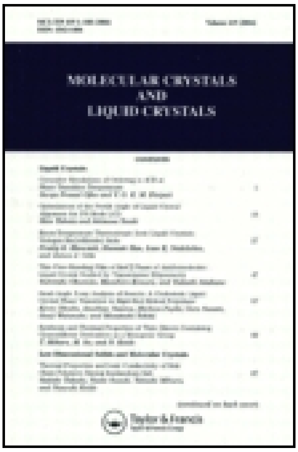

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Optical Properties of Thin Films of DNA-CTMA and DNA-CTMA Doped with Nile Blue

Edyta Hebda [a], Małgorzata Jancia [a], Francois Kajzar [b c], Jacek Niziol [d], Jan Pielichowski [a], Ileana Rau [b] & Alexandrine Tane [b]

[a] Cracow Technical University, Department of Chemistry and Technology of Polymers, ul. Warszawska 24, 31-155, Kraków, Poland

[b] POLITEHNICA University of Bucharest, Faculty of Applied Chemistry and Materials Science, Str. Polizu nr. 1, Bucharest, Romania

[c] Université d'Angers, Institut des Sciences et Technologies Moléculaires d'Angers, MOLTECH Anjou - UMR CNRS 6200, Equipe Interaction Moléculaire Optique nonlinéaire

[d] AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, al. Mickiewicza 30, 30-059, Kraków, Poland

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Optical Properties of Thin Films of DNA-CTMA and DNA-CTMA Doped with Nile Blue

EDYTA HEBDA,[1] MAŁGORZATA JANCIA,[1]
FRANCOIS KAJZAR,[2,3] JACEK NIZIOL,[4,*]
JAN PIELICHOWSKI,[1] ILEANA RAU,[2,*]
AND ALEXANDRINE TANE[2]

[1]Cracow Technical University, Department of Chemistry and Technology of Polymers, ul. Warszawska 24, 31-155 Kraków, Poland
[2]POLITEHNICA University of Bucharest, Faculty of Applied Chemistry and Materials Science, Str. Polizu nr. 1, Bucharest, Romania
[3]Université d'Angers, Institut des Sciences et Technologies Moléculaires d'Angers, MOLTECH Anjou - UMR CNRS 6200, Equipe Interaction Moléculaire Optique nonlinéaire
[4]AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, al. Mickiewicza 30, 30-059 Kraków, Poland

Refractive index dispersion of thin films of deoxyribonucleic acid (DNA)-surfactant (CTMA) and doped DNA-CTMA-Nile Blue (NB) (5 w%) complexes are reported and discussed. The thermal variation of the thin film thickness was measured by ellipsometry. The DNA-CTMA complex exhibits a rarely observed negative thermal expansion between room temperature and ca. 85°C. Doping with NB decreases the temperature range of negative thermal expansion to between room temperature and ca. 70°C. The dopping by 5 w% of NB lowers the absolute value of negative thermal expansion of DNA-CTMA system from 5% to 2% within this temperature range.

Keywords Deoxyribonucleic acid; DNA-CTMA complex; negative thermal expansion; Nile Blue; refractive index dispersion; thermal dilatation; thin films

Introduction

The bio-derived materials represent uncommon properties that are virtually impossible to be reproduced in industrial organic or inorganic materials. Among all available natural polymers, a range of rare properties are characteristics of deoxyribonucleic acid (DNA). Its structure has already been thoroughly studied owing to fundamental biological role of this supramolecule in heritage and development of living world [1]. DNA can be precisely copied in living cells. This replication provides mono-dispersed molecular mass of the bulk DNA sample–a feature impossible to achieve for any of industrial polymers. DNA can be

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[*] Address correspondence to Jacek Niziol, AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, al. Mickiewicza 30, 30-059 Kraków, Poland. E-mail: niziol@agh.edu.pl; Ileana Rau, University POLITEHNICA of Bucharest, Faculty of Applied Chemistry and Materials Science, 1 Polizu street, Bucharest, Romania, ileana_brandusa@yahoo.com

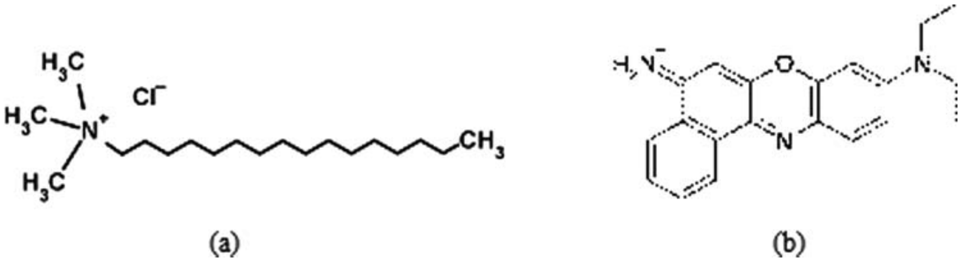

Figure 1. Chemical structures of CTMA surfactant (a) and of Nile Blue (b).

viewed as a polymer built of elementary blocks referred to as nucleobase pairs (adenine (A) + guanine (G), cytosine (C) + thymine (T)) bind by hydrogen bonds, the deoxyribose sugar and the phosphate.

Neat DNA is soluble exclusively in water. High surface tension and low water evaporation rate make film processing through standard spin-coating technique impossible in ambient conditions. Moreover, DNA is very sensitive to hydration [2] what could deteriorate final device performance. A breakthrough in DNA-based technology was made by demonstrating a series of DNA-cationic surfactant complexes [3]. It was already known that DNA, which is an anionic polyelectrolyte, could be quantitatively precipitated with cationic surfactant in water by an ion exchange reaction [4]. A smart choice of cationic surfactant - cetyltrimethylammonium chloride (CTMA) (see Fig. 1(a)) led to DNA–lipid complexes insoluble in water insoluble and more mechanically stable than crude DNA. Indeed, the obtained complexes were soluble in a range of common alcohols. Now, this complex is considered as a flagship of DNA derived materials for application in photonics and molecular electronics. Such applications include: devices based on second and third order nonlinear optical effects [5], low loss optical waveguides [6], holography [7], organic photovoltaics [8], organic field effect transistors [9] and organic lasers [10].

The molecular structure adopted by DNA is the so-called double helix composed of two inter-twined strands. All of the bases of a nucleotide can participate in hydrogen bonding. Under heating the double-stranded deoxyribonucleic acid unwinds and separates into single strands through the breaking of hydrogen bonding between the bases. This denaturation process is often called as DNA melting, although it is not the same phenomenon as melting in the case of aliphatic polymers. The melting temperature (T_m) is understood as the temperature at which half of the helical structure disappears. Melting of DNA has been thoroughly studied in solution, but much less in the solid state and it is almost an unexploited subject in the case of solid DNA-complexes.

In this paper we report the results of our studies of melting process in solid thin films of DNA-CTMA and DNA-CTMA doped with 5%wt of Nile Blue dye (Fig. 1(b)). In the present study the cetyltrimethylammonium bromide was used, instead of cetyltrimethylammonium chloride as done by Wang et al. [3] (Br^- instead of Cl^- as counterion, cf. Fig. 1(a)).

For future practical applications the thermal stability of the used materials is a one of the more vital issues. Nile Blue is a dye important for many practical reasons. It has a positively charged, oxidized, phenoxazine system and has a 9-diethylamino substituent to donate electron density across the ring [11]. Nile Blue is water soluble what facilitates incorporation of this dye to the system during the ion exchange reaction of DNA and a surfactant in water environment.

Experimental

The DNA sodium salt, extracted from salmon milt and roe, was purchased from Ogata Research Laboratory, Ltd (Chitose, Japan). The claimed molecular weight was $M_W = 10^6$ Daltons (Da) or 1500 base pairs and the purity better than 96%. A portion of DNA sodium salt was put in deionized water and mechanically stirred. The solution became clear and homogenous but extremely viscous. It contained entrapped air bubbles and didn't let them off. This viscosity was reduced by sonication, a process which according to the literature [12] significantly reduces the DNA molecular mass. In less viscous solution the cationic surfactant penetrates easier to the reactive centers of DNA. Next CTMA was dissolved in deionized water, added dropwise to the solution of DNA and both were constantly stirred for a longer time. Because DNA-CTMA is not soluble in water, it precipitates when formed. At the end of reaction the precipitate was recovered by filtration, washed with deionized water and dried. The DNA-CTMA-NB complexes were obtained in a similar way with butanol used as solvent of DNA-CTMA and Nile Blue.

Thin films were manufactured on silicon wafers through classical spin coating technique. Samples underwent a repetitive train of heating/cooling cycles (see Fig. 5). The thickness and refractive indices were monitored with the help of spectroscopic ellipsometry using Wollam M–2000 instrument. The spectroscopic ellipsometry is a very versatile technique because enables simultaneous measurement of thickness and of optical density variations induced by an external or an internal factor.

Results

Ellipsometric parameters Ψ and Δ were measured for a series of 200 nm thick films of both studied materials. Dispersion relations were calculated using Wollam patented software. The averaged values of $n,k(\lambda)$ dependence found for DNA-CTMA and DNA-CTMA/NB 5 w% are shown in Figs 2 and 3, respectively.

Comparing these graphs one, one can conclude that the wavelength dependence of extinction coefficient of DNA-CTMA/NB 5 w% shown in Fig. 2.

Figure 3 is a sum of the graph of DNA-CTMA and superposed absorption of Nile Blue, centered at c.a. 610 nm. In both pictures a peak at ca. 285 nm is present, which arises from the absorption of DNA bases. Taking into account, that the extinction coefficient is a molecule density depending parameter, its higher value of corresponds to a better "volume packing" of DNA macromolecules. This behaviour in DNA-CTMA-NB 5 w% complex can be be explained by smaller volume occupied by Nile Blue, a more compact molecule than CTMA bearing a long aliphatic chain.

Figure 4 shows the dependence of the refractive index on film thickness measured for DNA-CTMA system. Series of studied films were processed from different alcohols and according to different protocols. This explains error bars shown in the figure. The data show an increase of refractive index with film thickness t smaller than 100 nm. At larger thicknesses ($t > 100$ nm) the refractive index stabilizes and remains constant. It shows influence of substrate on the arrangement of DNA chains. In spin coated polymer films usually the polymer chains orient, with usually a small degree, preferably parallel to the substrate, with larger transverse electric index of refraction. In DNA the largest contribution to refractive index comes from conjugated π electrons, thus from phenyl rings. It is well known that the aromatic rings orient preferably perpendicular to the substrate, what may be the case here. At higher thin film thickness the substrate-DNA interaction influences less

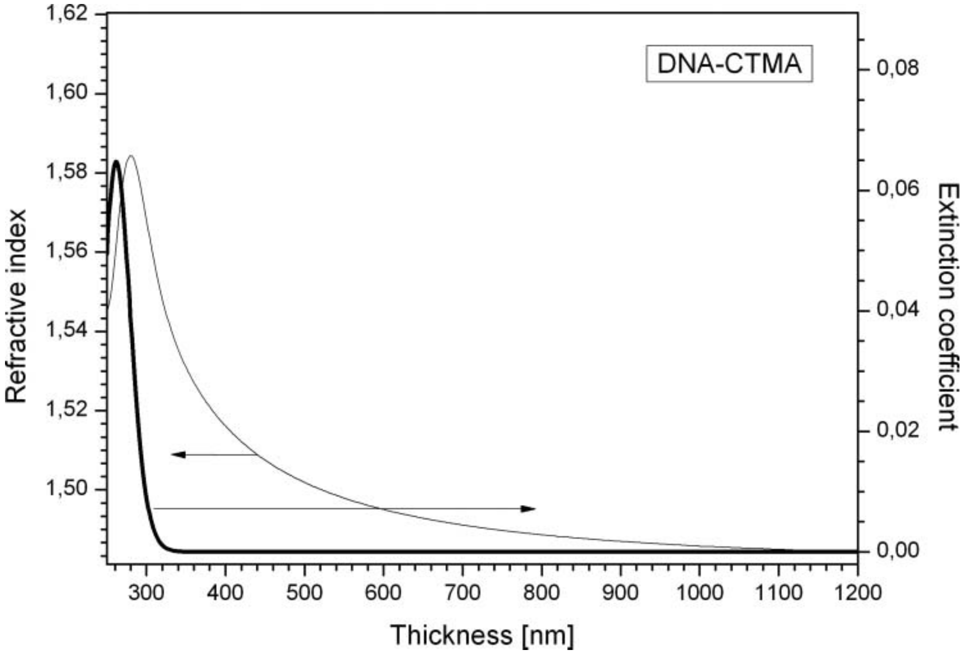

Figure 2. DNA-CTMA. Dispersion relations. Refractive index and extinction coefficient are respectively real and imaginary parts of complex index of refraction of material.

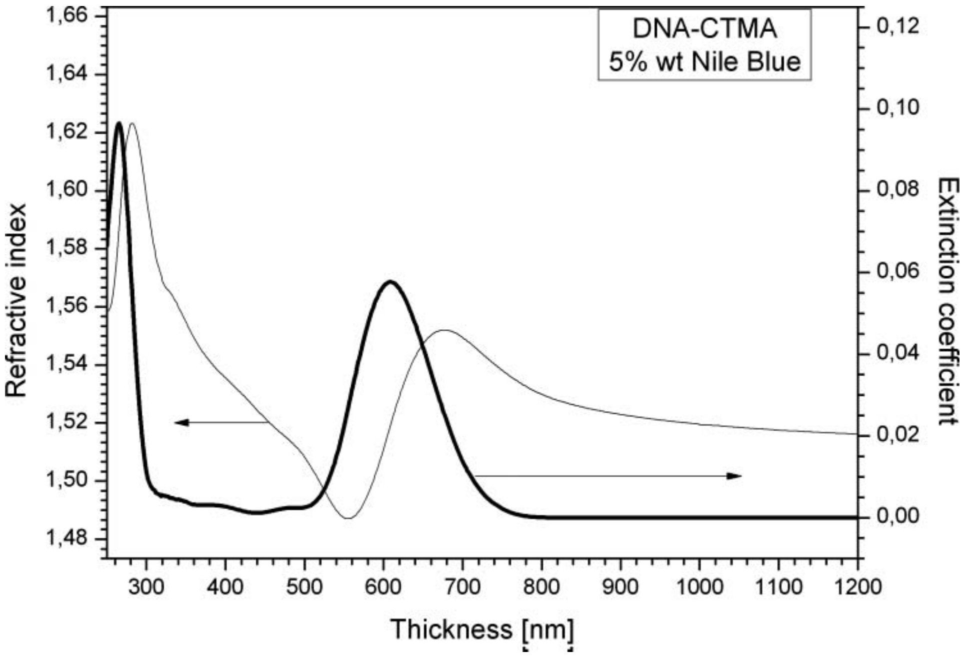

Figure 3. DNA-CTMA/NB5%. Dispersion relations. Refractive index and extinction coefficient are respectively real and imaginary parts of complex index of refraction.

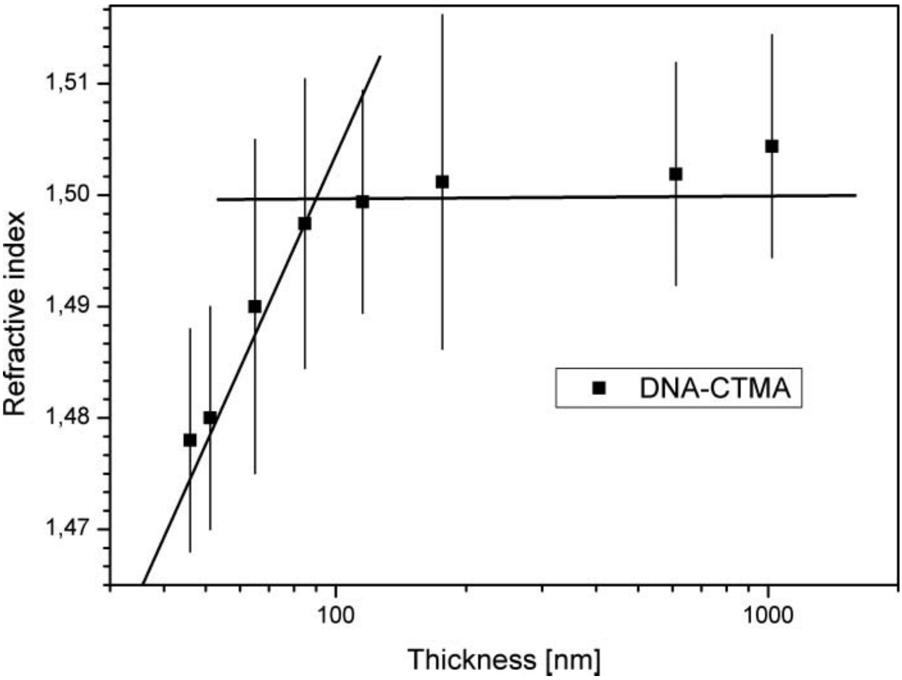

Figure 4. Dependence of DNA-CTMA refractive index(632 nm) on film thickness.

and less their structure, and refractive index becomes to be that of bulk material. We note that the influence of substrate on orientation of molecules was already reported (e.g. Refs. [13,14]).

In order to check whether the decrease of the thickness is not due to the release of solvent trapped in thin films they were subjected to a heating/cooling procedure as shown in Fig. 5. It consisted of initial slow heating and cooling followed by two rapid heating and cooling cycles (from the ambient to 85°C) and ended with heating up to 180°C, a temperature close to thermal degradation.

Figures 6 and 7 show an irreversible initial decrease of the thickness in effect of the first heating/cooling cycle. It may be attributed to release of residual solvent. Next two cycles data move back and forth on the same curve going to a minimum somewhere between 60°C and 70°C in the case of DNA–CTMA/NB5% and 10°C more in the case of DNA-CTMA. This minimum can be understood as a sign of DNA helix unwinding. Separated strand may adopt more compact structure. This assumption is supported by reversibility of this process. Once DNA "melting" is completed, the sample thickness increases, as can be seen for temperatures superior to 85°C. It means that DNA strands behave like classical polymer macromolecules since then.

Interesting results were obtained when studying the influence of Nile Blue addition on thermal kinetics of DNA-CTMA complex. Between the room temperature and ca. 70°C, one observes a relative thickness decrease by 5% in contrast to less then 2% in the case of DNA-CTMA-NB 5%w. This observation can be explained by less stiff conformation of macromolecules doped with Nile Blue, which enhances more compact packing at room temperature. This qualitative picture finds continuation in further heating. At higher temperatures, DNA-CTMA-NB 5%w expands more then DNA-CTMA. Macromolecules

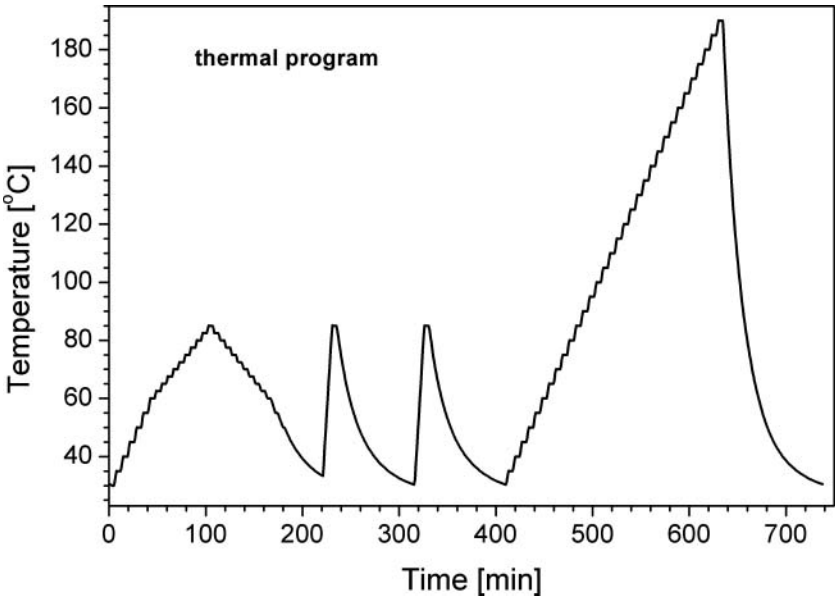

Figure 5. Representation of heating and cooling program.

of DNA-CTMA-NB 5%w at the state of film's minimum thickness, being more compacted, have less room to move than macromolecules of DNA-CTMA. Similar reasoning may be also applied for the analysis of the observed refractive indices dependence on temperature.

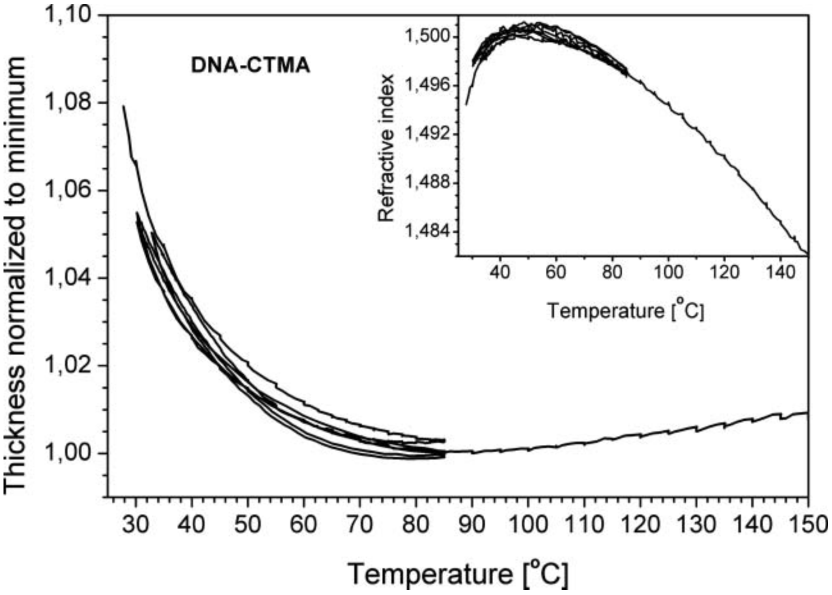

Figure 6. DNA-CTMA. Thickness and refractive index variations due to thermal treatment.

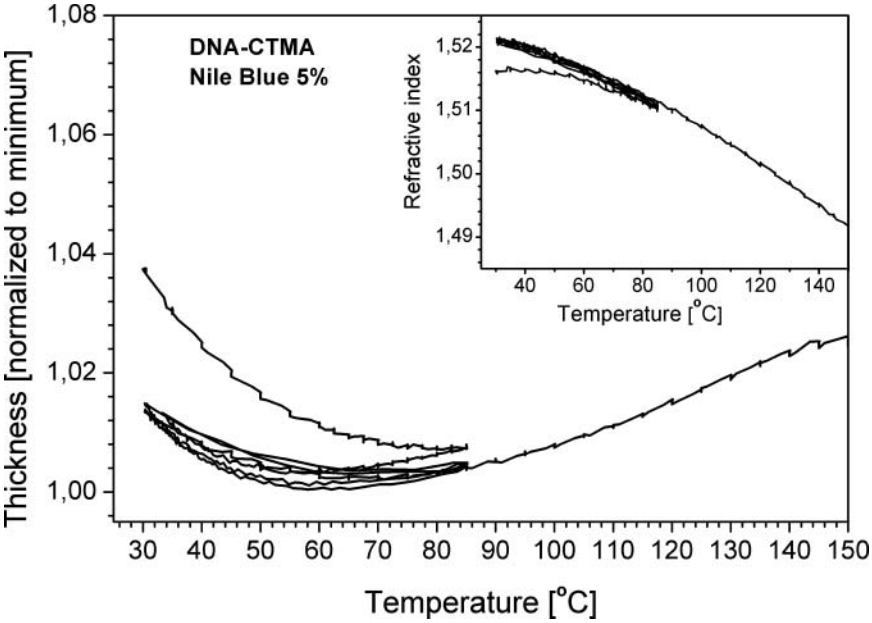

Figure 7. DNA-CTMA (5% NB). Thickness and refractive index variations due to thermal treatment.

Conclusions

In the present work thin films of DNA-CTMA and doped DNA-CTMA-NB films were prepared and studied for their refractive index dispersion as well as for their thermal expansion. A negative thermal expansion coefficient in thin films of DNA-CTMA complex for the double stranded helical structure (room temperature −85°C) was observed. Above this temperature, called also melting point or denaturation temperature, when the double strand helical structure transforms into a single strand one, the thermal expansion coefficient is positive. The negative thermal expansion is diminished when doping with Nile Blue. For 5 w% doping the thermal expansion in the temperature range room temperature −70°C changes from 5% for DNA-CTMA to 2% for DNA-CTMA-NB complex, respectively. This result is interesting for potential application of this biopolymer in photonics and in molecular electronics. Also influence of substrate on refractive of thin films up to 100 nm of their thickness was observed, leading to some kind of arrangement of DNA with respect to the substrate.

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