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Solvatochromic Determination of Second-order Polarizabilities of Chromophore-functionalized Dextran and Amylose Derivatives

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Linear dextran and helix amylose were covalently bonded with nonlinear optical (NLO) chromophores. The influence of the conformation of the polymer matrix on the NLO behavior of the supramolecular structure has been studied. The second order hyperpolarizability depends not only on the secondary structure of the biopolymer, but also on the position of the chromophore towards the polymeric backbone. Functionalization of NLO-phores with biopolymers led to increased thermo- and photostability.

Keywords: Dextran; Amylose; Solvatochromism; Conformation; Nonlinear optical properties

INTRODUCTION

It has been proposed that supramolecular structures can lead to improved nonlinear optical (NLO) properties [1]. The present challenge in materials development for second-order nonlinear optics is to find noncentrosymmetric molecules that have a large molecular hyperpolarizability and that can be organized in a noncentrosymmetric macroscopic arrangement to give rise to a nonvanishing second-order susceptibility. For a long time, scientists have been fascinated by biopolymers and intrigued by the fact that they can fulfil so many functions. Biopolymers have many advantages over conventional synthetic polymers since they are able to assemble hierarchically into stable ordered conformations. One of the most intriguing dissymmetric shapes is the helix. It was developed in natural systems in the early stages of evolution and used as the structural motif for the biomacromolecules (DNA and RNA, polypeptides and polysaccharides). The rod like structure of the polar α-helix gives rise to some unique properties such as a high persistence length, large optical and mechanical anisotropy and additive dipole moments of the individual repeated units [2].

In our previous work, we have synthesized poly-L-tyrosine which was organized in an α-helix structure (FTIR) and functionalized with different NLO-phores [3]. Surprisingly, these compounds which have preserved the α-helix structure showed lower solvatochromic shift in comparison with those with a partially destroyed α-helix structure. It is known that the well-expressed influence of solvents on UV/VIS spectra is an indication of NLO-activity [4]. We have concluded that this anomalous behavior of the organized polypeptide structure could be due to hydrophobic stacking interactions.

For this reason, we have decided to compare the solvatochromic behavior of differently organized natural biopolymers, such as linear dextran and helix amylose, functionalized with NLO-phores.

EXPERIMENTAL

Dextran T-150 (M_r 150,000, light scattering) was supplied by Pharmacia Fine Chemicals (Sweden). Amylose (M_r ca. 150,000, light scattering) was supplied by Serva Fine Biochemicals (Germany). *p*-Nitroaniline (>99%) was obtained from Merck (Germany). *p*-Nitrophenylhydrazine (>99%) was purchased from Loba-Chemie (Austria). All other chemicals were of reagent grade or better.

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TABLE I Absorption data of functionalized dextran (D) and amylose (A)

No.	Compound	Functionalization rate (w%)	λ_{cutoff} DMSObr (nm)	λ_{max} (nm)			$\Delta\nu$ (cm^{-1})	
				DMSO	Water	FA	H_2O/DMSO	H_2O/FA
1.	p-$NH_2C_6H_4NO_2$	–	434.0	390.0	383.3	385.5	−448	+149
2.	p-$NH_2NHC_6H_4NO_2$	–	454.0	405.2	391.1	396.3	−890	+336
3.	D-CH=$NC_6H_4NO_2$	11.5	464.0	387.7	383.3	385.0	−296	+115
4.	D-$CH_2NHC_6H_4NO_2$	11.5	476.0	404.4	401.9	404.0	−154	+130
5.	D-CH=$NNHC_6H_4NO_2$	98.0	446.0	395.2	388.5	393.4	−436	+321
6.	A-CH=$NC_6H_4NO_2$	4.7	438.0	383.9	372.5	376.3	−798	+272
7.	A-$CH_2NHC_6H_4NO_2$	4.7	451.0	395.0	392.7	392.7	−149	0
8.	A-CH=$NNHC_6H_4NO_2$	100	446.0	395.5	391.7	394.3	−246	+164

Chemical Activation of Dextran and Amylose

Dextran (5 g) was dissolved in 200 ml of 100 mM solution sodium periodate (pH 4.6), previously cooled to 5°C. The reaction was continued, with stirring, in the dark for 3 h at 5°C. The oxidation reaction was stopped by adding ethylene glycol and the reaction mixture was allowed to stand for 1 h at room temperature. The solution was concentrated under vacuum, subjected to dialysis against distilled water for 48 h and lyophilized.

Amylose (5 g) was dissolved in 50 ml DMSO and the solution was cooled to 5°C. To this solution was added 20 ml of 0.3 M solution of sodium periodate (pH 4.6), also cooled to 5°C. The mixture was stirred constantly for 20 h at 5°C in the dark. The oxidized amylose derivative was isolated as mentioned above.

The aldehyde groups in the oxidized dextran and amylose were determined quantitatively using the dinitrosalicylic acid method with D-glucopyranose as a standard [5].

Coupling of *p*-Nitroaniline (*p*-NA) with Dialdehyde Dextran (DAD) and Dialdehyde Amylose (DAA)

Dialdehyde derivative (2 g) was dissolved in 100 ml of 0.1 M $NaHCO_3$: DMSO (7:3, v/v), pH 9.3–9.5, containing a two fold molar excess of *p*-NA/moles introduced CHO groups. The mixture was stirred constantly for 18–20 h at room temperature. The excess of *p*-NA was eliminated by dialysis (48 h) and then the solution was lyophilized. The absence of *p*-NA in the conjugates was determined by TLC ($CHCl_3$: MeOH = 9 : 1, v/v). The compounds obtained, 3 and 6, are given in Table I.

Reduction of the Azomethine Group in Compounds 3 and 6

A measured amount (0.5 g) of compound 3 (resp. 6) was dissolved in 20 ml of 0.1 M and cooled to 5°C. To this solution was added 5 ml freshly prepared solution of $NaBH_4$ (10 mg/ml) in 0.1 M phosphate buffer. The mixture was stirred for 5 h at 5°C. The reaction mixture was desalted using dialysis and then lyophilized. Compounds 4 and 7 are given in Table I.

Coupling of *p*-Nitrophenylhydrazine (p-NPHyd) with DAD and DAA

Two fold molar excess of *p*-NPHyd (moles introduced CHO groups in the dialdehyde derivatives) was dissolved in 15 ml 96% ethanol, pH 3–3.5 (CH_3COOH) and heated to 60°C. To this solution was added 1 g DAD (resp. DAA) dissolved in 50 ml distilled water, pH 3–3.5 and the reaction mixture was stirred for 3–4 h at room temperature. After dialysis against water, the precipitate formed was discharged and the solution subjected to lyophilization. The absence of unreacted *p*-NPHyd was determined by TLC (see above).

Spectrophotometric Measurements

All compounds used were chromatographically pure and with a known moisture content, obtained by drying the sample for 3 h at 105°C until constant weight.

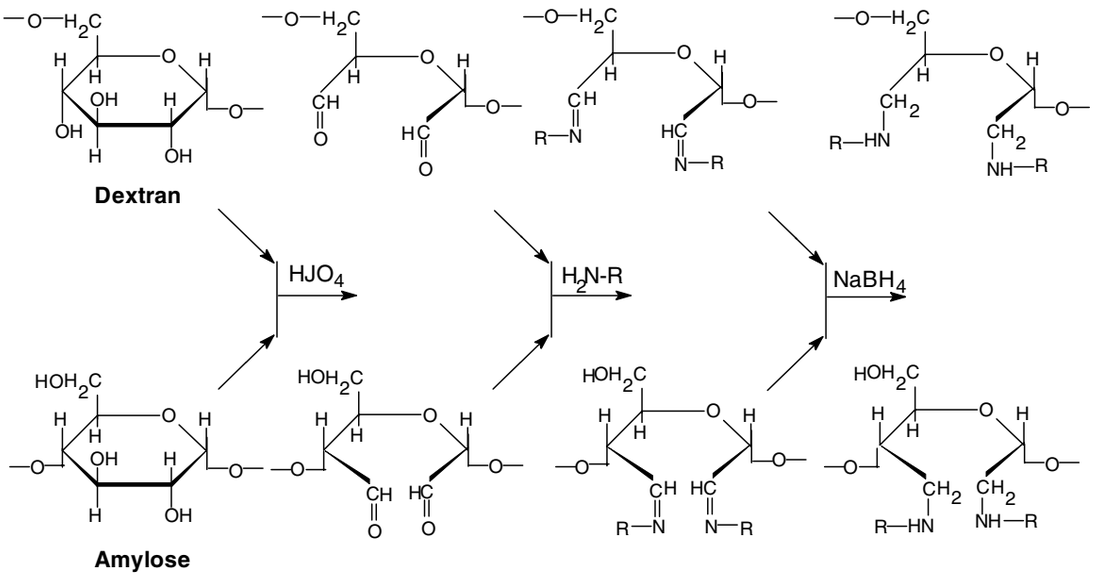
UV-VIS spectra were recorded on a Perkin–Elmer Lambda 2 spectrophotometer in the range 300–600 nm in analytical grade solvents. The amount of bound chromophore was determined in different solvents, using the molar extinction coefficients of the model chromophores in the respective solvent.

Solvatochromic Determination of β

The molecular second order hyperpolarizability was calculated from Eq. (1) for a laser wavelength of 1900 nm [4]. All calculations were made in CGS units.

$$\beta_{xxx}(2\omega) = (3/2)h^2\mu_{eg}^2(\mu_e - \mu_g)\omega_{eg}^2/(\omega_{eg}^2 - \omega^2) \times (\omega_{eg}^2 - 4\omega^2) \quad (1)$$

where h is Planck's constant, ω_{eg} is the frequency of transition from the ground to the first excited state,



SCHEME 1

μ_{eg} is the transition dipole moment between the ground and excited states, μ_g is the permanent dipole moment of the ground state, μ_e is the permanent dipole moment of the excited state, and ω is the laser frequency. The second order hyperpolarizability at zero frequency (β_0) was calculated using Eq. (2) [6].

$$\beta_0 = 6\mu_{eg}^2(\mu_e - \mu_g)/h^2\omega_{eg}^2 \qquad (2)$$

The data for ω_{eg}, μ_{eg}, μ_g and $\mu_e - \mu_g$ were estimated experimentally [4].

Photostability and Thermostability

A solution (5×10^{-5}–5×10^{-7} M of the compounds under study) in DMSO was prepared and then 4 ml of the solution was transferred to a UV cell. The cell was put in cell holders held at a temperature of 25 ± 0.5°C during irradiation, and was irradiated from outside with filtered radiation (>390 nm) using a 100 W high-pressure mercury lamp. The cell was kept at a distance of approx. 10 cm from the light source. The relative percentage photofading of the compounds under study was determined spectrophotometrically.

Thermostability was determined using differential scanning calorimetry (DSC), Mettler apparatus, heating rate 20°C/min in the range 20–250°C.

RESULTS AND DISCUSSION

It is well known that the biosynthesis of natural biopolymers occurs under genetic control, which offers defined molecular weight, monodispersity, purity, stereoregularity and conformational rigidity. For this reason, by study of the influence of the conformation on NLO-behavior it is better to compare products with known 3D structure. We have chosen two polysaccharides—dextran (random coil) and amylose (α-helix). The study of these molecules and the influence of their conformation on the second-order NLO response may provide an important step toward supramolecular engineering of NLO properties. The polysaccharides were activated by mild periodate oxidation to dialdehyde derivatives (Scheme 1).

The content of introduced aldehyde groups was determined spectrophotometrically and it was estimated to be 34.0 moles CHO-groups per mol dextran, which corresponds to 6.8% and 82.7 moles CHO-groups per mole amylose, resp., 4.3% degree of oxidation. Our assumption was to compare the behavior of the two polysaccharides by the same oxidation rate. For this reason amylose was subjected to rigid oxidation conditions (duration of the reaction and molarity of the oxidant). The impossibility to achieve a higher oxidation rate with amylose can be explained by the low accessibility of the vicinal HO-groups at C-2 and C-3 atoms due to the organized helical structure shown in Fig. 1 [7].

Dialdehyde derivatives of dextran and amylose were functionalized with NH_2-group containing NLO-phores to obtain the azomethine group. In some cases the azomethine group was reduced to the CH_2NH-group for investigation of the donor–acceptor interactions [8]. The results are presented in Table I.

The absorption spectra of the functionalized polysaccharides in the present work display intense bands in the visible region with well defined peaks

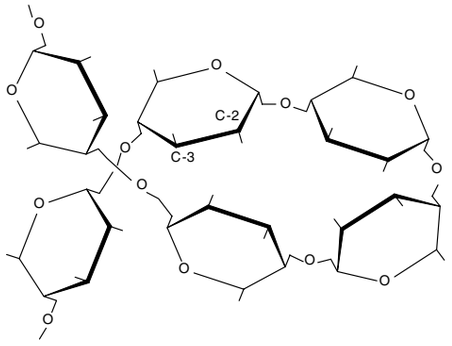


FIGURE 1 A view of the proposed model for helical V-amylose according to Hybl *et al.* [7].

as could be seen from λ_{cutoff} (Table I). All compounds showed positive solvatochromism with respect to formamide (FA, $\varepsilon = 109$) and negative solvatochromism with respect to dimethyl sulfoxide (DMSO, $\varepsilon = 46.7$). The inversion of solvatochromism (positive solvatochromism followed by negative solvatochromism) indicated the predominance of the neutral form in apolar solvents and of the zwitterionic form in polar solvents. Unfortunately, the polysaccharides do not dissolve in nonpolar solvents. The investigation of *p*-NA (the classical NLO-prototype) in different solvents showed that by transition from apolar solvents to moderately polar solvents ($\epsilon \approx 30$) the influence of solvents on spectral shift is significant. Working only with polar solvents gives rise to the "solvent limit" and the ICT transition is not directly proportional to the dielectric constant of the solvent. Nevertheless the comparison under equal conditions can yield some information. Taking into consideration that optical nonlinearity is also related to the oscillator strength (f) of the absorption band, we have calculated f (Table II). Hydrazine derivatives (compounds 5 and 8) showed large enhancement of the oscillator strength that does not depend on the molecular weight only. The best solvatochromic shift was exhibited by the organized structure of compound 6. Nevertheless, the disordered structure of compound 5 showed more solvatochromic shift than the organized structure in compound 8. It is interesting that donor–acceptor interactions affect the position of λ_{max} (bathochromic shift), but do not affect the solvatochromic shift (compounds 4 and 7). This can be attributed to the poor overlap between the electron lone pairs of the nitrogen atom and the aromatic ring. The solvatochromic shift of chromophores incorporated into a polymer with a flexible backbone was found to be independent of the polymeric environment (compounds 4 and 7).

As could be seen from Table II the best results were obtained with hydrazine derivatives. The helix conformation of amylose (with the exception of compounds 4 and 7) increased the hyperpolarizability only twice. Probably the explanation of this fact is the structure of the amylose. It is a single-threaded sinistral helix composed of six D-glucopyranose units per turn in the C1-chair conformation linked α-(1,4). The proposed model is like a cylindrical screw with a left-handed thread. It has an 8 Å pitch with a lead angle of 17.5°. The major and minor diameters are 13.4 and 11 Å. The crest and root contours of the thread are irregular and the packing diameter is close to 13 Å. The rod-like character, high aspect ratio of rod length to diameter and the length of the chromophores 6.8 Å of *p*-NA and 7.2 Å of *p*-NPHyd (AM1) [9] allow us conclude that the chromophores are situated inside the helix, in contrast to polypeptides, where the side chains of the amino acid residues are directed outside the helix [10].

Thermal Stability

Thermal stability is a major requirement for practical applications. The thermal stability of the compounds under investigation was measured by differential scanning calorimetry. DSC allowed the determination of T_m (melting point) as well as T_{di} (onset of decomposition) and T_{dm} (maximum of the decomposition). It should be noted that T_{di} values only provide a helpful upper limit of thermal stability. T_{dm} could not be observed. The DSC data are collected in Table III. In a number of cases (compounds 3 and 8), decomposition occurs prior to melting. However, thermal decomposition does not occur below 180°C.

TABLE II Solvatochromic determination of the second order hyperpolarizability

No	f	$\mu_e - \mu_g \times 10^{18}$ esu cm	$\mu_{ge} \times 10^{18}$ esu cm	$\beta_{(-2\omega;\omega\omega)} \times 10^{31}$ esu	$\beta_0 \times 10^{31}$ esu
1.	0.295	−4.8	4.95	−8.65	−6.90
2.	0.353	−14.0	5.51	−34.50	−26.93
3.	1.167	−3.0	9.83	−21.00	−16.79
4.	0.498	−1.4	6.55	−4.73	−3.70
5.	11.280	−6.9	30.80	−494.30	−391.50
6.	1.920	−8.1	12.53	−90.48	−72.71
7.	0.153	−1.5	3.52	−1.47	−1.17
8.	31.540	−3.8	51.49	−764.12	−613.42

TABLE III Thermal data from DSC experiments

Compound No	T_m (°C)	T_{di} (°C)
1	149–152	180
2	155–158	180
3	–	230
4	186–190	220
5	205–210	215
6	185–190	220
7	205–210	230
8	–	210

Photostability

Photostability is very important for practical applications. Little attention has been paid to this problem in the literature, but all applications are connected with light irradiation. For this reason we have investigated the photostability by irradiation with daylight and with UV-light. All the compounds investigated were photostable under irradiation with daylight for more than 180 days.

It is well known that the NLO-prototype *p*-NA is not photostable due to oxidation of the aminogroup. *p*-NPHyd showed lower photostability than *p*-NA. But in all cases the covalent bonding of the NLO-phore with polysaccharide increased the photostability (Fig. 2). We have observed the same effect by functionalization of poly-L-tyrosine with NLO-phores [11].

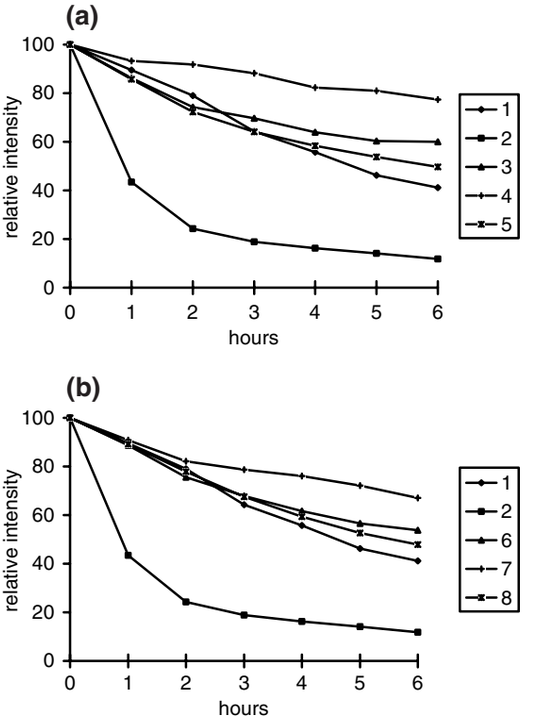


FIGURE 2 Photostability of the compounds under study (the numbering is according to Table I).

CONCLUSIONS

Biopolymers that maintain stable helical structures are DNA, some polypeptides and some polysaccharides. In the design of NLO-functionalized macromolecules, we have to recognize not only the secondary structure of the biopolymer, but the location of the chromophore with respect to the polymeric backbone too. In some cases, e.g. by construction of supramolecular wires and channels, self-assembled polysaccharides could find application [12]. In other cases, the orientation of the chromophore outside the polymeric backbone such as in polypeptides could be of interest [13].

This research may hopefully serve as a starting point for further research in the field of NLO-functionalized biopolymers, in particular with regard to use of these polymers as building blocks for the construction of novel dissymmetric architectures similar to those found in nature. Construction of the three-dimensional structure of biopolymers may achieve the arrangement of functional chromophoric side chains to afford artificial biopolymers such as biopolymeric electronic devices.

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