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# Second harmonic generation from Langmuir–Blodgett multilayers assembled from 'active' non-polymeric amphiphiles and 'inactive' polymeric amphiphiles

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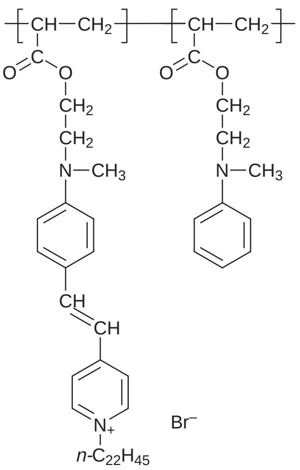
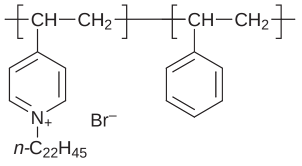
Alternating Langmuir–Blodgett (LB) multilayers have been prepared from a non-polymeric hemicyanine and a poly(4-vinylpyridine) 66% quaternised with docosyl bromide, and from a non-polymeric azobenzene and the same pyridinium polymer. With both types of multilayer the intensity of the SHG signal increased as the square of the number of layers up to a thickness of *ca.* 60 bilayers. The slopes of the plots correspond to second order susceptibilities of 17.5 and 9 pm $V^{-1}$ respectively. Although these properties and the stabilities of the films over time compare favourably with many other LB films described in the literature, these films prepared from 'active' non-polymeric amphiphiles and a 'passive' polymeric amphiphile are not as satisfactory as the closely related all-polymeric films described previously.

In recent years there has been great interest in materials for second harmonic generation (SHG), *i.e.* materials which on irradiation with light of a given frequency produce a significant intensity of light of twice the incident frequency. Such materials have many potential applications in optoelectronics.[1–3] To achieve SHG, materials generally need to contain good SHG chromophores macroscopically arranged in a non-centrosymmetric manner. One way[4] of achieving the latter requirement is to prepare Y-type Langmuir–Blodgett (LB) multilayers in which every alternate layer is 'active', *i.e.* has an SHG chromophore, and every alternate layer is 'inactive': see Fig. 1. Good SHG chromophores generally have a π-electron system substituted at one end with an electron-donor group and at the other end with an electron-withdrawing group. Examples are the hemicyanine chromophore, present in polymer **1** and compounds **3** and **4**, and the azobenzene chromophore, present in compounds **5** and **6**.



**1**



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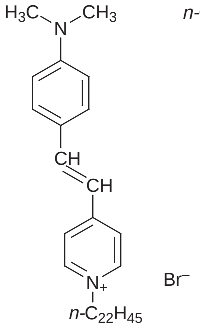

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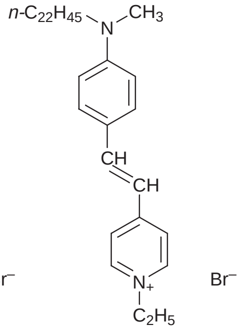
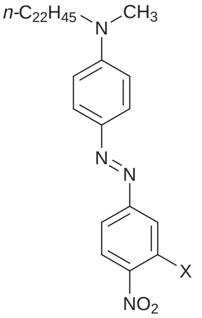


**4**



**5** : X = H
**6** : X = $CO_2H$

LB multilayers prepared from non-polymeric amphiphiles, although often highly organised initially, are in general physically fragile and prone, over an extended period of time, to molecularly reorganise.[5–7] LB multilayers prepared from amphiphilic polymers, although less well organised initially, are generally physically more stable and can be expected to be less prone to reorganisation. We have described recently the preparation of alternating LB multilayers from 'active' polymer **1** and 'inactive' polymer **2**.[8] With films containing up to a total of 600 layers the intensity of the SHG light, $I_{2\omega}$, increased as the square of the number of layers, as predicted by theory.[4] The macroscopic second order susceptibility, $\chi^{(2)}$, of these films was 12 pm $V^{-1}$. The films were stable at 20 °C for at least 8 months and at 60 °C for at least 96 h.[8] A Fabry–Perot device was successfully fabricated using the same active materials.[9]

We now describe the preparation of LB multilayers from 'active' non-polymeric amphiphiles and the 'inactive' polymer **2**. The main objective was to determine whether readily available non-polymeric SHG amphiphiles could be used just as successfully as less readily available 'active' polymeric amphiphiles such as **1**, *i.e.* to determine if it was really necessary to have both amphiphiles polymeric in order to obtain satisfactorily stable films.

## Experimental

Melting points were determined using an Electrothermal melting point apparatus and are uncorrected. $^1H$ NMR spectra were recorded on a Varian Gemini 200 MHz instrument using $CDCl_3$ solutions. Ultraviolet (UV) spectra were recorded on a Shimadzu UV-260 spectrophotometer. Elemental analyses were obtained using a Carlo-Erba CHNS-O EA instrument.

### Source of amphiphiles

**Polymer 2.** This polymer was available from the earlier studies.[10] It was prepared by reacting a poly(4-vinylpyridine) of $\bar{M}_v$ 25 000 with 1-docosyl bromide: 66% of the pyridine residues in the product were quaternised.

**Compound 3.** This compound, prepared as described previously,[11] had mp 237–239 °C (lit.,[11] 240 °C).

**Compound 4**

(*a*) *N-Docosyl-N-methylaniline.* A mixture of freshly distilled *N*-methylaniline (19.58 g, 0.18 mmol), 1-docosyl bromide (74.0 g, 0.19 mmol), potassium carbonate (25.53 g, 0.185 mmol), potassium iodide (0.76 g, 5.0 mmol) and *n*-butanol (150 ml) was heated at reflux temperature under nitrogen and vigorously stirred for 4 d. The mixture was then cooled and filtered. The solvent was evaporated off under vacuum and the residue treated with aqueous potassium hydroxide (150 ml of 50%) at 20 °C. After 2 h the mixture was extracted with diethyl ether (4 × 75 ml). The extracts were combined and dried over sodium sulfate. Removal of the solvent left *N*-docosyl-*N*-methylaniline (71% yield) as a white waxy solid, mp 41–42 °C. It had $\delta_H$ 7.3–6.6 (m, 5H, aromatic), 3.32 (m, 2H, $-CH_2N$), 2.90 (s, 3H, $CH_3N$), 1.34 (m, 40H, 20 $CH_2$), 0.92 (t, 3H, $CH_3$) (Found: C 83.8, H 12.6, and N 2.9%. Calc. for: $C_{29}H_{53}N$, C 83.8, H 12.8, and N 3.4%).

(*b*) 4-(*N-Docosyl-N-methylamino*)*benzaldehyde.* Phosphorus oxychloride (5.37 g, 35 mmol) was added dropwise to anhydrous *N,N*-dimethylformamide (12.77 g, 175 mmol) at 5 °C under nitrogen and the mixture was vigorously stirred for 30 min. *N*-Docosyl-*N*-methylaniline (7.47 g, 18 mmol) in *N,N*-dimethylformamide (25 ml) was added dropwise and the temperature kept at 5 °C for 30 min. The mixture was then heated at 90 °C for 3 h. After cooling, the mixture was added to crushed ice (400 g). Adjustment of the pH to 5 using sodium acetate precipitated the desired product, which was collected and dried (7.23 g, 90%). It had mp 55 °C, $\delta_H$ 9.71 (s, 1H, ArCHO), 7.73 (m, 2H, aromatic), 6.72 (m, 2H, aromatic), 3.45 (t, 2H, $CH_2N$), 3.01 (s, 3H, $CH_3N$), 1.33 (m, 40H, 20 $CH_2$) and 0.94 (s, 3H, $CH_3$) (Found: C 80.9, H 12.4, N 3.3%. Calc. for: $C_{30}H_{53}NO$, C 81.3, H 12.0, and N 3.2%).

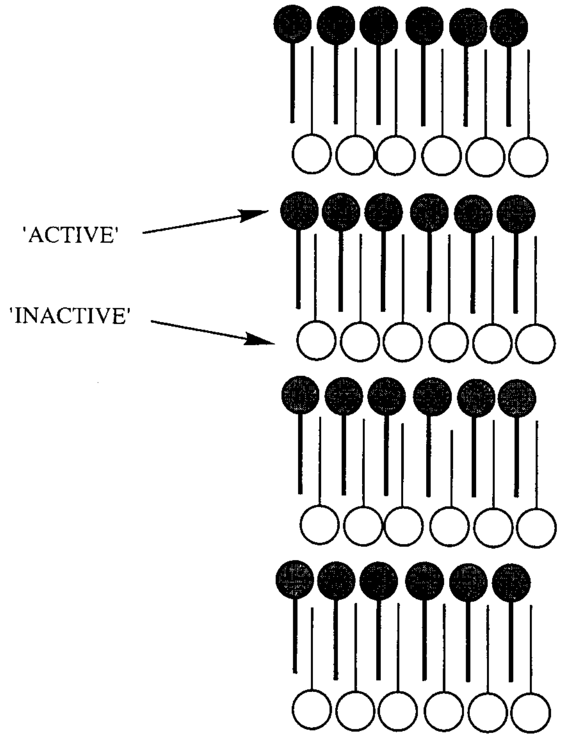


**Fig. 1** Scheme showing arrangement of 'active' and 'inactive' amphiphiles in an idealised Y-type Langmuir–Blodgett film which results in the film being non-centrosymmetric

(*c*) *N-Ethylpicolinium bromide.* Equimolar amounts of picoline and bromoethane were heated at reflux temperature for 4 h. The product was precipitated into diethyl ether, collected and dried. This gave the desired product, mp 122–123 °C (lit.,[12] 121 °C).

(*d*) *Compound* **4**. A mixture of *N*-docosyl-*N*-methylaniline (4.73 g, 11.4 mmol), *N*-ethylpicolinium bromide (2.31 g, 11.4 mmol), piperidine (1 ml) and methanol (50 ml) was heated under reflux for 18 h. The solvent was then evaporated off, the residue dissolved in a minimum volume of dichloromethane ($\sim$10 ml) and the product isolated by precipitation into hexane (400 ml). The product **4** was collected and dried (49% yield). It had mp 192–194 °C (Found: C 72.3, H 9.7, N 4.4, Br 12.4%. Calc. for: $C_{38}H_{63}BrN_2$, C 72.7, H 10.0, N 4.5 and Br 12.8%).

**Compound 5.** Using the general procedure given by Vogel,[13] *N*-docosyl-*N*-methylaniline was diazotized with the diazonium salt prepared from 4-nitroaniline. This gave 4′-*N*-docosyl-*N*-methylamino-4-nitroazobenzene **5**, mp 105–106 °C, in 57% yield. It had $\delta_H$ 8.3–7.7 (m, 8H, aromatic), 3.50 (m, 2H, $CH_2N$), 3.31 (s, 3H, $CH_3N$), 1.32 (m, 40H, 20 $CH_2$) and 0.93 (t, 3H, $CH_3$) (Found: C 74.0, H 9.8, N 9.6%. Calc. for: $C_{35}H_{57}N_4O_2$, C 74.3, H 10.1 and N 9.9%).

**Compound 6.** Using the general procedure given by Vogel,[13] *N*-docosyl-*N*-methylaniline was diazotized with the diazonium salt prepared from commercial 2-nitro-5-aminobenzoic acid. This gave 5-[4-(*N*-docosyl-*N*-methylamino)phenylazo]-2-nitrobenzoic acid **6**, mp 140–142 °C in 73% yield. It had $\delta_H$ 8.5–7.7 (m, 7H, aromatic), 3.33 (m, 2H, $CH_2N$), 3.02 (s, 3H, $CH_3N$), 1.34 (m, 40H, 20 $CH_2$) and 0.94 (t, 3H, $CH_3$) (Found: C 70.6, H 9.0, N 9.1%. Calc. for: $C_{36}H_{57}N_4O_4$, C 70.9, H 9.4 and N 9.2%).

### Measurement of isotherms, preparation of films and measurement of their properties

Details of the Langmuir troughs used,[14] and the general procedures for the measurement of isotherms[14] and for the preparation of LB multilayers[14] have been described before. In the present work all amphiphiles were spread from solutions in chloroform. The subphase was doubly-distilled deionised water with no additives, pH 5.2–5.6, at 20 °C. The LB films were deposited at a dipping speed of 8 mm $min^{-1}$ onto silanized silicon wafers or, for SHG materials, Pyrex glass microscope slides at a surface pressure of 30 mN $m^{-1}$. Deposition ratios were $1.00 \pm 0.05$ in all experiments. The alternating LB films were prepared by depositing the 'active' amphiphile on the upstroke and polymer **2** on the downstroke.

X-Ray reflectivity experiments[14] and SHG measurements (incident laser light of wavelength 1.064 μm) were carried out as described before.[15–17] All the LB films were stored in the dark at 20 °C because previous studies have shown that hemicyanines are sensitive to light.[18,19]

## Results and Discussion

### Synthesis and monolayer and multilayer properties of some non-polymeric amphiphiles containing SHG chromophores

The initial objective was to identify non-polymeric materials suitable for use in alternating LB films for SHG. These non-polymeric materials would ideally both (*i*) form well-ordered LB films, and (*ii*) contain excellent SHG chromophores. Four compounds were investigated: hemicyanines **3** and **4** and azobenzene derivatives **5** and **6**. All four were prepared using well-known types of synthetic reactions: see Experimental. For each compound, monolayers were spread at the air–water interface using chloroform solutions. The water was at 20 °C and pH 5.2–5.6. The isotherm was recorded. Attempts were then made to deposit the monolayers at a surface pressure of 30 mN m$^{-1}$ onto hydrophobic silicon wafers and/or other supports. X-Ray reflection studies were carried out on the LB multilayers obtained. The main data obtained from the isotherms and X-ray studies are summarised in Table 1.

The amphiphile **3** contains an excellent SHG chromophore, is readily available and as a consequence has been studied extensively.[11,20–29] The isotherm obtained in the present study, see Fig. 2, is essentially the same as that described in earlier studies.[23] It is evident that as the area available per repeat unit is decreased, beginning at quite a large surface area (*ca.* 160 Å$^2$ per repeat unit), the surface pressure rises steadily and eventually the isotherm becomes relatively steep. The area per repeat unit at a surface pressure of 30 mN m$^{-1}$ was 34 Å$^2$ and this corresponds well with the expected cross-sectional area of the molecule. Overall these results suggest that this amphiphile does not pack particularly well at the air–water interface. The monolayers transfer readily onto silicon or Pyrex glass on the upstrokes but not on the downstrokes. The multilayers obtained are therefore expected to be Z-type. In X-ray reflection studies of the multilayers one Bragg reflection was detected corresponding to a *d*-spacing of 47 Å. This value is very close to the length of the fully extended molecule, 45 Å, consistent with the multilayer being Z-type. Given that multilayers of, say, cadmium stearate often display more than ten orders of sharp Bragg reflections it is clear that LB multilayers of hemicyanine **3** have only modest order. It is likely that this, and the modest order in the compressed monolayer, is a consequence of the most hydrophilic part of the amphiphile being towards the centre of the molecule. It is interesting to note here that the isotherm of hemicyanine **3** has a shoulder at an area per repeat unit of *ca.* 95 Å$^2$ which corresponds approximately to the area of the hemicyanine chromophore.[23] This suggests, therefore, that the hemicyanine moiety initially lies flat on the water surface with the long alkyl chain out of the water. The fact that this hemicyanine does not form well ordered films prompted the study of hemicyanine **4**.

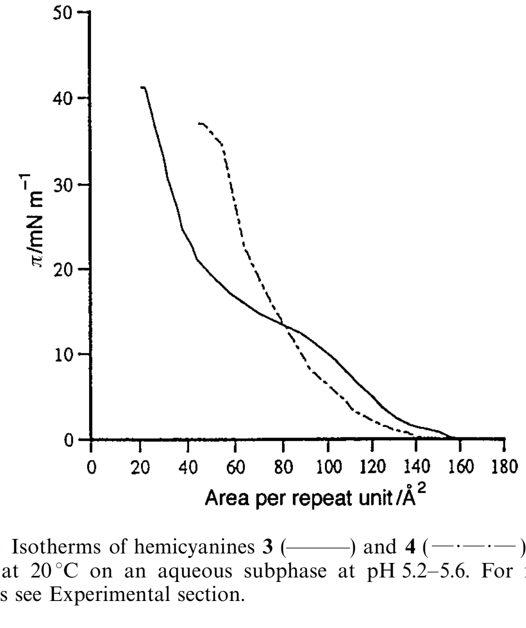


**Fig. 2** Isotherms of hemicyanines **3** (———) and **4** (—·—·—) measured at 20 °C on an aqueous subphase at pH 5.2–5.6. For further details see Experimental section.

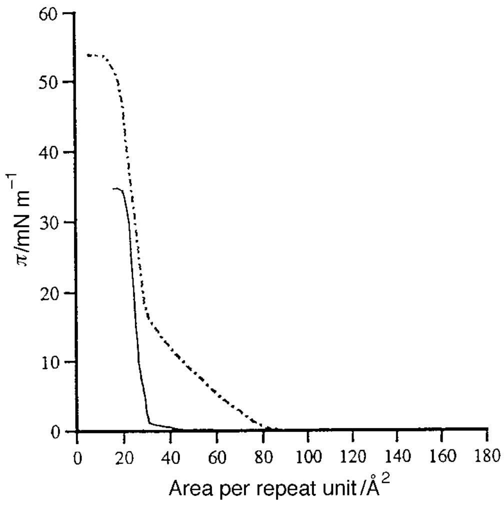


**Fig. 3** Isotherms of azobenzenes **5** (———) and **6** (—·—·—) measured at 20 °C on an aqueous subphase at pH 5.2–5.6. For further details see Experimental section.

The molecule of hemicyanine **4** is amphiphilic and in this case the hydrophilic moiety is close to one end. The isotherm of this compound, shown in Fig. 2, is good, *i.e.* as the area available to the monolayer is reduced the isotherm becomes steep. At this stage, however, the area per repeat unit is approximately twice that of the cross-sectional area of the amphiphile, suggesting it may form bilayers. The collapse pressure is relatively high (>35 mN m$^{-1}$). The isotherm lacks the shoulder present in the isotherm of hemicyanine **3**. Despite many attempts, hemicyanine **4** could not be deposited as a multilayer. The reasons for this are not clear.

Azobenzene derivative **5** contains the 4-*N*,*N*-dialkylamino-4′-nitroazobenzene SHG chromophore and similar compounds have been studied before.[30,31] Compound **5** gave a good isotherm, see Fig. 3, and the area per repeat unit at 30 mN m$^{-1}$ of 22 Å$^2$ is close to the cross-sectional area expected for this chromophore. Unfortunately, the monolayers deposited on both the upstrokes and downstrokes with deposition ratios of only 0.70. This is probably a consequence of the modest hydrophilicity of the nitro group and it prompted the synthesis of compound **6** in which the hydrophilicity of the nitro group is reinforced by a carboxylic acid group. It is interesting to note that the UV spectra of compounds **5** and **6** in chloroform have maxima at 488 and 489 nm respectively indicating that for steric reasons the carboxy moiety in compound **6** is not planar with the aromatic ring. Azobenzene derivative **6** also gave a good isotherm: see Fig. 3. The monolayers transferred well on both the upstrokes and downstrokes (deposition ratios 1.00 ± 0.05). In an X-ray reflection study, the multilayers gave two orders of Bragg reflections corresponding to a *d*-spacing of 48.5 Å. The UV spectra of the LB films of compounds **5** and **6** display $\lambda_{max}$ at 468 nm, suggesting that in both systems there is some aggregation of the chromophores.

On the basis of the above studies hemicyanine **3** and azobenzene derivative **6** were selected for the SHG studies though in both cases the multilayers are not especially well ordered.

### Preparation and properties of alternating multilayers

Polymer **2** was used to form the 'inactive' layers in the alternating LB multilayers. This polymer has an excellent

**Table 1** Properties of monolayers at the air–water interface and Langmuir–Blodgett films of various amphiphiles

| | | features of isotherm | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | area per repeat unit/Å$^2$ | | collapse pressure, $\pi_c$/mN m$^{-1}$ | LB film deposition ratio[b] | | X-ray data on LB film | | | UV spectrum $\lambda_{max}$nm | |
| entry | amphiphile(s) | at 0 mN m$^{-2}$,[a] $A_0$ | at 30 mN m$^{-2}$, $A_{30}$ | | Downstroke | Upstroke | no. of layers in LB film[c] | no. of orders of Bragg peaks | $d$/ spacing/Å | in solution | LB film |
| 1 | Compound **3** | 55 | 34 | 41 | 0.05 | 0.95 | 150 | 1 | *ca.* 47 | 497 | 378<br>470 |
| 2 | Compound **4** | 58 | 41 | 36 | — | — | — | — | — | 506 | — |
| 3 | Compound **5** | 28 | 22 | 34 | 0.70 | 0.70 | 150 | 1 | 40.1 | 488 | 468 |
| 4 | Compound **6** | 29 | 24 | 53 | 0.98 | 1.00 | 150 | 2 | 48.5 | 489 | 468 |
| 5 | Polymer **2**[d] | 44 | 37 | 47 | 1.00 | 1.00 | 150 | 5 | 45.4 | — | — |
| 6 | Compound **3** (upstroke) plus polymer **2** (downstroke) | — | — | — | 1.00 | 1.00 | 40 | 1 | 46.0 | — | — |
| 7 | Compound **6** (upstroke) plus polymer **2** (downstroke) | — | — | — | 1.00 | 1.00 | 40 | 1 | 46.7 | — | — |

[a] By extrapolation of the ‘solid’ section of the isotherm to zero pressure. [b] Values ± 5%. [c] Monolayers were transferred onto hydrophobic silicon at a surface pressure of 30 mN m$^{-2}$. [d] Data quoted is taken from reference 10.

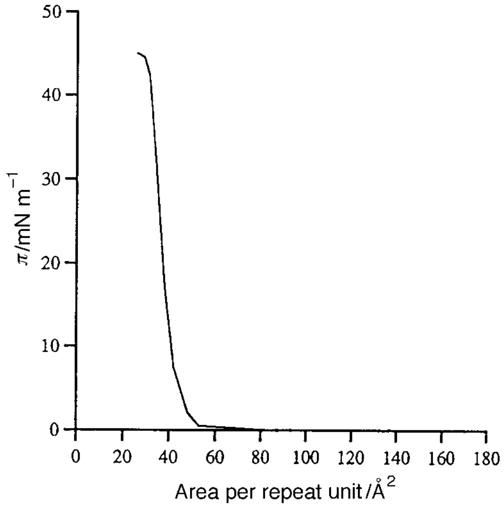


**Fig. 4** Isotherm of polymer **2** measured at 20 °C on an aqueous subphase at pH 5.2–5.6. For further details see Experimental section.

isotherm, see Fig. 4, and it deposits onto hydrophobic silicon wafers to give multilayers which display four or five orders of Bragg peaks.[10] As determined by X-ray reflection experiments the bilayer spacing is 45.4 Å. This value and FTIR measurements indicate that the films have a Y-type structure with the alkyl side chains interdigitated,[10] *i.e.* in the general arrangement shown in Fig. 1 but with both amphiphiles polymeric.

Alternating multilayers were prepared using each of compounds **3** and **6** with polymer **2**. The 'active' compounds were deposited on the upstrokes and the polymer on the downstrokes. For each system several separate films containing up to 70 bilayers were prepared. X-Ray reflectivity studies were made on examples of each type. In each case one order of Bragg reflections was observed. Thus, both types of alternating multilayers appear to be less ordered than those of polymer **2** alone. For the multilayers prepared using compound **3** and polymer **2** the Bragg peak corresponds to a *d*-spacing of 46.7 Å: for the multilayers prepared using compound **6** and polymer **2** it corresponds to 46.0 Å. These values are only slightly more than that of polymer **2** alone and suggest that in the alternating films the long side chains are either interdigitated and/or are greatly tilted from the normal.

Further alternating multilayers were deposited on fused quartz and their UV absorption measured. In each case the plot of absorbance at the wavelength of the main maximum, see Fig. 5, was a straight line up to thicknesses of *ca.* 60 bilayers, which is equivalent to *ca.* 0.33 μm. It is evident that beyond that thickness deposition was less regular. The all-polymeric SHG films studied previously deposited regularly up to at least 300 bilayers,[8] so the present films appear to be less satisfactory in this respect.

## SHG studies

SHG measurements were taken on the above alternating multilayers precisely as described in our previous papers.[15–17] The incident and detected light waves were linearly polarised in the plane of incidence and reflection, and a wavelength of 1.064 μm was used: $I_{2\omega}$ values were referenced to the signal from a quartz crystal and are considered accurate to $\pm 5\%$. The results are shown in Fig. 6 from which it is apparent that in each system $I_{2\omega}$ increases quadratically with the number of bilayers as predicted by theory up to at least 60 bilayers. The extent of scatter in the results is a measure of the reproducibility between samples. Interestingly, the best-fit straight line through both plots does not pass through zero. This has been found to be the case with a number of thick multilayers we have investigated,[8,32] and it suggests that the first 10 to 20 layers deposited pack differently to the subsequent layers.

Since the SHG signals are close to the longest wavelength maxima in the UV spectra of the chromophores, $I_{2\omega}$ may be partly resonance enhanced. This and the lack of knowledge of properties such as the local field effects within the layers makes it difficult to assess accurately the molecular chromophore hyperpolarisability response $\beta$. A study of the angle of incidence variation of the SHG response can allow an estimate of chromophore tilt assuming a one-dimensional model of chromophore non-linear response.[33] The conventional model for an LB film is that the chromophore axes are tilted from the perpendicular to the film with a very narrow angular distribution. A numerical fit to the incidence angle dependence of the SHG from these films indicates that using this model for the alternating multilayers prepared using hemicyanine **3** the chromophores are tilted at an angle of *ca.* 50° to the perpendicular and that in the multilayers prepared using azobenzene derivative **6** the tilt is 30°.

The slopes of the plots shown in Fig. 5 correspond to effective non-linear susceptibilities $\chi_{pp}^{(2)}$ of 17.5 and 9 pm V$^{-1}$ for the hemicyanine and azobenzene films respectively. The local modification to the optical field in these materials is difficult to quantify, but is often considered to be of the order of unity;[34] the local field effect might be discernible as an

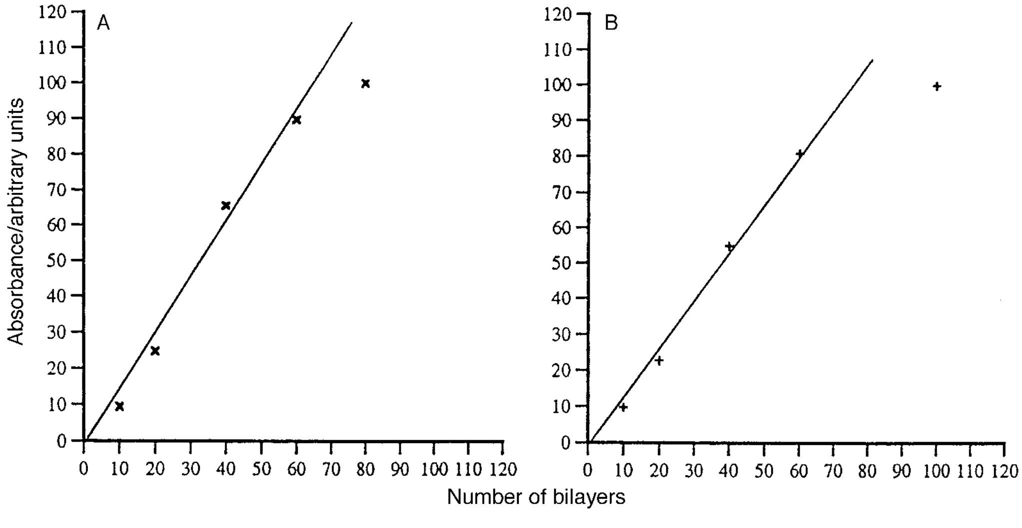


**Fig. 5** Plots of UV-absorbance *versus* the number of bilayers for Langmuir–Blodgett films prepared from: A, hemicyanine **3** and polymer **2**, and B, azobenzene **6** and polymer **2**. For further details see Experimental section.

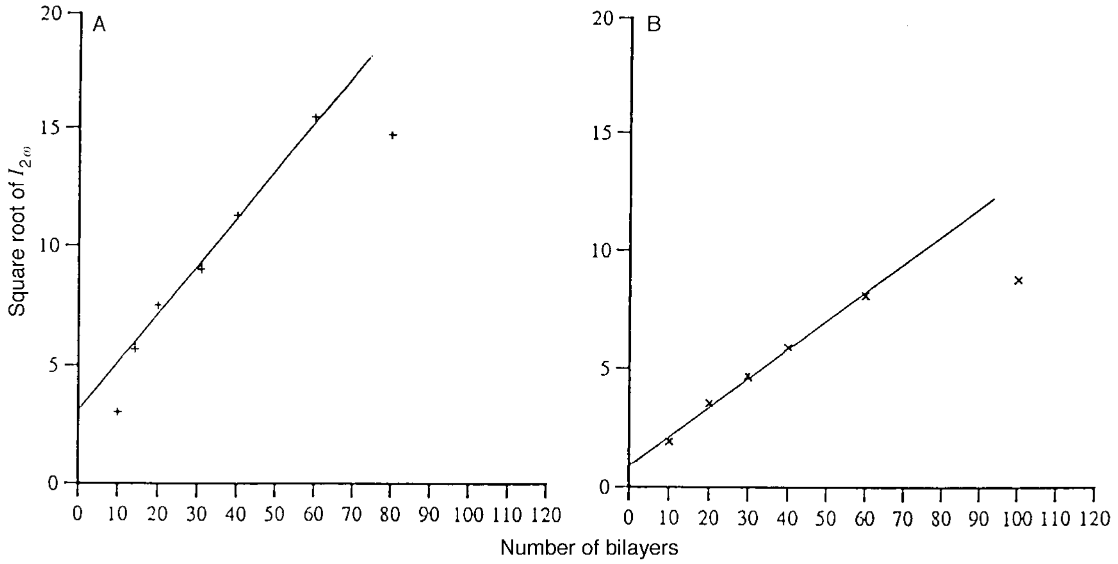


**Fig. 6** Plots of the square root of the intensity of the second harmonic light *versus* the number of bilayers for Langmuir–Blodgett films prepared from: A, hemicyanine **3** and polymer **2**, and B, azobenzene **6** and polymer **2**. For further details see Experimental section.

apparent change in the non-linear response of a chromophore. Without explicit allowance for the effects of local fields, the results indicate a unidirectional chromophore hyperpolarisability $\beta$ for hemicyanine **3** of $88 \times 10^{-50}$ $C^3$ $m^3$ $J^{-2}$ corresponding to a peak conversion efficiency to the second harmonic of $5 \times 10^{-5}$ per hemicyanine layer in the film, expressed relative to the conversion efficiency from the quartz. Estimation of a hyperpolarisability in this way is considered only accurate to about $\pm 30\%$, but our estimate corresponds closely to previous values quoted ($\sim 83 \times 10^{-50}$ $C^3$ $m^3$ $J^{-2}$) for hemicyanine molecules in LB films.[20] The corresponding hyperpolarisability for the azobenzene **6** is estimated to be $\beta = 30 \times 10^{-50}$ $C^3$ $m^3$ $J^{-2}$. This compares with a value of $17 \times 10^{-50}$ $C^3$ $m^3$ $J^{-2}$ determined[35] for Disperse Red I, which has the same chromophore as compound **5**. Thus the presence of the carboxy group in compound **6** appears to result in a modest increase in the $\beta$-value over that of compound **5**.

### Stabilities of alternating SHG multilayers

As a check on the stability of the films prepared from hemicyanine **3** and polymer **2** an LB film consisting of 30 bilayers was kept in the dark[18,19] at 20 °C for 12 months. The intensity of the SHG light was then remeasured. $I_{2\omega}$ was found to be only 50% of the value when it was freshly prepared. Heating the film at 50 °C for 72 h caused $I_{2\omega}$ to fall to 20% of the original value. The stability of the film prepared from azobenzene derivative **6** and polymer **2** was checked similarly. After 12 months at 20 °C it fell to 50% of the original value, and after heating at 50 °C for 72 h, $I_{2\omega}$ fell to zero. In our earlier work[8] the multilayers prepared from polymers **1** and **2** showed no detectable loss of the SHG signal either after being stored at 20 °C for 8 months or after being kept at 60 °C for 96 h. It is clear that the films studied in the present work are of similar stability to each other, but that both are significantly less stable than the all-polymeric films described previously.[8] Whilst this is not entirely surprising, since in a tightly packed molecular arrangement polymer molecules, being large, will move less freely than small molecules, the magnitude of the difference is, in the present context, disappointing.

It should be noted here that electrically poled polymer films have been described recently with comparable non-linear coefficients, of the order of $\sim 10$ pm $V^{-1}$, capable of a stable response throughout at least 1000 h at 100 °C.[36]

## Conclusions

Alternating LB multilayers have been prepared from hemicyanine **3** and polymer **2** and from azobenzene derivative **6** and polymer **2**. With both types of multilayer the intensity of the SHG signal, $I_{2\omega}$, increases essentially with the square of the number of layers up to a thickness of *ca.* 60 bilayers: see Fig. 6. The slopes of the plots correspond to $\chi^{(2)}$ values of 17.5 and 9 pm $V^{-1}$ respectively. Although these properties and their stabilities over time compare favourably with many other LB films described in the literature, these films prepared from 'active' non-polymeric amphiphiles and a 'passive' polymeric amphiphile are not as satisfactory as the all-polymeric films described previously.[8] Thus, whilst readily available non-polymeric amphiphiles are more convenient to use, the derived LB films are less stable.

We thank EPSRC for financial support.

### References

1 (*a*) *Organic Materials for Non-Linear Optics*, ed. R. A. Hann and D. Bloor, Royal Society of Chemistry, London, 1989; (*b*) *Organic Materials for Non-Linear Optics II*, ed. R. A. Hann and D. Bloor, Royal Society of Chemistry, London 1990; (*c*) *Organic Materials for Non-Linear Optics III*, ed. G. Ashwell and D. Bloor, Royal Society of Chemistry, London, 1993.

2 *Nonlinear Optical Properties of Organic Molecules and Crystals*, ed. D. S. Chemla and J. Zyss, Academic Press, New York, 1987.

3 P. N. Prasad and D. J. Williams, *Introduction to Non-linear Optical Effects in Molecules and Polymers*, John Wiley, New York, 1991.

4 P. Hodge and N. B. McKeown, in *Nonlinear Optical Materials*, ed. R. W. Munn and C. N. Ironside, Blackie, London, 1992, p. 226.

5 M. J. Grundy, M. R. Musgrove, R. M. Richardson, S. J. Roser and J. Penfold, *Langmuir*, 1990, **6**, 519.

6 P. Stroeve, D. D. Saperstein and J. F. Rabolt, *J. Chem. Phys.*, 1990, **92**, 6958.

7 M. Shimomura, K. Song and J. F. Rabolt, *Langmuir*, 1992, **8**, 887.

8 P. Hodge, Z. Ali-Adib, D. West and T. King, *Thin Solid Films*, 1994, **244**, 1007.

9 J. P. Cresswell, M. C. Petty, C. H. Wang, B. S. Wherrett, Z. Ali-Adib, P. Hodge, T. G. Ryan and S. Allen, *Opt. Commun.*, 1995, **115**, 271.

10 F. Davis, P. Hodge, X. H. Liu and Z. Ali-Adib, *Macromolecules*, 1994, **27**, 1957.

11 I. R. Girling, N. A. Cade, P. V. Kolinksy, J. D. Earls, G. M. Cross and I. R. Peterson, *Thin Solid Films*, 1985, **132**, 101.

12 T. Takahashi and K. Sato, *Yakagaku Zasshi*, 1958, **78**, 467.

13 *Vogel's Textbook of Practical Organic Chemistry*, Longmans, London, 1978, 4th edn., p. 687–720.

14 F. Davis, P. Hodge, C. R. Towns and Z. Ali-Adib, *Macromolecules*, 1991, **24**, 5695.

15 P. Hodge, Z. Ali-Adib, D. West and T. King, *Macromolecules*, 1993, **26**, 1789.

16 R. H. Tredgold, S. D. Evans, P. Hodge and A. Hoorfar, *Thin Solid Films*, 1988, **160**, 99.

17 M. Bishop, J. H. R. Clarke, L. E. Davis, T. A. King, F. R. Mayers, A. Mohebati, R. W. Munn, M. M. Shabat, D. West and J. O. Williams, *Thin Solid Films*, 1992, **210/211**, 185.

18 F. H. Quina and D. G. Whitten, *J. Am. Chem. Soc.*, 1975, **97**, 1602.

19 P. Hodge, Z. Ali-Adib, D. West, A. Mohebati and T. King, in ref. 1(*c*), pp. 61–67.

20 I. R. Girling, N. A. Cade, P. V. Kolinsky, R. J. Jones, I. R. Peterson, M. M. Ahmad, D. B. Neal, M. C. Petty, G. G. Roberts and W. J. Feast, *J. Opt. Soc. Am. B.*, 1987, **4**, 950.

21 J. S. Schildkraut, T. L. Penner, C. S. Willand and A. Ulman, *Opt. Lett.*, 1988, **13**, 134.

22 P. Stroeve, D. D. Saperstein and J. F. Rabolt, *Thin Solid Films*, 1989, **179**, 529.

23 M. C. J. Young, R. Jones, R. H. Tredgold, W. X. Lu, Z. Ali-Adib, P. Hodge and F. Abbasi, *Thin Solid Films*, 1989, **182**, 319.

24 H. Ancelin, G. Briody, J. Yarwood, J. P. Lloyd, M. C. Petty, M. M. Ahmad and W. J. Feast, *Langmuir*, 1990, **6**, 172.

25 P. Stroeve, D. D. Saperstein and J. F. Rabolt, *J. Chem. Phys.*, 1990, **92**, 6958.

26 J. Y. Fang, S. J. Xiao, Z. H. Lu, Y. Wei, Z. M. Sun and P. Stroeve, *Solid State Commun.*, 1991, **79**, 985.

27 X. Liu, L. Liu, Z. Chen, X. Lu, J. Zheng and W. Wang, *Thin Solid Films*, 1992, **219**, 221.

28 W. F. A. Su, T. Kurata, H. Nobutoki and H. Koezuka, *Langmuir*, 1992, **8**, 915.

29 M. A. Carpenter, C. S. Willand, T. L. Penner, D. J. Williams and S. Mukamel, *J. Phys. Chem.*, 1992, **96**, 2801.

30 D. W. Kalina and S. G. Grubbs, *Thin Solid Films* , 1988, **160**, 373.

31 I. Ledoux, D. Josse, P. Vidakovic, J. Zyss, R. A. Hann, P. F. Gordon, B. D. Bothwell, S. K. Gupta, S. Allen, P. Robin, E. Chastaing and J. C. Dubois, *Europhys. Lett.*, 1987, **3**, 803.

32 D. West, D. Dunne, P. Hodge, N. B. McKeown and Z. Ali-Adib, *Thin Solid Films*, in press.

33 S. Allen, *Inst. Phys. Conf. Ser.*, 1989, **103**, 163.

34 N. Wiser, *Phys. Rev.*, 1963, **179**, 62.

35 K. D. Singer and J. H. Andrews, in *Molecular Nonlinear Optics: Materials, Phys. and Devices*, ed. J. Zyss, Academic Press, London, 1994, ch. 6, p. 252.

36 Y. Shi, W. Wang, W. Lin, D. J. Olsen and J. H. Bechtel, *Appl. Phys. Lett.*, 1997, **70**, 1342.

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