

Structure and molecular orientation of tetramethoxy-tetraoctoxy phthalocyaninato-polysiloxane Langmuir–Blodgett films*

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We present new results on tetramethoxy-tetraoctoxy phthalocyaninato-polysiloxane macromolecules. We have been led to the conclusion that there is substantial realignment of the macromolecules in individual dipped layers after their transfer from the subphase. The mechanism of this realignment involves the reorientation of the aliphatic sidegroups. The main reasons for this conclusion are two-fold:

- 1 the in-plane inter-backbone spacing increases by a significant proportion from its value on the subphase to the value in deposited films. There is evidence that this spacing increases with substrate hydrophobicity;
- 2 when a single monolayer is transferred to a substrate the characteristic multilayer spacing is seen in X-ray diffraction, indicating that multilayer regions are present. The presence of such regions is interpreted as being a consequence of the restructuring responsible for the increase in in-plane spacing: lateral expansion of the macromolecules in a tightly packed monolayer must force some of them from that layer. The presence of these multilayer regions does not appear to adversely affect the film structure.

(Keywords: structure; molecular orientation; Langmuir–Blodgett films)

INTRODUCTION

A Langmuir–Blodgett (L–B) film consists of a series of monolayers transferred in succession from an air–water interface to a solid substrate. Conventional L–B materials consist of amphiphilic molecules (i.e. possessing both hydrophilic and hydrophobic endgroups), such as fatty acids, and film formation involving such molecules is well documented¹. The material reported here, tetramethoxy-tetraoctoxy phthalocyaninato-polysiloxane, is unusual in L–B terms in that it is uniformly hydrophobic and rotationally symmetric.

The investigation of phthalocyaninato-polysiloxane macromolecules at Queen Mary College was instigated in an attempt to find a material which combines the desirable electronic properties of protoporphyrin IX dimethyl-ester² (PPDME) with the relative ease of L–B film preparation of materials such as 22-tricosenoic and stearic acids. A further objective was to eliminate the post-deposition recrystallization which is consistently observed in the PPDME films. The phthalocyaninato-polysiloxane macromolecules have been favourably reported on by Orthmann and Wegner³ who indicate that these materials combine the electric and photoelectric attributes of previously reported phthalocyanines⁴ with good L–B properties.

A detailed investigation of the film structure was carried out when it appeared that there were anomalies

in the transfer of the monolayers from the subphase to the substrate: the transfer ratio indicated a decrease in the area per monomer unit whereas the inter-backbone spacings measured directly from the films indicated an increase. The investigation so far has yielded many novel data and we have been led to the radical conclusion that there is substantial realignment of the macromolecules in individual dipped layers during their transfer from the subphase. This realignment creates a high degree of long-range order, both within and between the individual layers. The mechanism of this realignment involves the reorientation of the aliphatic sidegroups and is thought to occur in the transferred material in the region immediately behind the meniscus.

MATERIAL PREPARATION

Tetramethoxy-tetraoctoxy phthalocyaninato-polysiloxane exists as macromolecules, with a typical macromolecule consisting of 15 monomer units³. A schematic diagram of a monomer unit is shown in *Figure 1*. The material was synthesized using the same methods as, and in strict accordance with, the procedures of Orthmann and Wegner^{5–7}.

The monomer units consist of a silicon-substituted phthalocyanine ring with four pairs of sidegroups attached in a random cyclic order. Each pair consists of a methoxy and an octoxy group, resulting in four isomers.

The polymerization results in straight siloxane bonds linking the silicon atoms at the ring centres. The resultant macromolecules therefore consist of random assemblies of the four isomers on rigid siloxane backbones. Consequently, the backbone and rings form a rigid, incompressible core surrounded by a deformable outer shell comprising the aliphatic sidegroups. The resultant

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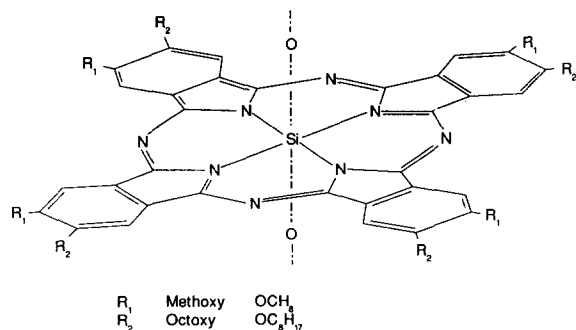


Figure 1 Schematic diagram of a monomer unit. Estimated dimensions – phthalocyanine ring: minimum and maximum diameters, 11 and 16 Å, respectively. Side groups: methoxy, 1 Å diameter, 1 Å length; octoxy, 3 Å diameter, 6 Å length. Molecules/macromolecular: minimum and maximum diameters, 18 (16 + 1 + 1) and 28 (16 + 6 + 6) Å, respectively

cylindrical molecule is rotationally symmetric about the backbone axis.

The diameter of a macromolecule in any given direction is dependent on its immediate environment and is, therefore, difficult to predict. It is however possible to estimate maximum and minimum limiting values of the diameter from the known structure of the monomer units. Consideration of the maximum and minimum ring diameters, which are approximately 16 and 11 Å, respectively, and of the dimensions of the sidegroups indicates that the maximum and minimum molecular diameters are approximately 28 and 18 Å, respectively.

Briefly, the synthesis involves the polymerization of phthalocyaninatosilicon hydroxide monomers. The monomer is synthesized by the hydrolysis of the dichloro compound produced from the cyclization of 5-methoxy-6-octoxy-1,3-isoindolediimine in the presence of SiCl_4 in Chinolin. The polymerization is performed via condensation in toluene containing a 5% FeCl_3 catalyst.

A powder camera was used to analyse the material as used for the spreading solutions, this being the most accurate means of measuring the inter-ring spacing along the siloxane backbones. The camera has a nickel-filtered copper source, with radiation at the $K\alpha$ wavelength of 1.541 Å. The value obtained was 3.31 ± 0.01 Å.

Due to the nature of the synthesis, only restricted quantities of the material were available for this investigation. Therefore, because the purpose of this investigation was the characterization of the films and not of the material in isolation, priority was given to the acquisition of data from the films. The known characteristics of the material^{3,5}, coupled with the reported consistency of the material with synthesis, provided sufficient data for this investigation.

FILM PROPERTIES AND ISOTHERMS

Film spreading

All trough work described herein was conducted using a Lauda Filmbalance. The subphase was water with pH ≈ 5.5 as obtained from a Milli-Q system. Aristar chloroform was used for all spreading solutions.

Measurements were made from π -A (area) isotherms obtained from spreading five solutions at concentrations of 0.685, 0.342, 0.137, 0.068 and 0.034 mM, (monomer units per litre) at a subphase temperature of $18.5 \pm 0.5^\circ\text{C}$. Two films were spread at each concentration.

Two films were spread from a solution of concentration 0.137 mM at a subphase temperature of 2°C to (partially) investigate the effects of temperature on the film properties.

A typical π -A isotherm is shown in Figure 2. With the exception of the collapse phase, the mode of which is discussed below, the isotherm appears similar to those obtained from conventional L-B materials. The values of pressure and area per monomer unit as obtained from the π -A isotherms are presented in Table 1.

The area per monomer unit in a fully compressed mono-layer on the subphase, π_1 , is 63.8 \AA^2 with the value at the dipping pressure, 25 mN m^{-1} , being 71.1 \AA^2 . The corresponding in-plane spacings are therefore 19.3 and 21.5 \AA respectively. The value for the fully compressed state is in good agreement with the estimated value of the minimum molecular diameter (18 Å) and, because of the

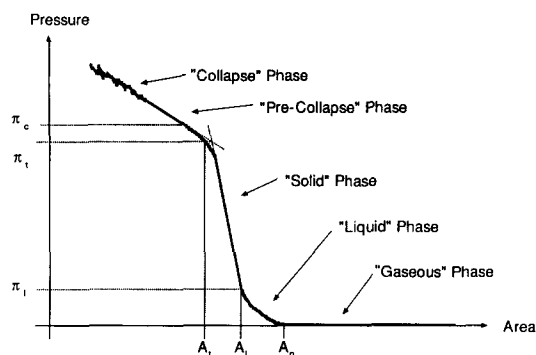


Figure 2 Typical pressure–area isotherm. Symbols: π_1 , pressure at which compression becomes linear, i.e. area reduction is proportional to pressure increase; π_t , transition pressure, from solid phase to pre-collapse phase; π_c , collapse pressure, where vibrations are apparent in film and pen trace shows pressure variations; A_0 , area/monomer unit where pressure rises above zero; A_1 , area/monomer unit where linear compression commences, at π_1 ; A_t , area/monomer unit when film fully compressed, at π_1

Table 1 Isotherm data

Pressure (mN m^{-1})	Area (\AA^2)		Ratio
	2°C	18.5°C	
25	74.6	71.1	1.05
π_t	64.7	63.8	1.02
π_c	51.2	52.2	0.98

Pressure (mN m^{-1})	Pressure (mN m^{-1})		Ratio
	2°C	18.5°C	
π_1^a	17.1	13.0	1.32
π_t	41.0	42.0	0.98
π_c	48.9	49.4	0.99

Variation of π_1 at 18.5°C	
Solution (mM)	Pressure (mN m^{-1})
0.685	14.5
0.342	18.8
0.137	13.0
0.068	10.1
0.034	10.4

The 'random' measurement errors correspond to ± 0.5 mm on millimetric graph paper, i.e. approximately 0.5 mm per 10 cm or 0.5%
^a 136.9 μM solution only for this pressure

mutual attraction of the hydrophobic sidegroups, it is reasonable to assume that this value is the practical effective minimum diameter. The vertical, i.e. normal-to-surface, diameter of the macromolecules on the subphase is unknown.

With the exception of π_1 , all the parameters are independent of both solution concentration and temperature. This parameter shows a significant variation, being 32% greater at 2°C than at 18.5°C and, also, shows an overall tendency to increase with increasing concentration of the spreading solution. The definition of π_1 is the surface pressure at which the rate of area reduction becomes linear with the increase in surface pressure. Consequently, we interpret π_1 as being an indication of the ease with which the macromolecules can realign as the separation of the spread droplets decreases during compression. It is expected that decreasing the temperature reduces both the efficiency of the solvent in spreading the macromolecules and the flexibility of the sidegroups, both of which will decrease the ease with which macromolecules can realign.

It is deduced on the basis of experimental observation and measurements made on the L-B trough that, on spreading, the macromolecules lie with their backbones parallel to the subphase surface in the manner of logs on water. Such a structure would agree with that observed in dipped films.

Film characteristics

Tetramethoxy-tetraoctoxy phthalocyaninato-poly-siloxane macromolecules form highly stable monolayers on the trough which transfer easily to form multilayers on solid hydrophobic substrates. Furthermore, transfer rates in excess of $50 \mu\text{m s}^{-1}$ are possible compared with $\approx 2 \mu\text{m s}^{-1}$ for PPDME.

Solutions with concentrations greater than approximately 1 mM (monomer units per litre) did not spread evenly: individual droplets displayed a definite tendency to agglomerate and form distinct rigid areas of material which impeded the spreading of subsequent droplets of solution. The π -A isotherms obtained showed that when such agglomeration occurred the film parameters showed considerably more variation than when it did not, i.e. than when less concentrated solutions were spread. Also, it was observed that the tendency to agglomerate increases with increasing solution concentration. The data presented were obtained using solutions with concentrations less than 1 mM.

This tendency to agglomerate and form rigid areas indicates that the attractive forces between the macromolecules are greater than those between the macromolecules and the subphase, illustrating the uniformly hydrophobic nature of the macromolecular surface. The nature of these attractive forces is also thought to be a factor in the unusual collapse mode of these films.

Film collapse

The onset of collapse, at $\pi > \pi_c$, in the film is signalled by the occurrence of small, but distinctly visible, random vibrations of the compressed film. These vibrations are evident on the π -A isotherms as a blurring of the pen trace caused by small, rapid random pressure variations. Simultaneously with the onset of the vibrations, narrow denser blue stripes appear in the compressed film. These

are oriented parallel to the barriers and occur in the region closest to the moving barrier.

As the compression progresses, the vibrations become more marked, increase in frequency, and the stripes become more distinct, more numerous and their separation decreases. The stripes remain if the barrier motion is reversed to halt the compression and expand the area. Collapse resumes at the previous values of the pressure and area if compression is resumed.

The collapse mode of the film is unusual in that it is progressive, with the pressure increasing approximately linearly with area reduction during the collapse, and is not catastrophic as is generally the case with more conventional materials. The macroscopic collapse mode appears to be a series of localized collapses and restructurings of the film. These cause the vibrations and result in the appearance of the stripes of denser blue, thicker material.

It is hypothesized that the pressure increases during collapse because the localized collapse-and-restructuring events occur at progressively less weak points in the film: the film being locally more rigid subsequent to each such event. These events are thought to be either foldings or subductions occurring between two rigid regions of the film. Either mechanism will create the observed stripes of thicker, darker blue material and cause the observed pressure increase.

STRUCTURE OF DIPPED FILMS

All L-B film preparation was performed on films spread using the 0.137 mM solution transfer at a speed of $50 \mu\text{m s}^{-1}$ and a surface pressure of 25mN m^{-1} . The transfer ratio, measured as the ratio of the area occupied by the transferred material on the substrate to that it occupied on the subphase, was $95 \pm 2\%$ for all samples.

Inter-layer spacings were measured using X-ray diffractometry (XRD). Films were deposited on cleaved mica, silted cleaved mica and glass (Chance microscope slides) for this purpose.

In-plane inter-backbone spacings were measured using transmission electron diffractometry (TED). Carbon film coated grids were used as substrates for all the TED, with two methods being used to prepare the samples. One method involved dipping a grid directly into the trough to obtain a single L-B monolayer on the surface of the carbon film. The other method involved using polyacrylic acid, a water-soluble polymer, to transfer multilayers from the XRD substrates to the grids.

Small drops of polyacrylic acid were placed on the surface of the films and allowed to dry out. Once dry, they could be removed from the substrate surface using a scalpel with the multilayer films adhering to the bases of the drops. The drops were then inverted and placed in water and allowed to redissolve, leaving the multilayer films floating on the surface for transfer onto the grids.

X-ray diffraction

The X-ray diffractometer has a nickel-filtered copper source, with radiation at the $K\alpha$ wavelength of 1.541 \AA . The values obtained for the inter-layer spacings are presented in Table 2, in order of increasing substrate hydrophobicity. Although this was not quantified, it was apparent from the manner in which water droplets behaved on the relevant surfaces. There is some evidence that the inter-layer spacing is substrate dependent. The

Table 2 XRD and TED data

Inter-layer spacings, Å (± 0.4 Å)		In-plane spacings, Å (± 0.6 Å)	
Substrate	Spacing	Substrate	Spacing
Cleaved mica	19.4 (monolayer)	Cleaved mica:silated	23.8 (all samples)
Cleaved mica:silated	19.7 (monolayer)	Glass	25.1 (all samples)
Cleaved mica:silated	19.8 (multilayers)		
Glass	20.0 (16-layer samples)		
Glass	20.4 (22-layer samples)		

influence of the substrate hydrophobicity on both the inter-layer and in-plane spacings is discussed further in the following.

It is evident from the XRD of monolayers deposited on mica substrates that they contain multilayer regions, with the data indicating that these regions contain approximately six to eight layers and comprise < 5% of the total area.

These multilayer regions have to be individually large enough to possess the regular structure necessary to cause X-ray diffraction. This implies that the mechanism responsible for their creation must be more complex than a simple forcing of individual macromolecules from the monolayer which would result in only bilayer regions being formed by the comparatively simple process of the forced macromolecules aligning above those remaining in the monolayer.

It should be noted that the presence of multilayer regions does not appear to affect the deposition of subsequent layers. Also, it remains unknown whether, over many layers, the accumulation of multilayer regions in the individual layers results in the formation of extra complete layers. Capacitance measurements of films comprising up to 25 layers were inconclusive.

It was observed that the XRD peaks obtained from the multilayers on glass were less well defined than those obtained from multilayers on mica, indicating that the inter-layer spacings in the films on glass are less clearly defined than those in the films on mica. This is thought to be due to differences in the surfaces of the substrates. Cleaved mica has a surface consisting of parallel planes with steps and so the deposited layers are also parallel planes, yielding well defined peaks. Glass however, is polished and so has an undulating surface with irregularities and the deposited layers will not be parallel planes, with the consequent loss of definition.

Multilayer regions, as detected in monolayers deposited on mica, could also be present in those deposited on glass, with the irregular surface of the glass causing them to remain undetected. These regions occupy only a small proportion of the total area and any misalignment amongst them, such as that due to surface irregularities, will significantly reduce the intensity of any diffraction peaks and, hence, the probability of detection.

Transmission electron microscopy

A Jeol 200CX TEM with an accelerating voltage of 200 kV was used for all the TEM. High speed X-ray film was used to record all the data.

The in-plane inter-backbone spacings of dipped films were measured from the diffraction patterns obtained from TED. The general form of these patterns was a central bright spot with two perpendicular pairs of arcs (Figure 3). The outer pair correspond to the inter-ring

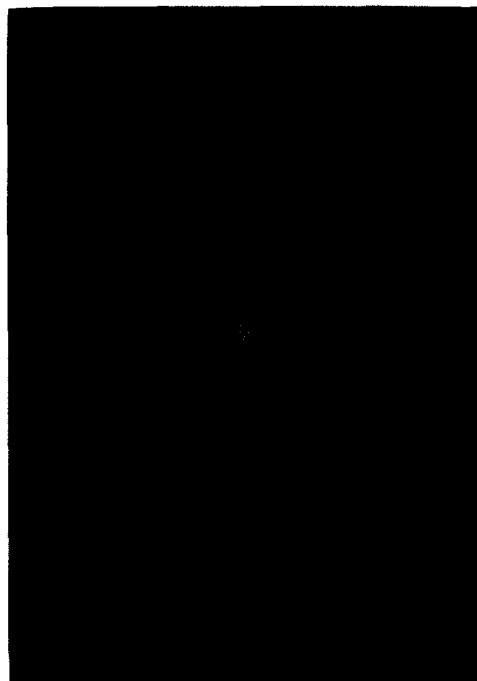


Figure 3 TED arcs from a 22-layer film on glass

spacing along the siloxane backbone and the inner pair to the in-plane inter-backbone spacing between adjacent (aligned) macromolecules. The calibration for the measurement of the in-plane spacing was provided by the previously measured value of the inter-ring spacing, with this value itself being confirmed by a calibration using TED of an evaporated aluminium film.

Using TED and TEM to investigate L-B films presents practical problems because they are sensitive to electron beam damage, necessitating that very low exposures be used. This is frequently allied with the use of high speed films, such as that used for this work, in partial compensation for the low exposures⁸. The use of such films does however, result in a loss of resolution because of their inherently large grain size compared with slower films.

An additional complication arises when TED is used. L-B films, because of their small depth, produce very little diffraction of the electron beam causing the central spot to be comparatively bright; proportionally brighter than is the case for many other types of sample. High speed film is necessary to record many of the features caused by diffraction but a consequence of this is saturation of the photographic emulsion in the region of the central spot with loss of definition where this occurs. This was unavoidable in the data we obtained and the saturation and loss of definition of the inner arcs, even though the outer arcs are only lightly exposed, is evident in Figure 3.

The values obtained are presented in Table 2. The diameters of the arcs were initially measured using a millimetre scale. Due to the poor definition, subsequent confirmation was obtained by analysis of the optical densities of the photographic negatives with an image processing system. The layers on mica substrates yielded TED arcs which were less well defined than those yielded by the layers on glass, indicating that the layers on mica were more disordered than those on glass. This was confirmed by visual inspection of the films under the TEM and is shown in the corresponding micrographs, as discussed below.

The in-plane spacings show a substrate dependency that is similar to, but more marked than, that of the inter-layer spacings. This is also attributed to substrate hydrophobicity. Although the variations in the XRD and TED data are small, being only of the order of 5%, they are highly consistent and are, therefore, thought to indicate a real effect and not an artefact introduced by experimental error.

Figures 4 and 5 are representative high resolution TEM micrographs of typical regions of directly dipped monolayers and transferred-from-glass multilayers, respectively. Micrographs of both types of specimen have the appearance of log-jams, with the specimens prepared by transferring films from glass showing more long-range alignment than the directly dipped specimens. It should be noted however, that only certain regions comprising approximately one-third of the total area of the transferred-from-glass films showed such alignment, with the remaining areas resembling the directly dipped specimens. This is attributed to the method of preparation: stripping the layers is likely to produce stress with the corresponding probabilities of structural damage and reduction in the size and number of the ordered regions.

In both types of specimen the width of the 'logs' is approximately 25 Å, with no apparent variation. There is some variation in the length of the 'logs' but the majority have lengths in the range 50–150 Å. Closer inspection of all the micrographs reveals that the longer 'logs' appear to comprise segments, with many of these segments having lengths of approximately 50 Å.

The observed width of the 'logs' corresponds to the measured in-plane spacings of the macromolecules. Also, the apparent prevalence of unit lengths in the region of 50 Å, corresponding to macromolecular lengths of 15 units, provides some confirmation of the expected peak in the macromolecular weight distribution at this value. The micrographs are, therefore, interpreted as showing both individual macromolecules and macromolecules end-to-end.

The depth of focus of the TEM is approximately 200 Å, which implies that at least 10 layers of the transferred-from-glass multilayers contribute to the images. Therefore, a high degree of inter-layer alignment must be present in these multilayer films as significant misalignment would lead to a loss of definition in the micrographs. Close inspection of the micrographs reveals that there are regions which are noticeably less distinct, implying that in such regions there is a degree of misalignment between layers.

The different degrees of long-range alignment of the two types of specimen are thought to be direct consequences of the substrates used for dipping. The amorphous carbon film is a very poor substrate for



Figure 4 TEM micrograph from a directly dipped monolayer

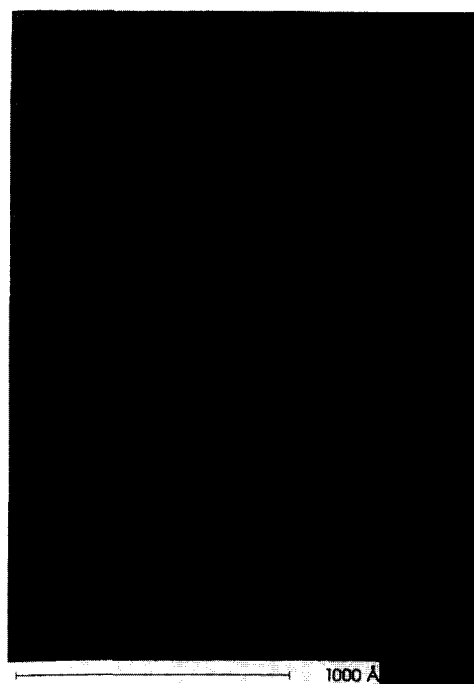


Figure 5 TEM micrograph of a 22-layer transferred-from-glass film

dipping: the interaction between the film and the grid is poor and the film has a tendency to lift off if the grid is dipped into the trough a second time. This implies that the interaction between the macromolecules and the substrate is too weak to induce a realignment and, consequently, the structure observed in the directly dipped monolayers is expected to be approximately that which exists in the film on the trough surface.

Glass, however, is a good substrate with the film showing good adhesion. Consequently, the interaction between the layer and the substrate, or preceding layer, is sufficiently strong to influence the alignment of the macromolecules during the transfer. This is confirmed

by the higher degree of alignment evident in the micrographs of the transferred-from-glass specimens, with the long-range alignment presumed to be in the direction of dipping as a result of the motion of the substrate through the air-water interface.

Film structure

The diffraction data indicate that the deposited films have a quasi-orthogonal structure: the macromolecules in successive layers align with their backbones directly above those in the preceding layer. These data also indicate that the structure has distinct in-plane and inter-layer spacings which are substrate dependent.

The TEM micrographs provide some confirmation of the TED measurements and provide a clear illustration of the manner in which the macromolecules form films with long-range order when deposited on hydrophobic substrates. The micrographs also indicate the high degree of inter-layer alignment present in these films.

The substrate dependence implies that the spacings are determined in the first layer and are not solely dependent on the molecular size (cross-sectional area). Also, the high degree of inter-layer alignment implies that this spacing is propagated throughout the entire multilayer. This has an important implication in that this material must be one which adapts its structure to the substrate whereas the majority of L-B materials form films with substrate-independent structures.

There is an apparent contradiction between the measured transfer ratio and the measured in-plane spacings in the deposited films. The measurements from the dipped films show that the in-plane spacing increases by approximately 17 and 11%, for glass and silylated mica, respectively, from the value derived from the area per monomer unit measurements of the films on the subphase at the dipping pressure. The transfer ratio however, was $95 \pm 2\%$ for all samples, implying a decrease in in-plane spacing of approximately 5% on dipping.

We hypothesize that this apparent contradiction indicates that restructuring occurs as part of the transfer process and that the mechanism by which this occurs involves reorientation of the sidegroups to achieve the most energetically favourable configuration for the surface on which they reside. The sidegroups are uniformly hydrophobic and on the subphase it will, therefore, be energetically favourable for them to minimize their area of contact, thus minimizing the in-plane spacing. On a hydrophobic substrate or a preceding layer however, it will be energetically favourable for them to maximize their area of contact. Any such increase in the area so occupied necessitates that the in-plane spacing must also increase and this spacing is propagated throughout the film.

The value of the transfer ratio indicates that the restructuring occurs in the material that has already been deposited, probably in the region immediately behind the meniscus.

This hypothesis also predicts that the in-plane spacing should, if it shows any dependence on substrate hydrophobicity, increase with increasing hydrophobicity and there is evidence supportive of this in the TED data.

The predicted effects of substrate hydrophobicity on the inter-layer spacing are less obvious. The data shows that, whilst its variation is less marked than that of the in-plane spacing, the inter-layer spacing also increases with increasing hydrophobicity. This contradicts what is

perhaps the most obvious prediction, i.e. that the inter-layer spacing should decrease if the in-plane spacing increases, and *vice versa*. The reasons for this apparent contradiction are, at present, unknown.

A possible explanation, however, is that increasing the substrate hydrophobicity, in addition to maximizing the area of contact between the sidegroups and the substrate, also increases the tendency for the sidegroups to collect between the ring and the substrate, forcing the ring away from the substrate. This would imply that the inter-layer spacing is governed by the minimum molecular diameter with only a small dependence on the substrate hydrophobicity.

This hypothesis can also explain the presence of the multilayer regions observed in transferred monolayers. The film area, as indicated by the value of the transfer ratio, actually decreases on dipping implying that the transferred film is initially more closely packed than when on the subphase. This is attributed in part to a reduction in the number of voids. To permit an increase in in-plane spacing, therefore, some material must be forced from the monolayer and any such material is available for the formation of multilayers. As already noted, the mechanism by which this occurs must be more complex than the relatively simple forcing of isolated macromolecules from the layer. It is proposed that the increase in spacing is accommodated by large areas of the film buckling away from the substrate and then collapsing back onto the expanded film. Such a mechanism involves discrete groups of many macromolecules and would permit the formation of distinct multilayer regions.

COMMENTS AND CONCLUSIONS

The investigation so far has shown that tetramethoxy-tetraoctoxy phthalocyaninato-polysiloxane macromolecules, whilst being a good L-B material in terms of spreading well and forming ordered multilayers, display complex and unusual properties. These properties are attributed to their size and shape and to the uniformly hydrophobic nature of their surface.

The macromolecules reorientate as part of the transfer process such that the in-plane inter-backbone spacing increases by an amount which appears to be substrate dependent and is greater than 10% for the substrates investigated in this work. This occurs in the film after dipping, probably in the region immediately behind the meniscus. Also, a deposited monolayer contains multilayer regions, containing approximately six to eight layers but comprising only a very small proportion of the total area. It is thought that they are formed as the result of the restructuring mechanism responsible for the increase in spacing.

There is a high degree of molecular alignment in the dipped films. The macromolecules align both within individual layers and between successive layers, with the alignment between layers being preserved through at least 10 or so layers. The structure of the dipped films is quasi-orthogonal, with distinct in-plane and inter-layer spacings. Both spacings show a degree of dependency on the nature of the substrate, increasing with increasing hydrophobicity. The variation in the in-plane spacing is more marked than that in the inter-layer spacing, which appears to be primarily governed by the ring diameter.

The collapse mode of a monolayer on the subphase is a series of localized foldings or subductions which result in visible stripes of thicker material. There is no catastrophic collapse as commonly observed for conventional L-B materials.

It would be rewarding to investigate similar phthalocyaninato-polysiloxane macromolecules with different sidegroups, e.g. tetrabutoxy-tetramethoxy and tetradodecoxy-tetramethoxy. This would yield more data on the inter-backbone spacings and would confirm or deny some of the explanations and hypotheses presented herein.

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