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

Schoondorp, Monique Annette

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SUMMARY

This thesis describes the structure and second order nonlinear optical behaviour of several Langmuir-Blodgett films. Langmuir-Blodgett (LB) films are ultra thin films produced by the Langmuir-Blodgett technique, named after their inventors (Irving **Langmuir** and **Katharina** Blodgett). According to the LB-technique, compounds are spread from a dilute solution at the air-water interface. The solvent evaporates and a monolayer is formed. Upon compression of the monolayer, the molecules are oriented at the interface. The oriented monolayer can be transferred onto a substrate by dipping the substrate perpendicular through the water surface. In this way highly ordered ultra thin films can be obtained where the thickness is controlled exactly by the number of dipping cycles. The Langmuir-Blodgett technique realizes the construction of well defined molecular architectures which are necessary in second order non linear optical active systems.

Second order nonlinearity can be observed when a strong electro-magnetic field interacts with material. When an electro-magnetic wave interacts with material, a polarization P is induced. When the electro-magnetic field is not very strong, the induced polarization can be described with:

$$\mathbf{P_{ind}} = \chi^{(1)} \mathbf{E}$$

P_{ind} = induced polarization in the material   (1)

$\chi^{(1)}$ = susceptibility tensor

E = electro-magnetic field

The susceptibility $\chi^{(1)}$ is linear dependent with the refractive index of the material (linear optical behaviour). When the electric field is strong, the induced polarization cannot be described any longer with equation (1) but with a power series as is given in equation (2).

$$\mathbf{P_{ind}} = \chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E}^2 + \chi^{(3)} \mathbf{E}^3 + \ldots\ldots$$ (2)

$$\chi^{(2)} = \text{nonlinear suscepibility}$$

In this **case** there is no linear dependence of the induced polarization and the electro-magnetic field and here we speak of nonlinear optical behaviour. In second order nonlinear optical behaviour the refractive index of the material is a function of E. According to equation **(2),** second order nonlinearity can only be observed when $\chi^{(2)} \neq 0$, which is only the **case** when the

system has a noncentrosymmetric structure. So, noncentrosymmetry in a film is a requirement for second order nonlinear optical behaviour. A major application area for second order nonlinear optical materials are electro-optic devices that will be used in optical fiber networks. The structure of LB mono- and multilayers is extremely important for possible applications. The very limited amount of material involved in LB-films needs special analytical tools. In this thesis the surface morphology of mono- and multilayers is characterized by transmission electron microscopy and electron diffraction. Orientation of parts of the molecules is mainly detected by (polarized) transmission- and grazing angle reflection infrared spectroscopy. When dye molecules are incorporated in LB-films, **UV/Visible** light spectroscopy gives additional information about the structural and **orientationa**l features of these molecules. The layer structure of the LB-films can be detected with X-ray diffraction.

In the past only amphiphilic low molecular weight compounds were known as monolayer forming compounds at the air water interface. During the last decade a variety of polymers showed film forming properties. Polymeric thin films have attractive properties compared to low molecular weight compounds like high thermal and mechanical stability. In this thesis the best of both, the high NLO-activity of low molecular weight compounds and the stability of polymers are combined. In Chapter 2, the behaviour and structure of mono- and multilayers of a series of amylose-esters with various alkyl side chains is studied. Amylose was chosen because the possible tuning of properties by substitution of the OH-groups on the glucose-unit.

Ester derivatives of amylose showed excellent film forming properties. The amylose-esters with short alkyl side chains appear to have a helical conformation at the air water interface which can be transferred into multilayers. Multilayers are obtained by Z-type transfer, that means deposition during the upstroke. The amylose palmitate however, as an example of an amylose-ester with long alkyl side chains forms partly ordered Y-type (deposition on both the up and down stroke) multilayers with side chains that have a preferential orientation perpendicular to the surface.

A dilute solution of amylose-acetate in chloroform was mixed with a chiral p-nitro-azo benzene **KMES**16 (an ester of **palmitic** acid and **4-nitro-4'-[(3R)-hydroxypyrrolidine-]azobenzene).** This dye fulfills the requirements for high second order nonlinear optical activity. The dye alone forms an unstable layer at standard conditions (23°C and $\pi = 7$ **mN/m)** at the air-water interface. However, mixtures of the dye with amylose-acetate do form stable monolayers when the amount of dye does not **exceed** 50 **mol%.** This behaviour deviates from additive behaviour of the

components. Deviation of additive behaviour is only found in the literature when the different compounds **are** mixed on a molecular scale. Transmission electron microscopy shows that the dye molecules and the polymer are not mixed molecularly. It is argued that the boundary lines between **amylose-acetate** and the dye domains play an important role in the stabilization process. The dye molecules are packed in a crystalline arrangement. Electron diffraction reveals an anti parallel packing of the molecules in the unit cell (plane group pg). The dye domains in the monolayer behave like H-aggregates. Aggregates are molecular assemblies where exciton effects may be observed when strong electronic interaction exists in molecular subunits. According to the exciton theory, spectral shifts can appear in absorption spectra. When only a blue shift is observed, one of the features of H-aggregates, it is suggested that the transition moments must be **parallelly** aligned, perpendicular to the grow direction of the aggregate.

The structure of multilayers of the mixture described in Chapter **3** is studied **in** Chapter 4. The structure of the amylose-acetate in the **mixed** multilayers corresponds to the structure found in Chapter 2. The azo-benzene units of the dye molecules are tilted about **30°** to the surface normal. The aliphatic chains are tilted about **60° to** the surface normal. The aliphatic chain of the dye molecule exhibits a special orientation as revealed by infrared spectroscopy. The all trans **CH$_2$** chains **are** tightly packed and they have a unique orientation around the chain director. The dye molecules are packed anti-parallelly in the crystals. The crystalline domains in the mixed multilayer behave also like H-aggregates. When the multilayers are heated above the melting point of the dye and cooled down, a more well defined layered structure is obtained. The helical structure of the amylose-acetate is not influenced by the heating cycle.

The structure that is found for the mixed multilayers in Chapter 4 is far from ideal regarding the normally accepted conditions for high second order nonlinear activity in thin films. But the system is not centrosymmetric because the dye molecules are packed in a **non-centro-symmetric** crystal point group **(P2$_1$)**. To study the second order non linear optical activity, second harmonic generation (SHG) is used as an indication of the nonlinear optical efficiency in Chapter 5. The LB-films show no significant SHG when measured as deposited. After heating and **cooling** the LB-multilayers unexpected large SHG is measured when the dye content is **70 mol%**. The morphology of the film changes dramatically after heating and cooling. Before heating very small **crystallites** (0.1-2 μm) can be observed under crossed **polarizers** in an optical microscope. After heating large crystalline plates (150-200 μm) show up. The structural features of the molecules in the film, like the tilt angle of the dye molecules to the surface normal, orientation and specific **packing** of the **alkyl** chains and the blue shift in the **UV/Vis** spectra do not change

significantly. The physics of the SHG might be almost similar to that of a **poly** crystalline powder (Powder theory of **Kurtz** and **Perry,** see p 103). According to this theory the second harmonic intensity can depend on the average particle size. This might explain the enhancement of the SHG going from a LB-film with small crystallites to a heated film with large crystalline sheets. Because the packing of the molecules in the crystalline sheets is almost anti parallel a larger signal than expected was obtained. To quantify the magnitude of the signal it is compared with that of the system described in Chapter 6. Based on this comparison it is argued that the H-aggregates may enhance the second order nonlinearity. The literature does not give a definite answer whether this is found before or not.

When mixtures of KMES 16 (70 **mol%**) and amylose-acetate in a dilute chloroform solution were spread onto a glassplate and heated above **129°C,** also SHG-active films can be obtained. The structure of these kind of films are almost similar to those of the heated LB-films of the mixtures. This indicates that the mixture is also a selforganizing system.

Chapter 6 describes the properties and structure of two new amphiphilic **NLO-materials** with stereogenic **(chiral)** centers (**KZ16** and **KDEZ16,** formulas on p 111). These molecules show LB properties as can expected from amphiphilic compounds. KZ16 mono and multilayers give homogeneous structures (no aggregation). Multilayers are built by Y-type transfer. An Y-type bilayer does not show any SHG, indicating a complete destructive interference of the oppositely packed molecules. The stereogenic centers in the bilayer do not contribute to any measurable extent to a **noncentrosymmetric** structure. When an alternating bilayer is measured (**KZ16/arachidic** acid), a nearly quadratic enhancement of the SHG with the number of bilayers is obtained. **Quadratical** enhancement is the ideal behaviour according to the generally accepted theory of SHG of thin layers.