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Properties of DNA-Based Organic Dyes Doped Membranes

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Received: October 1, 2014. Accepted: October 29, 2014

The deoxyribonucleic acid (DNA) sodium salt was reacted with hexadecyltrimethylammonium bromide (CTMA) to obtain DNA-CTMA organic-solvent soluble complex. The DNA-CTMA was then mixed with three organic dyes such as Nile Blue A (NB), Disperse Red 1 (DR1) and Disperse Orange 3 (DO3) resulting in colored membranes, that were characterized by UV-Vis, FTIR, X-ray, ionic conductivity and fluorescence analysis. The FTIR and UV-Vis spectra confirmed DNA-CTMA formation. The X-ray diffractograms show that the dye molecules accommodate between adjacent base pairs of DNA-CTMA chains promoting their separation. It is evidenced by increase of macromolecular chains spacing and the size of interplanar distance in comparison with DNA membranes. The ionic conductivities of DNA-CTMA-NB and DNA-CTMA-DR1 were found to be of 4x10⁻⁸ S/cm and 1.6x10⁻⁷ S/cm at 27 °C and 1.3x10⁻⁴ and 2.4x10⁻⁵ S/cm at 96 °C, respectively. DNA-CTMA-DO3 ionic conductivities are of 6.7x10⁻⁸ S/cm at 26 °C and 1.5x10⁻⁶ S/cm at 75 °C. The photoluminescence spectra show that all the DNA-CTMAdye membranes exhibit fluorescence with intensities in agreement with structural analysis, being respectively of 40, 54 and 180 for DNA-CTMA-Disperse Red 1, DNA-CTMA-Nile Blue A and DNA-CTMA-Disperse Orange 3, in the same order as the observed increase of crystallinity of the samples.

Keywords: DNA-CTMA-dye complexes, natural macromolecule derivative, conducting membranes, UV-VIS spectra, fluorescence

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1. INTRODUCTION

The natural macromolecules are known ever since long time already but only recently a growing interest to study them as potential materials for food industries [1, 2], medical applications and opto-electronic devices is observed [3, 4]. In this context the biological systems and biologically important molecules such as polysaccharides [3, 5], gelatin [6] and DNA are also investigated [7, 8]. It was already shown that the natural macromolecules are very interesting materials as charge injection interlayers for light emitting diodes (OLEDs) [8] or ionic conducting membranes on substitution of liquid electrolytes in electrochemical devices, such as batteries, solar cells or electrochromic devices [9]. For such purpose, different polysaccharides and their derivatives [10-12], proteins [6, 13] and DNA [4, 14, 15] were investigated.

Among the natural polymers membranes [9, 16, 17] DNA attracted an increasing interest because of its high availability, as this macromolecule can be easily obtained from the waste produced in fish processing industry [18]. DNA is a water soluble natural macromolecule which forms in solution polyanions. It is due to the presence of phosphate groups. Thus, this macromolecule in water solution behaves as polyelectrolyte. Moreover, DNA's biodegradability, non-toxicity and electrical properties led, among the others, to its investigation for opto-electronic applications, such as field-effect transistors [19], solar cells [20], OLEDs [21] or optical waveguides [22], among the others. Additionally, DNA was also studied for endocrine disruptors [23], and for organic compounds [24] or metal ions like Cu²⁺, Ag⁺, and Zn²⁺ removal [25]. Beside this, the DNA-based ionic conducting membranes were already applied and tested in small electrochromic devices (ECDs) either without or with dyes [26, 27]. The main interest in the development of polymer electrolytes is the search of new and modern devices [28], among the others: electrochromic rear mirrors for cars [29], smart windows for architecture [30] or camouflage [31]. The basic configuration of an ECD consist of five layers sandwiched type electrochemical cell with conductive substrates, such as glass-ITO (indium tin oxide) or glass-FTO (fluorine tin oxide), electrochromic (EC) layer, such as Prussian blue or WO₃, a solid, liquid or gel electrolyte and counter electrode, for example CeO₂-TiO₂ [28]. Polymer electrolytes in the form of ionically conducting membranes can be used in other electrochemical devices including previously mentioned OLEDs and/or dye sensitized solar cells (DSSC). Thus, the research on new environmentally friendly macromolecules is a goal for the development of modern devices. Aiming to advance in this field and develop new ionically conducting membranes for electrochemical devices and with light emitting properties, organic solvent soluble membranes based on modified DNA and organic dyes were prepared and characterized in the present work.

2. EXPERIMENTAL

Sodium salt DNA extracted from salmon sperm (Ogata Research Laboratory, Japan/lot: 05055; average molar mass of $M_{\nu} = 1 \times 10^6 Da$); sodium chloride (99 %, Quemis); butyl alcohol (99.4%, Mallinckrodt); hexadecyltrimethyl-ammonium bromide (CTMA, 98%, Sigma-Aldrich); *Nile Blue A* (75%, Sigma-Aldrich); *Disperse Red 1* (95%, Sigma-Aldrich) and *Disperse Orange 3* (90%, Sigma-Aldrich) were used as received.

DNA-CTMA complex was obtained by dissolving DNA in water (500 mL; 6.1 g/L) under constant stirring for 72-120 h. Then, the aqueous solution of the CTMA (500 mL; 6.1 g/L) was slowly dropped to DNA solution under constant stirring resulting in DNA-CTMA complex precipitation. The product was then filtered and washed extensively with Milli-Q water until the unreacted CTMA complete removal. Finally, the DNA-CTMA complex was dried under reduced pressure at 40 °C.

DNA and DNA-CTMA membranes were prepared by dissolving 0.18 g of DNA and DNA-CTMA, respectively in 30 mL of Milli-Q water under constant stirring for about 120 h. Then, this solution was poured into Petri dish and dried under reduced pressure at 40 °C.

DNA-CTMA-dye membrane was obtained by dissolving 0.18 g of DNA-CTMA and $9x10^{-3}$ g (5 wt%) either of *Nile Blue A* (NB), *Disperse Red 1* (DR1) or *Disperse Orange 3* (DO3) in 30 mL of butanol under a constant stirring for about 96 h. Finally, the solution was poured into Petri dish and dried under reduced pressure at 40 °C.

The UV-Visible spectra were registered with UV-Vis JASCO V 630 spectrometer in the range of 200 - 900 nm.

The FT-IR spectra were collected with Bomem/MB-102 apparatus.

The thermal analyses were performed with TGA Q50 TA Instruments equipment with heating rate of 10° C/min in the range of 25 to 500 °C under 50 mL/min of N₂ flow.

The X-ray diffractograms were obtained on silicon wafer with Rigaku Rotaflex RU-200B and λ (CuK_a) = 1.54 Å; power of 40 kV/ 80 mA; speed 1.2 degree/min and angle of 5 to 60 °.

The impedance measurements were performed by sandwiching the 1.54 cm round and about 5 μ m thick membranes between two mirrorpolished stainless steel 304 electrodes. The measurements were performed in vacuum using a home-made Teflon® sample holder and a computer controlled Solartron SI 1260 Impedance/Gain Phase Analyzer. The frequency range was of 10 MHz to 0.1 Hz with amplitude of 5 mV. The studies were performed in the temperature range from 303 K to 373 K using a EDG 5P oven.

The fluorescence spectroscopy analysis was performed with Hitachi F-4500 fluorimeter operating with 60 nm/min scan rate, excitation and emission slit of 2.5 and 5 nm, respectively.

3. RESULTS AND DISCUSSION

Aiming to develop new natural macromolecule-based membranes it was proposed to add the dyes as *Nile Blue A*, *Disperse Red 1* and *Disperse Organge 3* (Figure 1) to DNA-sodium salt solution. However, such molecules do not dissolve in water that is the only solvent for the DNA. Thus, it was necessary to modify DNA by reacting it with CTMA (Figure 2) resulting in DNA-CTMA organic soluble complex [32].

In order to check the nature of DNA-CTMA-dye interaction, the obtained samples were first characterized by FTIR spectroscopy and the results are shown in Figure 3. In this figure the DNA spectrum (Figure 3 a) reveals a broad absorption band around $3000 - 3600 \text{ cm}^{-1}$ that can be attributed to several molecular vibrations, such as NH stretching at 3358 cm⁻¹ [33], C=N at 3217 cm⁻¹ and CH₃ stretching at 2945 cm⁻¹. Intense bands around 1560-1740 cm⁻¹, involving several modes of molecules deformation and stretching, are observed for C=N in imines and oximes at 1691 cm⁻¹ and for amide C=O at 1652 cm⁻¹. Bands at 1606 and 1485 cm⁻¹ are due to C=C stretching vibration



FIGURE 1 Nile Blue A (a), Disperse Red 1 (b) and Disperse Orange 3 (c) chemical formula.



FIGURE 2 Reaction scheme of DNA- CTMA formation.



FIGURE 3

FTIR spectra of DNA (a), DNA-CTMA (b), DNA-CTMA-*Nile Blue A* (c), DNA-CTMA-*Disperse Red 1* (d) and DNA-CTMA-*Disperse Orange 3* (e).

attributed to purine imidazole ring. Band at 1531 cm⁻¹ can be attributed to N-O stretching of secondary amine groups [34], while that at 1236 cm⁻¹ to asymmetric and at 1088 cm⁻¹ to symmetric stretching of PO_2^- groups. Moreover, in the wavenumber range of 800 to 900 cm⁻¹ appear absorptions, which are due to vibrations of the sugar-phosphate groups [33]. According to Hebda et al [33], the bands discussed above are traditionally attributed to the B form of DNA.

Comparing the FTIR spectra of DNA and DNA-CTMA membranes (Figure 3 a and b) it is possible to verify the presence of absorptions at 2916 and 2849 cm⁻¹. These bands are assigned to the symmetric and asymmetric stretches of the CH₂ groups of CTMA and are evidence of the DNA-CTMA complex formation. It is also confirmed by the bathochromic shift of PO₂⁻ symmetric stretching band at 1095 cm⁻¹. Additionally, the shift of the DNA band at 1088 and shoulder at 1067 cm⁻¹ to 1065 and 1095 cm⁻¹ is observed after modification of DNA with CTMA [33].

Figure 3 c-e shows the DNA-CTMA-dye spectra. In the case of DNA-CTMA-NB there is no change in the spectrum, but in the case of



FIGURE 4 TGA analysis of DNA (—), DNA-CTMA (---), DNA-CTMA-*Nile Blue A* (····), DNA-CTMA-*Disperse Red 1* (-----), and DNA-CTMA-*Disperse Orange 3* (------).

DNA-CTMA-DR1 and DNA-CTMA-DO3 new bands at 1342 and 1339 cm⁻¹, respectively, are observed. The absence of other bands is probably due to a small amount of dye used and to the presence of similar groups in both, DNA-CTMA and dye chemical formula.

The thermal stability of the DNA-based membranes was studied by TGA and the results are shown in Figure 4. In this figure, one can see that DNA and DNA-CTMA membranes have lost about 18% and 15% of weight, respectively. The DNA weight loss is comparable with observations made with other DNA-based membranes [27], but is higher when compared to the DNA-CTMA-dye samples, for which the mass loss was only of 10% in the temperature range of 25 to 200 °C. This weight loss can be due to the removal of remaining solvents in the samples. The principal mass loss of DNA, attributed to the degradation process, starts at 215 °C and lasts up to 324 °C. At this stage, the sample weight loss is of about 37% and increases to 42% at 500 °C. The degradation process of DNA-based samples can be related to the dissociation of the DNA-double helix, resulting in the decomposition of nucleotide bases. The remaining residues at this temperature were of 38% of DNA. This result is very similar to that reported previously [27, 33]; however, the remaining weight at 500 °C was larger in the present work. The difference can be due to the

composition of the membranes, whereas the reported previously samples contained glycerol as additive.

The DNA-CTMA membrane lost 15% of the weight when heated up to 200 °C. Above this temperature the degradation process started and 56% of weight loss was registered at 300 °C. More than 9% was lost when the temperature was raised to 500 °C. The remaining about 20% were ashes [12].

The DNA-CTMA-dye weight losses as function of temperature were very similar (Figure 4). The samples lost 10% of weight when heated up to ~200 °C. This weight loss can be attributed to the presence of residual solvent. The degradation process starts at 200 °C and the weight loss is of about 60% when the sample is heated up to 300 °C. A further heating to 500 °C promotes a greater weight loss in all samples. The measured remaining weights parts are of 25, 22 and 20% for DNA-CTMA-NB, DNA-CTMA-DR1 and DNA-CTMA-DO3 complexes, respectively. These results are very similar to the previously reported ones for DNA-PEDOT and DNA-POEA samples [27]. From Figure 4 one can see a small decrease of the degradation temperature after DNA modification. This result indicates that the complex formation modifies the thermal stability of the membranes.

The influence of dye incorporation into DNA-based membranes on their structure was studied by X-ray diffraction. The obtained results are shown in Figure 5. The DNA diffractogram (Figure 5 a) reveals presence of a very large band attributed to the amorphous phase. The large bands centered at 17, 21 and 33 degree originate from the crystalline regions. These results are different to those obtained for DNA-glycerol-based samples where only one band at $2\Theta = 21^{\circ}$ was observed [27]. Analyzing the data for the DNA and DNA-CTMA membranes (Figure 5 a and b) one observes that the DNA-CTMA complex formation promotes an increase of crystallinity of the samples. Evidence of it is the appearance of two sharp peaks at $2\Theta = 22$ and 24 degrees. The DNA double helix is a rigid structure and becomes more rigid after attachment of large aliphatic chains to the DNA-backbone.

The DNA-CTMA-dye samples (Figure 5 c, d and e) exhibit a decrease of the crystallinity as compared with DNA-CTMA sample. This can be explained in terms of dye molecules intercalation between the bases pairs of DNA-CTMA adjacent strands, which causes a separation of the interplanar base pairs and increases average separation between the chains ($\langle R \rangle$). Moreover, a modification of the torsion angles and possibly an elongation of the DNA double helix is observed.

The ionic conductivities measured as a function of temperature in the temperature range of 24 to 100 °C and for the DNA-based samples with different compositions are displayed in Figure 6. An evaluation of this property is important for future application of the material as ionic conductor in electrochemical devices. As one can observe in Figure 6 the DNA membranes show an increase of ionic conductivities from 1.3×10^{-6} S/cm at 26 °C to 1.5×10^{-4} S/ cm at 100 °C. These values are lower than observed for DNA-glycerol sam-



FIGURE 5

XRD results of DNA (a), DNA-CTMA (b), DNA-CTMA-*Nile Blue A* (c), DNA-CTMA-*Disperse Red 1* (d⁻) and DNA-CTMA-*Disperse Orange 3* (e).

ples [27], but similar to those obtained for other DNA-based samples [14, 35]. Modification of DNA with CTMA leads to a two orders of magnitude decrease of the ionic conductivity to 4×10^{-8} S/cm at 29 °C and three orders of magnitude, i.e., to 9.4×10^{-7} S/cm at 96 °C, respectively. Addition of dyes to the DNA-CTMA composition formula, such as *Nile Blue* and *Disperse Red 1* results in an increase of the conductivity in almost the whole range of temperature used in this study. The DNA-CTMA-NB and DNA-CTMA-DR1 samples exhibit ionic conductivities of 4.9×10^{-7} and 1.6×10^{-7} S/cm at 27 °C and 1.3×10^{-4} and 2.4×10^{-5} S/cm at 96 °C, respectively. The sample of DNA-CTMA-*Disperse Orange 3* displays slightly better values of 6.7×10^{-8} S/cm at 26 °C and 1.5×10^{-6} S/cm at 75 °C when compared with DNA-CTMA sample, but lower in comparison with the other ones. Unlike in the previous studies, the samples studied in this work evidence nonlinear behavior of the ionic conductivity in function of temperature. Usually, this is interpreted as due to the ionic motion coupled to the segmental motion of the polymeric



FIGURE 6 Log of ionic conductivity as a function of inverse of temperature of DNA (\blacksquare), DNA-CTMA (\blacklozenge), DNA-CTMA-*Nile Blue A* (\blacktriangle), DNA-CTMA-*Disperse Red 1* (\blacklozenge) and DNA-CTMA-*Disperse Orange 3* (\bigstar).

chains [36] and is in agreement with the decreased crystallinity observed by X-ray diffraction (Figure 5).

As mentioned above, Figure 6 reveals a decrease of ionic conductivities after modification of DNA with CTMA. The DNA material used in this research was in a sodium salt form, thus incorporating small mobile Na⁺ ions serving as charge vehicles. The modification of DNA by reaction with CTMA eliminates such ions, decreasing in this way the ionic conductivity of the samples. The addition of dyes promotes an increase of ionic species. However, the dye quantity used is small and the size of such ions is large (Figure 1). Therefore, only a small increase of the ionic conductivities is observed.

Analyzing nonlinear behavior of ionic conductivity of the samples it should be noted that similarly to chitosan-ionic conducting membranes other complex behaviors, such as hopping mechanism between coordination sites or local structural relaxations could be simultaneously involved in the segmental motions of the macromolecule [37]. Moreover, an increase of temperature promotes faster internal modes of macromolecule in which the bond rotations produce segmental motions [38].

Aiming to verify the possibility to obtain DNA-based membranes for opto-electrochemical devices the samples were analyzed by UV-Vis absor-



FIGURE 7 Pictures of DNA-CTMA (a), DNA-CTMA-*Nile Blue A* (b), DNA-CTMA-*Disperse Red 1* (c) and DNA-CTMA-*Disperse Orange 3* (d).

bance and photoluminescence in the liquid and solid state, respectively. The optical properties of the DNA-CTMA complexes are primarily dependent on the type of tensoactive agent used, DNA molecular weight and concentration of reactants. DNA modified by quaternary surfactants, particularly hexadecy-ltrimethylammonium chloride or bromide (CTMA) produces transparent films with excellent optical properties, including high transmission in the visible and near infrared electromagnetic spectrum region (Figure 7 a). This advantage, in particular, allows the use of DNA-CTMA membranes for photonic and optoelectronic device application [33, 39]. The DNA-CTMA-*Nile Blue A, -Disperse Red 1* and *-Disperse Orange 3* membranes are blue, red and orange colored, respectively due to the added dyes (Figure 7 b-d).

The membranes photoluminescence can be obtained by doping with fluorescent dyes, which intercalate in the DNA structure [40]. It is well known that the fluorescence depends strongly on the environment in which the chromophore is inserted as well as on the molecular interactions with the polymer matrix. Depending on the macromolecule-dye interaction the light emission can be suppressed. Absorbance of DNA, DNA-CTMA and DNA-CTMA-dye solutions and fluorescence spectra of the DNA-CTMA-dyes membranes, are shown in Figure 8. Analyzing the spectrum of DNA solution (Figure 8 a) one can see that the maximum absorption wavelength of 258 nm is close to 260 nm, as already reported [39]. This band originates from conjugated π electron absorption of the double bond. The DNA-CTMA complex present a larger extinction coefficient than pure DNA indicating changes in the π - π transition of C=C electrons bond of the DNA strands stacking structure [39, 41].

The UV-Vis absorption spectrum of DNA-CTMA-*Nile Blue A* of the solution and fluorescence of the membrane are shown in Figure 8 b. The dye *Nile Blue A* in butanol (not shown here) shows an absorption maximum at 629 nm and an emission at 656 nm after excitation at 629 nm. The emission is present in only one stage evidenced by single band with Stokes shift of 27 nm. The DNA-CTMA-*Nile Blue A* solution reveals absorption and emission maxima at 629 and 656 nm, respectively and the membrane emission with maximum



FIGURE 8

UV-Vis absorbance of DNA and DNA-CTMA solution (a); absorbance of solutions in butanol (solid lines) and membranes emission (-o-) of DNA-CTMA-*Nile Blue A* (b); DNA-CTMA-*Disperse Red 1* (c) and DNA-CTMA- *Disperse Orange 3* (d).

at 676 nm after excitation at 629 nm (Figure 8 b). The Stokes shift for the solution is of 27 nm and for the membrane 47 nm, in comparison with Nile Blue in butanol. This shift difference can be attributed to the polarity of the medium as the fluorescence quantum yield is very sensitive to the environment, its pH, structure stiffness and solvent effects [42]. The UV-Vis absorption spectrum of Disperse Red 1 (not shown here) reveals an absorption maximum at 482 nm considered as a charge transfer band between the electron donor and electron acceptor groups [39, 43]. The fluorescence spectrum after excitation at 482 nm shows two peaks located at 558 and 590 nm. Moreover, the emission takes place in two stages evidenced by two bands with Stokes shift of 108 nm. The UV-Vis absorption of the DNA-CTMA-Disperse Red 1 solution (Figure 8 c) shows a maximum absorption and emission at 482 and 554 nm, respectively. The maximum emission wavelength for the membrane is at 719 nm after excitation at 482 nm. The Stokes shift is of 71 and 238 nm in solution and in membrane, respectively (Figure 8 c). The results show a suppression of emission at 558 nm and a significant difference in Stokes shifts between DNA-CTMA-DR1 solution and membrane, when compared with the DNA-CTMA-Nile Blue A system. This indicates existence of another factor than the polarity contributing to this difference.

Finally, the UV-Vis absorption and fluorescence spectra of *Disperse Orange 3* in butanol solution (not shown here) reveal an absorption maximum at 447 nm, an emission maximum at 515 nm and a second peak at 595 nm for excitation at 447 nm. Again, in this case the solution emission takes place in two stages with Stokes shift of 148 nm and with respect to the maximum absorption wavelength.

Figure 8 d shows the UV-Vis spectra of DNA-CTMA-*Disperse Orange 3* solution with maximum absorption wavelength of 447 nm and emission at 513 nm. For membrane, the maximum emission wavelength is of 669 nm. The Stokes shift in solution is of 66 nm and for the membrane of 222 nm, respectively.

Comparing the results presented in Figure 8 b-d, obtained for the same concentration of dyes, i.e., 5% of the DNA-CTMA mass one can evaluate the influence of the structure stiffness on photoluminescence. The structural rigidity decreases the rate of nonradiative relaxation giving the time to fluorescence relaxation and favoring the fluorescence of rigid molecules [42]. From the obtained results, it can be stated that the fluorescence intensity (in brackets) decreases as follows: DNA-CTMA-DO3 (180); DNA-CTMA-NB (54) and DNA-CTMA-DR1 (40). From the X-ray analysis it is seen that the rigidity, resulting from the increased crystallinity of the membranes, decreases in the same order. Thus, the results obtained by the fluorescence spectroscopy corroborate those got from X-ray diffraction.

4. CONCLUSIONS

Thin films of DNA, DNA-CTMA and DNA-CTMA-dye being Nile Blue A, Disperse Red 1 and Disperse Orange 3 were prepared and characterized by IR and UV-Vis spectroscopy, thermal analysis (TGA), X-ray diffraction, ionic conductivity and fluorescence spectroscopy. The FTIR and UV-Vis analysis confirm the DNA-CTMA complex formation as well as incorporation of dyes into the macromolecular matrix. The FTIR spectra show presence of peaks at 1920 and 1850 cm⁻¹ assigned to the CH₂ asymmetric and symmetric stretching of CTMA alkyl chains and evidencing the DNA-CTMA complex formation. The TGA analysis revealed that DNA-CTMA and DNA-CTMA-dye have lost less mass than DNA after heating up to about 200 °C. The degradation process started above 200 °C for all samples and a lower thermal stability was observed for DNA-CTMA-dye membranes as compared with DNA ones. The differences in thermal stability of the samples were explained in terms of a double helix dissociation resulting from the long alkyl groups (CTMA) insertion. This probably promotes van der Waals and hydrogen bonds disruption and as consequence exposition of nucleotide bases.

The X-ray analysis of the DNA-based membrane's samples showed that the modification of DNA with CTMA increases the membrane crystallinity.

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However, the dye molecules intercalate between the adjacent base pairs of DNA-CTMA chains promoting their separation, and consequently a decrease of crystallinity. Moreover, a modification of DNA-CTMA-dye torsion angles and double helix stretch is also taking place.

The ionic conductivity measurements in function of temperature of the membranes revealed lower values for DNA-CTMA, i.e., $4x10^{-8}$ S/cm at 29 °C and $9.4x10^{-7}$ S/cm at 96 °C when compared to DNA membranes. The addition of dyes to the DNA-CTMA composition formula, such as *Nile Blue* and *Disperse Red 1* promotes an increase of the conductivity in almost the whole range of temperature used in this study, being $4.9x10^{-7}$ and $1.6x10^{-7}$ S/cm at 27 °C and $1.3x10^{-4}$ and $2.4x10^{-5}$ S/cm at 96 °C, respectively. DNA-CTMA-DO3 membranes exhibit ionic conductivities of $6.7x10^{-8}$ S/cm at 26 °C and of $1.5x10^{-6}$ S/cm at 75 °C.

Finally, the results of fluorescence study show that all DNA-CTMA-dye membranes are fluorescent with intensities in agreement with structural analysis, being of 40, 54 and 180 for DNA-CTMA-*Disperse Red 1*, DNA-CTMA-*Nile Blue A* and DNA-CTMA-*Disperse Orange 3*, respectively, i.e., in the same order as the observed increase of crystallinity in these samples. The membranes are also promising candidates to be applied in new electrochemical devices.

5. ACKNOWLEDGEMENTS

The financial support of the Brazilian agencies CNPq, Capes and FAPESP, and FP7-PEOPLE-2009-IRSES Biomolec – 247544 are gratefully acknowledged. The authors are grateful to Driele R. Vicentin from IQSC-USP for samples preparation.

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