Langmuir-Blodgett films of amylose-esters and chiral azo-dyes

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CHAPTER 1

Introduction

The first experiments with ordered monolayers at the air water interface by Agnes Pockels [1] in 1891 and ordered multilayers by Katharina Blodgett [2] in 1935 have stimulated intensive research activities in this area, especially the last 10 years. Irving Langmuir developed the theoretical basis on surface science [3,4,5] for which he was awarded the Nobel prize in Chemistry in 1932. Langmuir and Blodgett pioneered in the field of mono-molecular films during 1934-1952 and for that reason, these films are named after them. A great deal of their pioneering work is summarized in the book of Gaines [6].

The Langmuir-Blodgett (LB) technique offers the possibility to obtain highly ordered well defined multilayers and realizes the construction of molecular architectures which allow the study of physical phenomena on a molecular level. Nature uses the ordering of organic molecules with great efficiency in biological membranes, essentially lipid bilayers with adsorbed proteins. Transfering the concepts of the biological membranes to synthetic organic ordered films, novel structures with special properties can be prepared via the LB-technique. The renewed interest in this old technique has been inspired by the many potential technological applications of such films [7]. Examples of possible applications are optical devices, sensors, microlithography, protective layers, conducting layers and surface modification. Reviews on the possible applications of LB-films have appeared in the literature [8,9,10,11,12,13].

This thesis focusses on LB-films with second order nonlinear optical properties. A major application area for second order nonlinear optical (NLO) materials will be in electro-optic devices [14]. These include optical switches and both amplitude and phase modulators. These devices will be used as optical switches in optical fiber networks.

Nonlinear optics.

There are several review articles and books describing nonlinear optical behaviour in detail [15,16,17], a short survey of the relevant theory is given below.

When an electromagnetic wave interacts with a molecule, a polarization **p** is induced in that molecule by the electric field component **E** of the electromagnetic wave. The polarization p can be described by equation (1).

$$\mathbf{p} = \mathbf{a}\, \mathbf{E} + \beta\, \mathbf{EE} + \gamma\, \mathbf{EEE} + \ldots \tag{1}$$

With $p = $ microscopic polarization and the electric field vector E having three components $\mathbf{E_x}$, $\mathbf{E_y}$ and $\mathbf{E_z}$. Each of the electrical field vectors can contribute to the polarization in each of the three directions of the molecule. $\boldsymbol{\alpha}$ is a second rank polarizability tensor with 9 elements $(\alpha,$ $\alpha_{xy}, \ldots \alpha_{zz})$, β is proportional to $\mathbf{E^2}$, and for that it is a third rank polarizability tensor with 27 components $(\beta_{xxx}, \beta_{xxy}, \ldots \beta_{zzz})$. In most cases, molecular symmetry reduces the number of significant tensor elements.

From equation (1) it follows that the second order polarizability is large when β is large. The origin of the hyperpolarizability β of a molecule has been attributed to charge transfer resonances involving appropriate substituted π-electronic systems. A lot of research has been focussed on the design of molecules with high @-values[18,19,20].

Turning from the microscopic to the macroscopic domain, the macroscopic polarizability P can be written according equation (2).

$$\mathbf{P} = \chi^1\, \mathbf{E} + \chi^2\, \mathbf{EE} + \chi^3\, \mathbf{EEE} \ldots \tag{2}$$

where χ^1, χ^2 and χ^3 are tensors with similar meaning to α, β and γ but here they describe the polarization induced in a whole system.

Second order non linearity can only be observed when $\chi^2 \neq 0$ and this is only the case when the system is non centro-symmetric. So, non-centro-symmetry in a film is a requirement for second order non linear optical behaviour.

In second order NLO, the interaction of the light and the molecules induce dipoles in the NLO-material that will emit radiation. For example, when a single beam of a monochromatic light of λ impinges on an appropriate NLO-material, second harmonic light (½ X) can be generated (SHG). This experiment is explained in more detail in Chapter 5 and 6 of this thesis.

Another effect that occurs through χ^2 is the electro-optic or Pockels effect, which is important in integrated electro-optic devices. In such devices the optical signal is modified by the application of an external electric field. The applied external electrical field induces a change

in the dielectric constant of the material [21]. The change of the dielectric constant by the electrical field *can* be very fast in organic materials compared with inorganic materials what makes them attractive materials for devices.

Non-centro-symmetry.

The noncentrosymmetry in a NLO-material is a minimum requirement, and several approaches to obtain such a system have been studied. The classical NLO-materials are inorganic crystals like lithium niobate (**LINbO$_3$**) and KTP (**KTiOPO$_4$**), but an increasing number of organic materials are shown to exhibit second order non linear efficiencies that are several orders of magnitude higher than in **LiNbO$_3$** [15]. Organic materials often exhibit physical properties which are superior to those of inorganic materials like higher damage thresholds to laser beams and **thin** film processing properties.

Organic molecules with high **hyperpolarizabilities** (β) tend to crystallize in centrosymmetric space groups and therefore show no second order linear optical effects. However, organic molecules *can* crystallize in one of the seventeen noncentrosymmetric space groups and Oudar and Zyss [22,23] have made progress in the understanding of the optimal packing of molecules in noncentrosymmetric structures. One absolute way to ensure the absence of a center of symmetry in a crystalline structure is to grow a crystal made of optically pure chiral molecules. This concept was applied by Oudar and Hierle [24] but the resulting structure is not necessarily very much off a centrosymmetric one. **A** complete review of organic crystals in relation to non linear optics is given by Chemla and Zyss [25].

Another approach to obtain noncentrosymmetric structures is the orientation of NLO-dyes in a polymer matrix which offers significant fabrication advantages relative to single crystals. Non linear materials are incorporated in a polymer matrix and the NLO-dye is oriented by heating the system above the **T$_g$** of the polymer and applying a strong DC electrical field. The dye molecules with relative high dipole moments will orient in a noncentrosymmetric manner. By cooling the polymer below the **T$_g$** under the applied DC field, the noncentrosymmetric alignment of the dye molecules is maintained in the polymer matrix. The first published results on this kind of NLO-systems **came** from Meredith, van Dusen and Williams [26]. The **polymer/dye** systems have been improved since then. Much attention has been paid to the number density of the dyes and to the temporal stability of the noncentrosymmetric order. Reviews are given by **Sohn** et al. [27], **Stamatoff** et al. [28] and **Flipse** [29].

Another, hardly described method to obtain ordered NLO-systems is the molecular assembly method [30,31]. Self assemblies generally consist of a head group that is reactive towards a specially prepared substrate and a reactive tail group to activate the deposition of subsequent layers. Up to now the chemistry involved, is associated with serious practical problems and further research is needed [8].

The fourth method to produce noncentrosymmetric structures is the **Langmuir-Blodgett** technique where this thesis is focussed on and this technique will be discussed in more detail on the following pages.

Langmuir-Blodgett technique.

According to the LB-technique, compounds are spread from a dilute solution of a volatile solvent at the air interface on a so called **Langmuir** trough. The solvent evaporates and a monolayer is formed.
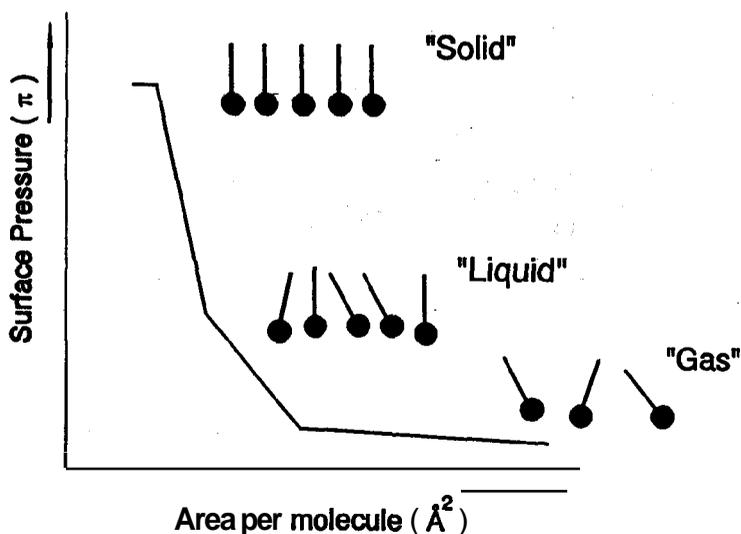

Figure *1.1* *Example of a pressure-area isotherm.*

Compounds suitable for monolayer formation at the air interface are amphiphiles consisting of a **hydrophilic** head group and a long chain hydrophobic substituent which are excellently described in the book of **Gaines** [6]. During the last decade, molecules with complete different structures such as polyphorins [32] and phtalocyanines [33] have been reported to form stable monolayers and LB-films. Also a variety of polymers are suitable for ordered LB-film formation [34], including amphiphilic polymers, for example **poly-(octadecyl)methacrylate** [35,36] but **also** helical forming polymers like poly-isocyanide [37], **poly-(methyl)methacrylate** [38,39,40], **poly-lactide** [41], **poly-glutamates** [42,43] and recently polysilanes [44].

Upon compression of the monolayer the molecules are oriented at the interface. The process of **compression** of a monolayer can be followed by the pressure-area isotherm. An idealized pressure area isotherm of a low molecular amphiphilic compound is shown in Figure 1.1.

In the oriented state, the monolayer can be transferred onto a substrate by dipping the substrate perpendicularly through the water surface. In this way highly ordered ultrathin films can be obtained where the thickness is controlled exactly by the number of dipping cycles. Figure 1.2 shows 1 dipping cycle.
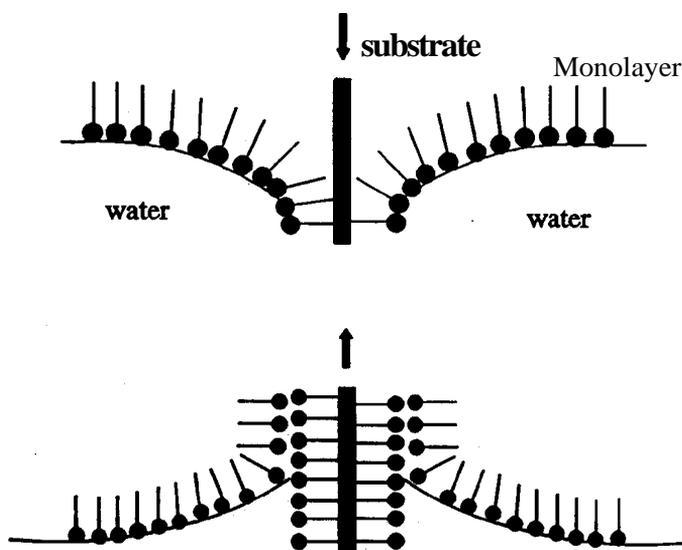
Figure *1.2 Schematic representation of one dipping cycle.*

Depending on the molecules spread at the air water interface, deposition occurs either during the up and down stroke (Y-type deposition), only during the upstroke (2-type deposition) or only on the downstroke (X-type deposition). As a consequence, different molecular orientations are obtained. Figure 1.3 shows the Y-, Z- and X-type structures. Besides these structures, mixed and alternate films can be prepared and examples of these are also drawn in Figure 1.3.

A great advantage of LB-films is that noncentrosymmetric structures can be produced in a controlled way and the highly oriented films that can be obtained. A disadvantage often said, is the in plane domain structure of LB-films wich disturbs the optical applications due to high scattering losses at the domain boundaries. However, polymeric LB-films appeared to have improved properties [45].
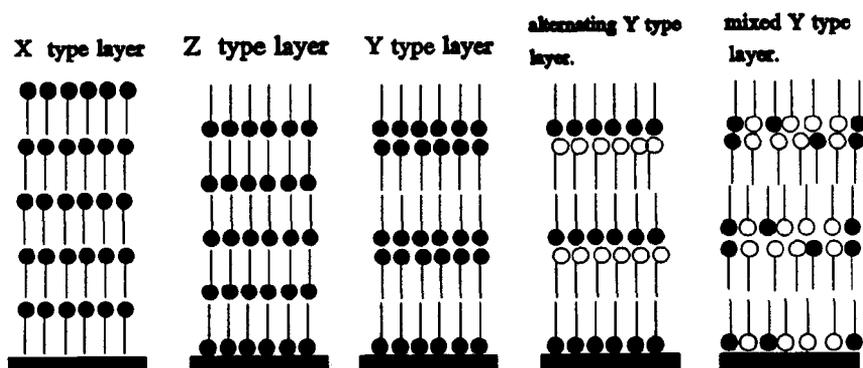
Figure 1.3 *Structures that can be obtained by the Langmuir-Blodgett technique.*

LB-films with non linear optical properties.

A brief review of relevant LB-systems in relation to NLO is given. Aktsipetrov et al. reported the first SHG from a LB-monolayer of 4-octadecylamino-4'-nitro-azobenzene [46]. They were also able to build up 5 layers of the same dye in the Z-mode, resulting in an enhanced SHG [47]. After Aktsipetrov et al., several groups reported on the SHG of LB-monolayers of different dye molecules [48,49,50]. A comparison of different stilbazium salt derivates and phenylhydrazone derivatives was made by Lupo et al [20]. They showed the importance of the tilt angle of the molecule to the substrate normal and the SHG enhancement by resonance if either or both the

fundamental and harmonic frequencies are close to an absorption band of the dye molecule. The pioneering work of **Girling** et al. on hemicyanine dyes [51,52] led to important results. Girling et al. studied SHG of mixed monolayers of a hemicyanine dye with arachidic acid. They showed that the SH intensity of a pure LB-monolayer of dye was ≈ 50% of that measured for a mixed monolayer **dye:arachidic** acid 1:1. This was not expected from the theory [53]. Linear optical absorption spectra [54,55] showed that H-aggregates were formed in the pure dye monolayer.

Aggregates are molecular assemblies often observed in dye molecules. The absorption spectra of dye molecules can vary with their concentration and substrate composition. An absorption spectrum of a dye in a diluted solution is normally adressed as molecular absorption (monomeric or M-band). When the solution is concentrated, the absorption can shift to lower (H-aggregates) or higher (J-aggregates) wavelengths and become sharper compared with the M-band. Aggregation can be considered as the formation of dimers, **trimers** and n-mers. A popular explanation of the changing absorption properties of the molecules is the theory of delocalized electronic states (exciton **theory**)[56,57]. When electronic states of molecules interact strongly, significant electronic overlap between the molecules may occur causing an electronic degeneracy. Whether a transition is allowed to the lower or higher excited state depends on the angle between the transition dipoles and the grow axis of the aggregate. In case of H-aggregates (higher excited state), the transition dipole is perpendicular to the aggregate grow axis.

Experiments with aggregates have interested several groups [54,55,58] but the interpretation of the results are not uniform. Three effects are thought to play an important role: (i) local field effects, (ii) resonance enhancement and (iii) aggregation. (i) Local field effects have been studied by **Hayden** [59] and Cnossen et **al.**[60] and **are** well understood. (ii) Facts about resonance enhancement can be obtained experimentally without too much trouble. (iii) The effect of aggregation on the NLO-activity of organized assembles is an important question but is still not well understood. Chapter 5 of this thesis gives a more extensive discussion on this subject.

A complete different approach to introduce noncentrosymmetry in a LB-film was reported by Decher et al. [61]. They built up regular Y-type layers of pyridine derivatives and obtained a herringbone structure that lacks a center of symmetry. The **SHG** of this herringbone structured films is highly sensitive to the **film** morphology and showed no thermal and mechanical stability. So far, only LB-films of monomeric compounds have been discussed and that is because most research activities have been focussed on monomeric materials. However the use of polymers is more attractive because of the thermal and mechanical stability and the possible amorphous

nature of the polymer films. The first report of SHG of a polymeric monolayer came from **Cam** et al.[62]. They synthesized polysiloxanes with azo side chain groups but did not investigate the multilayer deposition. Reports on related amphiphilic polymers with comparable NLO-activities appeared in the literature [63,64,65]. The first results on SHG of polymeric multilayers with quadratic enhancement of the SHG with the number of layers was given by Anderson et al.[66]. They designed noncentrosymmetric Y-type structures by producing alternate layers of two different substituted NLO-active side chains on polyether backbones. The authors reported an excellent quadratic behaviour for 4 alternating bilayers. So, an encouraging **start** was made. Hsiung et al. developed the idea of Anderson et al. and synthesized two polymers having **hydrophilic** backbones and hydrophobic **perfluor** carbon terminal groups in the side chains [67]. They **succeeded** in **transfering** good quality multilayers with **SHG** response up to 80 bilayers. Another approach to use the excellent properties of polymers concerning stability is mixing suitable polymers with NLO-active dyes. To my best knowledge, one study has been reported in the literature concerning a poly-(methyl)methacrylate LB-film mixed with a NLO-active merocyanine dye [68]. The noncentrosymmetric LB-film appeared to be homogeneously mixed but showed only SHG in an ammonia atmosphere because of the choice of the NLO-dye. The merocyanine dye is **protonated** in air and Daniel and Smith found that this meracyanine dye only shows significant SHG in the deprotonated state [69].

Characterization of LB mono- and multilayers.

The structure of LB mono- and multilayers is extremely important for the possible applications. Various experimental techniques have been employed for determining the packing and molecular orientation in the LB-films. The very limited amount of material involved in LB-films needs the improvement and development of special analytical tools.

During the last decade, a lot of progress has been made in the development of new techniques. Up to now most of the new techniques have been applied to study the model system of cadmium **arachidate** layers. Examples of new techniques in relation to LB-films are scanning tunneling microscopy (STM) [70,71], atomic force microscopy (AFM) [72], high resolution electron energy loss spectroscopy (HREELS) [73], surface **plasmon** microscopy (SPM)[74] and **secondary-ion** mass spectroscopy (SIMS) [75] all suitable for LB-films deposited on special substrates. Recently developed techniques to study monolayers on the air water interface are

surface second harmonic generation spectroscopy [76,77], ellipsometry [78], X-ray diffraction [79] and fluorescence microscopy [80].

In the following section, analytical techniques applied in this thesis will be briefly discussed.

Surface-pressure isotherms   At the air water interface, the pressure area isotherm is still one of the most valuable measurements, giving information about the stability of the monolayer at the air water-interface, the reorientation of molecules in two dimensions, phase- and conformational transitions and molecular 2D dimensions.

Transmission electron microscopy   The surface morphology of a monolayer can be studied by transmission electron microscopy which is a powerful technique for visualization of domains, pinholes and defects. Direct observation of one monolayer is not possible because the lack of contrast [81,82]. A resolution in the order of a nanometer can be reached when appropriate sample preparation techniques are used. Electron diffraction is a useful technique for the determination of the in plane structure of organic film LB-films. LB-films of cadmiumstearate have been studied extensively by electron diffraction [83,84]. To study the two dimensional organic crystal structures, low dose electron diffraction must be used in order to reduce electron beam damage of the sample. Compared to X-Ray diffraction, the interaction with matter is stronger and the electron beam can be focussed down to 5 Å which makes scanning of small details possible.

Fourier Transform Infrared Spectroscopy   To study multilayers, Fourier Transform Infrared spectroscopy (FT-IR) is an excellent technique and has been used by many authors. Infrared spectroscopy has the capability to reveal various conformational features of the molecules in the LB-film and can also be used to determine the orientation of parts of the molecules directly. Different IR-techniques can be used to deduce orientational parameters in the LB-film. The FT-IR techniques used in this study are grazing angle reflection spectroscopy (GIR), sometimes called external reflection spectroscopy and (polarized) transmission spectroscopy. The optics of the GIR-spectroscopy is reported by Greenler [85] and pioneering work is done by Francis and Ellison [86] and Allara and Swalen [87]. P-polarized light reflecting on a metal surface, is only absorbed by vibration modes which have a component of the transition moment perpendicular to the substrate surface. Transition experiments on IR transparent substrates are sensitive to dipole transition moments that are oriented parallel to the substrate surface [88,89].

UV/VIS spectroscopy   When dye molecules are incorporated in LB-films, UV/visible light spectroscopy can give additional information about the structural and orientational features of these molecules.

X-ray *diffraction* X-ray diffraction is a powerful tool for investigating the layer structure of the LB-fdms and it provides accurate information about the thickness of the films [90].

Optical microscopy Optical microscopy in the polarized mode is very useful in the study of often seen domains in LB-films. The size, shape and orientation of domains of LB-films can be observed in **LB-multilayers.** In the polarization mode, the **polarizer** and analyzer are set 90° to one another and domains having optical axis in different directions are observed as contrasting regions [91].

Outline of this thesis.

This thesis focusses on LB-films with second order nonlinear optical properties. The idea of combining best properties of both, high NLO-activities of low molecular weight compounds and the thermal and mechanical stability of polymers, is attractive. Therefore, suitable polymers had to be found and in cooperation with the Organic Chemistry department of the University of Groningen new NLO-dyes with chiral (stereogenic) centers were designed. A mixed system composed of a polymer (arnylose-acetate) and one of the NLO-dyes is studied in detail and is reported in this thesis.

Chapter 1 gives a general introduction on Langmuir-Blodgett films, non linear optical behaviour and important analytical techniques suitable for the characterization of LB-films.

Chapter 2 describes the synthesis of amylose-esters with various alkyl side chains. Amylose-derivatives are chosen because the variety of substituents that can be attached to the OH-groups of the glucose-ring and the hydrophilic nature of the amylose-backbone. The monolayer behaviour is studied as well as the structure of the multilayers of these polymers. Amylose-acetate is a very stable polymer on the air water interface and forms **Z-type** multilayers and this polymer is used as a matrix polymer for the dye molecules studied in Chapter 3, **4** and 5.

Chapter 3 reports on the monolayer behaviour of amylose-acetate mixed with a specially designed NLO-dye, an ester of **palmitic** acid and 4-nitro-4'-[(3R)-hydroxypyrrrolidine-]-**azobenzene,** abbreviated in this thesis as **KMES16.** Attention must be paid to the chiral center (properly said: stereogenic center) of the dye. Unexpected monolayer behaviour of the mixtures is found.

Chapter 4 demonstrates the structural features of multilayers of the same mixture discussed in Chapter 3.

Chapter 5 shows the second harmonic generation of LB-multilayers of mixtures studied in Chapter 3 and 4. The results obtained by these measurements have led to the study of cast films of amylose acetate and **KMES16**. The properties of these films are also discussed in this Chapter.

Chapter 6 deals with a more classical system: two chiral, amphiphilic dyes, **4-[4'-[(3R)-palmitoylpyrrolidine-1-]-phenylazo]-3-nitro-benzoic** acid **(KZ16)** and **4-[4'-[(3R,4R)-dipalmitoylpyrrolidine-1-]-phenylazo]-3-nitro-benzoic** acid (KDEZ16). The structural features of the dyes in the LB-multilayers are reported. The dyes show ideal SHG which offers the possibility to study the influence of the chiral (stereogenic) centers of the dye molecules.

Parts of this thesis have been published (Chapter 2)[92], [93], have been accepted **(Chapter3)**[94], (Chapter 4) [95] or have been submitted for publication [96,97].

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