Rigid Rod Oligoimides Form Oriented Langmuir–Blodgett Films

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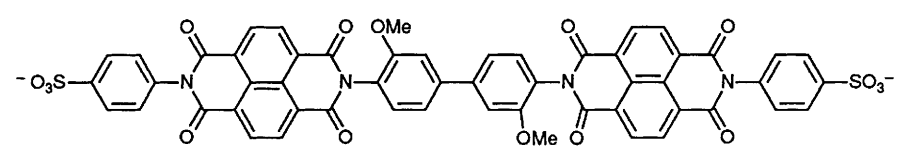
Organized monolayers of oligoimides were transferred from a water surface to solid substrates by horizontal lifting and studied by UV–VIS and polarized IR–ATR (ATR = attenuated total reflection) spectroscopy.

Langmuir–Blodgett (LB) films are traditionally formed from amphiphilic molecules composed of a polar head group and an aliphatic chain. It has been shown, however, that certain long, rigid aromatic compounds with no aliphatic tail (molecular lines) can be compressed on a water surface to form organized monolayers.[1] In this paper we report that linear oligoimides behave similarly and that mono- and multi-layer films can be produced on various substrates using the horizontal-lifting method. The spectroscopic studies demonstrate the anisotropic structure of these films. These oligoimide films are of special interest because of the importance of polyimide films in microelectronics,[2] and because there are so few examples of LB films made from molecules which lack the traditional aliphatic tail.[3]

We have previously reported the synthesis of soluble oligoimides.[4] The compounds B–A–B (**1**), B–A–B–A–B (**2**) and Bu_4N^+ ^-O_3SPh–A–B–A–$PhSO_3^-$ Bu_4N^+ (**3**) (where B is dimethoxybenzidine and A is naphthalene dianhydride), assayed to be pure by HPLC and NMR, were applied to a water surface in a Langmuir trough as chloroform solutions. After solvent evaporation, compression gave the pressure–area curves shown in Figure 1(a). Although the curves are steeply rising they do not represent true equilibria. This is demonstrated by the hysteresis, shown on expansion [Figure 1(b)]. It is of great interest that on recompression [Figure 1(b)], the expansion curve is retraced. Similar effects are seen at other pressures. These observations suggest that a very rigid film structure is permanently set at the smallest area achieved.



$^-O_3SPh—A—B—A—PhSO_3^-$

(3)

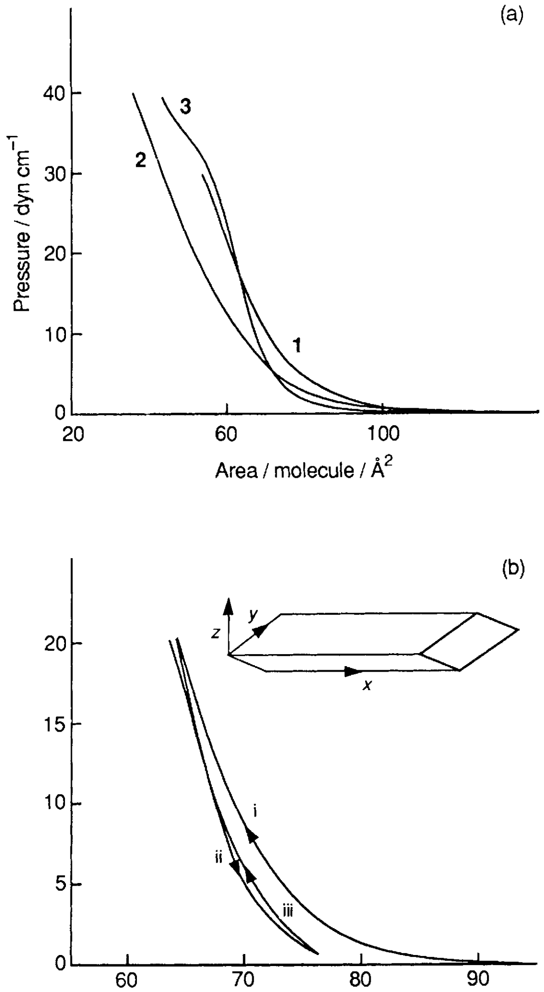


Figure 1. Surface pressure–molecular area curves on water at 20 °C, 5 mm min^{-1}. (a) Compounds (**1**), (**2**), (**3**); (b) compound (**3**) (i) compression, (ii) expansion, (iii) recompression. Inset shows ATR crystal.

On expansion the film might break into islands, but the structure within each island is retained. On recompression the islands are forced back together.

LB transfer experiments focused on (**3**). Vertical dipping was unsuccessful with a variety of substrates, but horizontal lifting[5] gave transfer ratios (change in area of trough : area of substrate), of 0.95 ± 0.05 for glass, quartz, germanium, aluminium, and gold. This was accomplished, at a constant surface pressure of 7 dyn cm^{-1},† quite simply, by mechanically lowering the substrate until the nearly parallel surfaces just made contact, waiting 0.1—1 min and raising the substrate.

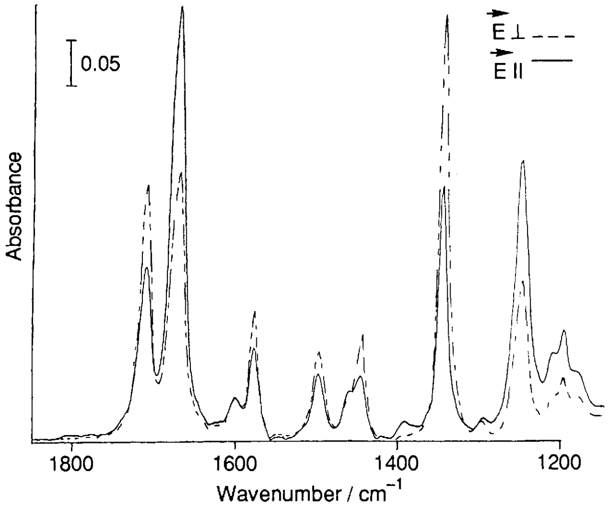


Figure 2. Polarized FTIR–ATR spectra of (**3**). Dashed line $\vec{E}$ in *y*-direction. Solid line $\vec{E}$ in *x–z* direction. Four layers on one side of a 50 × 10 × 2 mm Ge ATR crystal cut at 45°. Transfer performed at 7 dyn cm^{-1}, compressed at 10 mm min^{-1}, equilibrated for 1 h before the first transfer, at 23 °C.

Before lowering the substrate again to form a second layer, the water droplet clinging to the surface was removed. One or more layers made the surface more hydrophilic as expected if polar sulphonates were exposed. The excellent reproducibility for transfer was confirmed using UV–VIS spectroscopy on samples of (**3**), transferred to quartz, which showed that the spectral intensity of bands at 363 and 383 nm increased linearly as the number of layers increased from one to ten.

A germanium ATR crystal, which had been cleaned in an argon plasma and washed with $CHCl_3$, was used to determine if an organized, anisotropic film was transferred.[6] Usually, the long crystal axis was held parallel to the movable barrier. Using FTIR the background was subtracted and the peaks of interest were integrated. Reproducibility of the absorbance was ±5%. There was a linear dependence of absorbance on the number of layers. Compared to an isotropic sample, peaks were shifted by less than 2 cm^{-1}. The spectra were unchanged after the sample was left standing in air for three weeks.

Polarized IR (Figure 2) was used to measure dichroic ratios (*D*) in ATR (2—12 layers on each side) and transmission (20 layers on one side of the germanium crystal). The analysis used peaks due to the imide carbonyls[7]: ν^{sym} = 1715 and ν^{asy} = 1675 cm^{-1}. The symmetric vibration follows the long axis of the molecule; the asymmetric vibration is perpendicular to this long axis. In transmission $D = A_y/A_x = 1.18$ for ν^{sym} and 0.83 for ν^{asy}. This demonstrates a slight anisotropy in the *x–y* plane [the surface plane, Figure 1(b)]. The average molecule is rotated 47° from the *x* axis, not the 45° expected and determined for an isotropic film. This anisotropy is important for interpreting the *D* values from ATR. It presumably arises from the force of the moving barrier, but it is curious because

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† 1 dyn = 10^{-5} N.

the molecules are slightly ordered with their long axes parallel, not perpendicular to the applied force. The $D = A_y/(A_x + A_z)$ values from ATR were interpreted[8] using the x–y anisotropy, the refractive index of germanium (4.03) and an assumed value of the refractive index of the film (1.45). $D_{1715} = 1.23$ showed that the long molecular axis was tilted an average of 11° from the surface. The $D_{1675} = 0.61$ indicated that the carbonyl groups were held on average at 35° to the germanium surface.

Experiments with a germanium crystal coated by syringing on a solution of compound (**3**) and drying at room temperature, gave $D = 1.0$ for all bands in transmission and $D = 0.71$ for all bands in ATR. This demonstrates that the film is isotropic. It suggests, however, that the refractive index of the isotropic film is only 1.23. Using that value to reinterpret the LB film data has no significant effect on the tilt angle, but does change the average calculated angle for the dipole vector of the carbonyl groups to 49°. Thus, there is some uncertainty in our knowledge of the carbonyl group orientation.

These preliminary data provide the first indication that rigid-rod, aromatic molecular lines can form stable, anisotropic LB films on solid substrates. The success of the horizontal-lifting method is gratifying and suggests that interesting new thin films composed of molecular lines, dense in active functional groups, will be available from the LB approach. In this particular case the observed structure, with lines tilted up from the surface at only 11° is rather similar to that determined for polyimide films formed by heating a poly(amide-acid) precursor above 200 °C on glass.[9] Further spectroscopic and electrical measurements on films formed from various oligoimides under various conditions should be interesting in comparison with the properties of such polyimide films.

This work was supported by NSF and ONR. The Langmuir trough was provided by University of Minnesota Center for Interfacial Engineering. Help from J. Valentine, H. Brockman, T. Penner, R. Dluhy, J. Swalen, and J. Rabolt is acknowledged.

Received, 1st May 1990; Com. 0/01944E

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Typeset and printed by Black Bear Press Limited, Cambridge, England