPh films. Small differences in X-ray and electron diffraction results for Ba behenate L-B films may be caused by extra doses of radiation absorbed in a process of registration of electron diffraction patterns.

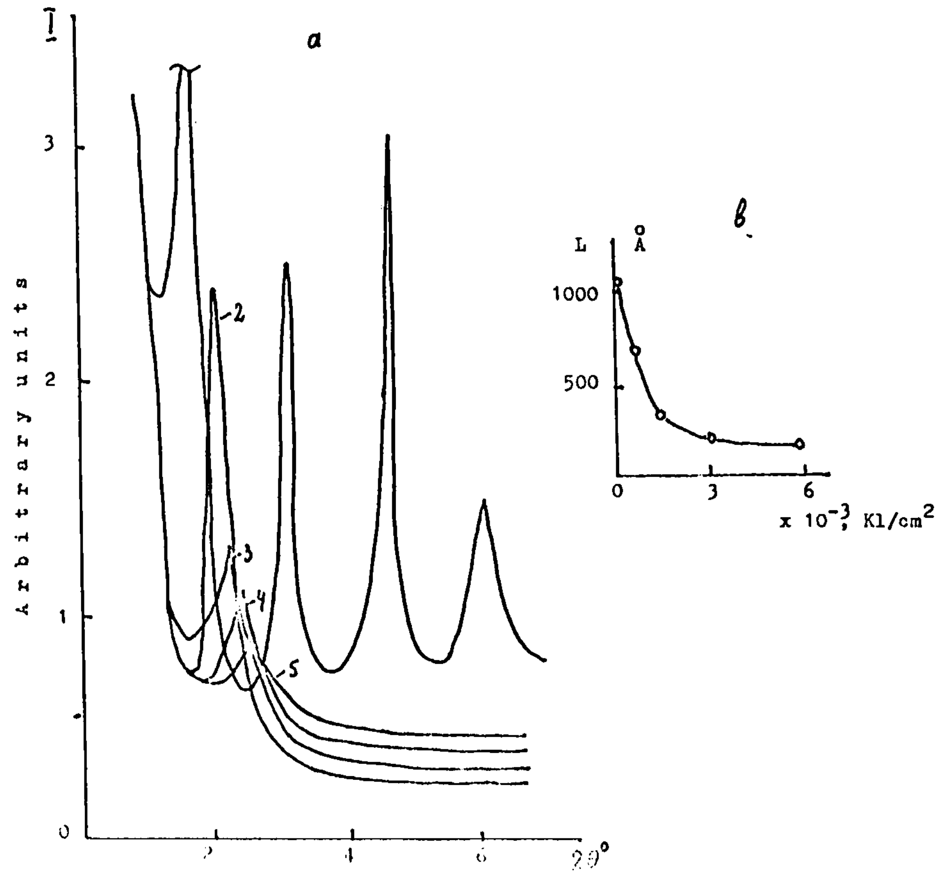

FIGURE 5 Small-angle X-ray diffraction patterns of Ba behenate L-B films in dependence on doses of irradiation, I = intensities of the meridional scattering, 2θ = scattering angles, 1 – $q = 0$, 2 – $q = 0.6 \cdot 10^{-3}$ cl/cm^2, 3 – $q = 1.6 \cdot 10^{-3}$ cl/cm^2, 4 – $q = 3 \cdot 10^{-3}$ cl/cm^2, 5 – $q = 6 \cdot 10^{-3}$ cl/cm^2; b) Long range order parameter – L in dependence on doses of irradiation by 3 keV electrons.

However, the dose of irradiation which destroys L-B films of Ba behenate is far less than the dose required for crosslinking of ODPh in layers. This result suggested that we might construct an L-B superlattice by crosslinking molecules in every other layer of ODPh with electrons of low energy (100 eV). These electrons have an energy which is enough for inducing chemical transformations in organic molecules, but not sufficient to penetrate into the bilayer of Ba behenate lying under ODPh bilayer, preserving the behenate Ba layer from destruction.

Irradiation "layer by layer"

Six L-B superlattices (ODPh bilayer + bilayer of Ba behenate)$_{10}$ and six (ODPh bilayer + bilayer of Ba behenate)$_5$ where every odd bilayer (ODPh molecules) were crosspolymerized separately by low energy electrons were prepared. Results

TABLE I

Dependence of Structural parameters of L-B films (bilayer ODPh + bilayer Ba behenate)$_{10}$ on doses of irradiation by low energy electrons

q (cl/cm^2)	D (Å)	L (Å)	N	x (Å)
1. 0	109	900	14	8
2. $0.14\ 10^{-3}$	109	800	14	8
3. $0.28\ 10^{-3}$	109	700	10	11
4. $0.42\ 10^{-3}$	109	500	9	12
*$0.42\ 10^{-3}$	107	600	9	12
5. $0.69\ 10^{-3}$	96	260	2	—
6. $0.83\ 10^{-3}$	no reflections			

q = dose of irradiation, D = spacing, L = long range order parameter, N = number of reflections, Δx = resolution.

*The sample from another series.

of small-angle X-ray diffraction analysis of these samples are presented at Table I. In Figure 3 the corresponding electron diffraction patterns are shown.

It was shown that when a dose of low-energy electron irradiation for every ODPh layer is more than $0.2 \cdot 10^{-3}$ cl/cm^2 the ODPh molecules are crosslinked and are not soluble in organic solvents (this value is less than previously mentioned for irradiation in bulk). At this step reflections from two-dimension packing of molecules of ODPh in layers may be seen in an electron diffraction pattern (Figure 3b). There is still long range ordering when molecular layers are stacked in the film (L = 700 Å) and 10–14 reflections are recorded on X-ray diffraction patterns (Table I).

When we increased a dose up to $0.42 \cdot 10^{-3}$ cl/cm^2 the ordering changes for the worse (L = 500 Å) and only 9 reflections were recorded on the X-ray diffraction pattern. Density spacing remains (except one sample where D decreases on 2 Å, which may be caused by decreasing of the thickness of ODPh bilayers). ODPh bilayers become amorphous at this stage (Figure 3c).

At a dose of $0.69 \cdot 10^{-3}$ cl/cm^2 long range ordering in the film disappears, the spacing sharply decreases. It seems that at this dose the radiation destroys the layers of behenate Ba lying under ODPh layers, as shown by the electron diffraction pattern (Figure 3d).

After further increasing the time of irradiation, all X-ray reflections are absent, so suggesting no ordering in the film.

So, the best samples in which odd bilayers are crosspolymerized, and in which good ordering occur are samples 3–4 (Table I).

Such L-B superlattices are of the most interest for applications in molecular electronics, "volume" lithography, for preparing lattices with large spacings for analyzers of soft cosmic radiation and others.

Acknowledgements

We should like to thank Prof. B. K. Vainshtein for useful discussion of the results.

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