Slow Structural Rearrangement of a Side-Chain Phthalocyanine Methacrylate Polymer at the Air–Water Interface

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ABSTRACT: A polymethacrylate with dodecoxy-substituted phthalocyanine units in the side chains has been used to form Langmuir–Blodgett monolayers at the air–water interface. The monolayers are highly crystalline. They expand slowly even when a constant surface pressure is applied. The structural change coupled with this process has been studied by electron microscopy, electron diffraction, and ellipsometry. It is proposed that the expansion is the result of a change in conformation of the peripheral alkoxy chains on the phthalocyanine rings. The polymer can be deposited on various substrates with Y-type transfer if it is mixed with arachidic acid. The resulting multilayers have been characterized by UV/vis and FT-IR spectroscopies and ellipsometry. No flow-induced orientation was observed during the transfer process.

Introduction

The Langmuir–Blodgett (LB) technique is a very promising method to obtain highly ordered multilayer systems. More and more literature is currently being published about the formation and applications of these LB multilayers from different classes of molecules.[1] Most of the applications are in the field of molecular electronics, molecular optics, and chemical sensors. Initially, only classical amphiphiles were used to construct multilayers, as these molecules had been shown to form stable monolayers at the air–water interface. More recently, other low molecular weight molecules have also been tested as building blocks for LB films, *e.g.*, alkyl- or alkoxy-substituted phthalocyanines.[2] The latter molecules are of interest because of their special optical and electrical properties.[2] For some applications it is very important to have materials with a controlled thickness in which the phthalocyanine molecules are oriented in a well-defined way. This can be achieved by the LB technique.

Polymers are also gaining more and more attention in the literature on LB films.[3] The best level of orientation for phthalocyanines has recently been obtained with a rigid-rod phthalocyaninatopolysiloxane.[4] In a LB multilayer of this polymer the molecules were shown to be oriented with the siloxane axis parallel to the substrate surface. They displayed a preference to be aligned in one direction. The multilayers have been used to construct a very stable chemical sensor.[5] So far, polysiloxanes are the only type of phthalocyanine polymers that have been studied by the LB technique.

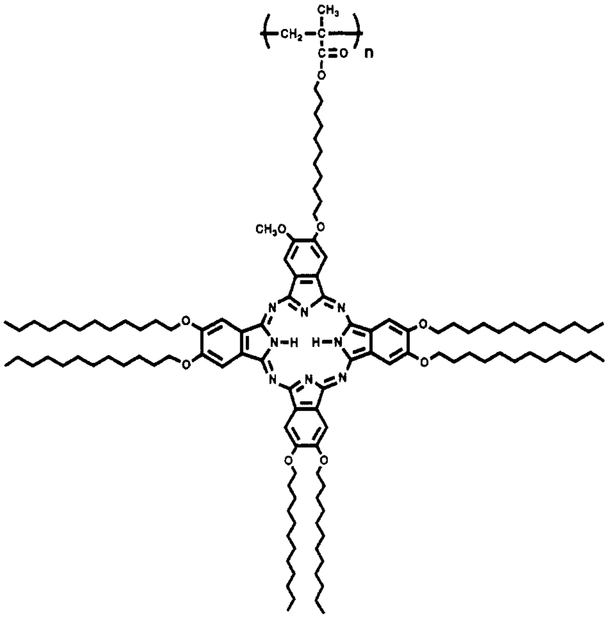

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Figure 1. Chemical structure of the phthalocyanine side-chain polymethacrylate 1 used in this work.

Recently, we synthesized a polymethacrylate with dodecoxy-substituted phthalocyanine side chains (1, Figure 1).[6] This polymer is more flexible than the phthalocyanine polymer mentioned above. It has a molecular weight of 47 000 which corresponds to a degree of polymerization of ≈24. The phthalocyanine units in the polymer are stacked in columns due to strong intramolecular interactions. Because of our current interest in sensor applications of substituted phthalocyanines,[7] we studied the monolayer properties of this methacrylate polymer at the air–water interface and the subsequent deposition of the monolayer film onto various solid substrates. The results are presented here.

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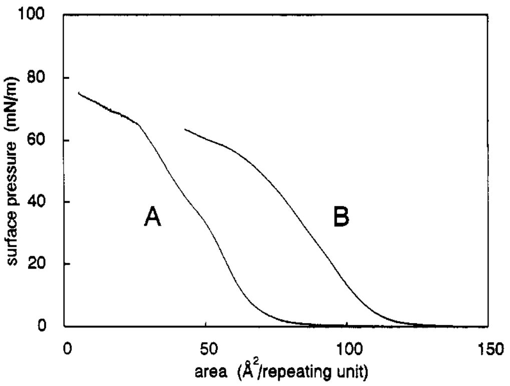


Figure 2. Isotherms of pure polymer 1 at $T = 20$ °C: (A) directly after spreading the solution; (B) after 1 night of expansion at zero pressure.

Experimental Section

The synthesis of poly[2-[[11-(methacryloyloxy)undecyl]oxy]-3-methoxy-9,10,16,17,23,24-hexakis(dodecyloxy)phthalocyanine] (1) has been reported elsewhere.[6]

The monolayer properties were studied by measuring pressure–area isotherms on a computer-controlled Lauda Film Balance (FW 2) with water, purified by a Milli-Q filtration system, as the subphase. The polymer was dissolved in chloroform (spectroscopic quality, about 1 mg mL^{-1}), and isotherms were recorded at a speed of 10 $Å^2$ (repeating unit)$^{-1}$ min^{-1}. The stability curves were obtained by measuring the surface area as a function of time at 20 °C using a constant pressure.

Transmission electron microscopy (TEM) and electron diffraction (ED) were performed on monolayers, picked up from the water surface by horizontally touching the monolayer with a Formvar/carbon coated grid at a surface pressure of 20 mN m^{-1} and a temperature of 20 °C. The samples were blotted dry by touching the edge of the grid with filter paper and subsequently dried in air. For the TEM experiments part of the specimens were shadowed with platinum at an angle of 20°. Electron micrographs of the shadowed specimens were recorded on a JEOL 1200EX electron microscope at 80 kV and a magnification of 5000× or 10 000×. Electron diffractograms of unshadowed specimens were recorded on a Philips CM20-FEG microscope at 200 kV and a camera length of 500 mm, using a Gatan 626 cryo-specimen holder at −170 °C.

Glass, silicon, and gold substrates were prepared as described in the literature.[8] Zinc sulfide plates, also used as substrates, were cleaned by washing thoroughly with chloroform. Deposition was performed by spreading a mixture of polymer 1 and arachidic acid in chloroform on the LB trough and subsequently dipping the substrate through the monolayer at a constant surface pressure with a speed of 4–10 mm min^{-1}.

FT-IR measurements were carried out as described in the literature.[8] UV/vis spectra were recorded on a Unicam SP-8 spectrophotometer.

Ellipsometry experiments were carried out with a Gaertner L117-C single-wavelength ellipsometer ($\lambda = 632.8$ nm) as well as with a home-built spectrometer. The latter was an automated four-zone ellipsometer[9] with a spectral range between 214 and 2300 nm and a resolution of 0.01 nm (typically chosen at 1 nm). The measured parameters Δ and Ψ had a relative accuracy of 2×10^{-4} deg and an absolute reproducibility of 10^{-3} deg. For the measurements at the air–water interface a monolayer was spread on demineralized water in a Teflon Petri dish with a diameter of 8 cm. The amount of polymer solution that had to be spread to obtain a monolayer was calculated from the pressure–area isotherms.

Results

Monolayer Properties and Deposition. The pressure–area isotherm of polymer 1, measured directly after spreading the solution, is shown in Figure 2, curve A. By extrapolation to zero pressure an occupied area per repeating unit of 67 $Å^2$ is obtained. This value is very close to the areas per repeating unit reported in the literature for tetrakis(decyloxy)-substituted phthalocyaninatopolysiloxanes.[10] In monolayers of these polymers the planes of the closely packed phthalocyanine rings are perpendicular to the water surface. Because one alkoxy chain in our polymer 1 occupies an area of at least ≈20 $Å^2$, the seven alkoxy groups in one unit of the polymer cannot all contribute to the occupied area. Therefore, some of them must lie between the phthalocyanine unit and the subphase. This will cause unfavorable contact of the hydrophobic chains with the water phase. This can be compensated for if a strong intramolecular interaction exists between the phthalocyanine units. It is most probable that the side of the phthalocyanine ring bearing the methoxy and methacrylate functions will face the subphase, because of the hydrophilic nature of these functions.

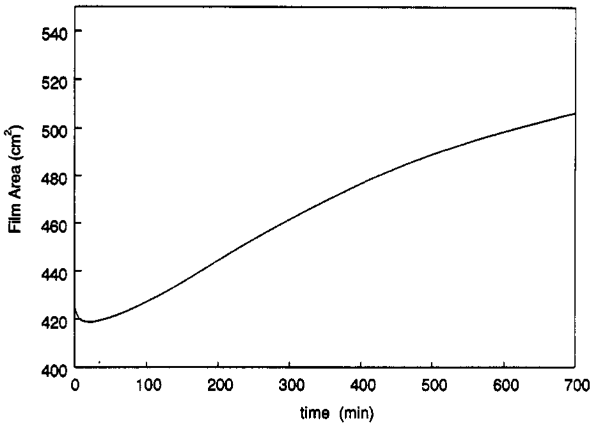


Figure 3. Film area as a function of time recorded during stabilization experiments with a film of polymer 1. The surface pressure was kept constant at 15 mN m^{-1}.

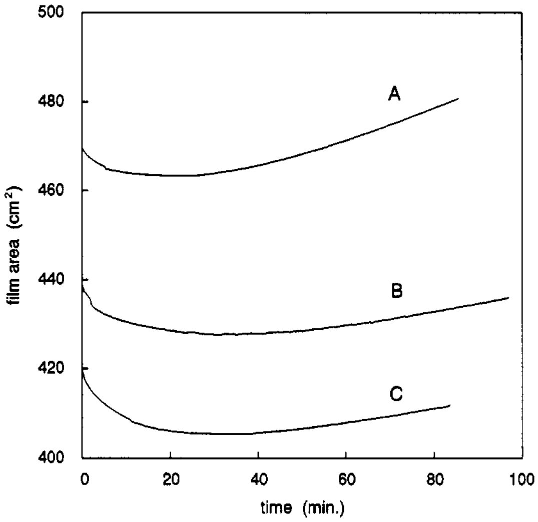


Figure 4. Film area as a function of time recorded during stabilization experiments with polymer 1 at different surface pressures: (A) 7.5 mN m^{-1}; (B) 15 mN m^{-1}; (C) 20 mN m^{-1}.

Stabilization experiments revealed that a very unusual effect took place. As is shown in Figure 3 the total area of the monolayer gradually increased with time after an initial small decrease. This increase took place against the applied pressure of 15 mN m^{-1}. Even after 16 h this process was continuing. The rate of area increase depended on the applied pressure, as can be seen in Figure 4.

To obtain some information about what was happening during the expansion of the monolayer, we spread a solution of the polymer on the subphase and allowed the

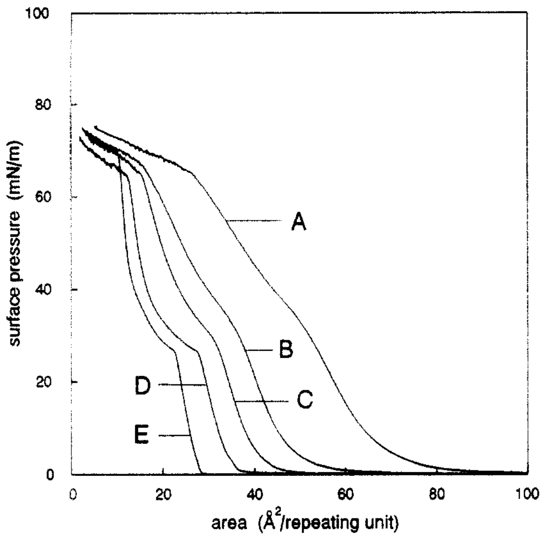


Figure 5. Isotherms at 20 °C of various polymer 1–arachidic acid mixtures: (A) pure polymer; (B) 2:1; (C) 1:1; (D) 1:2; (E) 1:4 mixtures.

layer to expand at zero pressure overnight. Subsequently, the isotherm shown in Figure 2, curve B, was recorded. As one can see, the calculated area per repeating unit is appreciably higher than in case of curve A, *i.e.*, 120 Å^2. When the film was fully compressed directly after spreading, a rigid and bright green collapsed monolayer was obtained. However, when this compression was carried out after 1 night of expansion, the green was less bright and the rigidity of the collapsed film had diminished.

At this point these results can be explained in three ways: (i) It is possible that the phthalocyanine units in the polymer slowly change from an "edge-on" to a "side-on" orientation with regard to the water subphase. (ii) The phthalocyanine units may retain their edge-on arrangement, but the hydrophobic alkoxy chains rise up from the water surface and become aligned beside the phthalocyanine units. (iii) Another unknown deaggregation process is taking place.

Information about the arrangement of the phthalocyanine units in polymer 1 can be obtained by studying transferred LB multilayers of 1 by spectroscopic methods. However, attempts to transfer the monolayer before expansion onto substrates resulted in only a partial and irregular deposition. This suggests that the polymer molecules are strongly aggregated, resulting in a rigid film. Also after overnight expansion the monolayer could not be transferred uniformly. Therefore, it was necessary to mix the polymer with a transfer promotor, *viz.*, arachidic acid. It is known that this compound reduces the rigidity of LB films.[2] One has to take into account, however, that the promotor may also influence the film morphology.

Various mixtures of polymer 1 and arachidic acid ranging from 2:1 to 1:4 (=repeating units:arachidic acid) were prepared and isotherms were recorded at 20 °C (Figure 5 and Table I). As can be seen in Table I, the presence of arachidic acid hardly changes the calculated area per polymer repeating unit. This indicates that the arachidic acid probably has no influence on the arrangement of the phthalocyanine units and that the arachidic acid and the polymer phases are segregated. Moreover, the mixed monolayers showed the same properties as discussed above; *i.e.*, the monolayer area increased gradually with time, and after overnight expansion the isotherms showed higher areas per repeating unit than before expansion.

Table I. Calculated Areas from Pressure–Area Isotherms of Polymer–Arachidic Acid Mixtures

ratio[a]	measd area[b]/Å^2	area per repeating unit[c]/Å^2
pure polymer	67	67
2:1	48	62
1:1	40	60
1:2	34	62
1:4	28	60

[a] Polymer 1 repeating unit:arachidic acid. [b] Obtained by extrapolation of the isotherms to zero pressure. [c] Calculated assuming an area of 20 Å^2 for one arachidic acid molecule.

Transfer of the mixed monolayers onto glass, gold, silicon, and zinc sulfide substrates was found to be possible with the 1:2 polymer–arachidic acid mixture at a pressure of 20 mN m^{-1} and was carried out directly after spreading as well as after overnight expansion. Unlike the pure polymer films this mixture gave good transfer results. The first downward movement of the substrate gave almost no transfer, but after that a Y-type transfer with a transfer ratio close to unity was possible. At least 59 layers could be deposited in this way.

FT-IR Spectroscopy. A total of 39 layers of the polymer–arachidic acid (1:2) mixture was built on zinc sulfide and gold substrates. For transmission (TM) and grazing incidence reflection (GIR) FT-IR measurements spectra were recorded with polarized incident light. This allowed us to obtain the absorbances in the film in three perpendicular directions. The spectra of multilayers, prepared directly after spreading, were compared with those of samples that had been prepared after 1 night of expansion. This was done to see if the orientation of the phthalocyanine units had changed during monolayer expansion (see Figure 6).

In order to be able to compare the TM spectra with the GIR spectra, we calculated a reflection spectrum from the TM spectrum in Figure 6D according to the procedure of Brinkhuis *et al.*[11] This was possible because the thickness of the film was exactly known from ellipsometry measurements (*vide infra*). The calculated spectrum was almost identical with the measured one, so no dispersion effects were present in the GIR spectra.

The largest difference between the TM and the GIR spectra is the higher absorbance in the C–H stretching region between 2800 and 3000 cm^{-1} in the former spectrum. This is due to the orientation of the phthalocyanine side chains and the arachidic acid molecules perpendicular to the film plane. These two cannot be distinguished from each other.

The phthalocyanine vibrational modes can be divided into two different classes: in-plane (i.p.) and out-of-plane (o.o.p.) vibrations. Table II shows the possible orientations that can be derived from the appearance of one or two of these classes of vibrational modes in single spectra, if the electric field vector **E** is polarized in one of the three different directions.

The only o.o.p. vibrations that occur in the measured range are the C–H and N–H vibrations at 870 and 1020 cm^{-1}, respectively. In the GIR spectra of the nonexpanded (Figure 6A) and expanded (Figure 6C) films, these o.o.p. vibrations are practically absent. However, in the TM spectra of parts B and D of Figure 6 these bands are clearly present. According to Table II, this suggests that the phthalocyanine rings in majority have an edge-on arrangement, which does not change during monolayer expansion.

We recorded TM spectra with polarizations in two different directions: perpendicular and parallel to the dipping direction **t**. Only one of these is depicted in Figure 6, because we observed almost no difference between the two spectra. From this we may conclude that the columnar

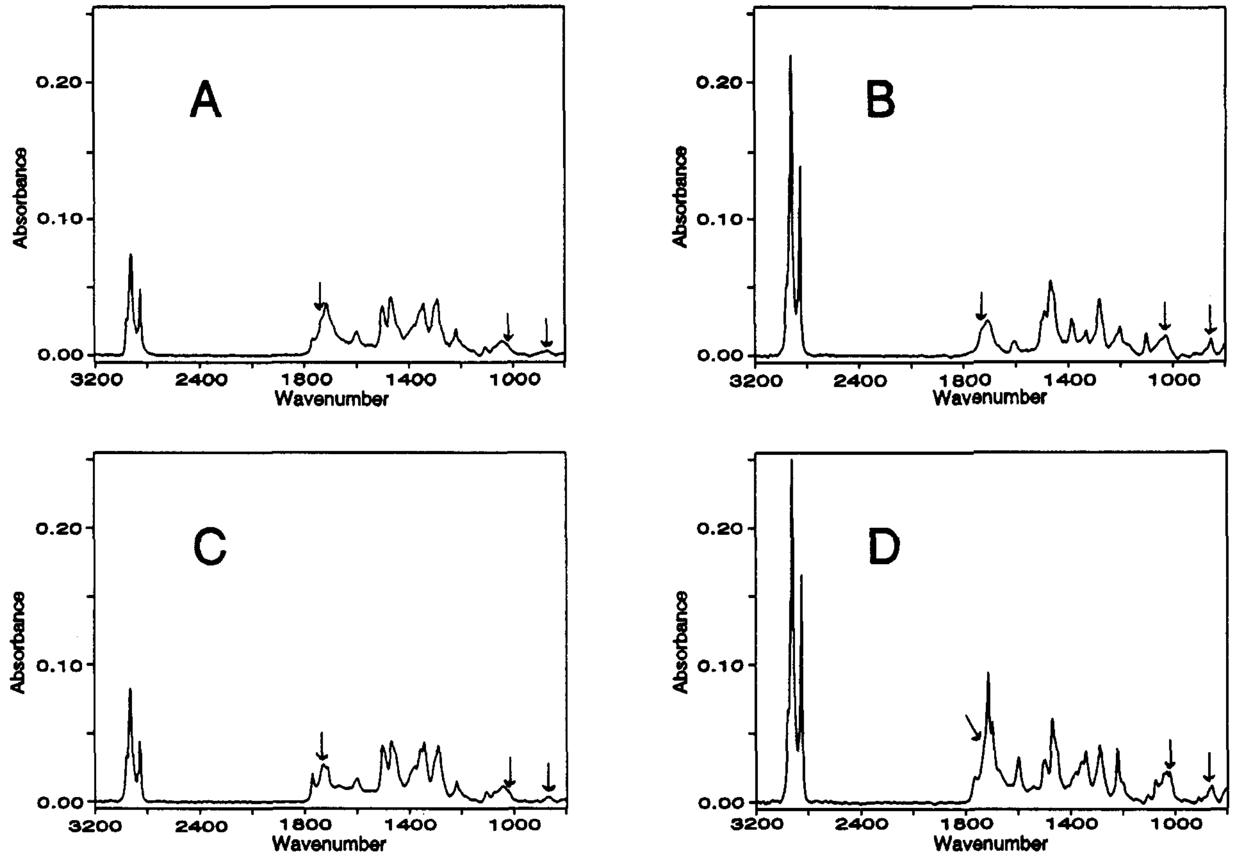
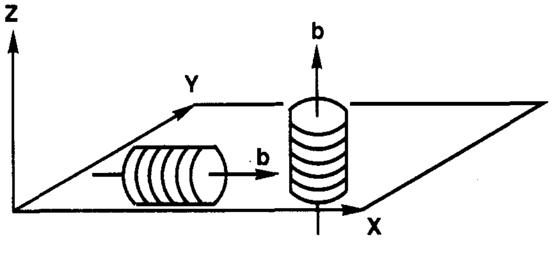


Figure 6. IR spectra of polymer 1–arachidic acid (1:2) mixed films consisting of 39 layers: (A) GIR spectrum of a nonexpanded film on a gold substrate; (B) TM spectrum with polarization parallel to the dipping direction of a nonexpanded film on a zinc sulfide substrate; (C) GIR spectrum of a film expanded overnight; (D) TM spectrum with polarization parallel to the dipping direction of a film expanded overnight. Peaks at 1735, 1020, and 870 cm^{-1} are indicated by an arrow.

Table II. Orientations of the Phthalocyanine Ring That Can Be Derived from the Occurrence or Absence of In-Plane (i.p.) or Out-of-Plane (o.o.p.) Vibrational Modes in the Polarized FT-IR Spectra[a]

direction of electric field vector **E**	i.p.	o.o.p.	i.p. + o.o.p.
z (GIR)	edge-on	side-on	tilted
y (TM)	edge-on (**b**//x) or side-on	edge-on (**b**//y)	edge-on or tilted
x (TM)	edge-on (**b**//y) or side-on	edge-on (**b**//x)	edge-on or tilted

[a] Direction of the columnar axis **b** with respect to the substrate plane (x, y) with the edge-on and side-on arrangements being as follows:



axis of 1 is not oriented relative to the dipping direction. This result is in contrast with the results obtained for LB films of phthalocyaninatopolysiloxanes and some other rigid-rod polymers, where a flow-induced orientation during the transfer process was observed.[4,8]

There are some small differences between the IR spectra of the transferred films obtained before (Figure 6, spectra A and B) and after (Figure 6, spectra C and D) monolayer expansion. Especially in the carbonyl region differences are observed due to either the polymeric ester carbonyl vibration at 1735 cm^{-1} or the arachidic acid vibrations at 1715 and 1750 cm^{-1}. Also in the region between 1100 and 1600 cm^{-1} some differences can be seen. It is very difficult and rather premature to draw conclusions from these findings.

UV/Vis Spectroscopy. The results presented above indicate that the orientation of the phthalocyanine units has not changed after monolayer expansion. The question now arises as to what effect causes the color change of the monolayer during expansion. To study this, we transferred nine layers of the nonexpanded mixed monolayer and nine layers of the expanded mixed monolayer to separate hydrophobic glass substrates and recorded the visible absorption spectra of the multilayers. As expected, a dramatic difference between the two spectra was visible (results not shown). The spectrum of the nonexpanded film was very similar to the solution spectrum of the polymer.[6] A broad Q-band was visible in the 610-650-nm region, suggesting strong interactions between the phthalocyanine rings,[6] and weak shoulders were visible at 664 and 700 nm. In contrast, the spectrum of the expanded film showed a large decrease in intensity over the whole spectral range. The maximum of the Q-band had shifted to the red. This result indicates that the number of absorption sites within the same area had decreased and that the interaction between the phthalocyanine units had become weaker after expansion.

Electron Microscopy. The IR and visible spectroscopic investigations were carried out on transferred mixed multilayers of polymer 1 and arachidic acid. To get information about the structure of the monolayer on the water surface in the absence of arachidic acid, we recorded electron micrographs and diffractograms of nonexpanded and expanded pure polymer monolayers that were picked

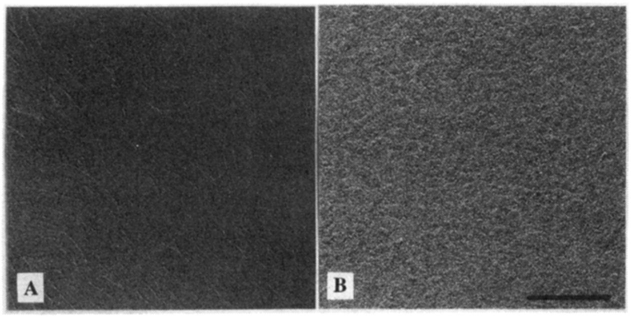


Figure 7. Electron micrographs of pure polymer monolayers, picked up on a Formvar/carbon coated grid at a surface pressure of 20 mN m^{-1}: (A) picked up directly after spreading; (B) picked up after overnight expansion at zero pressure. Scale bar = 1 μm.

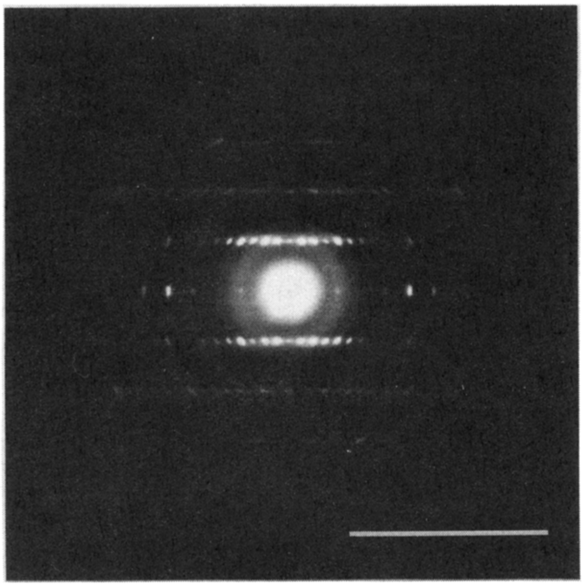


Figure 8. Electron diffractogram of a nonexpanded pure polymer monolayer. Scale bar = 1 Å^{-1}.

up from the water surface by a Formvar/carbon coated grid (see the Experimental Section). During the preparation of these specimens we observed that the surface of the monolayer facing the water phase was relatively hydrophobic before monolayer expansion and hydrophilic after expansion. This was evidenced by a larger contact angle of the water droplet on the grid during blotting before expansion than after expansion.[12]

Electron micrographs of the nonexpanded monolayer showed distinct smooth domains of different sizes and homogeneous thickness (Figure 7A). These domains were mostly separated by narrow boundaries. The expanded monolayer displayed much smaller domains that had a rough, grainy, and more irregular surface (Figure 7B). In addition to these small irregular domains, smooth domains were visible similar to those in the nonexpanded films, suggesting that the expansion had not been fully completed.

As the nonexpanded domains are homogeneous in thickness, we may conclude that the polymer on the water surface is not present in the form of multilayers. As a consequence, the expansion cannot be the result of a spreading out of stacked multilayer aggregates.

Electron Diffraction. To further characterize the different types of domains, we recorded electron diffractograms of both the nonexpanded and the expanded polymer monolayer, in the absence of arachidic acid. The specimens were cooled to −170 °C to decrease the radiation sensitivity. Figure 8 shows an electron diffractogram from a nonexpanded film. From the displayed pattern a rectangular unit cell of 3.9 × 16.6 Å can be derived. Assuming one polymer repeating unit per unit cell, the occupied area per polymer repeating unit is 64.7 Å^2, which is very close to the value calculated from the pressure–area isotherms. The 3.9-Å periodicity probably corresponds to the stacking distance of the phthalocyanine units and the distance of 16.6 Å to the lateral packing of the phthalocyanine stacks.

Table III. Monolayer Thickness (d_0) and Refractive Index (n) of Polymer–Arachidic Acid (1:2) Multilayers As Determined by Ellipsometry Measurements[a]

	sample 1	sample 2	sample 3
substrate	Au	Si	Au
N	0/19/59	0/21/39/59	39
λ (nm)	632.8	632.8	500
d_0 (Å)	29.0 ± 1.0	28.8 ± 0.5	28.5
n_1	1.46 ± 0.04	1.46 ± 0.02	1.450
n_2	0.08 ± 0.01	0.08 ± 0.01	0.018

[a] N is the number of monolayers deposited on the substrate.

The expanded film showed much less crystalline order. Only at a few positions of the sample was a diffraction pattern observed, which may be ascribed to nonexpanded areas as the diffraction pattern was indistinguishable from the pattern of the nonexpanded film. From these results it can be concluded that crystalline order is present before expansion and is lost when the monolayer of polymer molecules expands at constant pressure.

Ellipsometry. The observed monolayer expansion may be due to a change in the orientation of the alkoxy chains on the phthalocyanine rings. That increases the monolayer area and decreases the monolayer thickness. To investigate this, we studied the monolayer thickness by ellipsometry.[13]

In principle, the film thickness d and the refractive index n of the film can be determined by ellipsometry.[9] Each measurement at a given λ results in two ellipsometric parameters Δ (the phase difference between the light components perpendicular and parallel to the plane of incidence) and Ψ ($\tan \Psi$ is the ratio of the amplitudes of the perpendicular and parallel components), whereas there are three unknown quantities: n_1 (the real part of n), n_2 (the imaginary part of n), and the film thickness d. Furthermore, the dielectric constant ϵ_s of the substrate (+interfacing layers) is unknown, resulting in two additional quantities that must be determined. Four LB multilayer samples each containing a well-defined layer of different total thickness Nd_0 (d_0 is the monolayer thickness) provide eight experimental values for Δ and Ψ, enough to solve for n_1, n_2, and d_0. Samples of these compositions were prepared on silicon substrates as well as on gold substrates. Deposition was carried out after overnight expansion of the polymer–arachidic acid monolayer (1:2 mixture). We did not study nonexpanded samples because the monolayer expansion during transfer would result in films that are not fully uniform. The results are shown in Table III. Silicon substrates gave the most accurate results for n and d_0 at λ = 632.8 nm. For this substrate we obtained a monolayer thickness of d_0 = 28.8 ± 0.5 Å. However, we should mention that the in-plain refractive index probably differs from the refractive index perpendicular to the substrate surface, but we did not take this into account in our calculations. We performed measurements with the laser beam oriented parallel and perpendicular to the dipping direction of the substrate. No difference was observed between these two measurements, which is in agreement with the FT-IR results. Apparently, the crystalline monolayer domains with dimensions on the order of 1 μm (see Figure 7A) are randomly oriented. The beam spot of the ellipsometer has a diameter of at least 1 mm and therefore includes a large number of domains. As a result the sample is optically isotropic as seen by the ellipsometer.

Measurements were also carried out directly at the air–water interface. Two types of experiments were performed. First, an amount of a solution of the polymer in chloroform was spread on a water surface. This amount was calculated to be such that the whole surface could be covered with a "nonexpanded" monolayer. In a second experiment, the same water surface was only partly covered. This allowed the layer to become fully expanded after standing.

Ellipsometry measurements were carried out at a number of time intervals after the dissolved material had been spread on the water surface. From the Δ and Ψ data the product of n and d_0 was calculated using the standard three-phase model assuming temperature-corrected indexes of refraction for demineralized water of $n_1 = 1.332$ and $n_2 = 0.000$.

In experiments of the second type we observed directly after spreading domains that floated in and out of the narrow detection window of the ellipsometer on the water surface. These domains had the same value of nd_0 as the LB films in the first type of experiment. After a few hours we observed in the former case additional domains with a lower nd_0, and after 1 night we could only detect domains with this lower nd_0. Taking for this "expanded" film the same values for n_1 and n_2 as determined for our deposited LB films, *i.e.*, $n_1 = 1.46$ and $n_2 = 0.08$ at $\lambda = 632.8$ nm, we can calculate a film thickness of 29 ± 3 Å. This number is in good agreement with the number determined for the multilayer deposited on silicon, *viz.*, $d_0 = 28.8 \pm 0.5$ Å. Apparently, the presence of arachidic acid in the multilayer sample does not have a great influence on the results.

The higher nd_0 value measured for the nonexpanded film in the first type of experiment can be a result of a different n-value or a higher film thickness d_0. If we assume that the latter is the case and if we take for n_1 and n_2 the same values as from the expanded film, we may calculate a film thickness of 49 ± 5 Å. This number is an approximate value, as we observed a large change in the absorption spectrum of the LB film during expansion, as was outlined before (*vide supra*). The value of n_2 is therefore expected to be larger for the nonexpanded film than for the expanded film. However, our calculations revealed that a change in n_2 has only a minor influence on the ellipsometry parameters. So the 49-Å film thickness will be a good estimate.

Spectroscopic Ellipsometry. Once the film thickness d is well-known for a given LB multilayer sample, the dispersion $n(\lambda)$ can be calculated wavelength by wavelength using a standard three-phase model from Δ and Ψ values, provided that the refractive index of the substrate (n_s) is known. For gold the $n_s(\lambda)$ values are known from the literature.[14] The dispersion $n(\lambda) = [\epsilon(\lambda)]^{1/2} = n_1(\lambda) + in_2(\lambda)$ can subsequently be fitted to a series of optical transitions each characterized by an energy E_r, an oscillator strength ϵ_r, and a line width Δ_r.

The $n(\lambda)$ dispersion curves in the region between 214 and 800 nm of our multilayer sample 3 (Table III) on gold could easily be fitted by eight Lorentzian resonances (Figure 9, solid lines, and Table IV). Each of these resonances can be assigned to the well-known C, L, N, B, Q_y, and Q_x bands of phthalocyanines.[2] Following ref 2, we assigned the bands around 430 and 900 nm to vibronic bands. They can be described by Gaussian-type resonances (Lorentzian resonance multiplied by a Gaussian function). Note that the spectrum of Figure 9D is very similar to the visible absorption spectrum of the expanded film described in the UV/Vis Spectroscopy section, with the maximum at $\lambda = 700$ nm, corresponding to the Q_x band.

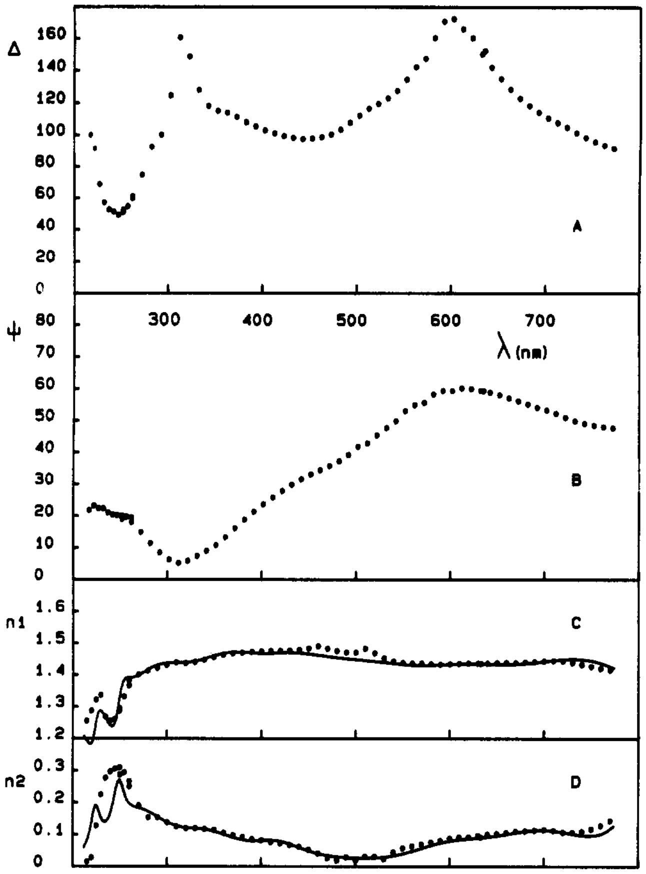


Figure 9. Ellipsometry parameters Δ and Ψ as a function of λ measured on sample 3 of Table III (curves A and B) (both in degrees, at an angle of incidence of 70°). The refractive indexes $n_1(\lambda)$ and $n_2(\lambda)$ (curves C and D) are calculated from $\Delta(\lambda)$ and $\Psi(\lambda)$ using a standard three-phase model (dotted lines) and fitted to a 10-harmonic-oscillator model (solid lines) using the parameters from Table IV and a monolayer thickness of $d_0 = 28.8$ Å.

Table IV. Values for E_r, ϵ_r, and Δ_r Used in the Harmonic-Oscillator Description of the Dispersion $n(\lambda)$ Curve from Figure 9

band	E_r/eV	$2\epsilon_r$	Δ_r/eV	assignt	line shape[a]
1	5.50	0.05	0.15	C	L
2	4.95	0.06	0.15	L	L
3	4.58	0.15	0.60	N_1	L
4	4.42	0.10	0.60	N_2	L
5	3.56	0.10	0.50	B	L
6	2.95	0.018	0.30	vibronic	G
7	2.05	0.026	0.27	Q_y	L
8	1.75	0.046	0.27	Q_x	L
9	1.51	0.040	0.10	vibronic	G
10	∞	3.60			L

[a] L = Lorentzian, G = Gaussian.

Discussion

The phthalocyanine polymer discussed in this paper has a rather flexible backbone and differs in this respect from the rigid-rod phthalocyaninatopolysiloxanes reported in the literature.[4,10] Its monolayer properties are unusual. The observed monolayer expansion is unprecedented. Our phthalocyanine polymer does not show any flow-induced orientation during monolayer transfer. This could be due to the fact that we are dealing with a polymer with a relatively low degree of polymerization, *viz.*, only 24. The

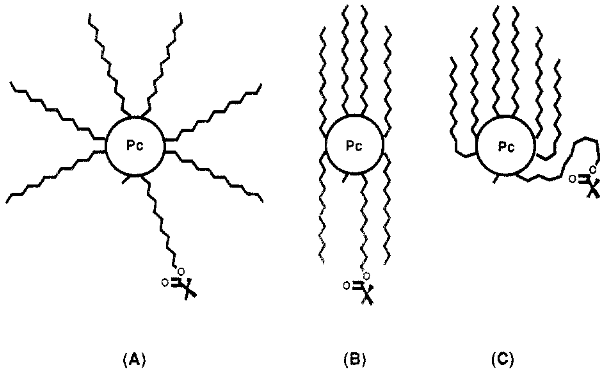


Figure 10. Schematic representations of the proposed molecular conformations of one polymer repeating unit: (A) in the solid state; (B) in a monolayer at the air–water interface directly after spreading and subsequent compression; (C) in a monolayer at the air–water interface after full expansion.

phthalocyaninatopolysiloxanes in the literature are more stiff and larger than our polymer, resulting in a better possibility for alignment in the transfer direction.

The UV/vis and FT-IR measurements reveal that before expansion the phthalocyanine units are closely packed with their planes perpendicular to the water surface. From the surprisingly good quality of the electron diffractogram we may conclude that there is a high degree of crystallinity in the nonexpanded film. Electron micrographs show that in this film no multilayer aggregates are present. The dimension of the unit cell calculated from the electron diffractogram is in very good agreement with the area per repeating unit derived from the pressure–area isotherms: 16.6 Å is the diameter of the phthalocyanine core,[10b] 3.9 Å is the interplanar distance. From these results a molecular conformation for the nonexpanded monolayer can be derived as schematically depicted in Figure 10B. The interplanar distance is somewhat larger than the value of 3.32 Å derived from solid-state X-ray diffraction measurements.[6] This can be explained by the fact that in the solid state the alkoxy chains in the polymer are stretched out in all directions (Figure 10A). In this state the phthalocyanine planes are stacked with a staggering angle of 45° to minimize the interplanar distance.[15] In the nonexpanded monolayer the alkoxy chains are forced to be closely aligned in vertical position (Figure 10B). This will cause steric repulsion between neighboring units, which explains the larger interplanar distance. The estimated 49-Å thickness of the monolayer from ellipsometry measurements on the nonexpanded film and the 67-Å^2 mean molecular area from the pressure–area isotherm are in line with the conformation proposed in Figure 10B.

FT-IR measurements indicated that the orientation of the phthalocyanine units does not change during monolayer expansion. The observed expansion therefore must be explained by a change in the orientation of the peripheral alkoxy chains, resulting in a loss of crystallinity and a decrease in interaction between the phthalocyanine units. The latter is possible because the spacer connection with the polymeric backbone is flexible. Ellipsometry measurements revealed that nd_0 decreased during expansion. From the calculated film thickness ($d_0 = 28.8 \pm 0.5$ Å) we may derive a conformation of the expanded monolayer as depicted in Figure 10C. The areas per repeating unit before and after expansion are 67 and 120 Å^2, respectively. The ratio of these numbers is 4:7, which corresponds to the number of alkoxy chains that probably contribute to the total area per repeating unit.

Our polymer is flexible and has asymmetrically substituted phthalocyanine units. As a consequence, the polymer molecules may initially orient themselves with their backbones toward the water surface. Apparently, this conformation is thermodynamically unfavorable, resulting in a very slow reorientation of the alkoxy chains away from the water surface. As a consequence the more hydrophilic phthalocyanine core becomes partly exposed to the water surface. This process will be slow because the reorientation requires a concerted movement of all the alkoxy chains in the polymer.

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