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Studies on the release of polymeric Langmuir–Blodgett multilayers from the solid supports on which they were prepared

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Dedicated to Professor Imanishi on the occasion of his retirement

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Abstract

It has been shown that polymeric Langmuir–Blodgett (LB) multilayers may be released from the supports on which they were prepared by first thermally evaporating thin films of stearic acid onto the support. The acid can subsequently be washed away, so undercutting the film and releasing it to float to the water surface. The films were redeposited onto fresh silicon wafers or onto glass microscope slides. Under the optical microscope, the films on the glass microscope slides were clear and featureless. By XRD the transferred films had the same or fewer orders of Bragg peaks and the corresponding bilayer spacings were the same or slightly larger than those of the original films. Thus, it appears that most films lose a small amount of their order in the transfer process. By second harmonic generation (SHG) the transferred alternating LB films formed from a poly(4-vinylpyridine) partially quaternised by reaction with *n*-docosyl bromide and from the poly(4-vinylpyridinium bromide) formed by the zwitterionic polymerisation of 4-vinylpyridine with 4(12-bromododecyloxy)-4′-trifluoromethylazobenzene displayed essentially the same SHG properties as the original films. Moreover, the SHG films could be stacked successfully to give thicker films. Several of the transferred films, but not all, contained traces of stearic acid, which appears to be present as small domains of Y-type layers. In one typical case, where the LB film consisted of 100 layers of a poly(4-vinylpyridine), it was shown that the amount of stearic acid present corresponded to an average of one monolayer. © 2002 Published by Elsevier Science Ltd.

Keywords: Langmuir–Blodgett films; Second harmonic generation; Release of Langmuir–Blodgett films from supports

1. Introduction

In recent years Langmuir–Blodgett (LB) films have been studied extensively [1–3], partly because, being organised nanostructures, they have a wide variety of potential applications. They may, for example, be used in sensors [4] or in electronic devices [5]. Polymeric LB films are generally expected to be more suitable than non-polymeric LB films for such applications because, even though they may be less well ordered, they are much more robust, less prone to reorganisation [6] and less prone to scatter light [7]. For various applications it would be attractive to be able to separate the film fabrication process from the device fabrication process. Thus, the LB film preparation, which is a relatively slow process and involves exposing the film to water repeatedly, could be carried out on a relatively large scale, then an appropriate small portion of the film could be transferred relatively quickly to the appropriate location on the device.

To separate the LB film fabrication process from the device fabrication process it is first necessary to develop methods to release the LB films from the solid supports on which they were prepared. This was first achieved by Langmuir and Blodgett who released palmitate, stearate and arachidate salt multilayers from glass supports to the water surface by careful treatment with hydrochloric acid [8]. Peters later carried out similar studies with multilayers containing dye molecules and monitored the process by fluorescence [9]. He concluded that whilst the multilayers were removed cleanly from the glass their organisation was disrupted somewhat by the procedure. In elegant studies monitored by fluorescence, Möbius and his colleagues have shown that arachidic acid-dye multilayers may be transfered from glass supports to the water surface with the aid of a poly(vinyl alcohol) film [10,11]. Rothen [12,13] carried out similar studies in which a slide was

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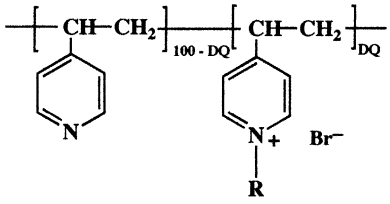
coated successively with a few layers of barium stearate, two layers of bovine albumin and a 100 Å thick coating of antibody. When a piece of Scotch™ tape was pressed onto the assembly and then stripped off all the layers remained fixed to the tape except the layer of barium stearate first deposited. The latter remained firmly attached to the slide. More recently Albrecht and Matsuda, at the Canon Research Centre, have successfully released LB multilayers of poly(lactic acid) less than 100 nm thick from silicon wafers using detergent solutions and have obtained free-standing LB films [14,15]. In closely related work it has been shown that LB multilayers prepared from various polymers are able to span the 200 nm pores of sintered filters [16] and that layers of poly(butylstyrene) and various other polymers can, as wet suspended membranes, span holes as large as a few millimetres [17]. After crosslinking, the suspended layers formed stable membranes 10–50 nm thick [18]. In the present paper, we describe our studies on the release of polymeric LB multilayers from the solid supports they were prepared on with the assistance of initial thin layers of stearic acid which can subsequently be dissolved away by washing with base, so undercutting the LB multilayers and helping them to float off the support.



(1) : R = -$(CH_2)_{21}CH_3$; DQ = 70

(2) : R = -$(CD_2)_{19}CD_3$; DQ = 60

2. Experimental

General experimental details were as given earlier [19,20].

2.1. Materials synthesis

2.1.1. Synthesis of polymer *1*

This polymer was synthesised by treating poly(4-vinylpyridine) (Polysciences: M_v 42,700) with docosyl bromide in methanol at reflux temperature for 72 h as described earlier [20]. By ^{1}H NMR spectroscopy, based on the relative areas of the signals due to aliphatic and aromatic protons, the degree of quaternisation (DQ) was 70%. By elemental analysis it had 14.8% Br.

2.1.2. Synthesis of polymer *2*

Poly(4-vinylpyridine) with M_v 25,000 [20] was reacted with fully deuteriated eicosyl bromide ($C_{20}D_{45}Br$) in methanol: THF (2 vols:1 vol) at reflux temperature for 72 h using a similar procedure to that used to prepare polymer **1**. By ^{13}C NMR spectroscopy (using appropriate conditions for integration), based on the relative areas of the signals due to the backbone carbons and the side chain carbon next to the quaternised N atom, the DQ was 60%. By elemental analysis it had 14.5% Br.

2.1.3. 4-Hydroxy-4′-trifluoromethylazobenzene *3*

p-Trifluoromethylaniline was diazotised and the diazonium salt coupled with phenol using the general procedure given in Vogel [21]. 4-Hydroxy-4′-trifluoromethylazobenzene **3** (74% yield) was obtained as a pale yellow powder. After two recrystallisations from methanol it had mp 130–131 °C; $\delta(CHCl_3)$ 6.90 (2H, m, ArH ortho to phenolic OH), 7.75 (2H, m, ArH ortho to CF_3) and 7.90–8.00 ppm (4H, m, ArH ortho to –N=N–).

2.1.4. 4-(12-Bromododecyloxy)-4′-trifluoromethylazobenzene *4*

1,12-Dibromododecane (2.00 g, 6.1 mmol) and K_2CO_3 (1.70 g, 12.2 mmol) were added to a solution of the azo compound **3** (1.50 g, 6.0 mmol) in dry acetone (50 ml) and the mixture was vigorously stirred and heated under reflux for 66 h. The mixture was then cooled to room temperature and filtered. Evaporation of the solvent left an orange coloured residue. This was dissolved in dichloromethane (20 ml) and the solution washed with NaOH (0.1 M, 20 ml) then water (20 ml) and dried. The solvent was evaporated off and the residue chromatographed over silica gel with dichloromethane as the eluent. This gave compound **4** (1.20 g, 69%) as an orange powder. It had mp 83–84 °C; δ 1.1–1.6 (18H, m, $[CH_2]_9$), 1.85 (4H, m, $[CH_2]_2$) 3.42 (2H, t, $J = 7.5$ Hz, CH_2Br), 4.08 (2H, t, $J = 7.5$ Hz, CH_2O), 7.05 (2H, m, ArH ortho to phenolic group), 7.79 (2H, m, ArH ortho to CF_3) and 8.00 ppm (4H, m, ArH ortho to –N=N–). Found C 58.5, H 6.4, N 5.4, Br 16.0% $C_{25}H_{32}N_2BrF_3O$ requires C 58.5, H 6.3, N 5.5 and Br 15.6%.

2.1.5. Synthesis of polymer *5* by quaternisation of a preformed polymer

This polymer was synthesised (82% yield) by treating poly(4-vinylpyridine) (Polysciences: M_v 42,700) with compound **4** isopropanol at reflux temperature for 72 h using the procedure described earlier [20]. By ^{1}H NMR spectroscopy it was 38% quaternised. By elemental analysis it had 12.8% Br.

2.1.6. Synthesis of polymer *6* via a zwitterionic polymerization

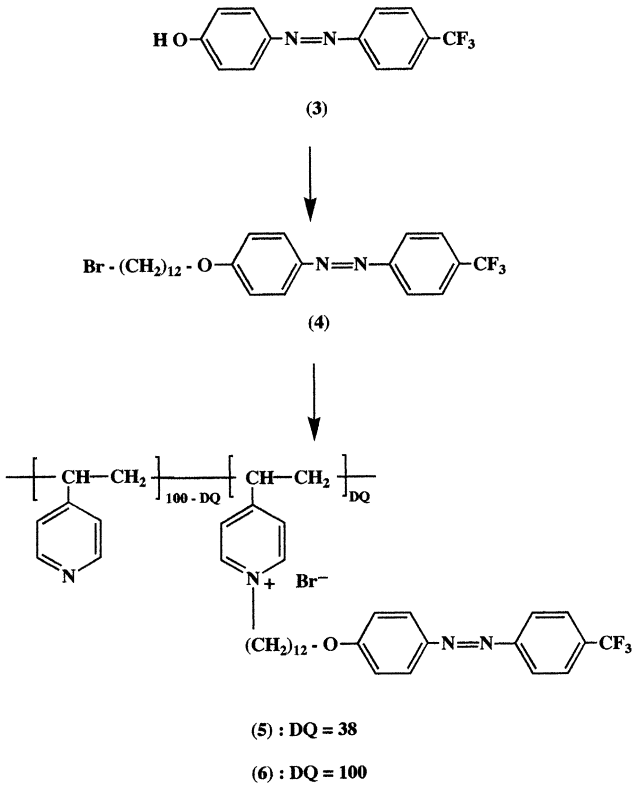
Compound **4** (288 mg, 0.56 mmol), freshly distilled 4-vinylpyridine (15 ml) and hydroquinone monomethyl ether (10 mg, 0.08 mmol) were placed in a sealable

Table 1
Properties of monolayers and Langmuir–Blodgett film properties of various polymers

Polymer	Monolayers: area per repeat unit (Å^2)		Collapse pressure (π_c, mN/m)	LB film deposition ratio[a]		X-ray data		
	At 0 mN/m (A_0)[b]	At 25 mN/m (A_{25})		Downstroke	Upstroke	No. of layers in LB film[c]	No. of Bragg peaks	*d* spacing (Å)
1	44	38.0	44	1.0	1.0	100	5	45.5
2	42	28.7	40	0.5	1.0	100	2	45.0
5	35	18.3	32	0.7	1.0	100	2	47.2
6	50	33.0	33	0.6	1.0	100	2	46.2
1 + **6**	–	–	–	1.0 (polymer **1**)	1.0 (polymer **6**)	80	2	45.9

[a] By extrapolation of the 'solid' section of the isotherm to zero pressure.
[b] Values within +5%.
[c] The monolayers were transferred at a surface pressure of 25 mN/m.

pressure tube. The mixture was degassed by 4 freeze-thaw cycles and then the tube was sealed under vacuum (1 mm Hg). It was heated at 50 °C for 1 h before being left at room temperature for 5 h. The seal was broken and unreacted 4-vinylpyridine distilled off. The residue was dissolved in chloroform and precipitated into diethyl ether (400 ml). This gave polymer **6** as an orange powder (308 mg, 89% yield). By ^{1}H NMR spectroscopy it was 100% quaternised. By elemental analysis, it had N 6.6% and Br 12.9%: calculated for 100% quaternised N, 6.7 and Br 12.9%. Due to the fact the polymer was a polyelectrolyte we were unable to determine the molecular weight. However, all the signals in the ^{1}H NMR spectrum were broad.



Scheme 1.

2.2. Langmuir isotherms and film deposition

Langmuir isotherms were measured for monolayers on water using the double-trough described earlier [19]. The subphase was water at 20 °C and pH 5.3–5.5 obtained by passing tap water through an Aquatron AFD deionisation column followed by double distillation in an Aquatron A4D distillation unit. Prior to use the purified water was filtered through 0.2 μ Millipore filters. The spreading solvent was HPLC grade chloroform (Aldrich Chemicals Ltd) and was used as purchased. In each case a 2.5×10^{-4} M solution of the polymer was spread carefully on the water surface of the Langmuir trough and the solvent was allowed to evaporate. The isotherm was then measured. The results are summarised in Table 1 and Fig. 1.

LB films were deposited onto either hydrophobic silicon wafers prepared as described earlier [19], onto pyrex glass

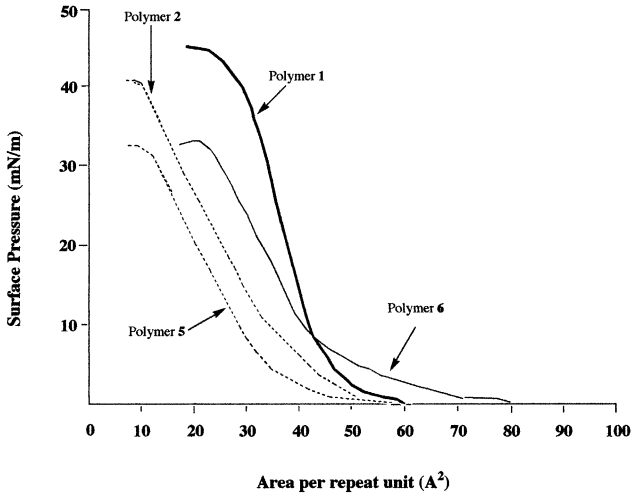


Fig. 1. Isotherms of polymers **1**, **2**, **5** and **6**. All isotherms were measured at 20 °C and pH 5.3–5.5.

microscope slides which had been cleaned thoroughly by washing overnight with ethyl acetate using a Soxhlet apparatus, or, when appropriate, chalcogenide glass plates. The surfaces of the slides were made hydrophobic by leaving them overnight on a PTFE support in a desiccator in an atmosphere saturated with the vapour of 1,1,1,3,3,3-hexamethyldisilazane. Deposition was carried out at 25 or 30 mN/m (see Table 1) and a dipping speed of 8 mm/min. The results are also summarised in Table 1.

2.3. X-ray studies

X-ray diffraction (XRD) measurements were carried out as described earlier [19] using a Phillips type PW 1730 X-ray diffractometer and nickel-filtered Cu K_α radiation. The results are summarised in Table 1.

2.4. Infrared studies of LB films

Transmission infrared (T-FTIR) spectra were measured for films deposited onto chalcogenide glass plates [19].

2.5. SHG measurements

Second harmonic generation (SHG) measurements were carried out by the Optics Group in the Physics Department of this University using the method described earlier [22]. The measurements were made using 1.064 μm radiation from a Q-switched Nd:YAG laser. Pulses of less than 1 mJ energy with a 10 ns duration were focused to an ca. 100 μm spot size on the sample. Incident and detected light were p-polarised and SHG was resolved in complete scans and angles of incidence onto the samples as described earlier [23]. The results were calibrated against the signal from quartz.

2.6. Evaporated films of stearic acid

An Edwards Auto 306 evaporator with a thickness monitor and a built in Peltier controller was used to prepare thermally evaporated (TE) films of stearic acid on silicon wafers cooled to −10 °C. Details of the procedure have been described earlier [24].

2.7. Release of LB films from supports

The following was found to be the most satisfactory procedure.

Stearic acid was deposited by thermal evaporation (described earlier) onto a silicon wafer so that the average layer thickness was 50 nm. An LB film, typically 100 layers thick, of the polymer under investigation was deposited on top of the stearic acid multilayer. To release the polymeric LB film the entire supported multilayer was soaked for 5 min in a solution of 1.0 M aqueous sodium hydroxide in a crystallising dish (ca. 25 cm diameter and 5 cm deep). The support plus LB film was then carefully removed and immersed in 1.0 M aqueous hydrobromic acid. By carefully passing the silicon wafer diagonally downwards through the water surface the polymeric LB film was released onto the water surface. The floating LB film was then redeposited onto a clean hydrophilic silicon wafer, glass microscope slide or chalcogenide glass as appropriate by passing it diagonally upwards through the air–water interface. The transferred LB film was studied by FT-IR, XRD and/or SHG as appropriate.

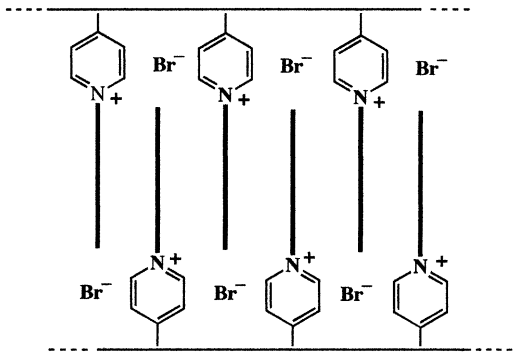


Fig. 2. Scheme showing general packing arrangement of various poly-(vinylpyridium salt)s in LB films and liquid crystals.

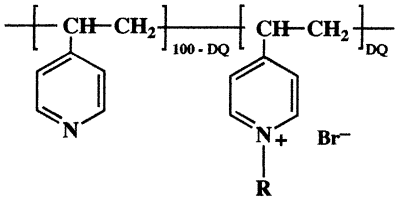
3. Results and discussion

3.1. Synthesis of polymers *1*, *2*, *5* and *6*, and their monolayer and LB film properties

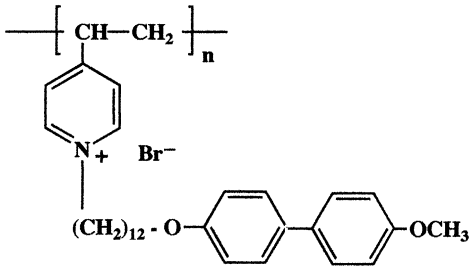
We have shown earlier that the polymers **7** formed by the quaternisation of poly-4-vinylpyridine with various long-chain alkyl bromides form excellent monolayers at an air–water interface and excellent LB films [20,25]. Measurements of average surface areas per repeat unit in the monolayers at the air–water interface (using a Langmuir trough), deposition ratios, bilayer thicknesses (XRD measurements) and average side chain tilt angles (FT-IR studies) indicate that in many cases the LB multilayers have an arrangement in which the lipophilic side chains interdigitate: see Fig. 2. The better LB films display up to five orders of Bragg reflections [20]. Accordingly they are some of the best-ordered polymeric LB films so far reported. It is interesting to note that Gramaine et al. studied the liquid crystal properties of polymers such as **8** and concluded the molecules pack in a manner closely analogous to that indicated in Fig. 2 [26,27].

More recent studies by the author's group [28] of polymers of the type **1** where the DQ was varied, indicate that the area occupied at the air–water interface per repeat unit increases as the DQ increases. This implies that the unquaternised repeat units contribute relatively little to the surface area and so, at the air–water interface, sit either above or below the quaternised repeat units. These studies also showed that, in view of the tendency for the polymers to be hygroscopic, the most satisfactory method to assess the

DQ is ^{1}H NMR spectroscopy. Given the overall excellent properties of polymers of type **7**, polymers of this general type were selected for the present studies.



(7) : R = various lipophilic chains ; DQ > 50



(8)

Polymer **1** was prepared by reacting a commercial sample of polyvinylpyridine (M_v 42,700) with docosyl bromide. By ^{1}H NMR spectroscopic analysis the DQ was 0.70. Monolayers were spread at the air–water interface from chloroform solution and the isotherm measured. The isotherm is shown in Fig. 1. The surface area per repeat unit at zero surface pressure (A_0) was 44 Å^2. The monolayers were transferred successfully (deposition ratios >0.95) on to silicon wafers to form Y-type LB multilayers. On XRD analysis the multilayers displayed five orders of Bragg reflections corresponding to bilayer thicknesses of 45.5 Å. These results are in excellent agreement with those obtained in our previous study [20].

Polymer **2** was prepared in a similar manner to polymer **1** but using perdeuteriated eicosyl bromide in place of docosyl bromide. Ultimately it is intended to use this polymer in neutron scattering studies. The isotherm was measured. The surface area per repeat unit and the bilayer thickness of the derived LB multilayer, summarised in Table 1, indicate it is also ordered as shown in Fig. 2.

For the present studies, it was considered advantageous to have available a coloured polymer of the same general type as polymer **7** because the derived LB multilayers would then be easier to see when being manipulated. To achieve this it was decided to prepare polymers containing azobenzene chromophores since it is known that such polymers give excellent LB films [25]. Furthermore, by using an azobenzene chromophore with both donor and acceptor substituents in the 4- and 4′-positions it would be possible to monitor the quality of the transferred films by SHG [25]. Accordingly azo compound **4** was prepared, as outlined in Scheme 1, and reacted with poly(4-vinylpyridine) to give polymer **5**. Despite the extended reaction period, by ^{1}H NMR spectroscopic analysis the DQ was only 0.38. In order to obtain a polymer with a higher DQ, the azo compound **4** was reacted with 4-vinylpyridine to bring about a zwitterionic polymerisation and hence the formation of the fully quaternised polymer **6**. Since polymer **6** is a polyelectrolyte we were unable to determine its molecular weight. However, the signals in the ^{1}H NMR spectrum were all very broad indicating the product was polymeric.

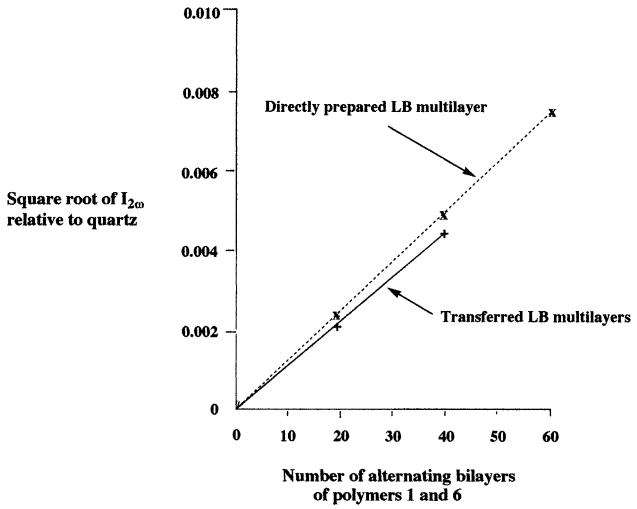


Fig. 3. Plot of the square root of $I_{2\omega}$ versus the number of alternating bilayers of polymers **1** ('passive layers') and **6** ('active layers'). $I_{2\omega}$ is expressed as intensity relative to quartz. Values of $I_{2\omega}$ have an error of +5%.

Monolayers of polymers **5** and **6** were spread from solutions in chloroform onto the water surface of a Langmuir trough and the isotherms recorded. The results are shown in Fig. 1 and summarised in Table 1. The monolayers were transferred satisfactorily (deposition ratios 1.00 on the upstroke: 0.7 and 0.6 respectively on the downstroke) on to silicon wafers to form Y-type LB multilayers. On XRD analysis the multilayers displayed two orders of Bragg reflections corresponding to bilayer thicknesses of 47.2 and 46.2 Å respectively. It is evident the LB films prepared from these two polymers are very similar to each other and also to those of polymer **1**. In all the subsequent work the LB films were prepared from the more readily prepared polymer **3**.

Finally, alternating LB multilayers were prepared from polymers **1** and **6**, the former being deposited on the downstroke and the latter on the upstroke. These LB multilayers displayed two orders of Bragg reflection on XRD corresponding to a bilayer thickness of 45.9 Å. As expected these multilayers displayed SHG properties. LB multilayers 20, 40 and 60 layers thick were prepared and their SHG properties measured relative to quartz as described earlier

[22,23,25]. The intensity of the second harmonic signal is expected to increase in proportion to the square of the number of active layers. It is evident from the plot shown in Fig. 3 that this was the case. We calculate a bulk nonlinear susceptibility in the experimental geometry used of $\chi^{(2)}_{pp}$ = ca. 2.5 pm V^{-1}. It should be noted, however, that it was not the object of the present work to obtain films with high $\chi^{(2)}_{pp}$ values. It was simply intended to prepare films with easily measured SHG properties.

3.2. Release of LB films from their supports

The object of the work was to prepare LB films in which several layers of stearic acid were followed by many layers of polymer, and then to release the LB multilayers from the solid supports by dissolving away the stearic acid with aqueous base, thus undercutting the polymeric LB films, so helping them to leave the supports and float to the water surface.

In the initial stages of the present project the stearic acid was deposited onto silicon wafers by the LB technique [24]. Typically 10 layers, with a total thickness of ca. 50 Å were deposited. We have shown, however, that TE films of stearic acid deposited under appropriate conditions have a similar quality and Y-type structure [24,29]. Since the TE films can be deposited more quickly it was more convenient to use this technique. In all the experiments described later a 50 nm thick film of stearic acid was deposited onto silicon wafers in this manner.

The first polymeric LB films to be studied were those of the coloured polymer **6**. LB films 100 layers thick were deposited on top of the stearic acid layers. The entire multilayer was then immersed in 1 M aqueous sodium hydroxide for 5 min. The silicon wafer plus the LB film was then transferred carefully to 1 M aqueous hydrobromic acid. By carefully passing the silicon wafer downwards through the water surface the polymeric LB was released and it floated to the water surface. The reason for using the acid was to neutralise any residual sodium hydroxide, which might otherwise react slowly with the polymer. Hydrobromic acid was chosen for this purpose because bromide anion was the counter ion in the original LB film. After 5 min on the surface of the acid, the LB film was picked up onto a fresh silicon wafer. XRD analysis of the transferred LB film showed two orders of Bragg peaks corresponding to a bilayer spacing of 47.0 Å. Thus, the transferred film appeared to be essentially as well organised as the original film. In a similar experiment the floating polymeric LB film was picked up on an aluminium plate with 2 and 3 mm holes. The film was able to span the holes when wet but it tended to break when dry. Finally with these films, it was noted that the transferred LB film showed, in addition to those due to the polymeric film, small but significant Bragg peaks (three orders; a good LB film of stearic acid alone would typically show ca. 10 orders) corresponding to the presence some Y-type layers of stearic acid (see later).

An LB film (100 layers) of polymer **1** was similarly prepared on a silicon wafer, released and deposited onto a fresh silicon wafer. On XRD it displayed three orders of Bragg peaks corresponding to a bilayer spacing of 46.2 Å. The original film had a bilayer spacing of 45.5 Å. The decrease in the number of Bragg peaks and the slightly greater bilayer spacing suggests that some of the order originally present in the LB film was lost. As with the transferred LB film of polymer **6**, the XRD indicated the transferred film contained some stearic acid. To estimate the amount present an FT-IR spectrum was measured and compared with that of an LB film consisting of a monolayer of stearic acid and 50 layers of the deuteriated polymer **2**. This polymer was used because the in the IR spectrum C–D bonds are weaker than C–H bonds and so the spectrum is relatively clear in the carbonyl region. The intensities of the carbonyl bands at 1710 cm^{-1} in the two spectra were almost identical. Thus, in the 100 layer LB film of polymer **1** the amount of stearic acid present corresponds on average to only one monolayer. Since the XRD displays peaks due to Y-type layers, the stearic acid must be present in small regions as multilayers.

An LB film (100 layers) of polymer **2** was similarly prepared on a silicon wafer, released and deposited onto a fresh silicon wafer. On XRD it displayed two orders of Bragg peaks corresponding to a bilayer spacing of 46.2 Å. The original film had a bilayer spacing of 45.0 Å. In this case there was no evidence for the presence of stearic acid.

Finally, several alternating LB films, each of 20 layers, were prepared from polymers **1** and **6**. One was transferred onto pyrex glass microscope slide to give a film 20 layers thick using the usual procedure. An LB film 40 layers thick was prepared by stacking two pieces of 20-layer thick film. By XRD analysis the films displayed two Bragg peaks corresponding to a bilayer spacing of 46.2 Å, a value very similar to that of the original films. The transferred LB films were clear and featureless. SHG measurements were made on the transferred films as they were earlier on directly prepared films. The results are shown in Fig. 3. It is evident that the films display SHG properties very similar to those of the directly prepared films and, particularly pleasing, that the 40 layer LB film prepared by stacking two 20 layer films displays 4 times the SHG signal of the transferred 20-layer film. This suggests it may be possible to prepare thick LB films successfully by stacking several thinner films.

4. Conclusions

In the work described in this paper, it has been shown that polymeric LB multilayers may be released from the supports on which they were prepared by first thermally evaporating thin films of stearic acid onto the support.

The acid can subsequently be washed away, so undercutting the polymeric LB film and releasing it to float to the water surface. The films were redeposited onto fresh silicon wafers or onto glass microscope slides. Under the optical microscope, the films on the glass microscope slides were clear and featureless. By XRD the transferred films had the same or fewer orders of Bragg peaks and the corresponding bilayer spacings were the same or slightly thicker than those of the original films. Thus, it appears that most films lose some of their order in the transfer process. By SHG the transferred alternating LB films formed from polymers **1** and **6** displayed essentially the same SHG properties as the original films. The SHG films could be stacked successfully to give thicker films. Several of the transferred films, but not all, contained traces of stearic acid, which appears to be present as small domains of Y-type layers. In one typical case, where the LB film consisted of 100 layers of polymer **1**, it was shown that the amount of stearic acid present corresponded on average to only one monolayer.

Acknowledgements

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