I. Polystyrene based materials

I.1. Synthesis and Properties of 2nd-order NLO-active Polystyrene and Amylose Based Materials

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INTRODUCTION

Second order non-linear optical effects in organic materials might lead to novel applications as integrated electro-optic devices, as blue lasers and so forth. Maximum effects can be expected from special designed materials that must have a non-centrosymmetric structure. There are several ways to achieve this non-centrosymmetry. The Langmuir-Blodgett technique and poling of NLO-active polymers are possibilities.

We have studied two kinds of NLO-active materials. The first is polystyrene based and is suitable for poling. The second is amyllose based and suitable for ordering with the Langmuir-Blodgett technique. In previous studies is shown that amyllose esters are good materials to be used as spreading material on the water surface. In this paper we will describe the synthesis of both kind of materials. We have studied the poling properties and NLO-activity of one of the synthesized polystyrene based materials. Of one of the amyllose based material some preliminary LB-properties will be described.

RESULTS AND DISCUSSION

I.1. Polystyrene based materials

We used polystyrene as starting material for preparing a polymer with covalently bound NLO-active groups. The advantage of this procedure above performing a polymerisation as the last step in the synthesis is that the degree of polymerisation is known. Other properties like solubility can then better be predicted. Polystyrene (Dow Styron 666, MW=100,000) was chloromethylated by a modified Galeazzi method. The polymer was treated with the sodium salt of a N-alkyl-aniline to provide the N-alkyl-anilinopolystyrene derivative (fig 1).

The functionalisation degree was determined by 1H-NMR spectroscopy and elemental analysis. The diazo-coupling reactions with in situ prepared diaziumsalts of some substituted anilines were performed in THF/DMSO mixtures of ratios of 1/1 to 4/1 depending on the functionalisation degree (DF). Cq solubility of used N-alkyl-anilino polystyrene was very important for this reaction mixture is that all used reactants and the buffer (acetic acid/solvent) are homogeneously dissolved. Product 5 shows good solubility in various solvents (table 1). In general, chloroform is the most suitable solvent. The solubility of 5 is dependent on the DF of 5 in such a way that above a certain DFsol the polymer does not form a clear solution anymore but a gel-like solution and is not suitable for any application. The highest achievable DFsol of the polystyrene based NLO-active materials is also dependent on DF. This means that a lower content of free N-alkylamine moieties (DF minus DFsol) improve the solubility of the polymer. For example, for 5 (R=Me) with DF=0.31 the maximal DFsol is 0.14 (entry 1) and for 5 (R=Me) with DF=0.25 the maximum DFsol is 0.16 (entry 3). Introducing a hydrophilic group on the polystyrene (entry 6) a drastic change in solubility is achieved. This polymer is only soluble in polar solvents as DMSO. The DFsol of this product is very high but unfortunately no usable films could be formed.

Two of these materials (entries 2 and 3) are used to study their poling and film forming properties. The effectiveness of the poling procedure is very

<table>
<thead>
<tr>
<th>entry</th>
<th>R′</th>
<th>Z′</th>
<th>X′</th>
<th>DF</th>
<th>DFsol</th>
<th>Solubility</th>
<th>Tg</th>
</tr>
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<tbody>
<tr>
<td>1. Me NO2</td>
<td>H</td>
<td>0.31</td>
<td>0.14</td>
<td>Chl, Chlb, Tol</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2. Me NO2</td>
<td>H</td>
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<td>Chl</td>
<td>115°C</td>
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</tr>
<tr>
<td>3. Me NO2</td>
<td>H</td>
<td>0.23</td>
<td>0.16</td>
<td>Chl</td>
<td>124°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Me NO2</td>
<td>H</td>
<td>0.37</td>
<td>0.18</td>
<td>ns</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Me SO2Me</td>
<td>H</td>
<td>0.25</td>
<td>0.05</td>
<td>Chl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Me COOH NO2</td>
<td>0.31</td>
<td>0.31</td>
<td>DMSO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. n-Bu NO2</td>
<td>H</td>
<td>0.28</td>
<td>0.16</td>
<td>Chl</td>
<td>104°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. n-Bu NO2</td>
<td>H</td>
<td>0.28</td>
<td>0.28</td>
<td>Chl</td>
<td>119°C</td>
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<td>9. n-Bu NO2</td>
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<td>Chl</td>
<td>95°C</td>
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<td>Chl</td>
<td>108°C</td>
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<td>11. n-Bu NO2</td>
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<td>0.37</td>
<td>0.33</td>
<td>Chl</td>
<td>120°C</td>
<td></td>
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</table>

a) see ref 7. b) DF= substitution degree of polystyrene with N-alkyl-aniline; c) DFsol is that part of DF that is substitution after the diazo coupling; d) chl= chloroform, chlb= chlorobenzene, toluene, DMSO=Methylsulfoxide; ns=not soluble; e) Tg is glass transition temperature.
In order to increase the content of the NLO-active compound without losing the solubility a n-butyl group was introduced at the donor nitrogen ($\text{R} = \text{n-Bu}$). The result was a 100% increase of the dye content. The $T_g$ of these polymers were lower than that of the N-methyl containing polystyrenes. Two polymers $5$ with different $R$-groups but comparative dye contents differ in $T_g$ in a value of about 20°C (entry 3 vs 7). An increase of $D_{\text{ foc}}$ results in a larger $T_g$ (entries 9,10,11). This effect neutralises the $T_g$ decrease due to the presence of a n-butyl group instead of a methyl group.

Another very important property for integrated optics is that the polystyrene based NLO-active materials are irreversibly bleachable. The chromophore is completely destroyed after bleaching. This can be seen by the disappearance of the absorption peak at 490 nm in the UV/VIS spectra before and after bleaching. The refractive index decreased 0.05 at 633 nm. This index lowering allowed us to make low loss ($\sim 1 \text{dB/cm}$) channel waveguides by exposure through photomasks in a standard mask aligner.

II. AMYLOSE BASED NLO-ACTIVE MATERIALS

Amylose can be functionalised in high degree with acid chlorides or acid anhydrides in a N-methyl-imidazole medium. Amylose esters form stable transferable Langmuir-Blodgett (LB) monolayers. We prepared amylose esters of NLO-active azo-dyes. The general procedure that was followed contains an introduction of a donor part on amylose followed by a diazo coupling and esterification of the still free hydroxy functionalities of amylose with acetic acid anhydride (figure 4). The acid chlorides $12$ were synthesized from the acid $11$ with $\text{PCl}_5$, were used immediately and without purification for the esterification of amylose. $11a$ was prepared via a Friedel-Crafts acylation of diphenyl-methyl-amine $6$ followed by hydrolysis of the ester $7$. $11b$ was synthesized by a reaction between $p$-bromomethyl-ethyl-benzoate $9$ with N-methylamidin. The ester $11b$ was immediately hydrolysed to the acid because of its instability.

Both acid chlorides could easily be coupled to amylose with a degree of substitution (DS) varying between 0.50 and 1.06. Using $13a$ (DS=0.73) the diazo-coupling with in situ prepared diazonium-salt of p-nitro-anilin resulted in low degrees of substitution. In similar diazo-coupling reactions the coupling rates (DS$_{\text{ foc}}$) were not consistent in and the best achieved was 0.17. This means that less than one fourth of the donor part is substituted. The position for the diazo-coupling reaction (para to the amine) is probably less activated because the amine functionality has a less strong donor capacity due to the electron withdrawing ester functionality. Using amylose derivative $12b$ (DS=0.50) the diazo coupling reaction went very smooth and a complete coupling was achieved. The product $13b$ (DS=DS$_{\text{ foc}}$=0.50) was not soluble in chloroform. So this polymer could not be used for the LB-technique so far.

Amylose derivative $14a$ (DS=0.73, DS$_{\text{ foc}}$=0.17) did form stable LB-monolayers (fig 5). The isotherm shows a much larger area per amylose unit than the stabilisation curve does. The stabilisation of the monolayer takes about six hours in contrast to amylose acetate that forms a stable layer in a few minutes. Probably the orientation of the azo-dye or the free donor parts proceeds very slowly. It is not clear if the amylose $14a$ forms a helix on the water surface like amylose acetate. Until now we did not achieve a complete transfer of the monolayer. We found a partial Z-transfer (0.6-0.8 upstroke, 0.0-0.1 downstroke) which is not good enough for a detailed structure research.

III. CONCLUSIONS

The polystyrene derivatives have attractive properties as bleachability and low conductivity, for applications in integrated electro-optic devices. Because of the low conductivity very high ordering degrees $\Phi>0.43$ can be reached. A relative low glass-transition temperature results in a big loss of ordering. Azo dye based amylose esters can be synthesised. Some of these esters form stable monolayers with hopefully a high non-centrosymmetric ordering.

IV. EXPERIMENTAL

A detailed synthesis of one of the polystyrene compounds has been published already. A detailed synthetic procedure for the other polystyrene based and the amylose based materials will be described elsewhere. Film preparation and measurements are described elsewhere. Langmuir Blodgett monolayer properties were studied using a computer controlled Lauda Filmbalance (FW2) as reported before.

V. LITERATURE


VI. ACKNOWLEDGEMENT

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