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Stability of Selected Chromophores in Biopolymer Matrix

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Photochemical and thermal stability of thin films formed from selected optically responsive chromophores embedded in deoxyribonucleic acid (DNA), Collagen and in the complex formed by DNA biopolymer and the surfactant hexadecyl ammonium (CTMA) matrix was studied by UV-VIS and compared with that observed when using some synthetic polymers (polymethylmetacrylate – PMMA, polycarbonate – PC). In particular the influence of external stimuli, such as heating and UV light on the chemical degradation process was investigated.

Keywords Aggregation; biopolymers; chemical degradation; DNA; kinetics degradation parameters; luminophores; photodegradation

Introduction

The deoxyribonucleic acid (DNA) is one of the most abundant biopolymers present in nature. It encodes all genetic information necessary for the survival and reproduction of a given living specie, through the genetic transmission (heritage), and its development. Its length (molecular mass) depends on the level of development of the species. It ranges from a few kbp (= 1000 base pairs ≈ 340 nm) for simplest species like viruses to about three thousands mbp for the most developed human chromosome [1,2].

Since the discovery of its double strand helical structure by Crick and Watson [3] DNA has attracted a lot of interest of scientists, not only of biologists, but also of chemists and physicists. Low molecular mass DNA are already synthesized in laboratories. Larger

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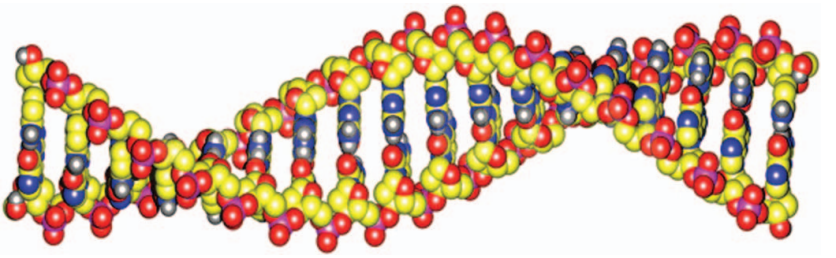

Figure 1. Schematic representation of the double strand chiral chemical structure of DNA. The stacking batons represent nucleobase pairs. The helical backbone is formed of sugar and phosphates molecules (cf. Fig. 2). Image retrieved from http://www.fotolibra.com/gallery/520577/dna-molecule-model-illustration/.

biopolymers are extracted from the waste of either fruits or meat processing industries [4,5].

As shown in Fig. 1 (see also Fig. 2) the structure of DNA consists of double helix formed by stacking nucleobase pairs (adenine-thymine, guanine-cytosine) along the developing double strand helix. The outside groups which are sugars and phosphates form the backbone of the helix. The DNA macromolecule presents a net negative charge compensated by sodium ions, non-localized counter ions, which can move freely along the macromolecular surface chain [6]. It provides strong ionic properties to DNA, which were already exploited

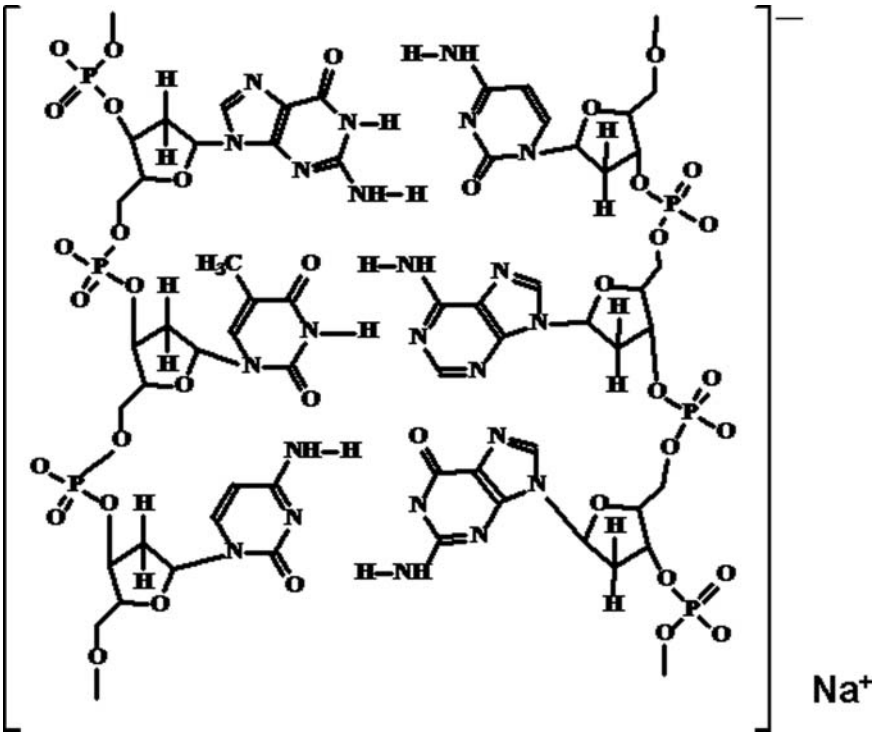

Figure 2. Chemical structure of a DNA segment with Na^+ counterion.

Figure 3. Chemical structure of hexadecyltrimethylammonium (CTMA).

in electrochromic display cells, as the conductivity of this macromolecule can be modulated by doping it with appropriate ions [7–10]. The electronic transport takes place essentially in the π electron stakes of nucleobases [11].

However one of the problems encountered with DNA is its temperature stability and solubility. DNA denatures at ca. 90°C, passing from double into single strand helix [12].

DNA is soluble in water only, which is also difficult to remove [13] and whose presence is technologically undesirable. Therefore the practical use of this polymer in photonics and in modern technologies seemed to be limited.

An important progress in view of using this materials in photonics was obtained by Ogata and coworkers [4,5] which have shown that DNA reacts with the surfactant hexadecyltrimethylammonium (CTMA) (cf. Fig. 3) forming a DNA-CTMA complex, stable up to ca. 230°C. Contrariwise to DNA the complex is soluble in a number of organic solvents and is insoluble in water [4]. Also it forms by solution casting excellent light propagation properties thin films with propagation losses between 0.1 dB/cm and 1.2 dB/cm in the large wavelength range of 600 to 1700 nm [14].

Recently it was shown that using another surfactants it is possible to obtain similarly stable complexes with better solubility [15].

However both DNA and DNA-CTMA macromolecules are only weakly light responding molecules, thus unusable as active materials in photonics. Although the fast electronic NLO susceptibility is one order of magnitude larger than for a commonly used in photonics poly(methyl methacrylate) (PMMA) [16], it is not sufficient to use it as a material for NLO devices. Therefore it has to be functionalized with optically responsive molecules. Indeed, such functionalization increases significantly the NLO response [16,17].

Because of its helical structure (cf. Fig. 1) DNA molecule (similarly as collagen) is very interesting for functionalization by doping. It exhibits a large free space in which molecule can be located. For DNA and DNA-CTMA complex four mechanisms of doping are possible:

(i) intercalation,
(ii) doping within the two helix grooves: larger and smaller (cf. Fig. 1),
(iii) statistical doping as in the case of synthetic polymers,
(iv) chemical reaction through the electrostatic attraction.

However one of the important questions to answer when using NLO chromophores in practical devices is that concerning their photochemical stability. They have to support large electric optical fields, particularly the UV light, as well as action of reactive molecules, such as e.g. oxygen. This problem is of primary importance when using synthetic polymers too. In the preceding papers [18,19] we have reported on the stability of several chromophores in DNA, DNA-CTMA and collagen. Here we report similar studies for other chromophores (DCM, Rhodamine 610, LDS 698, Nile Blue) dissolved in biopolymer: DNA, DNA-CTMA, Collagen and/or synthetic polymer matrices: PMMA, polycarbonate (PC), polyethylene glycol (PEG).

Materials and Methods

Materials

DNA used in this study was purchased in Japan from Ogata Research Laboratory, Ltd., Chitose. His molecular mass was reduced by controlled sonication process using the Sonic and Materials sonicator, model VC-250. The CTMA surfactant was purchased in Aldrich company and used as obtained. The chromophores used, whose chemical structures are shown in Fig. 4, were purchased either at Aldrich or at Exciton company.

The DNA-CTMA complex was obtained by reaction in water solution as described in Rau et al. [20]. The obtained by chemical reaction complex was carefully dried under vacuum in desiccator during two days.

The doping of collagen, DNA, DNA-CTMA, polymethylmethacryalete (PMMA), polycarbonate (PC) and plyethlene glycol (PEG) was done in solution. The same solvent was used to solubilise host and guest molecules. The lack of common solvents for some dyes, polymers or biopolymers limited the number of possibilities in synthesizing the functional complexes.

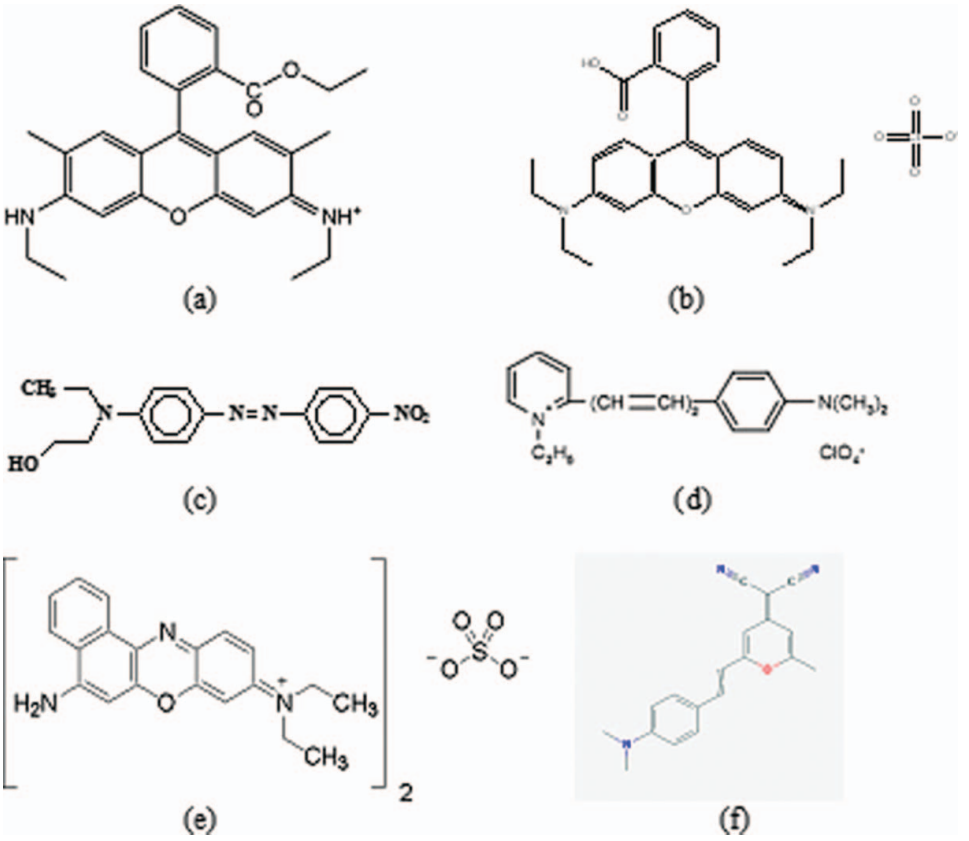

Figure 4. Chemical structures of studied chromophores: Rhodamine 490 (a), Rhodamine 610 (b), Disperse Red 1 (c), LDS 698 (d), Nile Blue (e) and DCM (f).

Apparatus

Thin films of studied compounds were obtained by spin coating of solutions on the carefully cleaned glass substrates. Spectroscopic grade solvents were used. The spin coating machine used was Laurell – Model WS – 400B – 6NPP/LITE.

The UV photodegradation measurements were performed using a commercial Vilber Urmat apparatus with two irradiation sources: UVA at 365 nm and UVB at 312 nm. In the present study only the photodegradation studies using UVB source were performed

The spectroscopic UV – VIS studies were performed with the JASCO UV – VIS – NIR spectrophotometer, model V 670.

Methodology

According to the Beer-Lambert law the transmission of a material T, defined as the ratio of transmitted I_T to incident intensity I_i decreases exponentially with its thickness l:

$$T = \frac{I_T}{I_i} = e^{-\alpha l} \tag{1}$$

where α is the linear absorption coefficient.

Eq. (1) is valid at low light intensities. At high light intensities, where multiphoton absorption takes place this equation is no more valid (see e.g. Ref. [21]).

In practice to describe absorption of a medium, one uses the notion of absorbance A (called also the optical density) defined as:

$$A = \log_{10} \frac{1}{T} = \alpha l \tag{2}$$

The advantage of this description is that the absorbance (for an isotropic medium like a solution) is directly proportional to the medium thickness l, i.e. to the number of molecules in optical beam, provided that the probing light beam is not completely absorbed. This linear relationship allows thus to determine and to follow the number of absorbing species in a solution, or in a thin film, provided that molecules are arranged in an isotropic way, as it is the case of solid solutions studied here. For ordered systems or partly ordered thin films the absorption measurements give information on the degree of orientation (see e.g. Page et al. [22]). Thus following the absorbance variation of a given material allows to monitor disappearance of molecules due to external stimuli: light, temperature, atmosphere, etc.

The optical absorption of any material dependes on the number of absorbing molecules. Therefore their decrease, due to the degradation, is reflected in the decrease of the material absorption. The kinetics of temporal degradation is usually described by the kinetic first order law:

$$\frac{dN(t)}{dt} = -kN(t) \tag{3}$$

where N(t) is the density of active species at time t and k is the kinetic degradation constant.

It means that the absorbing molecules density varies as

$$N(t) = N(t = 0)e^{-kt} \tag{4}$$

where $N(t = 0)$ is the initial concentration of absorbing species.

On the other hand, as it follows from the Lambert–Beer's law (cf. Eq. (2)), the optical absorption of a medium is proportional to the concentration N of absorbing species. The temporal variation of the optical absorption can be represented by the temporal variation of the optical density (absorbance) A(t) at the maximum absorption wavelength, provided there is no another competing phenomena. Thus Eq. (4) can be rewritten as follows

$$A(t) = A(t = 0)e^{-kt} \tag{5}$$

where $A(t = 0)$ is the initial absorbance.

Sometimes several phenomena contribute to the material degradation. In that case the degradation process is described by several degradation kinetics constants: $k_1, k_2, k_3, \ldots$. They can be determined by fitting the temporal variation of the optical density A(t) by two, or more exponential functions

$$A(t) = A_1e^{-k_1t} + A_2e^{-k_2t} + A_3e^{-k_3t} + \cdots \tag{6}$$

with

$$A_1 + A_2 + A_3 + \cdots = A(t = 0) \tag{7}$$

The kinetic degradation constant can be obtained from linear regression of measured temporal variation of log of optical density (cf. Eq. (3))

$$\ln A(t) = -k\,t + \text{const} \tag{8}$$

We have monitored and measured the optical absorbance at the maximum absorption wavelength λ_{max}. The methodology used is the same as that in a previous study [18]. Than the data were fitted using the Eq. (8).

An example of a least square fit of experimental data by Eq. (8) is shown in Fig. 5. The kinetic decay constant k is the slop coefficient of the straight line representing the fit.

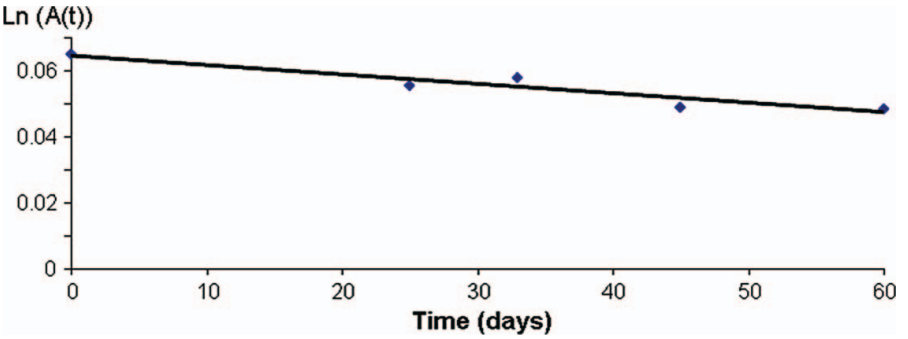

Figure 5. Example of a least square fit of the room temperature experimental data by Eq. (8).

Results and Discussion

As already mentioned the spectroscopic studies were done on thin films deposited on carefully cleaned glass substrates by spinning technique. This technique gives very regular, good optical quality thin films.

Glass BK7 was used as substrate. Obviously it cuts the UV part of absorption spectrum because of glass absorption but at the same time it provides a better heat conductivity and its evacuation.

Figures 6 and 7a–c show, as examples, thin film absorption spectra of DR1 chromophore, dissolved in DNA-CTMA matrix and Rhodamine 610 as function of dopant concentration, respectively. A significant variation of optical absorption spectrum of DR1 in DNA-CTMA with its concentration is observed. At small concentration (5 and 10 w%) the maximum absorption wavelength is situated at around 500 nm whereas at higher concentration it shifts to lower wavelength (ca. 450 nm for 20 w% of DR1). This behaviour may be due to the type of doping. As DR1 is a small molecule at low concentration it may intercalate at higher we have statistical doping. Other possible explanation is the aggregation, as DR1 is a dipolar molecule.

Figure 7 shows concentration variation of optical absorption spectrum of Rhodamine 610 chromophore embedded in 3 different biopolymers: DNA-CTMA (Fig. 7a), DNA (Fig. 7b) and collagen (Fig. 7c), respectively. In this case, in contrary to the previous, in all hosts matrices the maximum absorption wavelength doesn't change with dopant concentration, but the shape of the absorption band depends on host biopolymers. Also its value depends slightly on the host, both indicating importance of interaction with the matrix.

Thermal Degradation at Elevated Temperature

For the presently studied samples, the room temperature degradation was very slow therefore the kinetic degradation constants were not determined because of uncertainties in the

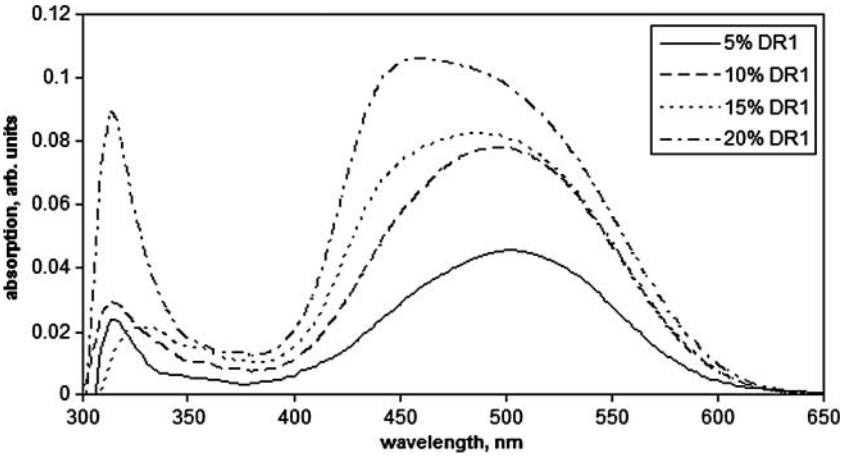

Figure 6. Chromophore concentration variation of optical absorption spectra of DNA-CTMA thin films doped with Disperse Red 1 (DR1) chromophore. The spectra are not normalized to the same thin film thickness.

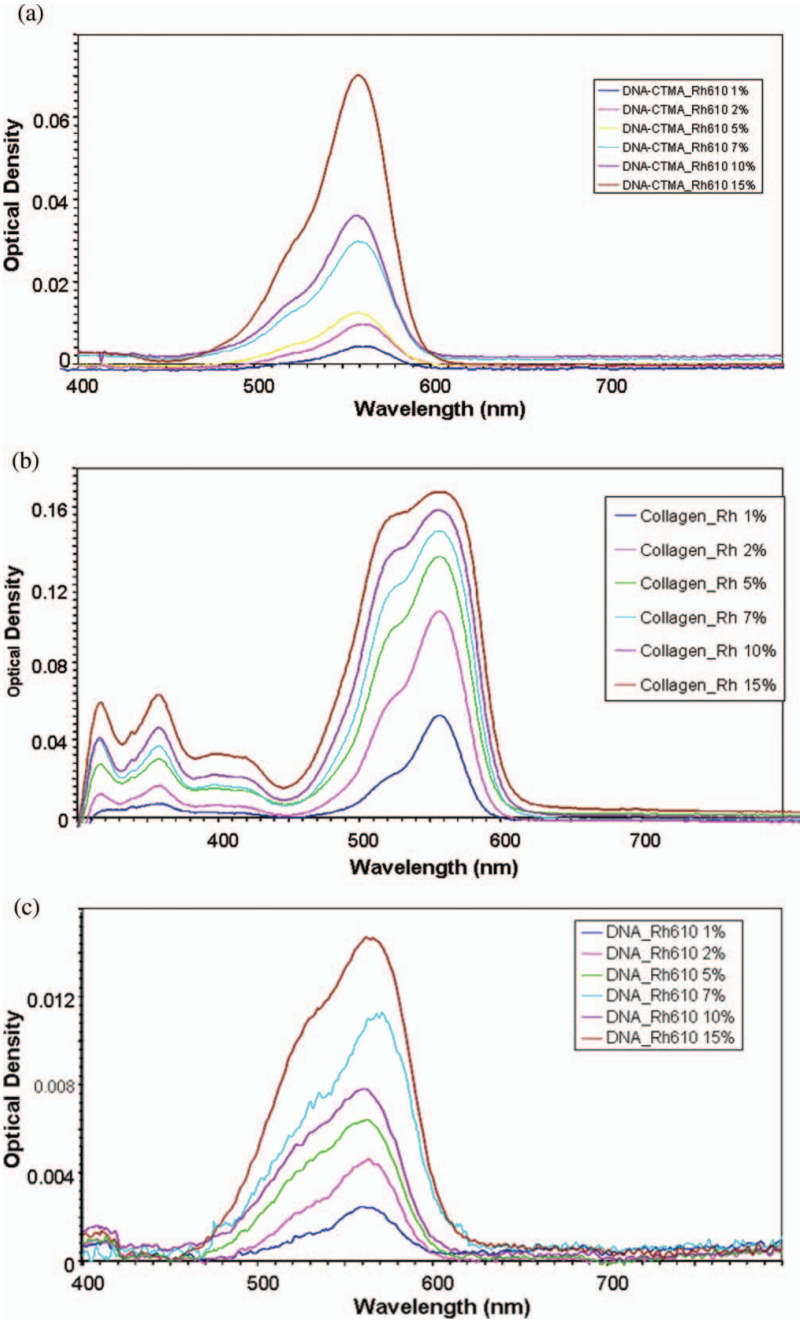

Figure 7. Concentration variation of optical absorption spectra for Rh610 in DNA-CTMA (a), DNA (b) and in collagen (c). The spectra are not normalized to the same thin film thickness.

measurements. Therefore the degradation process was accelerated by heating to higher temperature (85°C). From our previous studies [18] (see also Table 1) it follows that the degradation kinetic constants at this temperature are about three orders of magnitude higher than at room temperature.

Table 1. Room (k_{RT}) and elevated ($k_{85°C}$) temperature kinetic degradation constants, in min^{-1}, for studied chromophores embedded in different matrices

Chromophore	Concentration w%	Host	k_{RT} 10^{-6} (min^{-1})	$k_{85°C}$ (min^{-1})
Rh590[a]	5	DNA	2.78	6.68
Nile Blue	2	DNA-CTMA	NG	2600
	5			1300
	7			1200
	10			700
	15			400
	20			2600
Nile Blue	7	Collagen	NG	600
	10			400
	15			500
Rh590[a]	10	DNA-CTMA	2.57	40.0
	20		2.78	5.0
	5	Collagen	2.09	35
		Collagen + PEG	1.05	55
		PC	3.13	11000
		PEG	9.03	89000
LDS	5	DNA-CTMA		$k_1 = 27400$[b]
				$k_2 = 3600$
				$k_1 = 29000$[b]
	10			$k_2 = 5\,200$
	5	PC		2 600
	10			1 900
	15			2 400
DCM	5	DNA-CTMA		6 400
	10			6 300
	15			5 300
	5	PC		1 400
	10			1 700
	15			1 500

a – Ref. [18].
b – two decay constants were observed.
NG – negligible.

As already mentioned the chemical degradation of studied thin films was monitored by the temporal variation of their optical absorption spectra. An example of such a variation is shown in Fig. 8 for LDS 698 chromophore embedded in DNA-CTMA at the temperature of 85 °C and as function of the heating time. One observes a rapid decrease of absorbance with time and a small blue shift of the absorption spectrum, showing that the degradation process is associated with a decrease of the π electron conjugation length. The obtained data are listed in Table 1 and compared with some previously measured values [18]). One observes a good stability of Nile Blue in DNA CTMA and in DNA. For LDS 698 we observe two degradation kinetic constants showing that there is a fast and a slower degradation process.

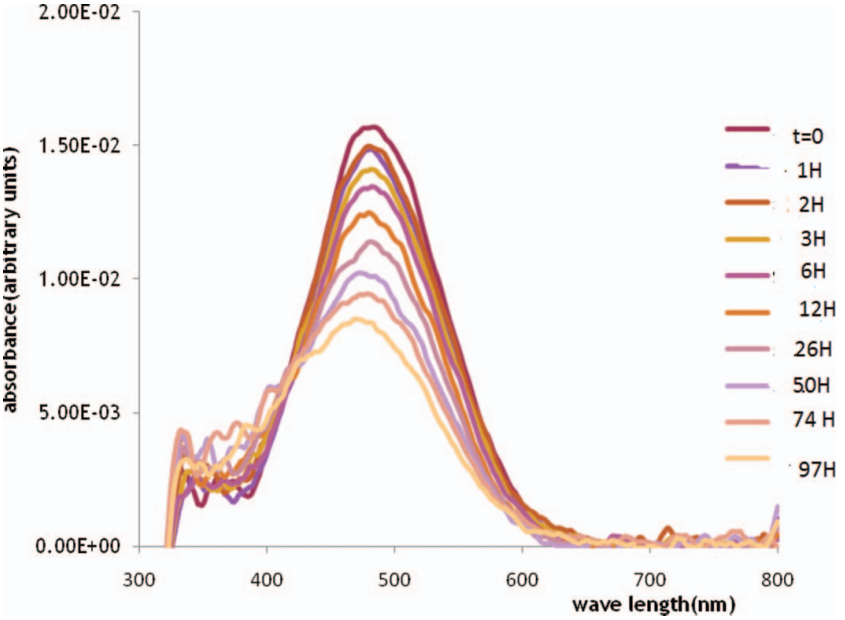

Figure 8. Temporal variation of optical absorption spectra of LDS698 in DNA-CTMA matrix under heating at 85°C.

It is also the less stable chromophore. Interesting is that the stability of this chromophore is better in PC than in DNA-CTMA.

The kinetic degradation constants, within experimental accuracy, depend little on the chromophore concentration.

Room Temperature Photo Degradation (Under UV Illumination)

As already mentioned, in the present study only the photodegradation at UVB(365 nm) was measured. The measured kinetic degradation constants are listed in Table 2 and compared with those determined previously for Rhodamine 590 and Disperse Red 1 [18].

Similarly as in thermal degradation studies LDS 698 chromophore is the less stable one and exhibits two degradation processes in DNA-CTMA complex. It is described by two kinetic degradation constants k_1 and k_2. One is large ($k_1 = 27400\ min^{-1)}$ and the second one is one order of magnitude smaller ($k_2 = 3600\ min^{-1}$ for 5 w% of LDS698 in DNA-CTMA). Rhodamine 610 exhibits a little better stability than Rhodamine 590. This is possibly due to the fact that Rhodamine 610 is an ionic compound and a kind of electrostatic interaction with the matix ensures its better stability. This molecule exhibits also a good stability in PMMA. Nile Blue is the most stable in two biopolymers DNA and Collagen. Nile Blue is also an ionic compound and the electrostatic interaction with these two biopolymers provides a kind of protection.

Similarly as in the case of thermal degradation the kinetic degradation constants, within experimental accuracy, do not depend on the chromophore concentration for a given matrix.

Table 2. Room temperature kinetic degradation constants in min^{-1} for studied chromophores embedded in different matrices and under UVA (312 nm) and/or UVB illumination

Chromophore	Concentration w%	Host	k_{UVA} 10^{-6} (min^{-1}) UVA 312 nm	k_{UVB} (min^{-1}) UVB 365 nm
Rh590[a]	5	DNA	3 800	2000
		Collagen	1600	2200
		PC	8900	2800
		PEG	5000	4500
		DNA + PEG	6100	4100
		Collagen + PEG	3330	2100
	10	DNA-CTMA	1000	2300
	20	"	800	1900
Rh610	7	DNA	NG	200
	15	"		470
	7	DNA-CTMA		1300
	15	'		800
	7	Collagen		1000
	15	'		1300
	1	PMMA		500
	15	'		400
DR1[a]	10	DNA-CTMA	880	2200
	20		1000	1800
Nile Blue	20	DNA		NG
	2	DNA-CTMA		2800
	5	"		1800
	7	"		1200
	10	"		1000
	15	"		900
	20	"		2300
	7	Collagen		600
	15	"		500
LDS698	5	DNA-CTMA		$k_1 = 27400$[a]
	"			$k_2 = 3600$
	10			$k_1 = 29000$[a]
	"			$k_2 = 5\ 200$
	5	PC		2600
	10			1900
	15			2400
DCM	5	DNA-CTMA		6400
	10			6300
	15			5300
	5	PC		1400
	10			1700
	15			1500

a – Ref. [18].
b – two decay constants were observed.
NG – negligible.

Conclusions

The spectroscopic studies performed on thin films reveal a significant interaction of guest molecules with the host matrix, as expected. This is seen particularly for DR1 molecule, where a significant blue shift and modification of the absorption band is observed as function of concentration. This observation is in favour of the doping mechanism by intercalation at small dopant concentration and a statistical one at higher concentration. Not such strong interaction is observed with other molecules. But this can be explained by their size making intercalation not possible.

The kinetic degradation depends on the composition, as we observed already. Heating and UV light accelerates the degradation, as expected. Among the studied chromophores the less stable is the luminophore LDS 698, which exhibits even two photo and thermal degradation processes, described by two distinct kinetic degradation constants. As previously observed these two degradation processes, within experimental, accuracy, do not show dependence on chromophore concentration.

The present studies confirm our earlier observations that DNA, and particularly the DNA-CTMA complex is a very interesting biopolymer to be used as matrix for active chromophores in view of their application in practical devices. The first order kinetic decay constants are smaller than if the chromophores are dissolved in PC or PEG. Also the laser damage thresholds; as determined previously [19] are very large for DNA and collagen, of few TW/m^2 for biopolymers.

Acknowledgments

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