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NLO properties of polymeric Langmuir–Blodgett films of sulfonamide-substituted azobenzenes

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The behaviour at the air/water interface of polymeric materials containing sulfonamide-substituted azobenzene chromophores has been investigated using surface pressure *versus* area measurements. Langmuir–Blodgett (LB) films of the polymers have been built up and then studied using X-ray diffraction. The polymer which gave the best organised LB film has been used to prepare an alternating Y-type multilayer structure with a polymer inactive in non-linear optics. The obtained film has a well-ordered polymeric LB structure giving three Bragg peaks. A series of films with various numbers of bilayers within the range from 2 to 80 has been prepared and the second harmonic generating properties of the films investigated. The measured intensity of the SH signal produced from incident light of wavelength 1064 nm was proportional to the square of the number of bilayers. The alternating LB films exhibited a non-linear susceptibility of up to 24 pm V^{-1} corresponding to a chromophore non-linear vector susceptibility of magnitude $\chi_{zzz}^{(2)} = 170$ pm V^{-1}.

Introduction

Non-linear optics has been recognised for several decades as a promising field with important applications in the domain of opto-electronics and photonics.[1–3] Inorganic crystals, such as $LiNbO_3$, or KH_2PO_4, have long been used as non-linear optical (NLO) materials and electro-optic devices that use them are already on the market. However, recent results suggest that organic materials might be a better choice for use in non-linear optical applications,[4–12] because they offer ultrafast response times, lower dielectric constants, better processability characteristics, and enhanced NLO responses relative to the traditional inorganic solids. NLO chromophores can be incorporated into a macroscopic environment in a variety of ways. Probably, the most important and most widely used methods are the incorporation of dipolar chromophores into a polymer host by simply dissolving the chromophore in a polymeric matrix (guest–host system),[13–15] by covalent attachment of the chromophores to a polymeric backbone (side-chain polymers),[16–21] or by incorporation of the chromophores into the backbone of a polymer (main-chain polymers).[22] Second-order NLO materials must not only contain second harmonic (SH) chromophores, but these chromophores must be arranged macroscopically in a non-centrosymmetric manner. This can be achieved in several ways, such as: formation of appropriate crystals, poling using an electric field,[16–18,23–26] production of certain types of Langmuir–Blodgett (LB) films, [15,24,27–40] and making artificial superlattices by self-assembly techniques.[41–44]

The LB approach offers the advantage of much greater chromophore alignment and chromophore density. Unfortunately, LB multilayers prepared from non-polymeric amphiphiles are generally physically fragile and prone, over an extended period of time, to molecular reorganisation.[45–47] LB multilayers prepared from amphiphilic polymers, although less organised initially, are generally physically more stable and can be expected to be less prone to reorganisation. Moreover, by the LB technique a non-centrosymmetric arrangement can be achieved easily using X- or Z-type deposition of the multilayers,[48–50] by deposition of a Y-type alternating film where just one component contains an SH chromophore,[51–55] or by alternately depositing two NLO-active materials whose chromophores are oppositely oriented with respect to SH generation.[27,56]

In this paper, we report the preparation and study of LB films with SH 'active' polymers in combination with 'passive' polymer (**5**) (Fig. 1). Polymers (**1**)–(**4**) contain chromophores, which according to semiempirical and *ab initio* calculation, possess high non-linear optical responses.[57] In our investigations we have chosen chromophores with sulfonyl moieties as the NLO-active groups, because they offer some advantages. Thus, the sulfonyl group exhibits strong electron withdrawing properties and being bifunctional, allows greater freedom in the design of an amphiphile for a specific application.[58] For example, it can form a link between a large conjugated π-framework like an aminoazobenzene moiety and a hydrophilic group (NH) which can anchor the molecule to an aqueous interface. Thus, molecules with such chromophores are expected to be useful in the LB approach. In addition, the increased transparency in the visible spectrum of the SH-compound where sulfonyl acceptor groups are used in place of NO_2 groups seems to be especially important for applications in non-linear optics.

Experimental

^1H NMR spectra were recorded on a Bruker AMX 300 MHz apparatus in $(CD_3)_2SO$ in the presence of TMS as a standard. IR spectra were recorded on ATI Mattson Genesis Series FTIR spectrophotometer for KBr discs. UV spectra were recorded on a Varian Cary 1 spectrometer. The GPC analyses were carried out using 4 × 30 cm Waters Styragel columns (10^6, 10^4, 10^3 and 500 Å) with tetrahydrofuran (flow rate 1 ml min^{-1}) as the elution solvent. The results were referenced to polystyrene standards.

Polymer (**1**) was obtained by the radical copolymerization of *n*-octadecyl methacrylate (1.1 g, 3.2 mmol) with the acrylate ester of 4-(4-*N*-methyl-*N*-2-hydroxyethylaminophenylazo)-*N*-(thiazol-2-yl)benzenesulfonamide (1.5 g, 3.2 mmol) in dioxane (60 cm^3) under nitrogen at 65 °C for 48 hours with AIBN (0.26 g) as the initiator. The final reaction mixture was poured into methanol, the precipitate collected by filtration and reprecipitated three times using a THF–methanol system. The

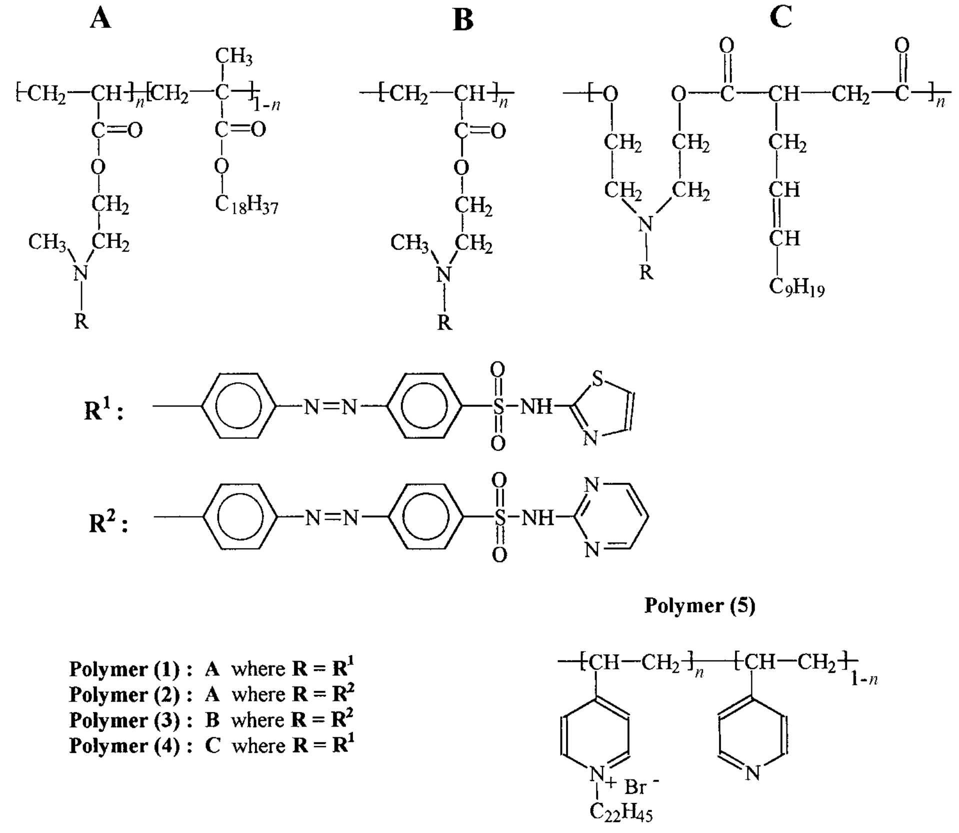

Fig. 1 Structures of polymers: polymer (**1**), polymer (**2**), polymer (**3**), polymer (**4**), polymer (**5**).

product had IR (KBr): 2923, 2851 (ν_{CH_2}); 1729 ($\nu_{C=O}$); 1602, 1583 ($\nu_{C=C_{arom.}}$); 1444 (δ_{CH}); 1384, 1166, 1135 (ν_{SO_2}); 947 ($\delta_{C=CH}$). UV (THF): λ_{max} 436. Found: C 64.39, H 8.54, N 7.09, S 6.23. Calculated for 1 : 1 copolymer ($C_{43}H_{63}N_5O_6S_2$) requires C 63.75, H 7.84, N 8.64 and S 7.92%. By GPC it had M_n 2803 and M_w 4481.

Polymer (**2**) was prepared by the radical copolymerization of *n*-octadecyl methacrylate (1.1 g, 3.2 mmol) with the acrylate ester of 4-(4-*N*-methyl-*N*-2-hydroxyethylaminophenylazo)-*N*-(pyrimidin-2-yl)benzenesulfonamide (1.5 g, 3.2 mmol) in dioxane (50 cm^3) under nitrogen at 65 °C for 48 h with AIBN (0.26 g) as the initiator. The final reaction mixture was poured into methanol, the precipitate collected by filtration and reprecipitated three times using a THF–methanol system. The product had IR (KBr): 2922, 2852 (ν_{CH_2}); 1723 ($\nu_{C=O}$); 1602, 1512 ($\nu_{C=C_{arom.}}$); 1447 (δ_{CH}); 1384, 1131 (ν_{SO_2}); 947 ($\delta_{C=CH}$). UV (THF): λ_{max} 430. Found: C 65.49, H 8.80, N 10.04, S 3.82. Calculated for 1 : 1 copolymer ($C_{44}H_{64}N_6O_6S$) requires C 65.64, H 8.01, N 10.44 and S 3.98%. By GPC it had M_n 2057 and M_w 3986.

Polymer (**3**) was synthesised by the radical polymerization of acrylate ester of 4-(4-*N*-methyl-*N*-2-hydroxyethylaminophenylazo)-*N*-(pyrimidin-2-yl)benzenesulfonamide (2.2 g, 4.7 mmol) in dioxane (150 cm^3) under nitrogen at 65 °C for 96 h with AIBN (0.26 g) as the initiator. The final reaction mixture was poured into methanol, the precipitate collected by filtration and reprecipitated three times using a THF–methanol system. The product had IR (KBr): 1727 ($\nu_{C=O}$); 1601, 1582, 1517 ($\nu_{C=C_{arom.}}$); 1444 (δ_{CH}); 1384, 1166, 1134 (ν_{SO_2}); 948 ($\delta_{C=CH}$). UV (THF): λ_{max} 434. Found: C 55.80, H 4.61, N 16.08, S 5.67. Calculated $C_{22}H_{22}N_6O_4S$ requires C 55.63, H 4.76, N 18.02 and S 6.87%. By GPC it had M_n 1113 and M_w 1343.

Polymer (**4**) was prepared by reaction of 4-(4-*N*,*N*-bis-2-hydroxyethylaminophenylazo)-*N*-(pyrimidin-2-yl)benzenesulfonamide (3.58 g, 8.0 mmol) with dodec-2-en-1-ylsuccinic anhydride (2.13 g, 8.0 mmol) in the presence of toluene (10 cm^3) and DMSO (15 cm^3) under nitrogen for 8 h at 150–160 °C. The final reaction mixture was poured into methanol, the precipitate collected by filtration and re-precipitated three times using a THF–methanol system. The product had IR (KBr): 2908, 2849 (ν_{CH_2}); 1713 ($\nu_{C=O}$); 1599, 1513 ($\nu_{C=C_{arom.}}$); 1384, 1135 (ν_{SO_2}); 1083 ($\nu_{C\text{-}O}$), 948 ($\delta_{C=CH}$). UV (THF): λ_{max} 434. Found: C 55.22, H 5.34, N 10.65, S 8.72. Calculated for 1 : 1 copolymer ($C_{35}H_{45}N_5O_6S_2$) requires C 60.40, H 6.52, N 10.06 and S 9.21%. By GPC it had M_n 1728 and M_w 3339.

Polymer (**5**) was available from the other studies.[59] It was prepared by reacting a poly(4-vinylpyridine) of M_v 25 000 with docos-1-yl bromide: 66% of the pyridine residues in the product were quaternised.

Monolayer studies and LB film preparation

All films were prepared on a commercial Langmuir trough (purchased from NIMA) equipped with Wilhelmy pressure sensors. Measurement of isotherms and LB multilayer depositions of individual polymer were carried out on a single-compartment trough (TYPE 2011) with one pressure sensor and a simple dipper. Deposition of alternating layer films was made on a double-compartment trough with two pressure sensors and an alternating dipper. This trough has been described in detail elsewhere.[60] The subphase was doubly distilled, 0.2 μm-filtered water with no additives, at pH 5.2–5.6 (due to exposure to atmospheric carbon dioxide) and at 20–24 °C. Surface films were prepared by dissolving polymer (**1**), (**2**), (**4**), or (**5**) in chloroform, and polymer (**3**) in the mixture of chloroform–THF (9 vol: 1 vol). In each case the concentration was known and was about 0.3 mg mL^{-1}. The LB films were deposited onto Pyrex glass microscope slides, which had been treated with 1,1,1,3,3,3-hexamethyldisilazane to make them hydrophobic.

LB film characterisation

The X-ray reflectivity experiments[61] and SHG measurements (incident laser light of wavelength 1064 nm) were carried out as described previously.[62–64]

Results and discussion

Preparation and properties of monolayers of polymers (**1**)–(**5**)

Monolayers of each of polymers (**1**)–(**5**) were prepared at an air/water interface by in each case placing a solution of the polymer on the water surface and then allowing the solvent to evaporate. Their surface pressure–area isotherms were measured and are shown in Fig. 2. Some properties of the monolayers are included in Table 1.

Polymer (**5**) has been described before.[59] Its isotherm measured in the present work (see Fig. 2) agrees well with that previously reported.

Polymer (**3**) gave an excellent steep isotherm (see Fig. 2) and the spread layer had a relatively high collapse pressure (40 mN m^{-1}). The isotherms of copolymers (**1**), (**2**), (**4**) were less steep and they were shifted to higher values of surface area (Fig. 2). These shifts are clearly due to the incorporation of additional groups (hydrophobic moieties) in the repeat units of the copolymers.

The isotherms of copolymers (**1**) and (**2**) show similar compression behaviour and suggest the monolayers are moderately well ordered. Moreover, the isotherms indicate that at higher surface area the molecules begin to pack into an extended state at the area of approximately 100–120 Å^2 per repeat unit. As compression continues the isotherms eventually become steeper with a limiting molecular area of about 60–70 Å^2 and collapse occurs at a pressure of above 30 mN m^{-1}. This behaviour suggests that at low surface pressure the polar side chains (NLO moieties) of the copolymers are lying flat on the aqueous subphase surface with the hydrocarbon chains (hydrophobic units) protruding away from the surface, and that at higher pressures the polar side groups are packed more tightly and are then also oriented away from the surface.

Copolymer (**4**) forms a film of lower quality monolayer on the water surface. The transition from the gaseous to the liquid phase takes place at the area of about 80 Å^2 per repeat unit, followed by collapse at 40 Å^2 per repeat unit, and a surface pressure of approximately 24 mN m^{-1}.

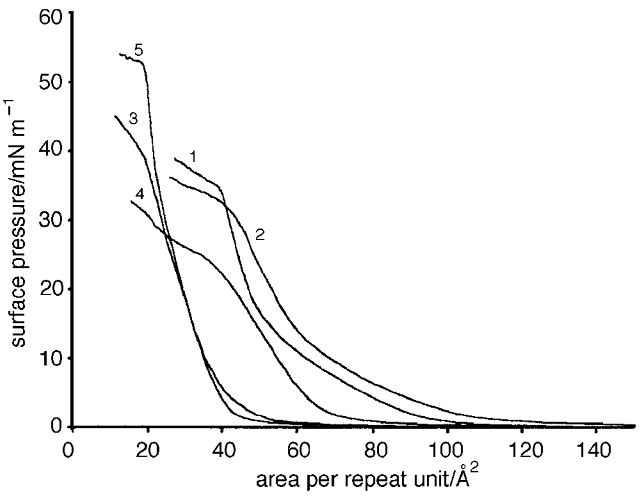

Fig. 2 Surface pressure–area isotherms for polymers measured at 20–25 °C on an aqueous subphase at pH 5.2–5.6.

Table 1 Summary of properties of monolayers and LB films

Film material	Langmuir film area of repeat unit/Å^2 At 0 mN m^{-1}	Langmuir film area of repeat unit/Å^2 At 30 mN m^{-1}	Collapse pressure π/mN m^{-1}	Deposition surface pressure/mN m^{-1}	LB film deposition ratio Downstroke	LB film deposition ratio Upstroke	No. of layers in LB film	X-Ray data No. of Bragg peaks	X-Ray data *d* spacing/Å
(**1**)	56	40	36	15	0.58	0.91	50	1	43.4
(**1**)				25	0.69	0.95	42	1	46.2
(**2**)	70	45	32	29	0.52	0.67	50	1	46.0
(**3**)	40.5	24	40	20	0.84	0.78	50	0	
(**4**)	72		24	15	0.45	0.35	50	1 (vw)[a]	34.3
(**5**)	30	25	53	30	0.47	0.99	60	4	44.3
(**5**)				35	0.50	1.07	60	4	46.8
(**5**)				35	0.99				
and (**1**)[b]				25		1.02	68	3	49.53

[a] vw—very wide. [b] (**5**) and (**1**)—alternate deposition.

LB multilayer deposition of individual polymers

Each polymer was deposited as a Y-type LB film. A summary of the deposition ratios and some properties of the films are given in Table 1.

Polymer (**2**) was deposited from the air/water interface onto a solid substrate at a surface pressure of 29 mN m^{-1}. The multilayers had a bilayer spacing of 46.0 Å as measured by X-ray reflectivity. Just a single diffraction peak was observed.

X-Ray reflectivity studies on the multilayer of polymer (**1**) showed one Bragg peak corresponding to a *d*-spacing of 46.2 Å when the deposition process was carried out at a surface pressure $\pi = 25$ mN m^{-1}. A lower value of the bilayer spacing (43.4 Å) was calculated from the single diffraction peak observed for a multilayer of polymer (**2**) deposited at a reduced surface pressure $\pi = 15$ mN m^{-1}.

The tendency of the bilayer spacing to decrease when the surface pressure at deposition is reduced is as expected. Thus, increase of the surface pressure decreases the area available to the molecules and forces the less hydrophilic parts away from the surface.

A small decrease in the thickness of a film deposited at reduced pressure was also observed in the case of polymer (**5**), which was deposited at surface pressures of 30 and 35 mN m^{-1}. In both cases X-ray reflectivity experiments showed four Bragg peaks corresponding to the bilayer spacing of 44.3 and 46.8 Å, respectively. These results confirm the good organisation of the film of polymer (**5**), which was reported earlier as the best ordered known polymer. In LB films of this polymer there is a tendency to form interdigitated multilayers.[59]

Although polymer (**3**) forms a stable monolayer on the surface of water, several attempts to deposit it onto a glass substrate at various surface pressures did not give any well organised LB films. Thus, the multilayers did not exhibit any Bragg peaks. The most probable reason for their poor ordering is the rigidity of the monolayer of polymer (**3**) mentioned earlier. Even at a low surface pressure the solid plate passing through the interface surface caused the ordered monolayer to disrupt and to collapse. This was evident from yellow streaks appearing on the water surface immediately after the first layer deposition.

Deposition of polymer (**4**) did not give good results. The obtained multilayer was not well-ordered since it showed just one very broad Bragg peak. In this case, the poor quality of the LB film is not surprising. The shape of the isotherm of polymer (**4**) has already suggested that the multilayer is not stable enough. Its deposition could be carried out only at a low value of surface pressure, but then transfer ratios were exceptionally low.

Deposition of alternating LB films

On the basis of the above studies, the polymer (**1**) was selected as the 'active' polymer for SHG studies and polymer (**5**) as the 'passive' polymer. Although multilayers of polymer (**1**) displayed only one Bragg peak it was very sharp and intense. Also the deposition ratios achieved in case of copolymer (**1**) were better than those obtained with the other 'active' polymers. Thus, multilayers of polymer (**1**) seemed to be the best ordered among all the 'active' polymers.

The 'active' copolymer was deposited onto Pyrex glass microscope slides on the upstrokes at a surface pressure of 25 mN m^{-1}, whereas the 'passive' polymer (**5**) was deposited on the downstrokes at a surface pressure of 35 mN m^{-1}. The X-ray reflectivity experiment carried out on the alternating layer film showed three Bragg peaks corresponding to a bilayer spacing of 49.5 Å. These results, summarised in Table 1, prove that the combination of copolymer (**1**) and (**5**) resulted in well organised LB films, which were only slightly less ordered than that of polymer (**5**) alone and much better ordered than that of 'active' polymer (**1**) alone.

Non-linear optical properties of alternating film

SHG measurements were taken on the alternating layer LB film samples ranging from 2 to 80 bilayers in thickness. The incident and detected light waves were linearly polarised in the plane of incidence and reflection, and a wavelength of 1064 nm was used. The intensities of the SHG signals, $I_{2\omega}$, were referenced to a quartz crystal and considered to be accurate within ±5%.

A study of the angle of incidence variation of SHG response makes it possible to estimate the chromophore tilt assuming a one-dimensional model of chromophore non-linear response.[65] 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 indicates that using this model for the alternating multilayers in question results in a chromophore tilt angle in the region of *ca.* 40° to the perpendicular.

Ideally, the intensities of second harmonic generation should depend on the square of the number of bilayers in the sample, for samples less than a micron in thickness. The square root of the maximum second harmonic signal from each sample is plotted in Fig. 3 as a function of the number of bilayers in the samples. A straight line would indicate a uniform and consistent structure in cross-section through the films. The slope of the graph of the peak SHG response with film thickness for these films (see Fig. 3) corresponds to an effective non-linear susceptibility $\chi_{pp}{}^{(2)} = 16$ pm V^{-1}. The chromophores within each layer are tilted 40 degrees from the perpendicular, with random azimuth, and using the assumption that the local field correction within the film is negligible this value of average bulk susceptibility corresponds to individual vector chromophore nonlinear susceptibility directed uniquely along the chromophore axis *z*, of magnitude $\chi_{zzz}{}^{(2)} = 114$ pm V^{-1}.

Interestingly (as can be seen in Fig. 4), the line, which is the plot of the variation in second harmonic intensity with the thickness of the alternating films of polymer (**1**) and (**5**), does not pass through zero, as would be expected for a film of zero thickness, deposited on a glass substrate. This behaviour has been investigated further by considering independently the thinner series of samples of alternating multilayers from two to 20 bilayers in thickness, with the results shown in Fig. 4. It is seen that the first 20 bilayers deposit as a film with better non-linear susceptibility, observed as an increase in the gradient of the signal variation with film thickness. This has been found to be the case with a number of multilayers investigated before.[53–55] and it suggests that the first few bilayers are arranged in a significantly different way to the subsequent layers, which is a phenomenon often encountered with LB films.

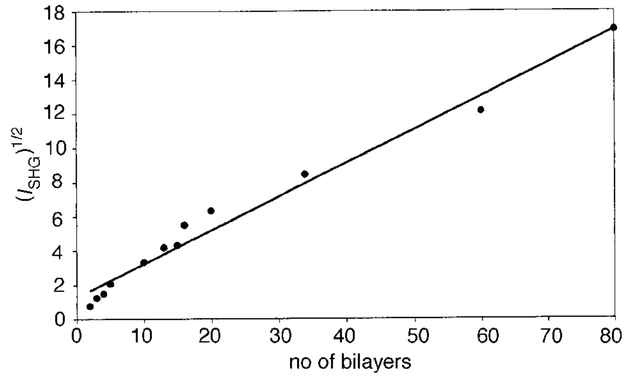

Fig. 3 Plot of the square root of the second harmonic signal *versus* the number of bilayers for the alternating Langmuir–Blodgett films.

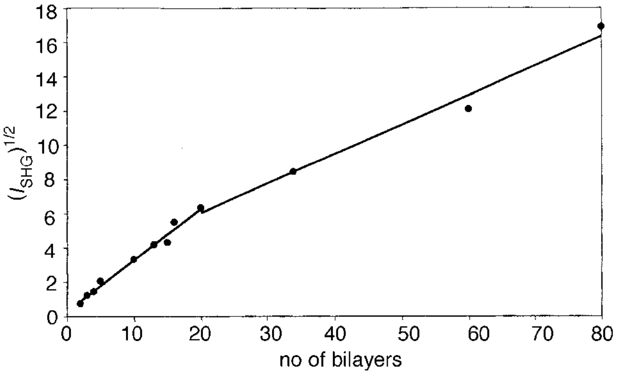

Fig. 4 Comparison of the square root of peak intensity of second harmonic from thin (<100 nm thick) and thicker LB film samples consisting of alternating layers of polymer (**1**) and (**5**).

The first 20 bilayers, corresponding to the first 100 nm of film deposited next to the substrate, exhibit a non-linear performance equivalent to a bulk susceptibility $\chi_{pp}^{(2)} = 24$ pm V^{-1} and chromophore non-linear vector susceptibility of magnitude $\chi_{zzz}^{(2)} = 170$ pm V^{-1}. This section of the line is seen to pass close to the origin as expected.

Conclusions

The homopolymer (**3**) gives a good quality isotherm, but the insufficient flexibility of its monolayer brings molecular disordering during deposition. Thus, the incorporation of long hydrocarbon chains into the polymeric backbone is undoubtedly necessary, although it reduces the density of non-linear chromophores. This situation has been met previously in the case of copolymers. Copolymers (**1**) and (**2**) exhibited a relatively good ability to form LB films. Moreover, the combination of polymer (**1**) as an 'active' and polymer (**5**) as a 'passive' polymer affords an excellent LB multilayer structure, exhibiting a high bulk non-linear susceptibility of 14 pm V^{-1}, comparable to some other results, but exceeding them with better ordering.[52–55] Thus, the X-ray reflectivity studies have shown three diffraction peaks, whereas the known NLO-alternating polymeric films reported earlier exhibited only one Bragg peak. The alternating film of polymers (**1**) and (**5**) may support several optical waveguide modes. The azobenzene chromophores with the sulfonyl group are almost transparent at the harmonic wavelength of 532 nm. The reduced absorption may extend the useful lifetime of devices through a lower operating temperature and improved operational stability.

Acknowledgements

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