

A SIMPLE METHOD FOR THE INCORPORATION OF LOW MOLECULAR WEIGHT DYES IN ULTRATHIN FILMS*

Yu-bao Zhang, C. Geraldine Bazuin**, Carmen M. Tibirna and Qing Lu

*Centre de Recherche en Sciences et Ingénierie des Macromolécules (CERSIM),
Département de Chimie, Université Laval, Québec (QC), Canada G1K 7P4*

Abstract A simple method for the fabrication of ultrathin films containing low molecular weight dye material is introduced (post-adsorption technique). The chromophore used is 4-nitro-4'-decyloxy azobenzene quaternary ammonium salt (azo-10Q). In classical layer-by-layer (LBL) procedures, where the substrate is dipped alternately into the chromophore solution and the complementary polyelectrolyte, the chromophore tends to desorb from the film during subsequent immersion in the polyanion solution, and there is little or no indication of multilayer growth. The extent of desorption depends somewhat on the selection of polyelectrolyte, the ionic strength and the pH of solution. An alternative approach is to first prepare conventional LBL films from a pair of oppositely charged polyelectrolytes, and then to soak this film into the chromophore solution, where adsorption by penetration into the LBL film may take place. In preliminary results, a linear dependence of UV absorbance on layer number of LBL film thus prepared was found, demonstrating the apparent effectiveness of the post-adsorption technique for the preparation of azo-10Q-containing ultrathin films.

Keywords Ultrathin films, Layer-by-layer, Azo derivatives, Polyelectrolytes, Supramolecular complexes

INTRODUCTION

Our laboratory has made extensive investigations of supramolecular complexes of functionalised mesogens with oppositely charged polyelectrolytes or other complementary functionalised polymers^[1]. We showed that thermotropic liquid crystalline (LC) materials can be generated by ionic complexation between two such components, even when neither are liquid crystalline by themselves^[2]. Our studies have been focussed mainly (but not exclusively) on supramolecular LC materials with *sidechain* architecture self-assembled by complementary *ionic* interactions. Most frequently, the non-covalent or ionic bonding takes place at or near the polymer backbone (see schematic a)^[2–6]. A major advantage of this approach is that a wide variety of simple, often commercially available, functional polymers can be used. The non-covalently attached sidechain is any typical low molar mass mesogen (or simple surfactant) that is fitted with an appropriate functional group promoting specific association with the polymer. The use of small molecules and simple polymers, from a synthetic standpoint, allows for ease and versatility in modifying many molecular parameters, and therefore in tailoring materials for particular applications. Furthermore, it opens the door to combining properties of polymers and of small molecules advantageously. In a second class of supramolecular polymers that we are developing, the noncovalent or ionic interaction is located far from the polymer backbone (see schematic b)^[7–9]. These give systems with greater polymeric character than those of the first class, again with much versatility by the choice and proportion of small molecules used.

* The financial support of NSERC (Canada) and FCAR (Québec) is gratefully acknowledged.

** Corresponding author: C. Geraldine Bazuin, E-mail: geraldine.bazuin@umontreal.ca

New address: Département de chimie, Université de Montréal, C.P. 6128 Succursale Centre-Ville, Montréal (QC), Canada H3C 3J7

Invited lecture presented at the China-Canada Bilateral Polymer Symposium, 2002, Tianjin, China

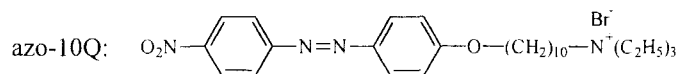
Received March 03, 2003



The above systems have been studied mainly in the bulk, but also at the air-water interface and as Langmuir-Blodgett multilayers^[10, 11]. In particular, a new type of (water-soluble) dye compound, ammonium-functionalized 4-nitro-4'-alkoxy azobenzene has been synthesized and studied in both the bulk^[12] and at the air-water interface^[10]. Besides the highly conjugated azobenzene group, which acts as an efficient nonlinear optical chromophore, this compound possesses both thermotropic liquid crystal and surfactant characteristics. In the bulk, the dye by itself is crystalline and melts directly into the isotropic phase, but, when complexed to polyelectrolytes, it forms a liquid crystalline phase of the single-layer smectic A type over a wide temperature range, with a prominent glass transition near ambient temperature, a weak second glass transition-like transition near 100–120°C, and a reversible mesophase – isotropic transition at high temperature. At the air-water interface, a stable polyion-complexed monolayer forms, and preliminary results show that the transferred LB film, which is of the Z-type, displays stable nonlinear optical properties (second harmonic generation), *i.e.*, ordered asymmetric ultrathin assemblies could be prepared by the LB technique. In this context, it was of interest to explore the possibility of preparing ultrathin films containing these chromophores by the layer-by-layer (LBL) technique.

The formation, structure and functionality of ultrathin films have attracted increasing attention in the past two decades. Various methods for thin film preparation, including the Langmuir-Blodgett (LB) technique, self-assembled monolayer (SAM) techniques and vapour deposition, have been employed. In many cases, ultrathin films with higher ordered or well controlled structure, as well as various functionalities, have been designed. Although sporadic studies were reported as early as the 1960's^[13], the novel method of electrostatic layer-by-layer (LBL) deposition was developed by Decher *et al.* in the early 1990's^[14] and has proven to be a versatile and simple way for thin film preparation of polyelectrolytes, proteins, nanoparticles and dye molecules^[15]. The LBL multilayers are obtained by consecutive adsorption of molecules of opposite charge on a solid surface. Their formation requires that at each step the adsorption inverses the charge of the multilayers. Thus, a limiting factor in LBL multilayer growth is in obtaining sufficient adsorption of each polyion so that complete charge reversal (and not merely neutralization) occurs at the surface after each step.

One of the methods to accomplish functionality of ultrathin films is the introduction of dye molecules into the LBL film. Usually, dye molecules are covalently bonded to the polyelectrolyte chain. There is also a report on the growth of multilayers where the dye molecule is ionically bonded to the polyelectrolyte chain prior to deposition^[16]. Successful multilayer growth has likewise been reported for LBL deposition of polyions and some specially designed dyes usually with bi- or multi-charged groups^[17].



In this paper, we present results of preliminary experiments to introduce one of the ammonium-functionalised azobenzene chromophores mentioned above (the decyloxy variant, azo-10Q, whose molecular structure is shown) into LBL films. We conclude with a particularly promising method based on post-adsorption of the chromophore into previously prepared LBL films. The advantages of this simple method are that, on the one hand, no complex chemical reactions are involved in the preparation of dyes of specially designed structure or polyelectrolytes with a covalently linked dye moiety, and, on the other hand, well controlled thicknesses and dye concentrations and distributions can, in principle, be accomplished by varying the preparation conditions of the LBL polyelectrolyte film and the dipping conditions of the dye molecules.

EXPERIMENTAL

Materials

The synthesis of 4-nitro-4'-alkoxy azobenzene quaternary ammonium salt with a 10-carbon alkyl chain (azo-10Q) is described elsewhere^[10, 12]. Sodium carboxymethyl cellulose (CMC, degree of substitution 0.9, viscosity 3,000–6,000 cps for 1% aqueous solution), sodium poly(vinyl sulfonate) (PVS, 25% solution in water) and poly(4-vinyl pyridine) (P4VP) of molecular weight 200,000 were purchased from Aldrich and used as received.

Pretreatment of Substrate

The glass slides used for LBL fabrication were pre-treated for 30 min in an ultrasonic bath at 25°C in a mixture of ethanol/acetone/chloroform (2/1/1, *V/V/V*) and then in a 2% KOH aqueous solution under the same conditions. After treatment, the slides were thoroughly rinsed with freshly filtered deionized water (Nanopure II, Barnstead) and also stored in this water prior to use. This pre-treatment procedure was used to partially hydrolyse the surface of the support substrate and render a net negative surface charge.

Multilayer Construction

First, a base layer for multilayer deposition was prepared. The pre-treated negatively charged glass slide was immersed in a 0.001 mol/L P4VP/HCl (denoted as P4VP • HCl) solution for 10 min, where the molar ratio of HCl to P4VP is 1:1. After thoroughly rinsing with deionized water and drying with a nitrogen stream, the glass slide was immersed in a 0.001 mol/L PVS solution for 10 min, and again rinsed with deionized water and dried by nitrogen. This base layer containing one layer of P4VP • HCl and one layer of PVS is denoted as (P4VP • HCl/PVS)₁. Subsequently, several series of LBL experiments were made, all at room temperature (about 22°C), with rinsing and drying between two consecutive immersions as described above.

In two series involving two different polyanions, slides covered with the (P4VP • HCl/PVS)₁ base layer were alternately immersed in the azo-10Q and polyanion (CMC or PVS) solutions. The solution concentrations were 1.71×10^{-3} or 5.5×10^{-4} mol/L for azo-10Q, 1.14×10^{-3} mol/L for CMC and variable for PVS (specified in Results). In another series, the effect of added NaCl and NaOH was tested: first, the LBL procedure was effected with 0.10 mol/L NaCl added to the azo-10Q and anion solutions (but not the base layer), and second, the procedure was repeated with 7.0×10^{-2} mol/L NaOH added to the NaCl-containing azo-10Q and anion solutions. The pH's of the solutions were measured by pH paper to be 7 and 13 for the NaCl- and NaCl/NaOH-containing solutions, respectively.

In the third set of experiments, LBL films of additional layers of (P4VP • HCl/PVS) were prepared according the above procedure for the (P4VP • HCl/PVS)₁ base layer. These (P4VP • HCl/PVS)_x films, where *x* indicates the number of (P4VP • HCl/PVS) layers, were then immersed in a 5.5×10^{-4} mol/L azo-10Q solution for about 6 h followed by rinsing and drying as above. It was checked that no significant increase in UV absorbance was obtained for longer soaking times (e.g. overnight, several days), and no additional desorption was observed after much more extensive rinsing than the usual.

Characterisation Method

The amount of adsorbed azo-10Q was monitored by UV-visible spectroscopy, using the UV-visible spectrophotometer HP8450A. The reference for the LBL film measurement was the (P4VP • HCl/PVS)₁ base layer, so that the possible contribution to UV absorbance from P4VP•HCl was subtracted.

RESULTS AND DISCUSSION

LBL Fabrication by Alternate Immersion in Azo-10Q and CMC Solutions

Figure 1 shows the UV absorbance spectra obtained after every two immersion cycles in azo-10Q and CMC solutions (one azo-10Q layer and one CMC layer), where the first immersion of the substrate covered with the (P4VP•HCl/PVS)₁ base layer was in the azo-10Q solution and the last immersion was in the CMC solution. The maximum UV absorbance increases with the number of immersions (dips); however, the increment is small and irregular. Figure 2 gives the intensity of the maximum at $\lambda = 372$ nm after each immersion; that is, after dipping

in the azo-10Q solution as well as after dipping in the CMC solution. It can be observed that, in some cases, the intensity of the absorbance maximum decreases after immersion in CMC compared to after the previous immersion in azo-10Q. This indicates that azo-10Q is washed off during immersion in the CMC solution, which was supported by a slight coloration of the CMC solution. One way this may occur is by complexation to CMC chains, which if non-stoichiometric (*i.e.*, only a fraction of the carboxylate groups of the CMC chains are complexed by azo-10Q) leaves the CMC chains water-soluble^[18] and thus able to drag the azo-10Q back into solution. On the other hand, some azo-10Q remains in the film, as indicated by the non-zero absorption. Since Figure 2 indicates that there is little multilayer buildup, the azo-10Q that is not washed off must be adsorbed in the $(\text{P4VP} \cdot \text{HCl}/\text{CMC})_1$ base layer. Possibly, these azo-10Q molecules have penetrated sufficiently into the base layer to be “out-of-reach” of the competing CMC chains in solution (This idea led to the novel route for preparing azo-10Q ultrathin films that is described in the last part of this paper). In any case, it is clear that immersion in the azo-10Q solution does not result in simultaneous adsorption and charge reversal by an azo-10Q layer that is necessary for adsorbing the subsequent polyanion layer, as has been mentioned for other small molecules with a low number of charges^[16].

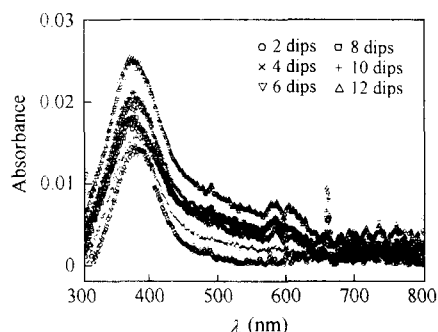


Fig. 1 UV absorbance spectra obtained after each immersion (dip) in the CMC solution for alternate immersions in CMC and azo-10Q solutions, where the number of immersions refers to the total number in both solutions (*i.e.* 6 dips means 3 in CMC and 3 in azo-10Q); the solution concentrations are $c_{\text{azo-10Q}} = 1.71 \times 10^{-3}$ mol/L and $c_{\text{CMC}} = 1.14 \times 10^{-3}$ mol/L.

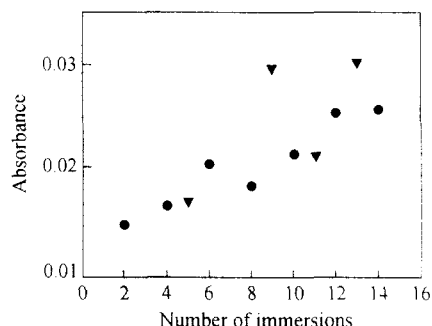


Fig. 2 Variation of the UV absorbance at $\lambda = 372$ nm with number of immersions, alternately in azo-10Q and CMC

The circles correspond to the data of Fig. 1 and the triangles give the UV absorbance measured after immersion in azo-10Q.

The formation and the quality of LBL films are highly influenced by the strength and extent of electrostatic interaction, which can be adjusted by varying the pH (for a weak polyacid or polybase) and the ionic strength of solution. Thus, LBL films were also fabricated, first, from azo-10Q and CMC solutions with added NaCl and, second, with NaOH added to the same solutions. The presence of NaCl was considered to screen the electrostatic interactions of azo-10Q and CMC and possibly to reduce the stiffness of the semi-flexible CMC chains. NaOH increases the charge density of the CMC by ionizing the hydroxyl groups on the CMC backbone.

Figure 3 shows the evolution of the UV absorption maximum with number of immersions for the LBL procedure from the NaCl-containing solutions (pH = 7) and the NaCl- plus NaOH-containing solutions (pH = 13). At pH = 7, the amount of adsorbed azo-10Q in the first immersion is increased (about 2 times) compared to that observed with no added salt (see Figs. 1 and 2) and there is little desorption in the following step; however, there is still no indication of significant multilayer growth during subsequent immersions. When the solution pH is increased to 13 by adding NaOH, the amount of azo-10Q deposited in the first layer is reduced compared to pH 7 (although it is higher than for no added salt or base). Furthermore, when dipped in the basic CMC solution, the azo-10Q is desorbed dramatically – *i.e.*, most of the adsorbed azo-10Q was desorbed back to solution. This may be related to the greater effectiveness of the more highly charged CMC chains to resolubilize the azo-10Q molecules.

LBL Fabrication by Alternate Immersion in Azo-10Q and PVS Solutions

Poly(vinyl sulfonate) (PVS), with its more strongly interacting sulfonate group and more flexible backbone (when the electrostatic interactions are screened by added salt), was also tested for fabricating LBL films with azo-10Q. Figure 4 shows the variation of UV absorbance at $\lambda = 372$ nm with number of immersions, where the even number is the measurement after dipping in PVS solution (see, in particular, the data for $c_{\text{PVS}} = 1.0 \times 10^{-2}$ mol/L). The overall amount of adsorbed azo-10Q is higher than for the corresponding data with CMC. However, the fluctuation of the UV absorbance around 0.04 for most of the immersions indicates that, again, almost no azo-10Q is adsorbed after the first layer. Furthermore, the (moderate) decrease in absorbance after each immersion in PVS indicates desorption of azo-10Q, as observed for CMC. As also shown in Fig. 4, the addition of NaCl or the reduction of the polyanion concentration by two orders of magnitude (or even smaller, not shown) does not affect the overall adsorption – desorption trend very much, and little multilayer growth is observed.

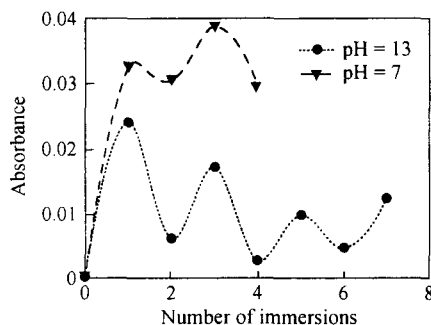


Fig. 3 Variation of the UV absorbance at $\lambda = 372$ nm with number of alternate immersions in azo-10Q and CMC solutions containing 0.10 mol/L NaCl (pH = 7) and 0.10 mol/L NaCl plus 7.0×10^{-2} mol/L NaOH (pH = 13), where $c_{\text{azo-10Q}} = 5.5 \times 10^{-4}$ mol/L and $c_{\text{CMC}} = 1.14 \times 10^{-3}$ mol/L.

The last immersion before measurement is in azo-10Q for the odd numbers and in CMC for the even numbers.

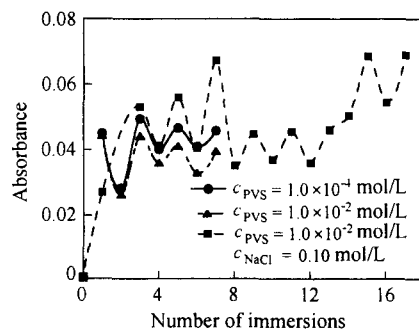


Fig. 4 Variation of the UV absorbance at $\lambda = 372$ nm with number of alternate immersions in azo-10Q and PVS solutions, where the even numbers give the measurements after dipping in the PVS solution, and the odd numbers after dipping in azo-10Q. Data are shown for two different concentrations of PVS (1.0×10^{-4} mol/L and 1.0×10^{-2} mol/L) and one concentration of PVS with added salt ($c_{\text{PVS}} = 2.0 \times 10^{-2}$ mol/L and $c_{\text{NaCl}} = 0.10$ mol/L), with $c_{\text{azo-10Q}} = 5.5 \times 10^{-4}$ mol/L in all cases.

LBL Fabrication of Azo-10Q-Containing Ultrathin Films by Post-Adsorption into Polyelectrolyte Multilayers

As demonstrated above, it is difficult to fabricate azo-10Q-containing ultrathin films using the conventional electrostatic LBL method. Azo-10Q is a small organic dye molecule, with a single ionic charge per molecule, and the adsorbed excess azo-10Q (if any), which is supposed to provide the charge inversion of the multilayer surface, is readily desorbed back to solution during subsequent immersion into the polyanion solution. Thus, the azo-10Q molecules appear to behave as conventional small counterions during electrostatic LBL film fabrication. By contrast, the preparation of LBL films using polyelectrolytes with opposite charges has become a routine method for thin film preparation. Due to the coil conformation of the polyelectrolyte chains, on the one hand, the adsorption inverts the charge of the multilayers at each step; on the other hand, there exists excess or free charges in the electrostatic LBL film, which are not complexed by the oppositely charged polyelectrolytes.

The presence of uncomplexed charges raises the possibility of fabricating azo-10Q-containing thin films by post-adsorption of azo-10Q into previously prepared electrostatic LBL films; that is, a selected number of LBL polyelectrolyte layers are first fabricated and then the resulting multilayer is soaked for some time in the azo-10Q solution, allowing the azo-10Q molecules to penetrate the multilayers and adsorb to the uncomplexed charges (*i.e.* ion-exchange with remaining Na cations). Preliminary results demonstrating the post-adsorption technique are shown in Fig. 5, for which previously prepared $(\text{P4VP} \cdot \text{HCl/PVS})_x$ LBL films were soaked in an azo-10Q solution, and the UV spectra recorded using bare glass slide as the reference. The background is the spectrum of

an LBL film with a single (P4VP • HCl/PVS) layer. Because the UV absorption due to P4VP • HCl is very weak compared with that of azo-10Q in the wavelength range recorded ($\lambda = 300$ to 800 nm), the UV absorbance maximum is considered as a good indication of the amount of azo-10Q adsorbed. Clearly, the UV absorption maximum is much higher than for the experiments described above, and it increases continuously with layer number. This is shown in Fig. 6 where the variation of the UV absorbance maximum as a function of PVS (or P4VP • HCl) layer number, x , in the (P4VP • HCl/PVS) $_x$ multilayer films is plotted. A linear dependence of UV absorbance with layer number is found. This demonstrates the effectiveness of the “doping method” for the preparation of azo-10Q-containing thin films. The experiment was refined by subtracting the UV absorption due to the P4VP • HCl/PVS multilayers for each layer number (that is, two sets of multilayers of each layer number were prepared, one of which was soaked in azo-10Q solution), which confirmed the increase in UV absorbance with layer number deposited. The modified shape of the curves may be indicative of some aggregation of azo-10Q. These preliminary but promising experiments will be followed up by more systematic investigations. The simple method can, in principle, be extended to charged dye molecules and polyelectrolytes of arbitrary structures and may find applications for ultrathin film fabrication with material combinations not possible by spin-coating.

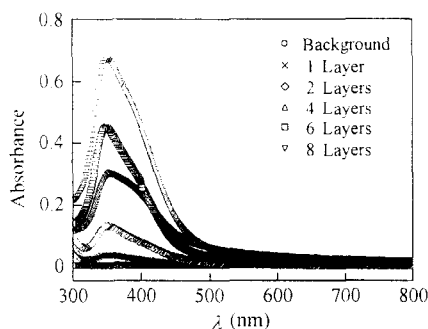


Fig. 5 UV spectra of P4VP • HCl/PVS LBL films after lengthy immersion (~ 6 h) in a 5.5×10^{-4} mol/L azo-10Q solution, where the layer number represents the number of PVS (or P4VP • HCl) layers deposited (*i.e.* each layer corresponds to one PVS plus one P4VP • HCl layer pair)

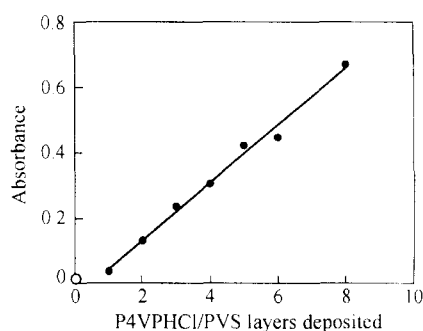


Fig. 6 Variation of the maximum UV absorbance with P4VP•HCl/PVS layer number deposited, as obtained from the UV spectra of Fig. 5 (plus those for 3 and 5 layers)

CONCLUSION

We have successfully prepared ultrathin films of small dye molecules by a simple post-adsorption method based on LBL polyelectrolyte films. The small organic dye molecule, azo-10Q with only one cation group, acts as a counterion during electrostatic LBL film fabrication from alternate dipping between solutions of this dye and a polyanion, and tends to desorb back to solution during subsequent immersion in the polyanion solution. The desorption can be depressed but not eliminated by adding salt to the solutions. There is, however, no indication of multilayer growth of azo-10Q and the polyanion on the substrate. On the other hand, an alternative approach to incorporate small molecules into conventional polyelectrolyte LBL films by post-adsorption provides a promising method for the incorporation of azo-10Q into ultrathin films. This simple method can be extended to charged dye molecules of arbitrary structure and allows the use of polyelectrolytes for ultrathin film fabrication with material combinations not possible by spin coating.

REFERENCES

- 1 Bazuin, C.G., “Design of PLCs with noncovalent bonds”, in “Mechanical and Thermophysical Properties of Polymer Liquid Crystals”, ed. by Brostow, W., Chapman and Hall, Vol. 3, Ch. 3, 1998, p.59

- 2 Bazuin, C.G. and Tork, A., *Macromolecules*, 1995, 28: 8877
- 3 Brandys, F.A. and Bazuin, C.G., *Chem. Mater.*, 1996, 8: 81
- 4 Tork, A. and Bazuin, C.G., *Macromolecules*, 2001, 34: 7699
- 5 Bazuin, C.G., Boivin, J., Tork, A. and Tremblay, H., *Macromolecules*, 2002, 35: 6893
- 6 Brandys, F.A., Masson, P., Guillon, D. and Bazuin, C.G., *Macromol. Chem. Phys.*, 2001, 202: 856
- 7 Vuillaume, P.Y. and Bazuin, C.G., *Macromolecules*, in press
- 8 Vuillaume, P.Y., Bazuin, C.G. and Galin, J.C., *Macromolecules*, 2000, 33: 781
- 9 Vuillaume, P.Y., Galin, J.C. and Bazuin, C. G., *Macromolecules*, 2001, 34: 859
- 10 Panambur, G., Robert, C., Zhang, Y., Bazuin, C.G. and Ritcey, A.M., *Langmuir*, in press
- 11 Garneau, S., Rondeau, Ph., Bazuin, C.G. and Ritcey, A.M., *Macromol. Chem. Phys.*, 2000, 201: 2535
- 12 Tibirna, C.M., "Development of New Supramolecular Polymers of Interest for Non-linear Optical Applications", Ph.D. Thesis, Département de chimie, Université Laval, Québec (QC), Canada, 2003
- 13 a) Iler, R.K., *J. Colloid Interface Sci.*, 1966, 21: 569
b) Tredgold, R.H., Winter, C.S. and El-Badawy, Z.I., *Electron. Lett.*, 1985, 21: 554
- 14 Decher, G., Hong, J.D. and Schmitt, J., *Thin Solid Films*, 1992, 210–211: 831
- 15 a) Decher, G., "Layered nanoarchitectures via directed assembly of anionic and cationic molecules", in: "Comprehensive supramolecular chemistry", ed. by Sauvage, J.P. and Hosseini, M.W., Pergamon Press, Oxford, U.K., 1996, Vol. 9, p.507
b) Advincula, R., "Polyelectrolyte layer-by-layer self-assembled multilayers containing azobenzene dye groups", in: "Handbook of Polyelectrolytes and Their Applications", ed. by Tripathy, S.K., Kumar, J. and Nalwa, H.S., American Scientific, Stevenson Ranch, CA, 2002, Vol. 1, p.65
c) Ferreira, M., Cheung, J.H. and Rubner, M.F., *Thin Solid Films*, 1994, 244: 806
- 16 Das, S. and Pal, A., *J. Langmuir*, 2002, 18: 458
- 17 a) Ariga, K., Lvov, Y. and Kunitake, T., *J. Am. Chem. Soc.*, 1997, 119: 2224
b) Cooper, T., Campbell, A. and Crane, R., *Langmuir*, 1995, 11: 2713
c) Advincula, R.C., Fells, E. and Park, M., *Chem. Mater.*, 2001, 13: 2870
- 18 Goddard, E.D., "Polymer–surfactant interactions part II" and "polymer–surfactant interactions – recent developments", in: "Interactions of Surfactants with Polymers and Proteins", ed. by Goddard, E.D. and Ananthapadmanabhan, K.P., CRC Press, Boca Raton, 1993, Ch. 4 and 5