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14. ABSTRACT This report results from a contract tasking Angers University as follows: The studies will be performed on thin films obtained by the spinning technique from DNA solutions. For the rotational and charge mobility measurements the films will be deposited on ITO coated glass substrates with an over deposited aluminium electrode. 1.Electro-optic Kerr effect. Experiments will be done at 632 nm using the variable frequency AC power supply. This will allow to determine the Kerr constant and its frequency dependence, assessing eventual resonance enhancements. 2.Phase conjugation measurements. Using a 20 ps pulsed laser the optical Kerr susceptibility and its temporal response will be measured. These experiments will allow to determine the contributions to the Kerr susceptibility coming from rotational mobility and/or charge transport. The experiments will be performed at 1064 nm and 532 nm. The second wavelength will allow to measure also enhancement of cubic susceptibility due to eventual multiphoton excitations. 3. Dynamic holography to measure the charge mobility. This technique, based on the study of the kinetics of grating inscription and decay permits to have information on the charge mobility. For doing that a 20 ps pulsed laser beam of 1064 nm wavelength will be used to write the grating in a two beam coupling geometry. The grating will be read with a cw laser at 632 nm. The film will be sensitized with photosensitive molecules like TNF or its derivative and C60 or its derivative. The response times obtained by fitting the write and decay curves will be obtained and from them the charge mobility. The experiments will be done changing the grating period and applying DC electric field to drive generated charges.					
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FINAL RESEARCH REPORT 4

Period February 16, 2006 - May 15, 2007

Research project: Photoconducting, Charge Mobility, and Nonlinear Optical Properties of DNA

FA8655-06-M-4003

REF: SPC 064003

1. Conductivity and photoconducting properties

1. 1. Material preparation

For DNA extraction can be used all animal tissues, however, some animal tissues are easier to extract than others. Calf thymus and chicken erythrocytes are one of the most well studied tissues for DNA extraction. In our investigation we used DNA sodium salts, extracted from salmon milt and rote (M_w : 1.3×10^6 , ca. 2000 base pairs), was provided by Chitose Institute of Technology to (CIST), Japan. The high molecular weight DNA rendered inhomogeneous film thickness due to high solution viscosity. In order to reduce the viscosity of the DNA-based solutions an ultrasonic procedure was used in 18 M Ω -cm deionized water. Figure 1 shows the distribution of molecular weights after different time of sonication process based on measurements of hydrodynamic volume.

In the continuation of the project we were using other PEDOT substance than those described in report 3. Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (Fig. 2.) aqueous dispersion of the intrinsically conductive polymer PEDT/PSS with solid content 1.0 to 1.4 %, PEDT :PSS ratio 1:2.5 (by weight) and viscosity max. 30 mPa·s. It is tailored to a high conductivity and forms conductive coatings. This kind of polymer has high conductivity, transparent, colourless to bluish coatings, good resistance to hydrolysis, good photo stability and good thermal stability, high absorption in the range of 900 to 2000 nm, no absorption maximum in the visible spectrum up to 800 nm.

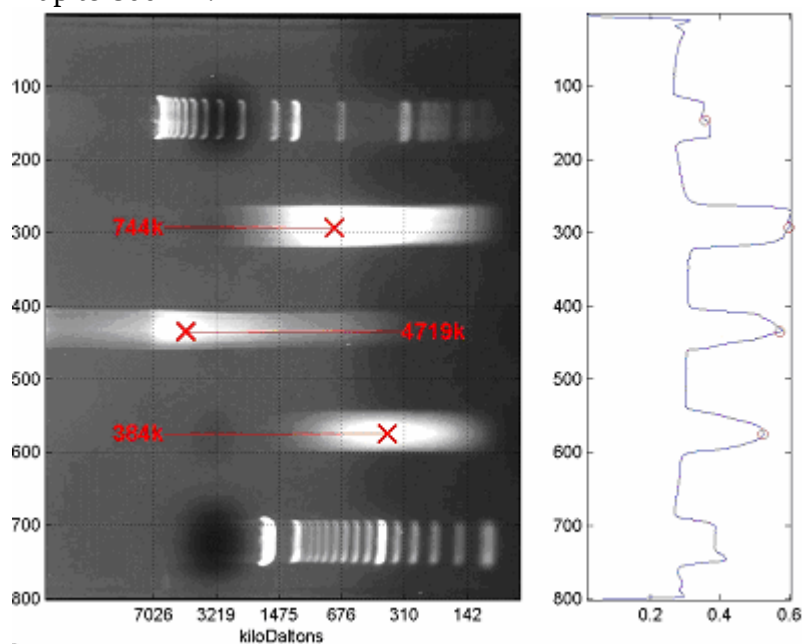


Fig. 1. Molecular weights distribution of DNA.

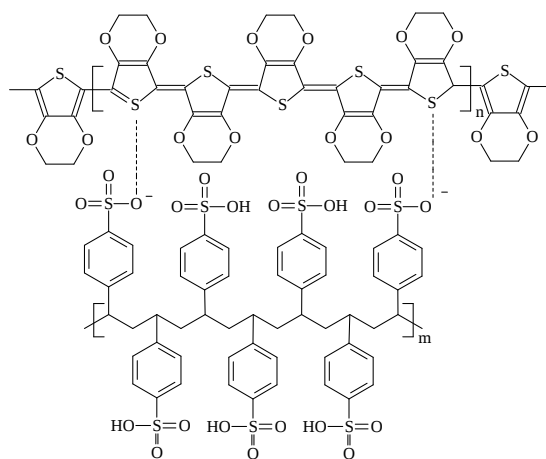


Fig. 2. Chemical structure of polymer complex PEDT-PSS.

Glass plates were cut in 3×5 cm substrates and rinsed successively with detergent solution, ethanol and deionized water. This cleaning procedure was repeated three times, always removing adhering solvent by centrifugation from the surface.

DNA solution was added to PEDT/PSS aqueous solution Baytron PH 500 and after filtration the solution was deposited by solution casting on comb electrodes deposited on pure silica substrates. Comb type electrodes were fabricated at CEA (intraelectrode distance of about 100 μm) or purchased at Nietsch company (intraelectrode distance of about 10 μm).

DNA-based solutions an ultrasonic procedure was used. After sonication, a 8 g/L concentration of DNA (0.8 g in 100 ml) deionized water, at 20°C, was blended using a magnetic stirrer overnight. After DNA in water was functionalized with PEDOT. (PEDT:PSS ratio 1:2.5 (by weight); solid content 1.0 to 1.4 %) with ration 1:0.1 and 1:0.01 and 1:0.05 DNA to PEDOT. Respectively PEDOT 1.8%; 8.5%; 15.7% by weight doped to DNA.

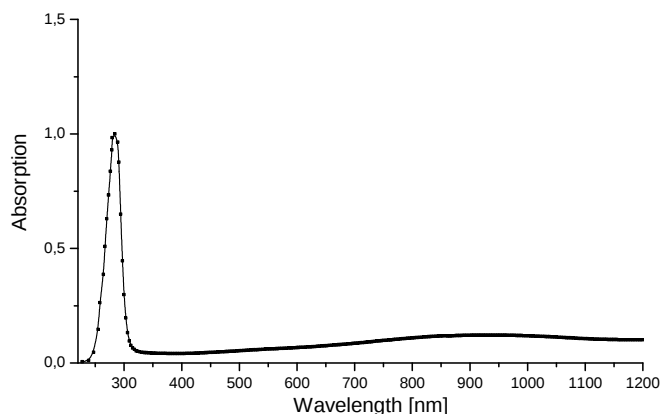


Fig. 3. Absorption spectrum of DNA-PEDOT (1:0.1) thin film.

1.2. Conductivity measurements

Electrical conduction properties of DNA-thin films doped with PEDOT were investigated. This study was realized by comparing thin films with different concentration of PEDOT: 1.8%, 8.5% and 15.7%. The aim of this study is to see how the PEDOT doping affects the DNA electrical conduction properties. Figure 4 shows the current voltage characteristic for highest studied concentration of PEDOT (15.7%). The applied voltage was two times stepwise increased (Iup1, Iup2) from 0 V to 85 V, and then stepwise decreased (Idown1, Idown2). During the first increase, and for low applied voltage ($20\text{V} <$), the sample exhibits an ohmic behaviour with a resistivity about $2.3 \times 10^6 \Omega$. For higher applied voltage, the sample becomes unstable and

the resistivity enhance considerably. During the decreasing I_{down1} the conduction starts to be stable, but its value decreased. This trend is confirmed by the second cycle (I_{up2} , I_{down2}) where the ohmic behaviour is observed.

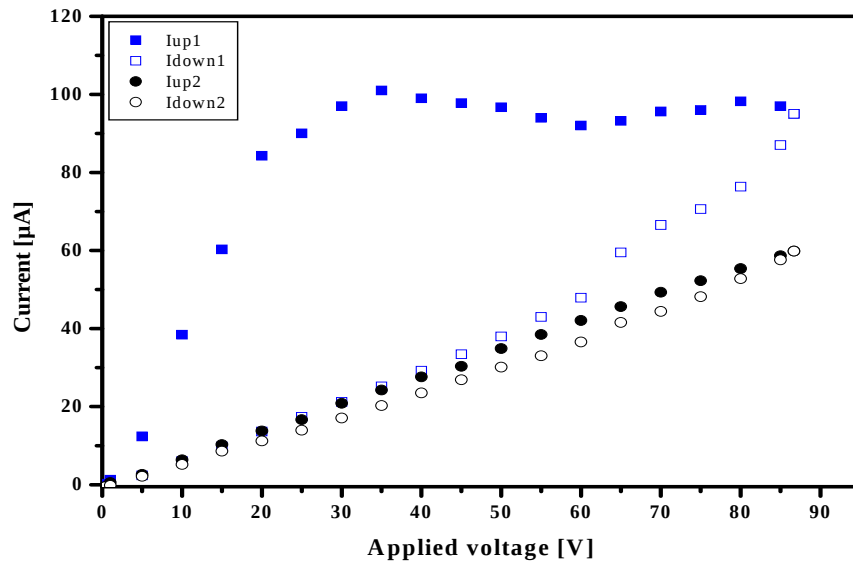


Fig. 4. Dependence of electric current on applied voltage for a thin film of a system DNA-PEDOT with a concentration of 15.7%

Figure 5 shows the current voltage characteristic for the 3 studied concentrations of PEDOT after stabilisation of the samples (2nd cycle of increasing and decreasing the voltage). The hystereses observed are very small and are connected with the contacts. As reference, we plotted also the signal measured the empty electrodes.

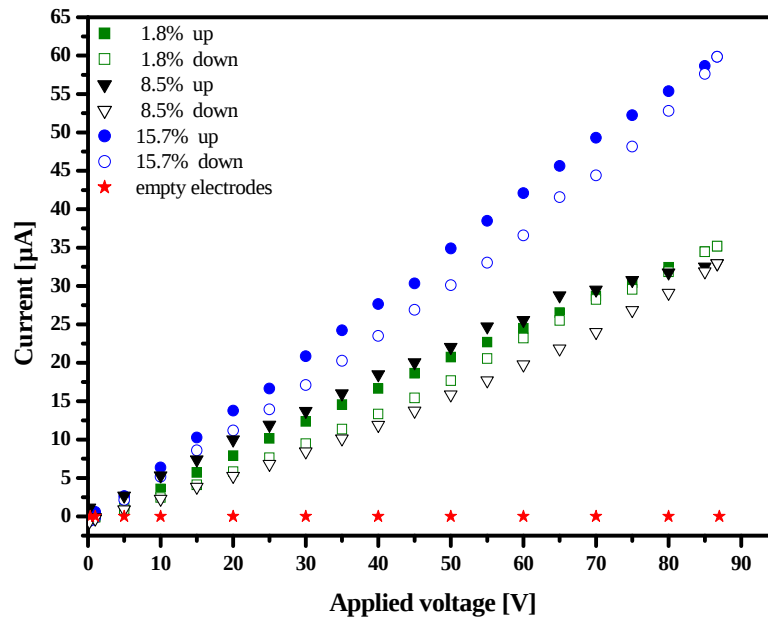


Fig. 5. Dependence of electric current on applied voltage for a thin film of a system DNA-PEDOT with different concentrations (1.8%, 8.5% and 15.7%).

Figures 6-8, show ohmic behaviour of the current voltage characteristics with resistivity about $10^6 \Omega$. The values of resistivity extracted from these figures are summarized in Fig. 9. As expected, the conduction increases with PEDOT doping. No dark current was observed.

DNA-PEDOT 15.7 %

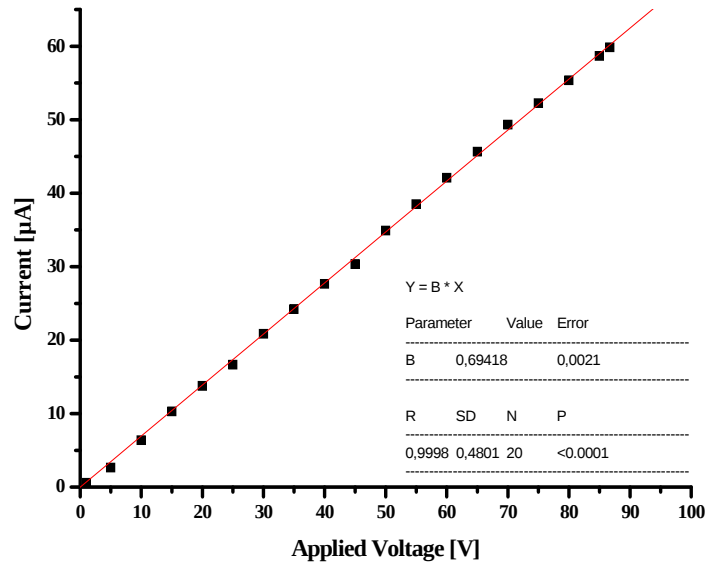


Fig. 6. Dependence of electric current on applied voltage for a thin film of a system DNA-PEDOT 15.7%.

DNA-PEDOT 8.5 %

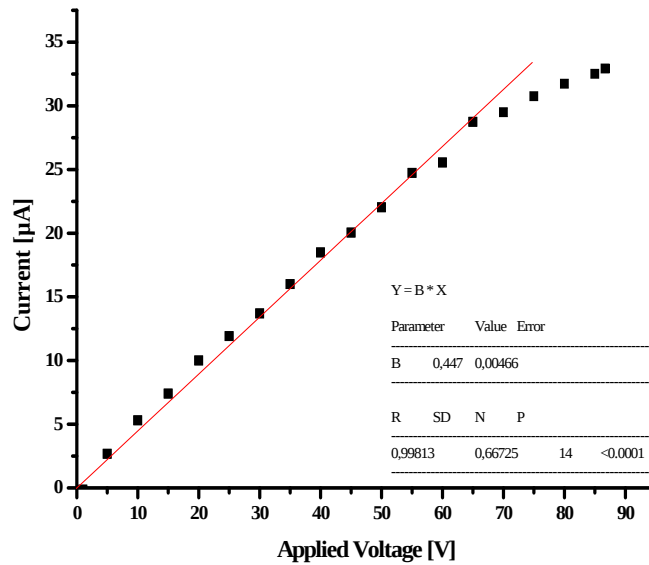


Fig. 7. Dependence of electric current on applied voltage for a thin film of a system DNA-PEDOT 8.5%.

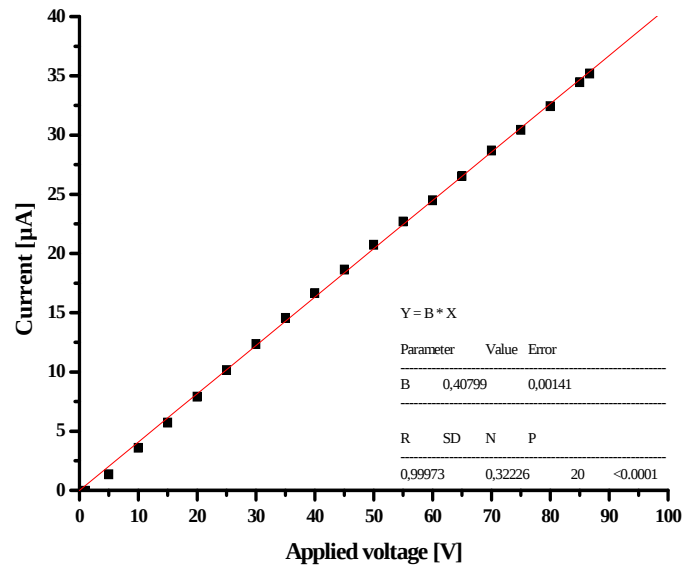


Fig. 8. Dependence of electric current on applied voltage for a thin film of a system DNA-PEDOT 1.8%.

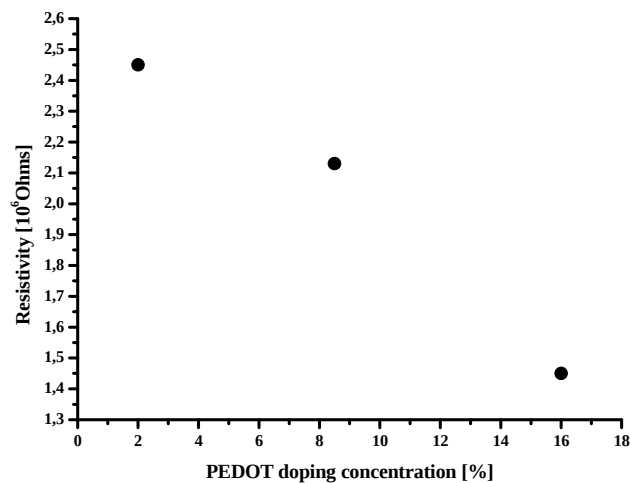


Fig. 9. Resistivity dependence of DNA-PEDOT thin films versus concentration.

2. Optical holography in picosecond regime on thin films of functionalized DNA

2.1. Fabrication of studied materials

The chromophore, 4-(4-Nitrophenylazo)diphenylamine (DR1), purchased from Aldrich, was purified by a double recrystallization from an absolute methanol solution. The hexadecyltrimethylammonium chloride (CTMA), poly(9-vinylcarbazole) (PVK), poly(methylmethacrylate) (PMMA) and used solvents were also purchased from Aldrich and used as supplied, without any further purification. The molecular weight measured $M_w = 106$ Daltons (Da) or 2000 base pairs.

The high molecular weight DNA (Fig. 10) rendered inhomogeneous film thickness due to high solution viscosity. After sonification, aqueous solution DNA- Na^+ was then added drop-

wise to one liter of aqueous CTMA solution and stirred at room temperature for 6 hours. The DNA-CTMA precipitate complex was collected by vacuum filtration through a 0.4 μm nylon filter, washed with 18 M Ω cm deionized water and then dried in a vacuum at 35°C.

The DNA-CTMA complex was dissolved in butanol and was also functionalized with DR1 (30% in weight). Also DR1 grafted with polymethylmethacrylate and polyvinylcarbazole in trichloroethane with the same concentration of chromophore. The resulting solutions of DR1-DNA-CTMA, DR1-PMMA and DR1-PVK were then filtered through a 0.4 μm pore size nylon syringe filter.

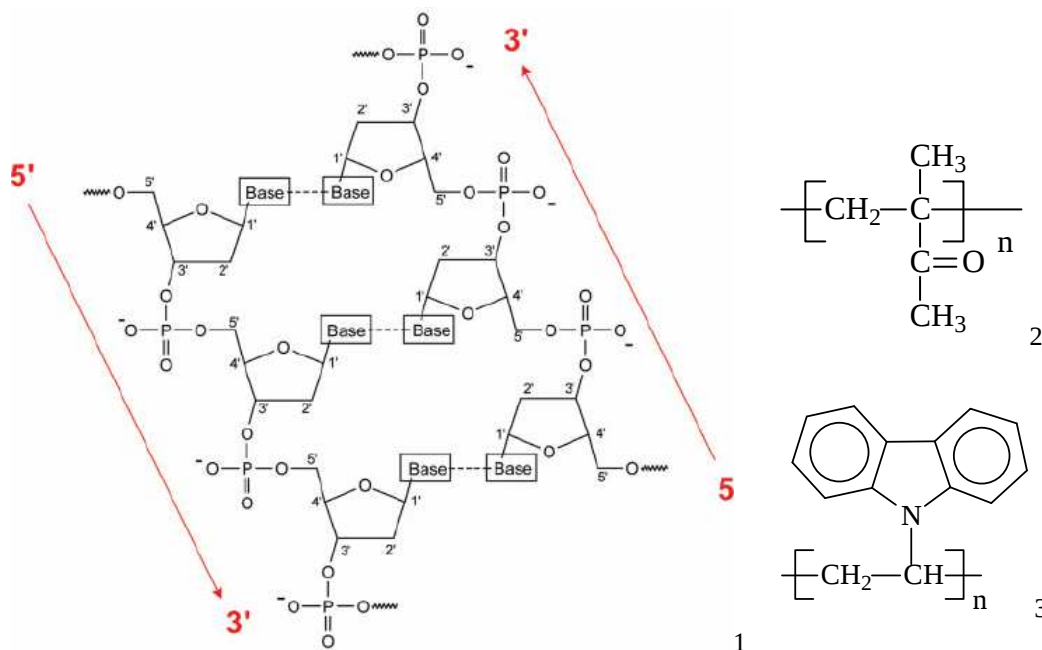


Fig. 10. Chemical structures of matrices DNA (1), PMMA (2), PVC (3).

Spin deposition was used to fabricate thin films of DR1-DNA-CTMA, DR1-PMMA and DR1-PVK with controlled thickness on glass slides. After the deposition, the thin films were heated for 60 min at 80°C to remove any remaining solvent.

UV-vis measurements in the 210-1200 nm spectral region were performed at room temperature in films with a PERKIN ELMER UV/VIS/NIR Lambda 19 spectrometer. The absorption spectrum of thin films present in the Fig. 11.

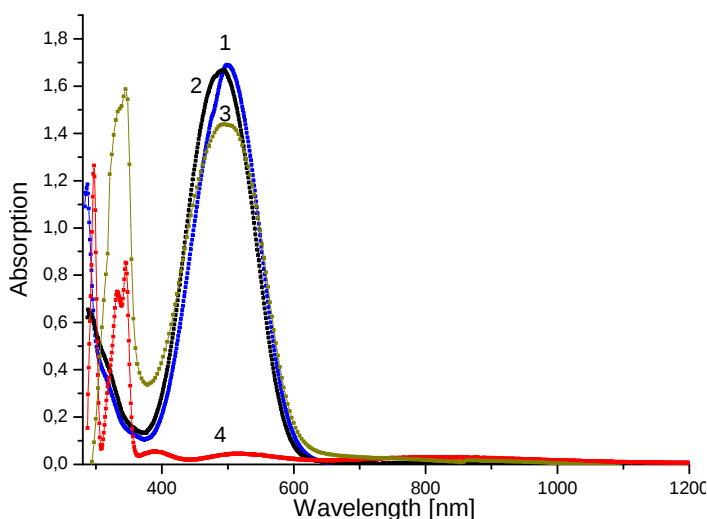


Fig. 11. The absorption spectrum of DR1-DNACTMA (1), DR1-PMMA (2), DR1-PVC (3), PVC (4) thin films.

2.2. Study of photoinduced surface organization

Materials which exhibit birefringence and dichroism can be used in applications as optical data storage and optical information processing. However the process of photoinduced modification/organization of material's surface is not easy for explanation. There is few different models which try explain this behaviour¹, but in the case of DNA structure these explanation is not sufficient because of their complicated structure. In general case molecules based on azobenzenes exhibit reversible trans-cis photoisomerisation and thermal relaxation. The most known representative of azobenzene derivatives with reversible photoisomerisation process is DR1. This molecules can be oriented during polarized irradiation, which describe hole burning model².

We used DR1 as guest in guest-host system. As a host we used different matrices: DNA-CTMA, PMMA and PVK.

The schematic experimental setup of the experiment for creation and studying of photoinduced surface organization (further called: diffraction grating) is shown in Fig. 12. Diffraction grating were recorded by two 16 ps pulses laser beams at wavelength of 532 nm from pulsed Nd:YAG laser (Continuum Leopard D-10) working at 10 Hz repetition rate pulse energy 1.3 mJ. Grating formation was monitored by cw He-Ne laser operating at 632.8 nm by measuring the intensity of the first-order diffracted beam in the transmission mode. The polarization of writing beams were controlled by systems: polarizer (P) - half wave plate ($\lambda/2$), placed on the pathway of beams before samples. The intensity signal of first order of diffraction was measured by photodiode (Centronic Series OSI 5) and this signal was fed to the digital oscilloscope (Tektronix TDS 3054). The sample (S) was mounted on stage.

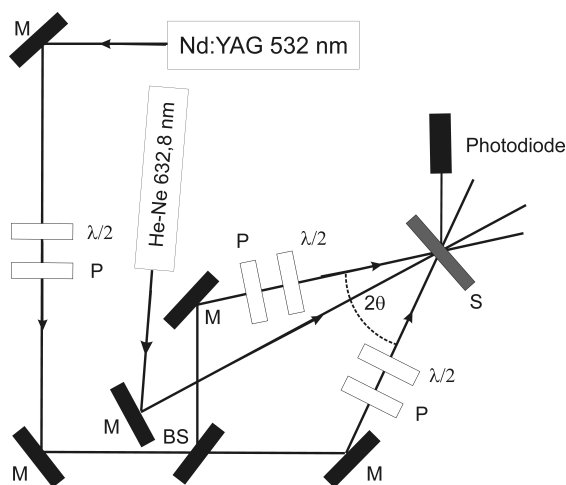


Fig. 12. Schematic setup of the grating experiment, M – mirrors, BS – beam splitter, P – polarizers, $\lambda/2$ – half wave plates, S - sample.

The surface structure of the grating of polymer film was investigated by Atomic Force Microscopy (with microscope Pico SPM of Molecular Imaging).

¹ K.G. Yager, C.J. Barrett, , "All-optical patterning of azo polymer films", Cur. Op. Sol. Stat. Mat. Sci. 5, 487 (2001)

² M. Dumont, A. El Osman, "On spontaneous and photoinduced orientational mobility of dye molecules in polymers", Chem. Phys. 245, 437 (1999).

First, the s-s polarization configuration was set-up and we compared dynamics of photoinduced inscription of diffraction gratings for guest-host systems: DR1-DNA-CTMA, DR1-PMMA and DR1-PVK (Fig. 13). We worked within the Bragg light scattering regime and we observed only first order of diffraction. The light (532 nm) absorption in the sample caused *trans-cis* isomerisation process of DR1. We observed the dynamics of build-up of diffraction grating in the sample in function of time by measuring the intensity of first order of diffraction (further called “the signal”).

The observed dynamic of the diffraction signal, which is directly connected to the inscription of grating shows very fast increasing (in the case of DR1-PMMA and DR1-DNA-CTMA immediately after switching on laser light). We can notice that inscription of grating for DR1-DNA-CTMA is the fastest (in comparison with than for known other studied matrices).

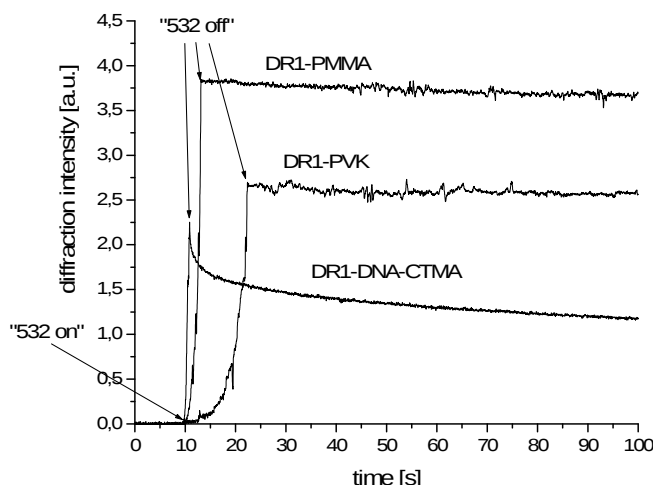


Fig. 13. Example of build-up grating process in compounds DR1-PMMA, DR1-PVK and DR1-DNA-CTMA using 16 ps pulses of 532 nm with 10 Hz repetition rate monitoring by He-Ne laser.

Also we observe different behaviour after switching off inscription laser light (523 nm): for DR1-PMMA and DR1-PVK there are almost stable gratings, while for DR1-DNA-CTMA we observed small relaxation of grating. After switching on 532 nm reading beams we noticed continuation of recording of grating.

We noticed that each pulse of laser is able to create a well readable grating. In the case of DR1-PMMA and DR1-PVK we do not observed relaxation after pulses of inscribing laser light, whereas in the case of DR1-DNA-CTMA this relaxation exists, but do not disturb for the fastest creation of grating.

In the second step we compared results from the same experiment but with different polarizations of inscribed laser light (s-s, p-p, and s-p). In the case of DR1-PMMA and DR1-PVK we obtained fastest build-up of signal when light was polarized in the same direction (s-s, p-p), than for light polarized perpendicularly (s-p), as we expected. However in the case for DR1-DNA-CTMA we do not noticed phase grating (polarization s-p) and almost the same speed during creation of intensity grating (Fig. 14).

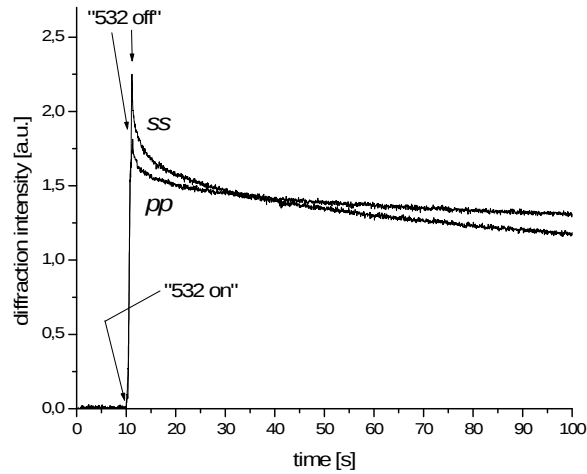


Fig. 14. Dynamics of build-up grating process in compounds DR1-DNA-CTMA. Two polarizations of writing beams: ss – upper curve, pp – lower curve.

Our samples was free to the deform (thin films on the substrate) and surface relief grating could be formed. We observed them using AFM. The scanner was used in the contact mode.

Figure 12 shows typical example of the three dimensional view of the surface relief grating and results from the same experiment for the DR1-DNA-CTMA thin films. For the case of DR1-PMMA we obtained typical results the relief pattern with a regular sinusoidal shape up to 90 nm depth. The grating spacing Λ , measured from AFM, was about 0.52 μm , and was consistent with the theoretically ones calculated using equation (1):

$$\Lambda = \lambda / (2 \sin \theta) \quad (1),$$

where λ is the wavelength of the writing beam, 2θ is the angle between the two writing beams.

From the Fig. 15 it can be seen also that the in the case of PVK matrix obtained SRG has not so regular shape as in the case of PMMA as the matrix and there is no SRG in the case of DR1-DNA-CTMA. However we can observe different view with comparison of surface before irradiation. We propose two explanation of this behaviour: we do not have creation of surface relief grating when we use DNA-CTMA as a matrix or our SRG can relaxes very fast (Fig. 13) and after we have only permanent changing in volume of material (we can observe signal of first order of diffraction even after few weeks after experiment).

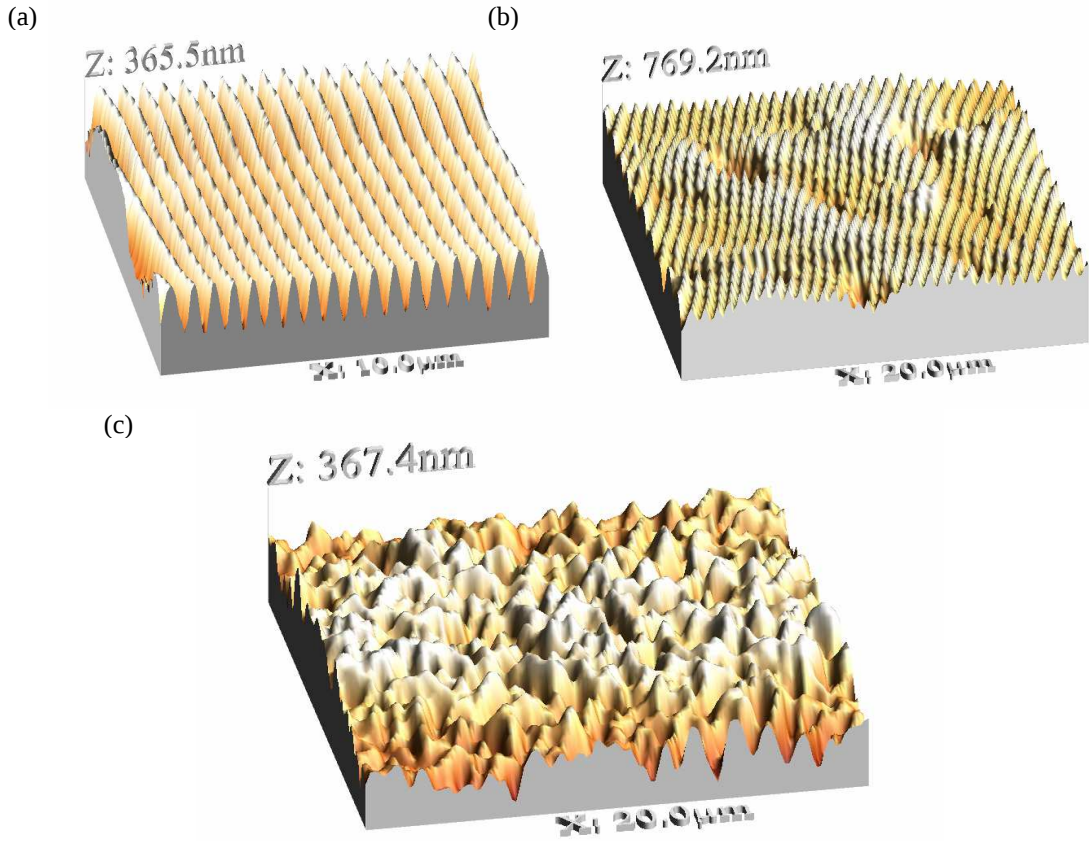


Fig. 15. AFM three-dimensional view of DR1-PMMA (a), DR1-PVK (b) and DR1-DNA-CTMA (c).

3. Conclusions

We have shown electrical conduction properties of DNA-thin films doped with different concentration of PEDOT: 1.8%, 8.5% and 15.7%. It's clearly seen that the conduction increases with PEDOT doping and we do not observe dark current was observed.

We have demonstrated also influence of DNA-CTMA, as the matrix for material which can be used for simple optical holography. We observed that guest-host system DR1-DNA-CTMA has faster response for light irradiation, but there is no surface relief grating formation as in the case of systems studied till now (in our case DR1-PMMA and DR1-PVK). Finally DR1-DNA-CTMA is very promising material in the field of dynamic holography, but need further studying, what is in our plans.

4. Dissemination

A part of the results was presented at the IX International Conference Nonlinear Optics Applications NOA 2007, Swinoujście, 17-20 May 2007. The obtained results will be published in Optics Express.