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

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INTRODUCTION

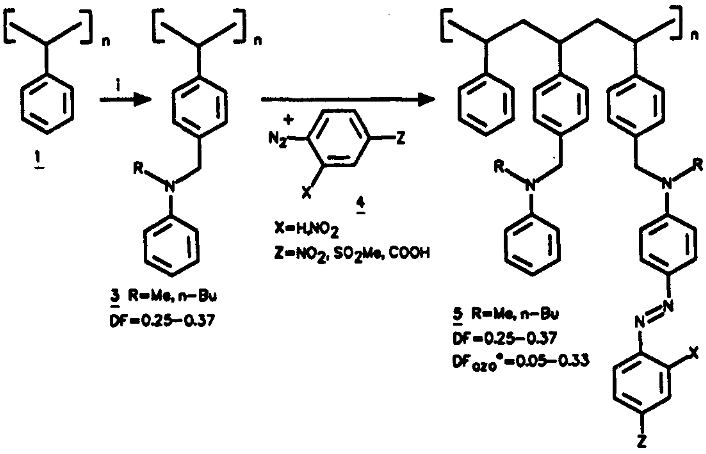
Second order non-linear optical effects in organic materials might lead to novel applications as integrated electro-optic devices[1,2], a blue laser[3] and so forth. Maximum effects can be expected from special designed materials that must have a non-centrosymmetric structure. There are several ways to achieve this non-centrosymmetry. The Langmuir-Blodgett technique[4] and poling of NLO-active polymers[2] are possibilities.

We have studied two kinds of NLO-active materials. The first is polystyrene based and is suitable for poling. The second is amylose based and suitable for ordening with the Langmuir-Blodgett technique. In previous studies is shown that amylose esters are good materials to be used as spreading material on the water surface[5]. 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 amylose based material some preliminary LB-properties will be described.

RESULTS AND DISCUSSION

I. 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[6]. The polymer 2 was treated with the sodium salt of a N-alkyl-aniline to provide the N-alkyl-anilinopolystyrene derivative 3 (fig 1).[6] The functionalisation degree (DF=0.25-0.37) was determined by ^{1}H-NMR spectroscopy and elemental analysis. The diazo-coupling reactions with in situ prepared diazoniumsalts of several substituted anilines 4 were performed in THF/DMSO mixtures of ratios of 1/1 to 4/1 dependening on the functionalisation degree (DF) cq solubility of used N-alkyl-anilino polystyrene 3. Very important for this reaction mixture is that all used reactants and the buffer (acetic acid/sodium acetate) 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 and DF$_{azo}$ in such a way that above a certain DF$_{azo}$ the polymer does not form a clear solution anymore but a gel-like solution and is not suitable for any application. The highest achievable DF$_{azo}$ of the polystyrene based NLO-active materials is also dependent on DF. This means that a lower content of free N-alkylaniline moieties (DF minus DF$_{azo}$) improve the solubility of the polymer. For example, for 5 (R=Me) with DF=0.31 the maximal DF$_{azo}$ is 0.14 (entry 1) and for 5 (R=Me) with DF=0.25 the maximum DF$_{azo}$ 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 DF$_{azo}$ of this product is very high but unfortunately no usable films could be formed.



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* DF is substitution degree of polystyrene can vary between 0.0–1.0
** DF$_{azo}$ is substitution degree of the complete NLO-active dye and can vary between 0.0–DF

Figure 1 Synthesis of Polystyrene based NLO-active materials

entry	R^a	Z^a	X^a	DF^b	DF$_{azo}$^{c}	Solubility^d	Tg^e
1	Me	NO$_2$	H	0.31	0.14	Chl, Chlb, Tol	
2	Me	NO$_2$	H	0.25	0.13	Chl	115°C
3	Me	NO$_2$	H	0.25	0.16	Chl	124°C
4	Me	NO$_2$	H	0.37	0.18	ns	
5	Me	SO$_2$Me	H	0.25	0.05	Chl	
6	Me	COOH	NO$_2$	0.31	0.31	DMSO	
7	n-Bu	NO$_2$	H	0.28	0.16	Chl	104°C
8	n-Bu	NO$_2$	H	0.28	0.28	Chl	119°C
9	n-Bu	NO$_2$	H	0.37	0.13	Chl	95°C
10	n-Bu	NO$_2$	H	0.37	0.23	Chl	108°C
11	n-Bu	NO$_2$	H	0.37	0.33	Chl	120°C

a) see figure 1; b) DF=substitution of polystyrene with N-alkyl-aniline; c) DF$_{azo}$ is that part of DF that is substitution after the diazo coupling; d) chl=chloroform, chlb=chlorobenzene, tol=toluene, DMSO=Methylsulfoxide, ns=not soluble; e) Tg is glass transition temperature

table 1 Properties of polystyrene based NLO-active materials.

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 important for the NLO-activity of the material. Because a better non-centrosymmetric ordening gives a higher NLO-activity. The degree of ordening (Φ_a=-(3[cos$^3\theta$]-1)/2) (cosθ is the average component of the dipole moment along the field direction) of the corona discharge poled films of the compound 5 (R=Me, DF=0.25, DF$_{azo}$=0.16) can be calculated from dielectric measurements[7]. A relative high value of Φ_a=0.45 was measured. This can be attributed to the low dc conductivity of the polymer through which a high poling field is effective in the polymer film.

It is also possible to measure directly the NLO-activity of poled films by performing Electro-Optic (EO) measurements. The EO-measurement after one hour contact poling of polymer 5 (R=Me, DF=0.25, DF$_{azo}$=0.13) showes a r_{33}=18.2 pm/V in a still working electric field. Switching the field off gives an instantaneous decrease of r_{33} to 12.9 pm/V. This value corresponds to a $\chi^{(2)}$-(ω,ω,o)=21.2 pm/V. This value is not completely off resonance and corrected for a wavelength of 1.52 μm, $\chi^{(2)}$(ω,ω,o) is 4.08 pm/V. The ordening Φ_b (Φ_b=1-cos$^3\theta$) of the dipoles that can be calculated from this value is 0.43. This value is almost identical to the Φ_a that was calculated using dielectric measurements.

The stability of the poled films is shown in figure 2. At 100°C the ordening is lost within one day. Storing the film at 80°C gives a relaxation to about 40% of the initial value of 12.9 pm/V. At room temperature the relaxation stabilizes at about 60% of the initial value. This instability is probably due to the relative low glass transition temperature (Tg) of the polymer (115°C).

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 5 (R=n-Bu). The result was a 100% increase of the dye content. The Tg 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 Tg in a value of about 20°C (entry 3 vs 7). An increase of DF_{azo} results in a larger Tg (entries 9,10,11). This effect neutralizes the Tg decrease due to the presence of a n-butyl group instead of a methyl group.

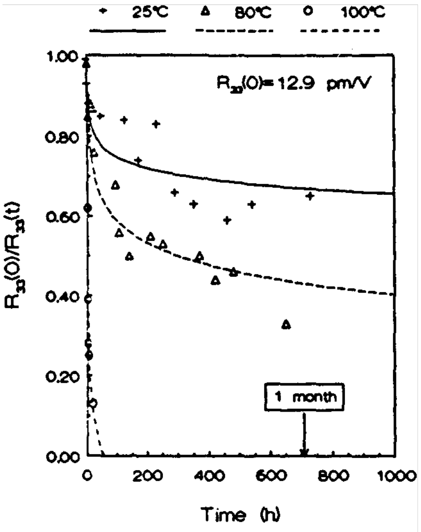


Figure 2 Relaxation of poled films

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 disapearance 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 (≈1dB/cm) channel waveguides by exposure through photomasks in a standard mask aligner.

II. AMYLOSE BASED NLO-ACTIVE MATERIALS

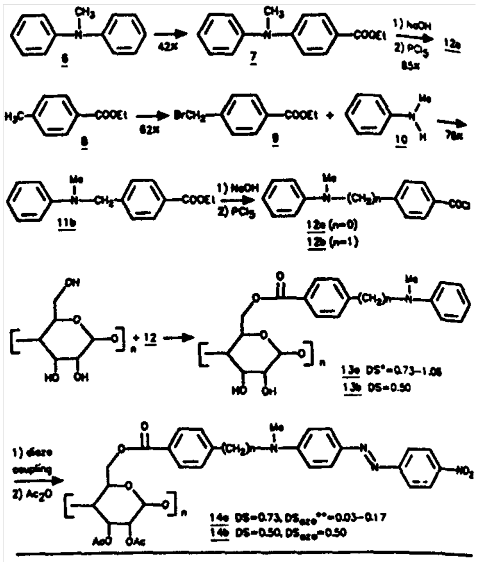
Amylose can be functionalised in high degree with acid chlorides or acid anhydrides in a N-methyl-imidazole medium. Amylose esters form stable transferable Langmuir-Blodgett (LB) monolayers.[5] We prepared amylose esters of NLO-active azo-dyes. The general procedure that was followed contains an introduction 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, synthesized from the acid 11 with 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-methylanilin. 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 diazocoupling reactions the coupling rates (DS_{azo}) 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 13b (DS=0.50) the diazo coupling reaction went very smooth and a complete coupling was achieved. The product 14b (DS=DS_{azo}=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_{azo}=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.[5] 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.

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 ordening degrees Φ=0.43 can be reached. A relative low glass-transition temperature results in a big loss of ordening. Azo dye based amylose esters can be synthesized. Some of these esters form stable monolayers with hopefully a high non-centrosymmetric ordening.



*DS is substitution degree per amylose unit and varies between 0.0-3.0
**DS_{azo} is substitution degree of the azo-dye per amylose unit and varies between 0.0-0.5

Figure 3 Synthesis of Amylose based NLO-active materials

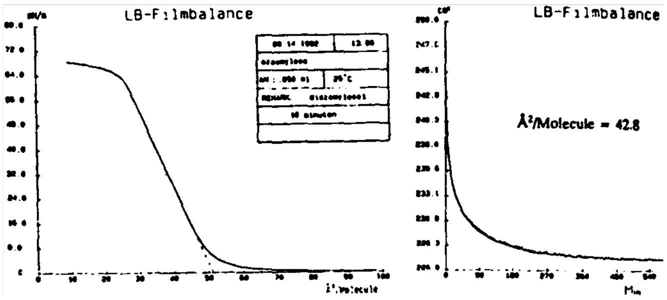


Figure 4 LB-isotherm and stabilisation curve of 14b

EXPERIMENTAL

A detailed synthesis of one of the polystyrene compounds has been published already [7]. 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[7]. Langmuir Blodgett monolayer properties were studied using a computer controlled Lauda Filmbalance (FW2) as reported before[5].

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