Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Tieke, Bernd , Enkelmann, Volker , Kapp, Harald , Lieser, Günter and Wegner, Gerhard(1981) 'Topochemical Reactions in Langmuir-Blodgett Multilayers', Journal of Macromolecular Science, Part A, 15: 5, 1045 — 1058

To link to this Article: DOI: 10.1080/00222338108056782

URL: http://dx.doi.org/10.1080/00222338108056782

J. MACROMOL. SCI.-CHEM., A15(5), pp. 1045-1058 (1981)

Topochemical Reactions in Langmuir-Blodgett Multilayers

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ABSTRACT

The topochemical polymerization of diacetylenes and the dimerization of cinnamic acid derivatives have been studied in Langmuir-Blodgett-multilayers. The resulting polymer films are of controlled thickness and morphology and exhibit excellent stability. Structure, morphology and phase changes occuring in monomer and polymer films have been investigated using spectroscopic methods, electron and x-ray diffraction. Possible applications of the polymer films are discussed.

INTRODUCTION

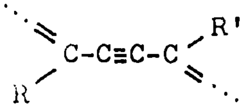
Reactions in monomolecular layers or in multilayers built up by the Langmuir-Blodgett technique (1) have recently become of interest because of the orientational effects obtainable in these structures. Polymerizations, in particular, have been demonstrated to be a way to effectively stabilize these normally quite unstable molecular assemblies (2-4).

Of special interest are topochemical, i.e. strictly lattice controlled reactions where minimal structural disorder is introduced by the reaction and the molecular packing is retained (5,6). Polymer films prepared by this technique could be effectively utilized as stable ultrathin coatings or membranes of controlled thickness in a variety of industrial or biomedical applications.

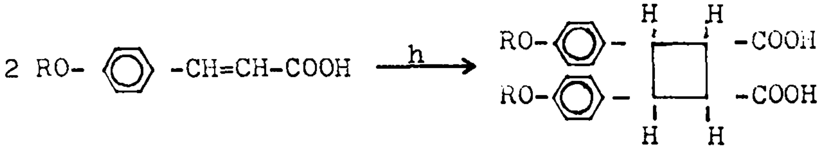
The topochemical reactions studied in built-up multilayers were the solid-state polymerization of diacetylenes and the four-center-type dimerization of cinnamic acid derivatives (5,6). The monomers used in this investigation were unsaturated long chain fatty acids of the general structure

$$C_mH_{2m+1}-C\equiv C-C\equiv C-(CH_2)_8-COOH$$

with m = 9 (1), m = 10 (2) and m = 12 (3), which polymerize upon ultraviolet radiation in a 1,4-addition reaction to form a planar, conjugated polymer backbone of the general structure



and long chain ether and ester derivatives of the 4-hydroxy-cinnamic acid which dimerize according to



with R = $C_{16}H_{33}$ (4), $C_{18}H_{37}$ (5) and $C_{16}H_{33}-\underset{O}{C}-$ (6).

Both reactions have in common that they are strictly lattice controlled, i.e. both the reactivity and the symmetry of the products are determined by the monomer packing. All reactivity comes about from very specific rotations of the monomer molecules on their lattice sites. Since these reactions take only place in the perfectly packed crystalline state they offer an excellent opportunity to study the state of order in mono- and multilayers.

EXPERIMENTAL

Chemicals

Diacetylene monocarbonic acids were prepared as described previously (7). Ether derivatives of the cinnamic acids were prepared according to the method described by Cray and Jones (8).

Mono-and Multilayer Formation

A commercially available Langmuir trough equipped with a film balance (MGW Lauda) was used. Monolayers were obtained by spreading the acid solutions in $CHCl_3$ (spectroscopic grade, concentration 1 mg/ml) on a subphase of triply distilled water (pH 5,9 - 6,1) or a 10^{-3} molar $CdCl_2$-solution. pH-variations were carried out by addition of 0,1 n HCl or NaOH, respectively.

Multilayers were built up by the Langmuir-Blodgett-technique (1). Transfer of the monolayers onto quartz- or germanium plates was performed at a surface pressure of 20 mN/m.

Polymerization

Diacetylene derivatives were polymerized using a medium-high-pressure mercury lamp (Heraeus Hanau Q

300). Cinnamic acid derivatives were polymerized using a 150 W Xe-lamp.

Multilayer Characterization
The UV-spectra were recorded from multilayers deposited on quartz plates (24 x 12 x 1 mm) using a Perkin-Elmer Hitachi 200 spectrometer.
Structure investigations were performed by SAXS using a Philips powder diffractometer and electron diffraction using a Philips EM 400 electron microscope. Details of sample preparation have been described previously (9,10).

MONOLAYER PROPERTIES

The monolayer properties of the derivatives 1-6 have been studied by measuring the surface pressure-area-isotherms. Isotherms of 1-3 have been described previously (11,12), those of 4-6 are shown in Fig.1. In general, the stability increases with increasing chain length and is maximal when the subphase contains counterions such as Cd^{2+}, which allow a salt formation of the polar head groups.
As it is known that the pH of the subphase has a marked effect on the salt formation in the monolayers (13), it was necessary to study the conditions of the Cd-salt formation more in detail. The results of such studies are shown in Fig. 2 for 3.
If the collapse pressure of the monolayer is plotted as a function of the pH in the subphase, the salt formation seems to be essentially complete at a pH of 6,5.
More direct evidence for a salt formation is obtained by means of ATR-IR-spectroscopy (9,10,14). In

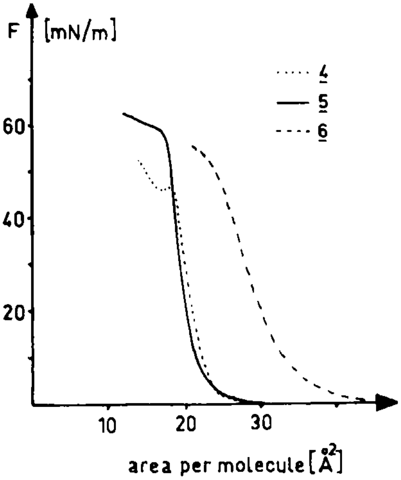


Fig.1. Surface pressure-area-isotherms of 4-6 on a 10^{-3} molar $CdCl_2$-solution, T=21°C, pH=6,5.

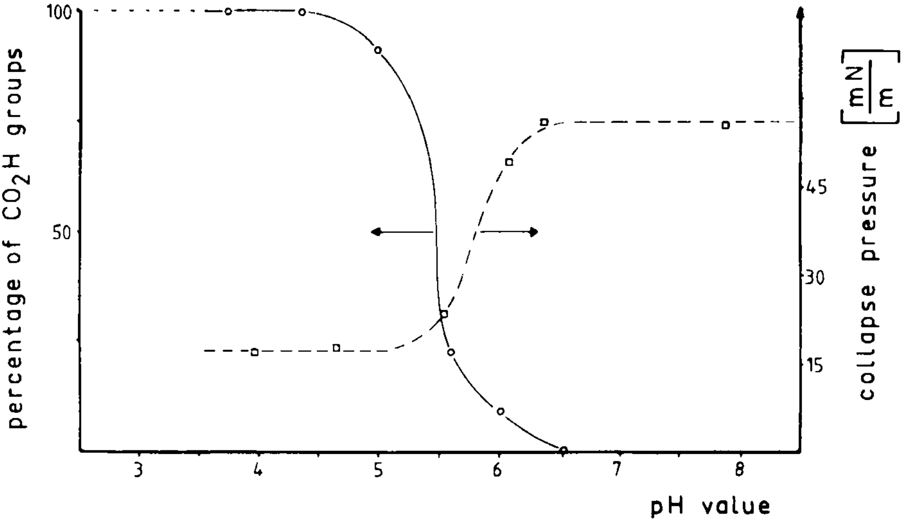


Fig.2. Percentage of free acid 3 in the multilayers (full line) and collapse pressure (broken line) as a function of the pH of the subphase; subphase 10^{-3} molar $CdCl_2$-solution, T=20°C.

the IR-spectra the C=O valence band of the free acid group occurs at 1710 cm^{-1} while the presence of an ionized carboxylate group gives rise to a strong band at 1550 cm^{-1}. Thus the relative amount of acid to carboxylate groups can be derived from the relative intensities of the two bands. The pertinent results obtained for 3 are also shown in Fig.2. They are in good agreement with the data derived from the surface pressure-area-isotherms indicating that about 95% of all acid groups are in an ionized state at a pH of 6,5.

REACTIONS IN MULTILAYERS

Both the reactions are initiated by ultraviolet radiation and can be detected by monitoring the uv- and visible absorption spectra after various irradiation times.

Fig.3a represents the spectra of the monomer and dimer derivatives of the cinnamic acid. During the reaction the 260 nm-peak decreases. The dimer, a derivative of the β-truximic acid, has a shoulder at 280 nm and a maximum at 223 nm.

Since the conjugated polymer chains reveal a strong absorption in the visible spectrum, the diacetylene polymerization can be monitored more directly. Fig. 3b represents spectra which are typical for the compounds 1-3. During the polymerization reaction the polymer absorption shifts towards shorter wavelengths by about 100 nm.

MORPHOLOGY OF THE MULTILAYERS

Investigations on the morphology were carried out using SAXS and electron diffraction.

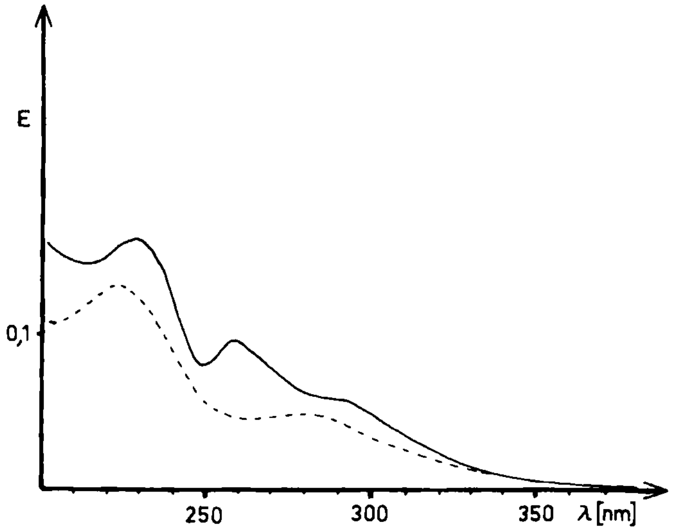


Fig.3a. Transmission spectra of a multilayer of 4 as Cd-salt before (——) and after (----) 30 min of UV-irradiation.

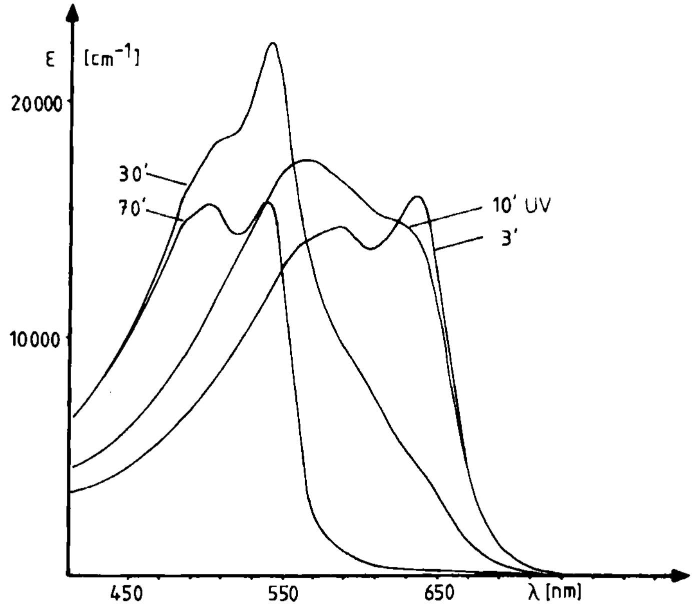


Fig.3b. Transmission spectra of a multilayer of 3 as Cd-salt after different UV-irradiation times.

The x-ray measurements revealed a head-head-tail-tail (Y-) structure of the multilayers (9-11). In both the diacetylene and cinnamic acid derivatives the Cd-Cd-long spacing increases during the reaction, but the layer structure is retained.
To prevent damage to the samples most of the electron diffraction studies were carried out at liquid nitrogen temperature. As a model compound multilayers of 3 have been studied. A typical diffraction pattern is shown in Fig.4. The spots are due to the crystalline packing of the aliphatic groups. Monomer and polymer films consist of perfect-crystalline domains of several microns in diameter. Individual domains in adjacent layers are not in register with each other. The Cd-ions are not located at fixed lattice sites which is probably caused by inclusions of water, due to a partial solvation of the ions. Fig.5 shows a model of the multilayer morphology parallel and perpendicular to the substrate.
Similar to the behaviour of saturated fatty acids and paraffins the monomer and polymer films show various phase transitions. Annealing above 60°C as well as the polymerization process itself cause a transition of the originally orthorhombic subcell (form A), also known from paraffins or polyethylene, into a triclinic cell (form B). This is due to a slip in the side chains connected with rotations of the individual paraffin chains, as shown in Fig.6.

The phase change is accompanied by a shift of the polymer absorption from 640 to 540 nm, as shown in Fig.3b. At the same time the domain size is reduced

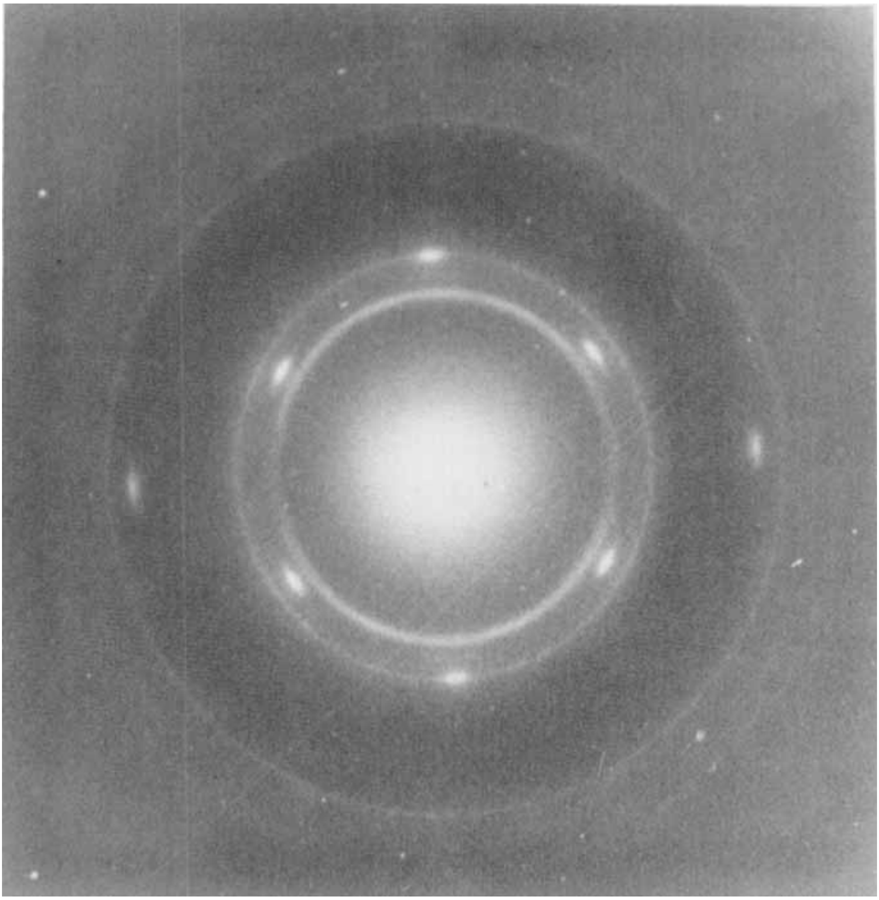


Fig.4. Electron diffraction pattern of a stack of ten monomeric double layers, specimen temperature -150°C.

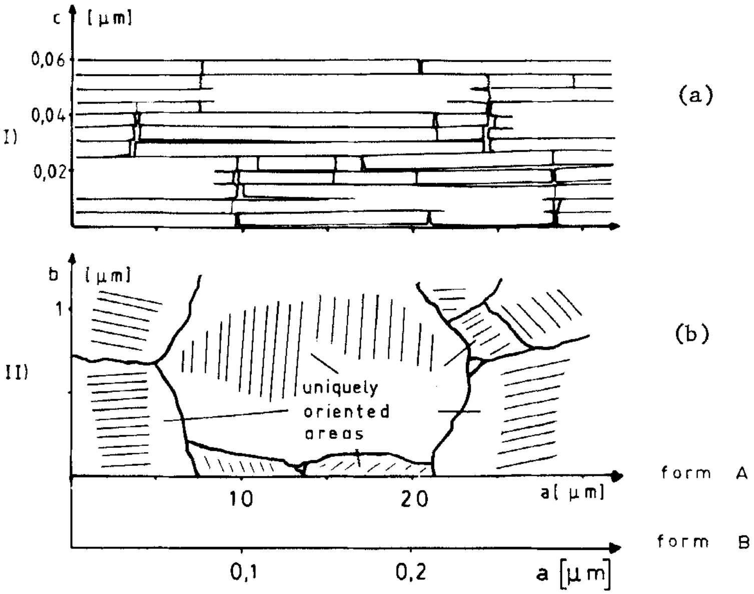


Fig.5. Model of a multilayer: a) parallel and b) perpendicular to the substrate.

and a polycrystalline texture of very small islands, less than 0,1 micron in diameter, is obtained (9,10).

Upon storage as monomers the multilayers tend to reorganize into microcrystals. UV-irradiation of these samples leads to a green-blue polymer with an absorption maximum at 700 nm which also shifts towards shorter wavelengths during the reaction process. The subcell of the final polymer (form C) is triclinic (Fig.6). Fig.7 shows absorption spectra of multilayers of <u>1</u>-<u>3</u> which have been uv-irradiated for 5 min. after a storage at 20^{o}C for three days. The

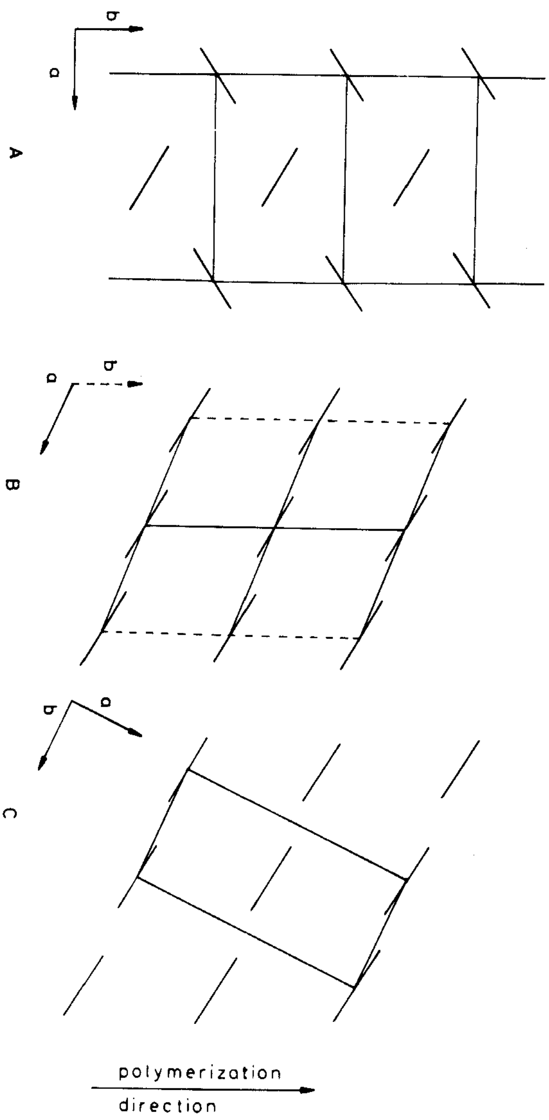


Fig.6. Projection along the paraffin chain axes. The bars represent the zig-zag planes (the setting angle is arbitrary).

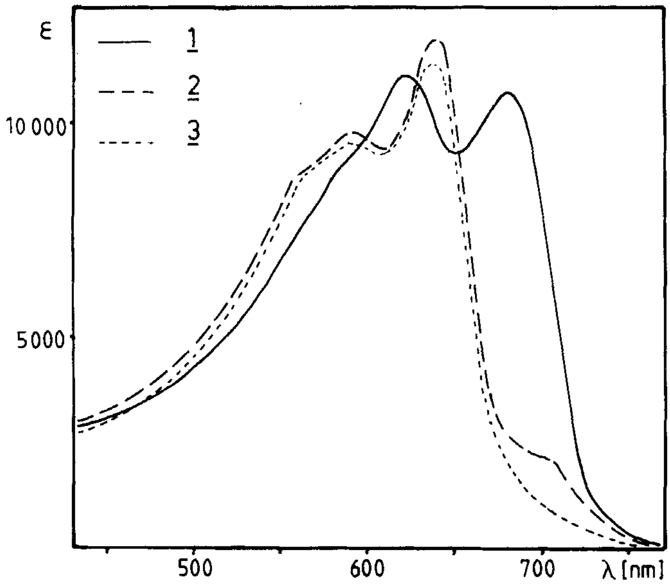


Fig.7. "Aging" of the multilayers. Transmission spectra of 1-3 as Cd-salts (40 layers). The samples were stored at 20°C for three days, followed by 5 min. of UV-irradiation.

intensities of the 700 nm-peak increase from 3 to 1 indicating that a decrease of the length of the aliphatic chain favours the tendency of the compounds to reorganize in form of microcrystals.

CONCLUSIONS

The ultrathin polymer films prepared by topochemical reactions in built-up multilayers exhibit excellent stability and could show potentially useful applications as coatings or membranes of controlled thickness and morphology. It should also be emphasized that multilayers are ideal systems for the investigation of solid-state reactions by spectroscopic methods. According to the special mechanism of multilayer deposition the number of monomer molecules per unit area and the number of layers are exactly known. The samples available by this technique are so thin that several problems arising in large, three dimensional crystals from inhomogeneous product distribution, effects of crystal optics and high extinction coefficients which complicate a quantitative spectroscopic investigation of solid-state reactions can be safely neglected. In the multilayers conversion to polymer, quantum yield and the detection of phase transitions can be evaluated easily from the transmission spectra (9,10,15).

ACKNOWLEDGEMENT

The authors gratefully acknowledge financial support for this work by the Deutsche Forschungsgemeinschaft.

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