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BIOPOLYMERS FOR APPLICATION IN PHOTONICS. PART 2

Keywords: Deoxyribonucleic acid, DNA, collagen, DNA-CTMA complex, linear optical properties, nonlinear optical properties, photoluminescence, photo-thermal stability, optical damage threshold, thin films.

Possibilities of utilization of biopolymers, and particularly of the deoxyribonucleic acid (DNA) are reviewed and discussed. The ways of their functionalization with photoresponsive molecules to get desired properties are described and illustrated on several examples as well as the processing of materials into thin films. Their room - and photo-thermal stability, studied by spectroscopic techniques is reported, together with optical damage thresholds. Physical properties, and more particularly linear, nonlinear and photoluminescent properties of obtained materials are also reviewed and discussed.

Ключевые слова: дезоксирибонуклеиновая кислота, ДНК, коллаген, комплекс ДНК-СТМА, линейные оптические свойства, нелинейные оптические свойства, фотолюминесценция, фототермическая стабильность, порог оптического разрушения, тонкие пленки.

Рассматриваются и обсуждаются возможности использования биополимеров, и в частности дезоксирибонуклеиновой кислоты (ДНК). На нескольких примерах дается описание способов их функционализации фоточувствительными молекулами для получения желаемых свойств, а также при переработке материалов в тонкие пленки. Спектроскопическими методами изучена стабильность при комнатных условиях, фототермическая стабильность, а также пороги оптических разрушений. Также рассматриваются и обсуждаются физические свойства, и, в частности, линейные, нелинейные и фотолюминесцентные свойства полученных материалов.

1. Introduction

In last 30 years time the synthetic polymers have found large applications in almost each domain of human activity, and particularly in construction, car industry, medicine, textile and more recently in advanced technologies. These polymers are obtained principally from coal and from oil by chemical transformation and synthesis. However, due to the fact that the coal and oil resources are limited on one hand and contribute to an important pollution of the planet on the other the scientists turns their attention to nature produced biopolymers. Indeed, the decay time for a thin foil of polyethylene (PET), used largely in fabrication of plastic bottles, is of 5 – 10 years. Also the largely used polystyrene (PS) decomposes in 50 years, low-density polyethylene (LDPE) in 500 – 1000 years. Polypropylene (PP), used in clothing and rope fabrication, practically does not degrade [1]. The fabrication of some polymers, like polyvinyl chloride (PVC), used largely in construction and in fabrication of toys is done with the use of toxic dioxin. Its degradation is associated with the production of unhealthy subproducts. These facts explain well the already mentioned switch of the scientists interest to natural biopolymers, originating from renewable resources and biodegradable.

One of these polymers which attracted recently some interest is chitosan which is a polysaccharide, occurring in the exoskeleton of invertebrates and in their internal structures. It was shown that it has some interesting optical properties [2, 3]. There are two biopolymers produced in a very large amount by nature which are the deoxyribonucleic acid (DNA) and collagen. Both are biodegradable, abundant and can be obtained from, *e.g.,* the waste of food producing industry.

In this Chapter some properties of obtained complexes as well as their practical applications also reviewed and discussed.

2. Materials

The deoxyribonucleic acid we are using in our studies was purchased at Ogata Photonics Laboratory, Chitose, Hokkaido, Japan. It is obtained from the waste produced in salmon processing [4, 5], particularly from roe and milt. Frozen roe and milt are first grinded. Then the grinded product is homogenized. Then starts the important and difficult process of protein elimination. The homogenized product is treated with enzymes DNA, dissolved in water and decolorized with active carbon. Finally the product is filtered and freeze-dried. The most delicate and difficult step in purification process is the separation of proteins. The final product contains usually *ca* 98 % of DNA and *ca* 2% of proteins ([5]).

Collagen is also obtained from the waste produced in meat processing. It is usually obtained from skin and bones of animals, principally such as beefs and porcs as well as from fish [6, 7]. The collagen used in our study was obtained at University Politehnica of Bucharest from beef skin using an original procedure described in Refs. [8, 9]. DNA is known to denature at around 90 °C, changing its helical structure from double stranded to single stranded [10, 11], limiting in this way the temperature range of applicability. Also thin film processing and water solubility only limits the possible range of its applications.

Collagen can be irreversibly hydrolyzed giving gelatine, which is largely used in food industry.

3. Stability of thin films in air

3.1 Kinetics of molecules degradation

One of the important problems with organic molecules is their chemical, thermal and photothermal stability. Although some molecules like benzene and one of the allotropic forms of carbon – diamond belong to the the most stable molecules/compounds, a lot of

others oxidize or decompose when heated to higher temperatures. This is essentially due to the reaction with oxygen which is omnipresent in the nature.

The material stability issue is one of the most important problems encountered with active molecules and materials. It determines whether or not they may be used in practical devices, as they have to operate in a given temperature range and for a given time duration. More strict requirements exist for materials to be applied in military devices. Therefore a lot of attention is devoted to the beahviour of materials under action of different factors, such as chemical environment, heating, light, and more particularly UV action. Some of these factors can be present simultaneously, influencing strongly the material behaviour. The materials have to support large electric optical fields, light illumination, 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.

One of the solutions envisaged to slow the degradation process is encapsulation protecting the material from the action of ambient oxygen. This appeared to be highly efficient in increasing the time of live of organic light emitting diodes (OLEDs), organic field effect transistors (FETs) and organic light emitting field effect transistors (OFETs), which are expected to revolutionize future light generation ways and lighting. Therefore the studies of the chemical and photothermal stability of new molecules and complexes envisaged to be used in such devices are important from the point of view of their practical utilization.

Moldoveanu et al [12] and Popescu et al [13] have studied the stability of several chromophores, such as Rhodamines 590 and 610, DR1, DCM, LDS698, Nile Blue (for chemical structures see Table 1.), dissolved in DNA, DNA-CTMA and in collagen matrices. For the sake of comparison they used for the same chromophores a few synthetic polymers, such as polyethylene glycol (PEG), polycarbonate (PC) and polymethyl methacrylate (PMMA). The chromophores degradation studies were performed in thin films by monitoring variation of their optical absorption spectra with time, at room temperature, at elevated temperature (85 °C) and under the action of UV A and B light (312 and 365 nm). The variation of optical absorption spectra under the action of different agents is the usually used technique for such kind of studies (see e.g. Refs [14-17]).

For these purposes the thin film absorption spectra of studied chromophores were monitored in visible light (the used matrices absorb in UV so their absorption does not interfere with the chromophore spectrum variation) at various time intervals. The films were obtained by solution casting (spinning) on transparent substrates (BK7 glass). The observed temporal variation of optical densities of studied films, for a given external degrading factor, were used to calculate the degradation constants, by assuming a pseudo-first order kinetic mechanism.

The advantage of this approach is that according to the Lambert – Beer's law the absorbance (optical density), at low light intensities and for an isotropic medium, like a solution or an isotropic thin film, 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. At high light intensities, where multiphoton absorptions take place this assumption is no longer valid [18].

This linear relationship between the absorbance and the number of molecules 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 considered here. For ordered systems or the partly ordered thins films the absorption measurements give information on the degree of orientation (see *e.g.* Page *et al* [19]). Thus following the absorbance variation of a given material allows monitoring the decay of molecules due to the action of external stimuli, such as: light, temperature, presence of reactive chemical agents, etc.

The kinetics of temporal degradation of a thin film can be described by the first order law:

$$\frac{dc}{dt} = -kc \qquad (1)$$

where c is the concentration of active species and k is the first order kinetic degradation constant.

It means that the concentration c(t) varies with time t as

$$c(t) = c(t=0)e^{-kt} \qquad (2)$$

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

On the other hand, as it follows from the Lambert – Beer's law, the optical absorption of a medium is proportional to the concentration c(t) 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. Thus Eq. (5.2) can be rewritten as follows

$$A(t) = A(t=0)e^{-kt} \qquad (3)$$

where A(t=0) is the initial optical density.

The kinetic degradation constant can be obtained from linear regression of measured temporal variation of optical density (Eq. (5.3))

$$\ln A(t) = -k\,t + \text{const} \qquad (4)$$

It may happen that 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, …..They can be determined by fitting the temporal variation of the optical density A(t) by two, or more exponential functions

$$A(t) = A_1 e^{-k_1 t} + A_2 e^{-k_2 t} + A_3 e^{-k_3 t} + \ldots \qquad (5)$$

with

$$A_1 + A_2 + A_3 + \ldots = A(t=0) \qquad (6)$$

3.2 Chemical degradation at room temperature

The discussed here thermal and photodegradation studies of spin coated thin films, deposited using Laurell – Model WS – 400B – 6NPP/LITE spin coater, were performed with a JASCO UV – VIS - NIR spectrophotometer, model V 670. Figure 1 shows, as an example, the variation of the optical absorption spectrum of DNA-Rh 590 thin film as function of time. Over the period of 39 days a slow, monotonic decrease of the optical density of studied film is observed.

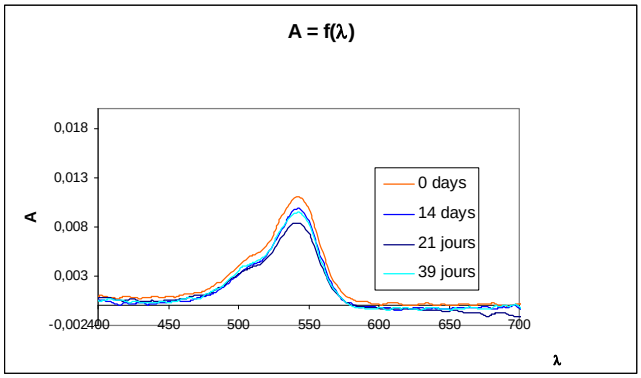
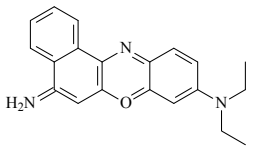
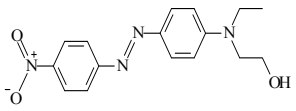
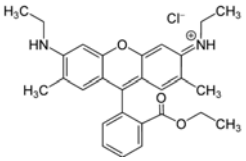
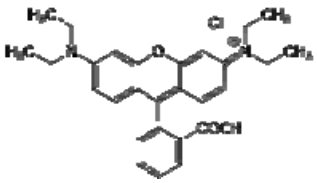


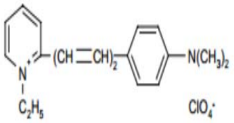
Fig. 1 - Variation of the optical absorption spectrum of DNA- Rh 590 thin film as function of time (in days)

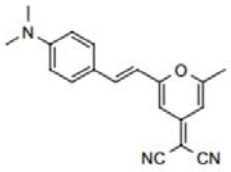

Nile Blue

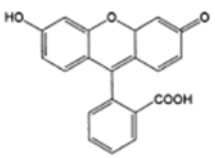

Disperse Red 1

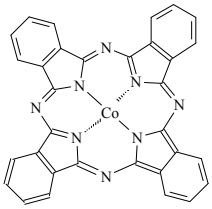

Rhodamine 590 chloride


Rhodamine 610 chloride


LDS 698 perchlorate


DCM


fluorescein


CoPc

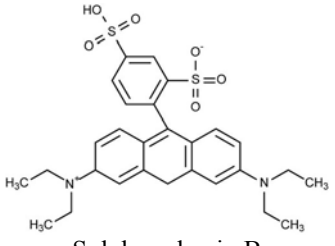

Sulphorodamin B

Figure 2 compares the least squares fit of Eq. (4) to the temporal, experimental variation of the maximum of optical density with time for Rhodamine 590 embedded in DNA (a) and in a synthetic polymer polyethylene glycol (PEG) (b). The observed much larger decay slope in the case of PEG matrix indicates a significantly faster (about 3 orders of magnitude difference) decay of Rhodamine 590 in the synthetic polymer as compared with the DNA –CTMA matrix.

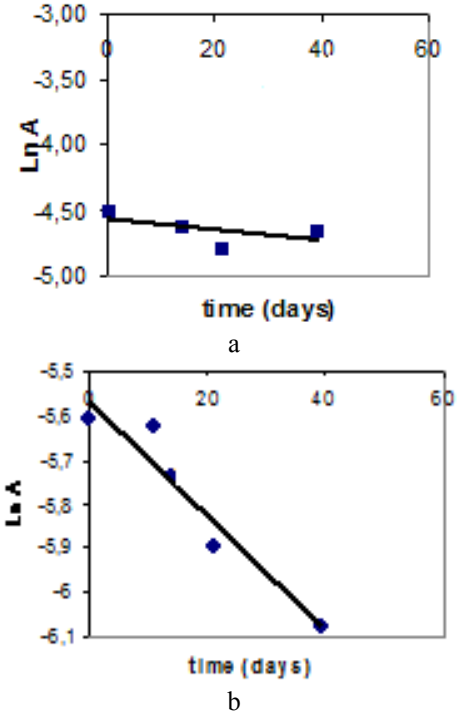


Fig. 2 - Least squares fit of Eq. (4) to neperian logarithm of experimental absorbances at room temperature for DNA-Rh590 and PEG-Rh590 thin films (b). Squares and diamonds show measured values while solid lines the fitted ones

Table 1 - Room and high (85°C) temperature kinetic degradation constant of Rhodamine 590 at different matrices (after Moldoveanu [12])

Host material	Room temperature kinetic degradation constant k_1 ($mins^{-1}$)	Kinetic degradation constant k_1 at 85°C ($mins^{-1}$)
DNA	$2.78x10^{-6}$	$6.68x10^{-6}$
DNA+PEG	$6.57x10^{-6}$	$51.7x10^{-6}$
Collagen	$2.09x10^{-6}$	$35x10^{-6}$
Collagen+PEG	$1.05x10^{-6}$	$55x10^{-6}$
PC	$3.13x10^{-6}$	$11000x10^{-6}$
PEG	$9.03x10^{-6}$	$89000x10^{-6}$

The determined in this way the room temperature kinetic degradation constants for Rhodamine 590 embedded in different matrices are given in Table 1. In all cases the chromophore decay can be described by a single exponential function. Although at room temperature the kinetic degradation constants are of the same order of magnitude for

different matrices however the lowest stability is observed in PEG (k_1 = 9.03x10^{-6} min^{-1}). Adding biopolymers improves significantly the chromophore stability (adding DNA: k_1 = 6.57x10^{-6} min^{-1}, with collagen one obtains the best stability for this chromophore k_1 = 1.05x10^{-6} min^{-1}, respectively). The stability of Rhodamine 590 in DNA is very similar to that in other two matrices: collagen and polycarbonate (PC), being close to the value of k_1 = ~ 3x10^{-6} min^{-1}.

Table 2 lists the room temperature decay constants for several chromophores embedded in different matrices and for different concentrations. Nile Blue, DCM and LDS 698 show very good stability, with negligible first order decay constants in biopolymers DNA – CTMA and in collagen. A good stability shows also DCM in PC.

Table 2 - Room ($k_{20°C}$) and elevated ($k_{85°C}$) temperature kinetic degradation constants, in min^{-1}, for studied chromophores embedded in different matrices

Chromophore	Concentration w%	Host	k_1(20 °C) 10^{-6}(min^{-1})	k_1(85 °C) (min^{-1})
Rh590[a]	5	DNA	2.78	6.68
Nile Blue	2 5 7 10 15 20	DNA-CTMA	NG	2600 1300 1200 700 400 2600
Nile Blue	7 10 15	Collagen	NG	600 400 500
Rh590[a]	10 20	DNA-CTMA	2.57 2.78	40.0 50.0
	5	Collagen	2.09	35
		Collagen + PEG	1.05	55
		PC	3.13	11000
		PEG	9.03	89000
LDS 698	5 10	DNA-CTMA	NG	k_1=27400[a] k_2=3600 k_1=29000[a] k_2=5 200
	5 10 15	PC	NG	2 600 1 900 2 400
DCM	5 10 15	DNA-CTMA	NG	6 400 6 300 5 300
	5 10 15	PC	NG	1 400 1 700 1 500

a - two decay constants observed
NG - negligible

3.3 Chemical degradation at elevated (85 °C) temperature

Since the room temperature degradation (20 °C) are usually very low, the measured values of kinetic degradation constants are affected by a large error because of high uncertainties in the measurements. Therefore the degradation process was accelerated by heating the films to higher temperature (85°C), however bellow the stability limit temperature of DNA (*ca*. 90°C).

Tables 1 and 2 gives also first order kinetic decay constants measured at elevated temperature (85 °C) and compare them with room temperature data Only in the case of LDS 698 chromophore, embedded in DNA - CTMA matrix, a double exponential decay was observed. In the case of biopolymer matrices and Rhodamine 590 chromophore the kinetic decay constants are less than one order of magnitude larger than at room temperature (Table 1). However in the synthetic polymer matrices PC and PEG this increase is by *ca* three orders of magnitude. Also adding of PC or PEG to DNA or to collagen increases the kinetic decay constants.

Table 2 lists the kinetic decay constants measured at 85 °C for different chromophores and their concentrations, embedded in various matrices. Their large increase, compared to room temperature data, is observed. The chromophore LDS 698, which shows an excellent stability at room temperature, decays rapidly at 85 °C in both used matrices: DNA – CTMA and in PC. Moreover, in biopolymer the decay of this chromophore is described by two kinetic decay constants, what means that there are two different processes behind. A very pecular is also the concentration dependence of kinetic decay parameter observed for Nile Blue embedded in DNA – CTMA matrix. It decreases with chromophore concentration up to 15 w% and increases at 20 w%. This may be due t intercalation or groves inclusion of this chromophore. Indeed Nile Blue is known to stain DNA and is used for this purpose.

3.4 Kinetics of photodegradation

Table 3 - Kinetic degradation constants k_1 (in min^{-1}) under UV irradiation for Rh610 in different matrices, irradiated at 312 nm

Concentration	DNA-Rh610	DNA-CTMA-Rh610	Collagen-Rh610
1%	0,0019	0,0022	0,001
2%	0,0021	0,0029	0,0009
5%	0,0014	0,002	0,0006
7%	0,0002	0,0013	0,001
15%	0,0047	0,0008	0,0013

The described here photodegradation measurements were performed using a commercial Vilber Urmat apparatus equipped with two irradiation sources: UVA at 365 nm and UVB at 312 nm. The illumination intensity was of 6.5 mW/cm^2 for UVA and 2.5 mW/cm^2 for UVB. It means that the ratio of photons illuminating the sample at UVA to that at UVB n_{UVA}/

$n_{UVB} \approx 2.6$. All measurements were done at room temperature. Table 3 lists first order kinetic degradation constants under UVB for Rhodamine 610 in 3 biopolymers: DNA, DNA-CTMA and collagen. No significant dependence on the matrix and on chromophore concentration is observed within experimental efficiency. However the the chromophore degradation is fast with kinetic degradation constants about three orders of magnitude larger as compared to room temperature values.

Table 4 shows the room temperature photodegradation constants for selected chromophores in bio- and synthetic polymer matrices for different chromophore concentrations.

Table 4 - Photodegradation kinetic constants, in min^{-1}, for selected chromophores embedded in different matrices and under both UVB (312 nm) and UVA (365 nm) irradiation

Chromophore	Concentration w%	Host material	k_{UVB} 10^{-6} (min^{-1})	k_{UVA} 10^{-6} (min^{-1})
Rhodamine 590	5	DNA	3 800	2000
		Collagen	1600	2200
		PC	8900	2800
		PEG	5000	4500
		DNA + PEG	6100	4100
		Collagen +	3330	2100
	10	PEG	1000	2300
	20	DNA-CTMA	800	1900
Rhodamine 610	7	DNA	NG	200
	15	"		470
	7	DNA-CTMA		1300
	15	"		800
	7	Collagen		1000
	15	"		1300
	1	PMMA		500
	15			400
DR1	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 - two decay constants observed
NG - negligible

The kinetic photodegradation constants are, generally, three orders of magnitude larger than in dark. Interesting is a very good stability of pure Nile Blue in DNA. This molecule is known to stain DNA, forming most likely, a stable complex with this biopolymer. It is less stable in two other matrices PC and DNA-CTMA, with a worse stability in the second. LDS also shows a better stability in PC than in DNA-CTMA. In DNA-CTMA it exhibits two kinetic photodegradation decay constants, similarly as when heating. The kinetic degradation constants increase with increasing NB concentration most likely due to its aggregation. Obviously the photodegradation of chromophores depends on the presence or lack of absorption bands at the illumination wavelength why the results shown in Table 4 will be different if shining with another wavelength. Therefore comparison at one wavelength of kinetic photodegradation constants may be misleading.

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

The kinetic degradation depends on the composition. 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 values listed in Tables 1 - 4 for kinetic photodegradation constants correspond to the specific experimental conditions, *i.e.* temperature, ambient atmosphere, etc. The measurements were performed in air and on thin films. In solution, bulk material and in neutral atmosphere they will be different. However they allow a comparison of the chemical stability of different chromophores in various matrices at the same conditions, although in the case of photodegradation the kinetic degradation constants are expected to depend strongly on the illumination wavelength.

3.5 Optical damage threshold

Another important parameter determining the usefulness of a given material in devices working in extreme conditions, like high intensity light sources delivered by lasers is the optical damage threshold. It is understood as the highest light intensity the material withstand without a permanent damage. For higher light intensitties a permanent damage to the illuminated material takes place. It is caused by very high optical fields leading to the dielectric breakdown in material. Figure 3 shows speckles created in a transparent biopolymer thin film by a high intensity laser beam.

High and ultrahigh light intensities are created by pulsed Q switched and mode locked lasers, although the optical damage to a material can be caused also by low intensity cw lasers if the light beam is absorbed. The light absorption causes increase of the temperature and decay of material through melting, photochemical reaction or even evaporation. These processed are not

considered here, assuming material with no absorption. The only damage possible, taken under consideration, is that produced through the dielectric breakdown or multiphoton NLO absorptions, thus heating.

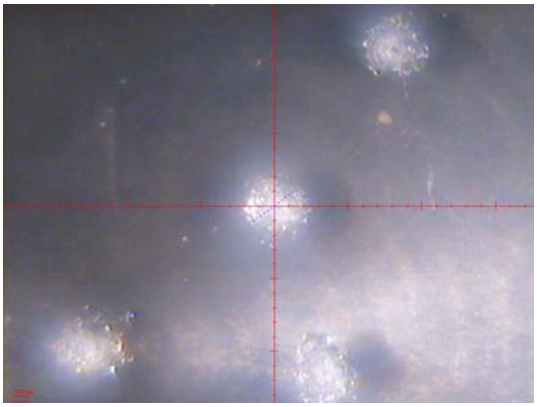


Fig. 3 - Optical microscope image of speckles created in a DNA thin film during the optical damage threshold experiment

The measured optical damage thresholds (GW/cm^2) for studied biopolymers are listed here.

1. DNA-CTMA-DR1 – 5 w% - 3.3
2. DNA-CTMA-DR1 – 10 w% - 3.6
3. DNA-CTMA-DR1 – 20 w% - 4.8
4. DNA-CTMA - 5.2
5. DNA - 5.3
6. collagen - 4.4
7. PC - 0.30
8. PEG - 0.78

They correspond to the specific experimental conditions, *i.e.* wavelength of 1064.2 nm; repetition rate of 10 Hz and pulse duration of 6 ns. At another wavelengths, pulse duration times and repetition rates they will be different. For shorter laser pulses the optical damage threshold will be higher. It will be similar for lower repetition rates. Higher repetition rates will induce a faster material degradation due to the heat accumulation. Also absorption will decrease the damage threshold. However they allow comparing the behaviour of different materials at the same conditions. The data shows, that compared to the thin films of studied synthetic polymers (polycarbonate (PC) and polyethylene glycol (PEG), the films three biopolymers: collagen, DNA and DNA– CTMA exhibits about one order of magnitude higher damage thresholds. Adding DR1 to chromophore decrease only a little the thin film DNA-CTMA complex damage threshold. This is a very interesting result showing a high potential for using biopolymers in photonics

4. Optical thin film properties

4.1 Linear optical properties

DNA and DNA-CTMA molecules exhibit a large transparency range, the lowest energy absorption being that of phenyl rings, located around 260 nm (cf. Figure 4). The absorption UV cut-off is around 325 nm whereas in near IR only the absorption of harmonics of high energy CH and OH vibrations are present.

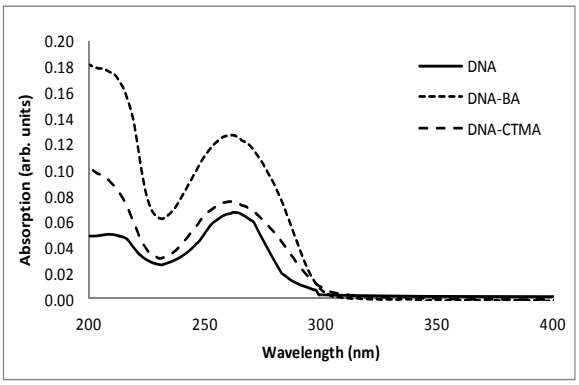


Fig. 4 - Optical absorption spectra of DNA and two DNA-surfactant complexes

Adding surfactant does not alter the transparency band as only the aromatic ones add absorption at 260 nm where absorb nucleobases. The refractive index of DNA-CTMA thin films varies between 1.582 in UV (300 nm) and 1.482 in NIR (1000 nm) [20].Compared to silica it is slightly higher in UV because of the absorption of nucleobases and lower in NIR.

DNA – CTMA thin films exhibit low propagation losses, particularly in the telecommunication wavelength range (1.3 – 1.55 μm). At 1.3 μm the propagation they are of 0.2 dB/cm, a value comparable to that observed in best synthetic polymers. It is even lower (0.1 dB/cm) at 800 nm, the wavelength used for interconnects and local area networks (LAN's).

The relatively low index of refraction and good transparency make these complexes interesting for application as cladding layers in Mach – Zehnder interferometer type in waveguiding configuration electro-optic modulator (EOM) [21, 22]. Indeed, in that case a better distribution of electric field in the EOM structure: buffer layer/active layer/buffer layer is obtained with its larger value in active layer. At allows to obtain a better orientation of chromophores in active layer.

Another interesting result concerning the temperature variation of refractive index of DNA – CTMA and DNA-CTMA doped with Nile Blue was reported by Hebda *et al* [20]. The refractive index of thin film DNA – CTMA alone increase between 0 and 40 °C showing negative thermal expansion in this temperature range. Adding 5 w% of Nile Blue compensates this negative expansion. It means that one can get a polymer with no thermal expansion. Such property is very important for practical applications.

4.2 Nonlinear optical properties

4.2.1 Second order nonlinear optical properties

As already mentioned collagen lacks centre of symmetry. Thus it is expected it will exhibit, not very important because of lack of conjugated p electrons, second – order nonlinear optical properties (NLO) properties. Indeed Vasilenko *et al* [23] reported already in 1965 the first observation of second harmonic generation (SHG) in protein – collagen complex. This observation was confirmed later (1971) by Fine and

Hansen [24]. Two other polypeptides, tubulin and myosin [25-27] were shown also to exhibit the second order NLO properties. Much more recently SHG measurements were reported for polysaccharides, such as starch and cellulose [28-34].

The ability of collagen and other biological species to exhibit SHG has attracted a lot of interest (for a review see Knoesen [35]), not only because of its interest for basic knowledge, but also because of the possibility it gives for imaging. Indeed a lot of research which followed was devoted to the use of nonlinear optical techniques for imaging of biological tissues (see *e.g.* Lee *et al*. [36]).

There are very little data on second-order NLO properties of DNA alone, although this chiral molecule should exhibit such effects, as observed in this type of materials (see *e.g.* Ostroverkhov *et al* [37], Sioncke *et al* [38], Iwamoto *et al* [39]) and the already mentioned for collagen. These authors have observed in chiral structure an intensity dependence of SHG signal on the polarization of incident laser beam with respect to the helix.

In several recent papers the second harmonic generation technique was used as a tool for studying the interaction of DNA with environment or for detection of its modifications. In fact, SHG is a very sensitive technique to study the interfaces [40], as the bulk centrosymmetry is broken there and the observation of frequency doubling is no more forbidden by symmetry, as it is the case of centrosymmetric structures. In particular Boman *et al* [41] reported on using SHG to study the formation of the DNA double helix at the quartz surface due to the pairing of adenine and thymine nucleobases. Zhuang Zheng-Fei *et al* [42] used this technique as a detection tool of the very early malignancy in prostate glandular epithelial cells. Williamson *et al* [43] reported observation of a humidity dependent optical SHG signal from spun films of DNA. Note that Yamada Satoru *et al* [44] performed theoretical calculations of NLO properties of modified guanine bases with a NLO group.

Using the experimental set up described in Ref. [45] we have attempted poling of spin deposited thin films of DNA-CTMA complex, doped with a highly responsive, noncentrosymmetric (3-(1,1-dicyanothenyl)-1-phenyl-4, 5-dihydro-1H-pyrazole) (DCNP) molecule. This is the commonly used way to create noncentrosymmetry in primarily centrosymmetric thin films by applying high DC electric field, and particularly in so called electro-optic polymers [46]. The polar orientation of chromophores is usually done at higher temperatures where the polymer chain mobility becomes relatively large and facilitates their orientation. Then it is by cooling the polymer thin film down to room temperature. The obtained degree of polar order depends on the used polymer matrix and on the strength of the applied electric field E_{DC} as well as on the ground state dipole moment of chromophore. In the present case it was done by *in situ* corona poling technique. Figure 5 presents the temporal variation of the *in situ* measured SHG intensities at different temperatures. At 60 °C, i.e well below the DNA denaturation temperature (ca 90 °C)) we observe after switching on the poling field an increase of SHG signal (triangles, black). But after reaching a certain value the SHG intensity drops to a low value and starts to increase again, drops, increase. These oscillation don't have a fixed period. Similar behaviour was observed in Electric Field Induced Second Harmonic Generation measurements on a polydiacetylene thin film and were explained by formation of electrets in studied material [47].

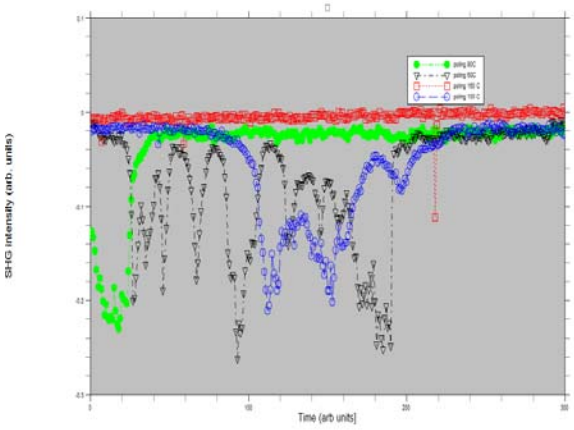


Fig. 5 - Temporal variation of SHG intensity during the poling process at different temperatures

After some number of oscillations no more the polar order formation is observed. This behaviour may be due to the existence of deep traps in DNA, a phenomenon we observed already with BioLED [48]. The poling process, accompanied by a flow of charges through the poled films is associated with formation of electrets, *i.e.* pairs of electron holes, because of electron trapping. Such pairs obviously create an electric field opposed to the applied poling field, cancelling it. This explains decrease of SHG signal. The charges are obviously created by two – and/or more photon absorption [16] process, and/or by SHG photons. The increase after is most likely due to the detraping of charges via a two (and/or more) photon absorption and/or harmonique photons..

4.2.2 Third-order nonlinear optical properties

There is a little research of third-order NLO properties of pure DNA. One of the first problems treated by NLO technique was the mobility of DNA helix under the applied electric field. This study is difficult for two main reasons: DNA is soluble in water only and exhibits a large ionic conductivity. This solvent is also necessary to maintain its integrity. DNA itself is a polyelectrolyte. Application of an external electric field induces an ionic dipole moment [49-52] and changes the conformation of DNA [53, 54].

There are no symmetry restrictions on third order NLO effects, such as for second order effects where lack of center of inversion is required. Obviously the third – order NLO susceptibilities depend on the order, as it is always the case. The number of non-zero tensor components depends on material crystallographic symmetry, but the NLO effect is present in any material medium.

Samoc *et al* [55] have measured real and imaginary parts of the nonlinear index of refraction of DNA in solution by wave dispersed femtosecond z-scan technique. They have found that it varies between $2x10^{-15}$ and 10^{-14} cm^2/W in the wavelength range 530–1300

nm. They report also observation of a weak two photon absorption (TPA) below 600 nm, with nonlinear absorption coefficient equal to 0.2 cm/GW at 530 nm. Apparently it corresponds to two photon transition to the first excited level of nucleobases phenyl rings. Such two photon transitions are allowed because of chiral structure of DNA. There is lot of experimental techniques allowing to measure third-order NLO susceptibilities. Hereafter we will describe few of them; particularly those which were used in studying NLO response of DNA based materials.

Rau *et al* measured third-order NLO properties of pure DNA-CTMA and DNA-CTMA-DR1 complexes by optical third harmonic generation (THG) technique (see *e.g.* Kajzar [56]). THG is an NLO process in which 3 photons with frequency ω generate a photon with triple frequency 3ω *via* interaction with matter. In other words a light beam with wavelength λ will be transformed into a beam with shorter wavelength λ/3. The main advantage of this technique is the fact that the response time is very fast as the harmonic field oscillations have to follow that of fundamental beam. Thus the response time is in the 10^{-15} s time domain when working in the visible and near IR electromagnetic field range. Therefore the THG technique is very interesting to measure the fast, electronic origin, third-order NLO susceptibilities of different materials as the other technique, *e.g.* z-scan, degenerate and non-degenerate two (TWM), four wave mixing techniques (FWM) give the values which may contain large orientation contributions[57]. Also the thermal contributions can be important when not using very short (fs) laser pulses, particularly when the excitation wavelength is within the material absorption band or a multiphoton absorption [16] is present.

The THG data obtained for thin films of DAN – CTMA and DNA – CTMA complexes doped with DR1 chromophore are reported in Table 5.

Table 5 - DNA – CTMA and DNA – CTMA – DR1 thin film thicknesses (in □m), fundamental wavelength refractive indices, coherence lengths and third order nonlinear optical susceptibilities $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$

Sample	Thickness [μm]	Refractive index n_ω	Coherence length [μm]	$\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ in 10^{-14} [esu]
DNA-CTMA	0.367	1.488[a]	7.4 [a]	11.5±1.2
DNA-CTMA-DR1 (5%)	3.484	1.488[b]	7.4	155±16
DNA-CTMA-DR1 (10%)	4.060	1.488[b]	7.4	69±7
DNA-CTMA-DR1 (15%)	3.484	1.488[b]	7.4	85±9
silica	1010	1.44967	6.71	1.43±0.14[c]
PMMA		1.4795[d]	8.28[d]	3.2[d]

a - Grote et al [60]
b - assumed (see text).
c - Gubler and Bosshard [58].
d - Morichere et al [59].

They are calibrated with recently determined THG susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ value [58] of silica used as standard and are compared with the value obtained for polymethyl methacryalate (PMMA) thin film [59]. In the screening procedure the refractive indices for DNA-CTMA complex thin films, reported by Grote *et al* [60] were used. We used the same refractive indices for DNA-CTMA-DR1 complexes as for pure DNA-CTMA. Indeed their expected modification is not large and the harmonic intensities do not depend on their difference but on their sum [61]. Therefore the error in $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ susceptibility of these complexes is expected to be small.

The DNA based thin films exhibits about one order of magnitude larger cubic susceptibility than silica and PMMA. This is due to the already mentioned contributions from the polarizability of π electrons in nucleobases, absent in these materials. Interesting is behaviour of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ susceptibility with dopant concentration (DR1). At 5 w% of DR1 one observes a large increase, up to $(155\pm16)\times10^{-14}$ esu from $(11.5\pm1.2)\times10^{-14}$ esu for pure DNA-CTMA thin film. At 10 w% of dopant $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ decreases to $(69\pm7)\times10^{-14}$ esu, to increase again at 15 w% of DR1 to $(85\pm9)\times10^{-14}$ esu, respectively. This strange behaviour was tentatively explained by Rau *et al* [62] within a three level quantum model as due to the blue shift of DR1 absorption band caused by aggregation of these molecules. As consequences the two photon resonant contribution of charge transfer (CT) band, predominant in NLO susceptibility is varying with the dopant concentration [62].

Samoc *et al* [63] determined the real and imaginary parts of the nonlinear index of refraction of DNA in solution by wave dispersed femtosecond z-scan technique. They found that it varies between 2×10^{-15} and 10^{-14} cm^2/W in the wavelength range 530-1300 nm. They have reported also an observation of a weak two photon absorption (TPA) below 600 nm, with nonlinear absorption coefficient equal to 0.2 cm/GW at 530 nm. Apparently it corresponds to the two photon transition in phenyl rings.

Derkowska *et al* [64] have reported the degenerate four wave mixing (DFWM) and nonlinear transmission measurements on DNA-CTMA complex, doped with several complexes, such as DR1, cobalt phthalocyanine (CoPc) and fullerene C_{60}. A different behavior of DFWM susceptibility than when these molecules are dissolved in other solvents was observed, indicating the influence of ionic environment of DNA on electronic structure of embedded chromophores.

Very interesting results on behavior of guest molecules were reported by Mysliwiec *et al* [65] by optical phase conjugation perfomed on DNA-CTMA-DR1 thin films which shows and about four orders faster response, due to the trans-cis-trans izomerization, than if the same chromophore is embedded in PMMA matrix [66]. It is even faster in the case of disperse orange (DO3) molecule [67], which isalso an azodye, but smaller than DR1. In that case the response time is in □s range, depending on beam intensity, about three orders of magnitude shorter than in the case of DR1. in

both cases the peculiar double strand structure of DNA and the large free volume are believed to be behind this short response time.

4.3 Photoluminescent properties of functionalized DNA and DNA – surfactant complexes

DNA and DNA-CTMA complexes appear also as an interesting matrix for luminophores. Several research groups reported enhancement of photoluminescence of certain luminophores when embedded in DNA or DNA-surfactant (usually CTMA) matrix. In particular Wang *et al* [68], reported enhanced photoluminescence of rare earths ions 6,6.7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5,-octanedionate, (Eu^{3+}-FOD) in DNA-CTMA matrix both in thin films and in optical fibers, with fluorescence lifetime of 750 □s. Both the fluorescence lifetime and the emission quantum efficiency were found to be larger in DNA-CTMA matrix than in the reference material PMMA.

Yu *et al* [69, 70] observed a a 17 times larger photoluminescence from Sulforhodamine (SRh) embedded in DNA matrix as compared when the matrix used was PMMA. The maximum of emission was realized with 1 wt % concentration of SRh in DNA. With a distributed feedback structure with 437 nm period they observed amplified spontaneous emission (ASE) at 650 nm wavelength and lasing with threshold of 30 $\mu J/cm^2$.

Massin *et al* [71] compared photoluminence quantum efficiency of three different luminophores (cf. Figure 6(a)), dissolving them in solid PMMA and in DNA – CTMA matrices. For two of them (for details see Ref. [68]) the pholuminescence quenching takes place at higher concentration when using DNA-CTMA as matrix, as compared with PMMA. Also a blue shift of the fluorescence spectra in the case of DNA-CTMA matrix is observed, showing influence of DNA environment. Figure 6 (b) displays the concentration variation of the photoluminescence quantum yield ratio in DNA-CTMA/PMMA for these three chromophores. In the chase of Chr 1 this ratio increases with concentration showing higher quenching limit when the chromophore is embedded in biopolymer matrix. For the other two the ratio is almost constant, being larger than 1.

Koyama *et al* [72] reported enhancement of photoluminescence of fluorescein in DNA –CTMA matrix, as compared to PMMA. Increase of photoluminescence efficiency was also observed for natural chromophores: green tea extract (GTE) in DNA [73] and sea buckthorn extract (SBE) in DNA-CTMA [74] as compared when using PMMA matrix

Very recently Kobayashi and co-workers have demonstrated an electric field steered, large emission wavelength range of a DNA based BioLED with AlQ_3 and $Ru(bpy)_3^{2+}$ as active molecules [75, 76].

DNA [77] and DNA– surfactant [78-81] thin layers were also used as electron blocking layers in Bio Light Emitting Diodes (BioLEDs) allowing to get a significant increase of luminance efficiencies

DNA and DNA-CTMA complexes are also interesting matrices for lasing [82-84]. Amplified spontaneous emission (ASE) was observed by several research groups [37,86-87] (for a recent review see Ref. [88]). In particular Mysliwiec *et al* [89] have observed photoluminescence and ASE from MR isomer of spiropyrane embedded in DNA-CTMA matrix. These effects are not observed when using synthetic polymers as matrix, such as, *e.g.* polymethyl methacrylate (PMMA). A two photon lasing was also demonstrated in a DNA-CTMA-chromophore complex [90].

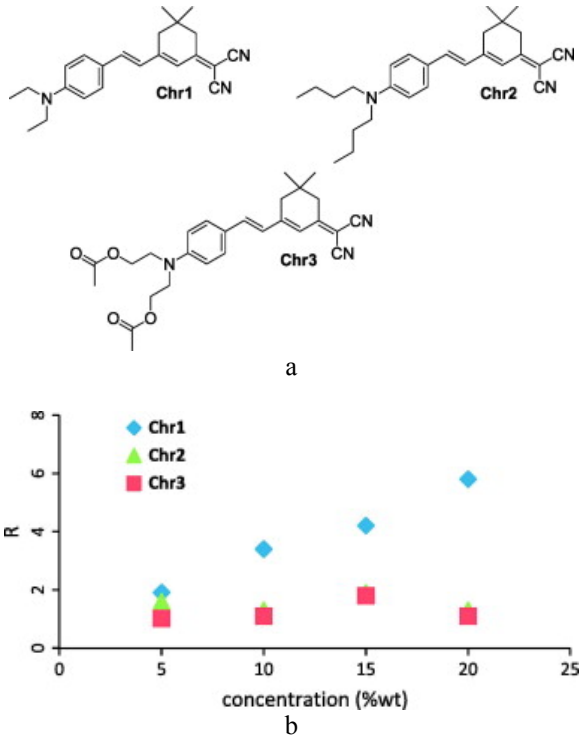


Fig. 6 - Chemical structures of the studied dyes and the concentration variations of their quantum yields ratios when embedded in DNA–CTMA or in PMMA matrices (after Massin et al [71], for details see text)

Random lasing in luminophore doped DNA based complexes was also recently demonstrated [91-94].

5. Conclusions

In this Chapter we review and discuss the recent work on two biopolymers: collagen and deoxyribonucleic acid in view of their application in photonics. Both are abundant, renewable, biodegradable and nature fabricated macromolecules. They can be obtained from the waste produced in food processing industry. That used in our studies originates from the waste produced in salmon processing industry. Thus they can be cheap and the renewable resources are practically unlimited. It can be used, at least partly, to replace synthetic polymers as matrix for photosensitive molecules, offering an interesting, ecologically friendly, alternative material for applications in photonics and in electronics.

. We have described and discussed linear and nonlinear properties of DNA based systems. One of the important observed property of this biopolymer is the fast response time, corresponding to the conformational transformations of a photoizomerisable molecule It is a few orders of magnitude faster than in PMMA matrix. This effect is due to a large free volume offered by DNA matrix. Also the specific environment of charged

DNA modifies electronic structure of embedded molecule and as consequence its physical properties.

There are also a large number of studies and application of DNA based complexes for their electrical properties. *Par excellence* DNA itself is a negatively charged anionic polyelectrolyte, with sodium ions Na^+ as counter ions. DNA. Application of an external electric field induces an ionic dipole moment [95-97] and changes the conformation of DNA molecule [98-100].

The electric conductivity of DNA, not discussed here, was subject of a continuous research interest and of controversies from the early sixties [101-103] with the first theoretical suggestion by Eley and Spivey [104] that the delocalization of π electrons in nucleobases may lead to an efficient electron transport along the DNA stacks [105].

A very interesting output here is obtaining of conducting, solid membranes as it was shown recently [106], with good ionic conductivities, controllable by an appropriate dopping. It is getting by plasticizing DNA with glycerol and introducing doping molecules to the system (for details see Refs. [107-109]) Of transparent membranes (in visible) with good ionic conductivities.

These membranes can applied in electrochromic cells for displays and in "smart windows". They are also potentially interesting materials for application in solar energy conversion as well.

The research on practical utilization of DNA is still at its beginning. But more and more researchers and laboratories join people already active in this field and a rapid progress is expected with new discoveries' and new practical applications.

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