

*Dedicated to Professor Alexandru T. Balaban
on the occasion of his 85th anniversary*

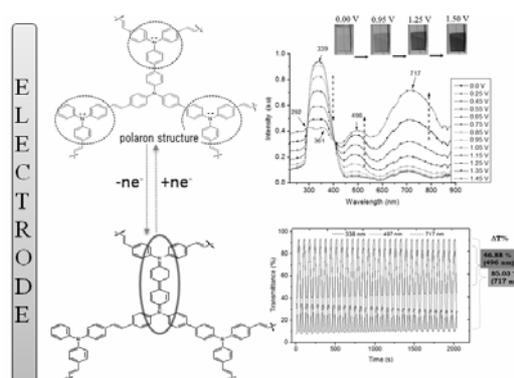
SPECTROELECTROCHEMICAL PROPERTIES OF LINEAR AND STAR-SHAPED TRIPHENYLAMINE OLIGOVINYLENES

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Three electroactive oligomers with linear and star-shaped structure containing triphenylamine moieties as ending group and/or core unit connected by vinyne segments were characterized in terms of the electrochemical polymerization and spectroelectrochemical behavior. Using cyclic voltammetry technique the oligomers were electropolymerized and deposited as electroactive polymeric films on the electrode surface. The polymers films have excellent electrochemical stability and exhibit color changes while the potential of the working electrode is swept between 0.0 V and 1.8 V. These color changes may be associated to various oxidation states that undergo the polymers during the oxidation/reduction processes. The electrochromic behavior of polymers was monitored, and the results confirm that the electrodeposited films present very good electrochromic properties preserving their electrochromic parameters even after a number of 45 continuous cycles operations. It can be anticipated that all three polymers can find applications in electrochromic devices, optical displays, smart windows or sensors.



INTRODUCTION

In the age of modern and rapidly developing electronics, novel materials such as conjugated molecules and polymers, featuring photo- and electroluminescent properties, are attracting exceptional interest in terms of the possibilities they offer for molecular optoelectronic applications such as potential elements of

electroluminescent diodes, displays and photovoltaic cells.¹ Nowadays, some conjugated organic materials can already be found in prototypes, and commercial chemical sensors, photovoltaic cells and display devices.²⁻⁶ The use of small conjugated oligomers as model compounds for conducting polymers has a great advantage because of their well-defined and defectless structure and better supramolecular

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organization in the solid state, facilitating thus their experimental and theoretical investigations, and gives the opportunity to tune the photophysical properties, solubility in common organic solvents, by changing easily the structure by introduction of side substituents, end-capping groups, insertion of certain specific functional groups and by changing the oligomer length.⁷ The combination between the triphenylamine which possess holes as charge carriers and the strong emissive vinyl moieties has led to new electroactive conjugated materials in which the tertiary amine does not interrupt the chain conjugation,⁸⁻¹¹ on the contrary, the lone pair of electrons from nitrogen atoms contributes to enlarge the effective conjugation.^{12,13} Triphenylamine can be easily mono, bi- or tri-functionalized by attaching substituents in the *para*-positions (the most reactive ones), making this molecule to be widely used as building blocks in the construction of linear, branched and hyperbranched, star and dendrimer conjugated architectures. The vinyl linkage not only forms a conjugated bridge between the aromatic units, but also acts as a spacer allowing the decrease of steric interactions between structural units. Because of the bulky propeller-like structure of triphenylamine molecule, the resulting polymers possess good solubility in many organic solvents and an increased ability to form good films for various optoelectronic applications. Having a pronounced electron-donor character, excellent redox and good hole-transport properties, triphenylamine derivatives are already used in the preparation of new materials with hole-transporting properties.¹⁴⁻¹⁶ Electrochemical behavior is an important part of the optimization process based on investigation of structure-activity relationships. Electrochemical and spectroelectrochemical methods allow a relatively easy evaluation of the properties such as the kind of charge carriers responsible for the process of conductivity and other parameters for optoelectronic applications of both monomers (small molecules) and polymers.¹⁷⁻²²

The objective of this communication is to present the electrochemical synthesis of poly(triphenylamine vinylene)s by anodic electropolymerization of three oligomers containing triphenylamine unit as ending groups connected by vinylene segments. These oligomers with linear and star-shaped structure exhibit

interesting electronic properties, reversible electrochemical process and stability.

RESULTS AND DISCUSSION

Three oligomers containing triphenylamine (TPA) as end groups and triphenylamine or benzene nuclei (Fig. 1) as cores were chosen to be investigated regarding their spectroelectrochemical behavior. Their synthetic method is published already elsewhere.²³⁻²⁵

Electrodeposition of polymeric films

The oligomers have TPA units as electroactive groups at the ends and therefore it is expected to exhibit electrochemical behavior ruled by these groups. In Fig. 2 are presented the consecutive cyclic voltammograms recorded for solutions of oligomers, by sweeping the ITO/glass working electrode potential from 0.00 V to 1.50 V and 1.80 V. In the first anodic scan, oligomer **L** exhibits two main oxidation peaks at $E_{pa1} = 0.872$ V and $E_{pa2} = 1.211$ V and two reduction peaks at $E_{pc1} = 0.992$ V and $E_{pc2} = 0.807$ V. The star-shaped oligomer **S1** exhibits two oxidation peaks $E_{pa1} = 0.926$ V and $E_{pa2} = 1.324$ V and two reduction peaks at $E_{pc1} = 0.729$ V and $E_{pc2} = 0.874$ V. The oligomer **S2**, undergoes oxidation and reduction process exhibiting two anodic peaks at $E_{pa1} = 0.898$ V and $E_{pa2} = 1.396$ V and two reduction peaks at $E_{pc1} = 0.632$ V and $E_{pc2} = 0.884$ V. In all three cases, the oxidation and reduction peaks are large and not very well defined and this is due to the large surface area of the ITO/glass working electrode used in this study. The first oxidation peak observed on the first scan is associated with the loss of electron from the atomic central nitrogen of TPA moieties leading to the formation of cation-radical (TPA^{•+}). The cation-radicals are unstable and can be involved in a dimerization reaction generating tetraphenylbenzidine species (TPB²⁺) (Scheme 1). This is an electroactive center that undergoes a reversible oxidation process, which is responsible of the additional cycles further observed in the cyclic voltammograms²⁶. The second scan shows a similar profile, but the redox current intensities increase suggesting that an electroactive polymer film is deposited on the ITO/glass electrode.

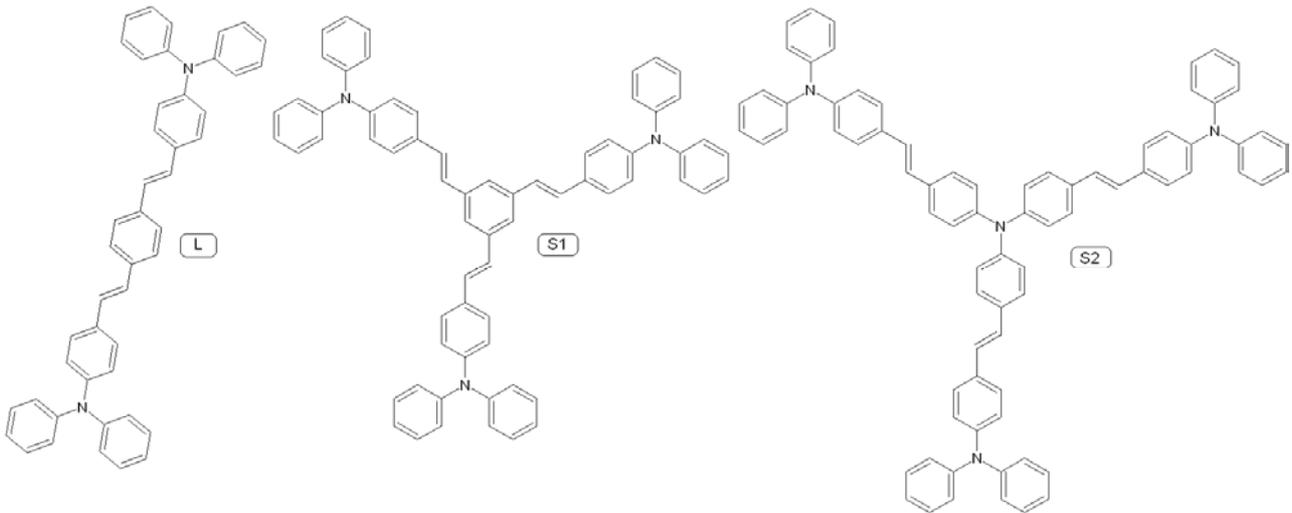


Fig. 1 – Triphenylamine oligomers with linear (L) and star-shaped (S1 and S2) structures.

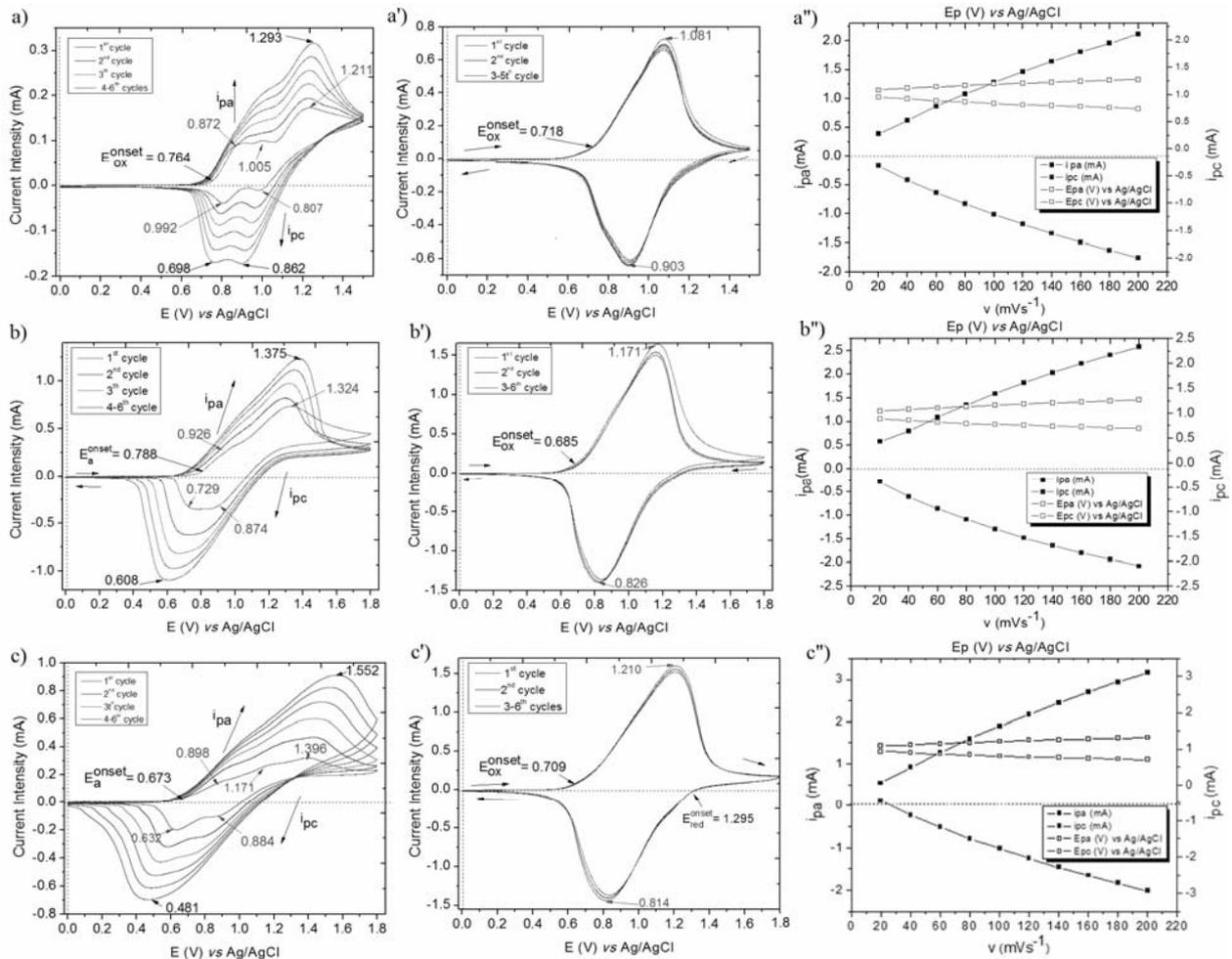
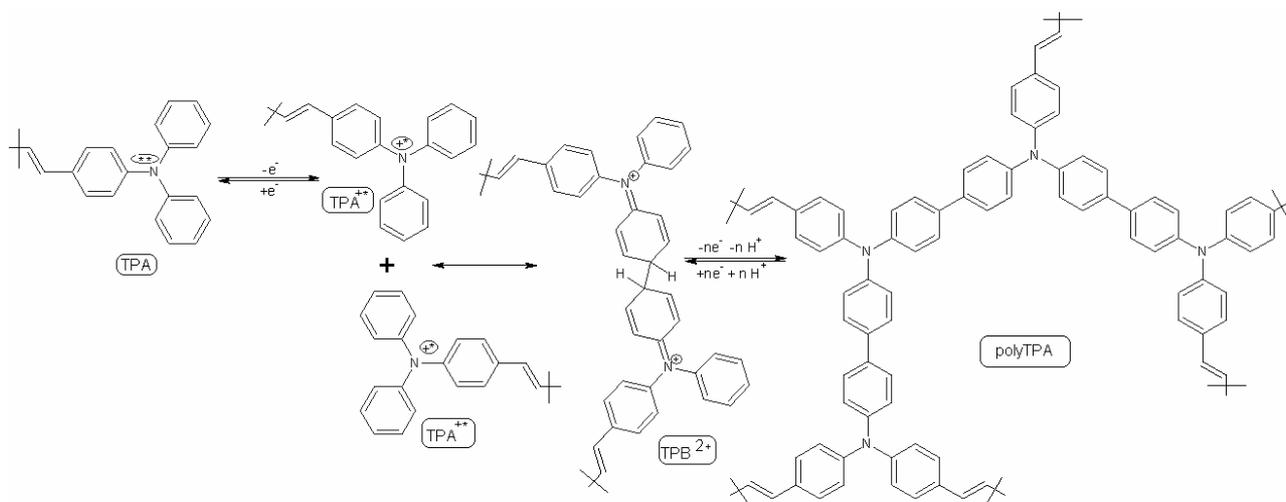


Fig. 2 – Repetitive CVs (10 or 6 cycles) for oligomers: a) L, b) S1 and c) S2, from CH_2Cl_2 solutions ($c = 10^{-3}$ M), containing 0.1 M TBAP, recorded at ITO/glass with 50 mVs^{-1} scan rate (v); the electrochemical stability of the electrodeposited polymers: a') polyL, b') polyS1, and c') polyS2 recorded in ACN solution containing 0.1 M TBAP, scan rate = 50 mVs^{-1} ; the i_{pa} and i_{pc} vs v (mVs^{-1}) graphs for polymers: a'') polyL, b'') polyS1 and c'') polyS2.



Scheme 1 – General mechanism proposed for electrosynthesis of polymers by electropolymerization of oligomers, using cyclic voltammetry technique.

By increasing the number of the scans until 6th or 10th scans, it can be observed that the first oxidation and reduction peaks (E_{pa1}) disappear and the second oxidation and reduction peak values are shifted to more positive and negative values, respectively. The intensity of the oxidation and reduction currents increases which indicates that new electroactive polymeric structure is formed on the electrode surface, by C-C bond formation between *para*-free positions of the TPA peripheral units at the ends of the oligomer structure (Scheme 1). Thus, at the end of the scans, yellow or green colored polymer films are formed and deposited on the ITO/glass working electrode surface, which are insoluble in methylene chloride and acetone. The thickness of the electrodeposited films depends on the number of successive scans. The presence of more TPA units and of central core makes the oligomer **S2** more easily oxidizable with an onset anodic potential of 0.673 V comparative to oligomers **L** ($E_a^{onset} = 0.764$ V) and **S1** ($E_a^{onset} = 0.788$ V). This can be explained by the fact that the **S2** oligomer has a more extended conjugation by [TPA-vinyl-TPA-vinyl] segments, through the involvement in conjugation of the lone electron pair from the N atom.

To investigate the electroactivity and stability of the electrogenerated polymers, the working electrodes ITO/glass with the films deposited on were immersed in ACN solution containing 0.1 M TBAP electrolyte and subjected to 5 scans on the 0.00 V -1.50 V or 1.80 V potential domain. The

redox response of these electrodes is shown in Fig. 2 (a', b') and c''), where it can be observed that all films have good electrochemical activity and stability, maintaining their electroactivity during all 5 repetitive cycles; the redox peaks current intensities are decreasing very little from the first scan. In addition, the intensities of the oxidation (i_{pa}) and reduction (i_{pc}) and the peak potential values (E_p) recorded for polymers increase linearly with the increasing of the scan rate between 20 to 200 mVs^{-1} (Fig. 2 a''), b''), c'')).

It is known that the morphology of organic materials films plays an important role when they are used as components in optoelectronic devices, and has great influence on their performance and stability. For this, the electrodeposited polymeric films were analyzed in terms of their surface morphology by AFM technique. The obtained images show that the polymeric films are uniformly deposited on the ITO/glass electrodes and the differences in their morphologies (smooth surface and without grains for poly**L** or boundary surface for poly**S2**) as well as the surface roughness are related directly to the molecular structure of electrogenerated polymers (Fig. 3). The AFM results for poly**S2** are in accordance with literature data, where the authors explain that the boundary surface is caused by the positive charge located in the central core which could produce coulombic repulsion between different polymeric branches which lead to affect both the nucleation and growing process of the film.²⁶

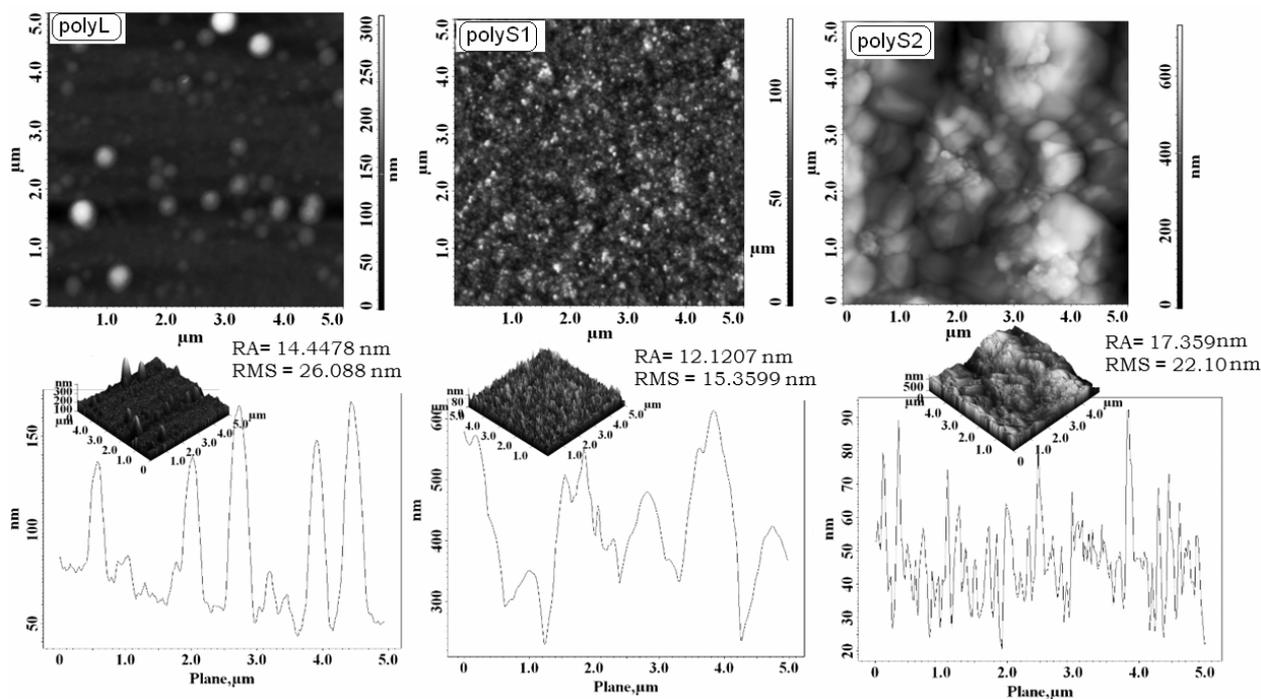


Fig. 3 – AFM images recorded for the electrogenerated polymers on the ITO/glass.

Spectroelectrochemical studies

It was observed that the color of the electrogenerated films changes during the cyclic voltammetry measurements, and thus, their electrochromic properties were further investigated. The absorption spectra of the films were obtained as a function of the applied potential between 0.00 V and 1.50 V or 1.80 V (Fig. 4). In their neutral state (0.0 V), the films are semitransparent showing a pale yellow or green color, visible with the naked eye and with a maximum of absorption in the range of 327-345 nm assigned to $\pi-\pi^*$ transition from the tetraphenylbenzidine units. Being electrodeposited films, the polymers maintain some of their oxidized structure (polaronic/doped state) recognized by the absorption maxima at higher wavelength values, 710 nm (for polyL), 686 nm (for polyS1) and 687 nm (for polyS2), but these bands have small intensities. As the potential is gradually increased to 1.50 or 1.80 V, the intensity of the first absorption bands (339 nm, 337 nm or

345 nm, respectively) decrease, while new absorption bands appear in the 498 -510 nm wavelengths and increase in intensity.

The absorption bands located at higher wavelength values which appear at 0.0 V, in the neutral state of the films, increase drastically in intensity until the potential reaches more positive values and are shifted to higher values at 717 nm, 695 nm and 723 nm, respectively. It can be stated that the first absorption band is associated to the neutral tetraphenylbenzidine unit of the polymers while the second and the third absorption bands (498-510 nm, and 695-723 nm) can be assigned to cation and dication structure of the polymers (polaron and bipolaron structures). These new bands appear as a result of the oxidation process of the films that produce visible change in the color of the films from yellow to orange/green and finally to intense blue.²³ When then potential was applied in reverse the film color returns to the semitransparent with pale yellow or green color.

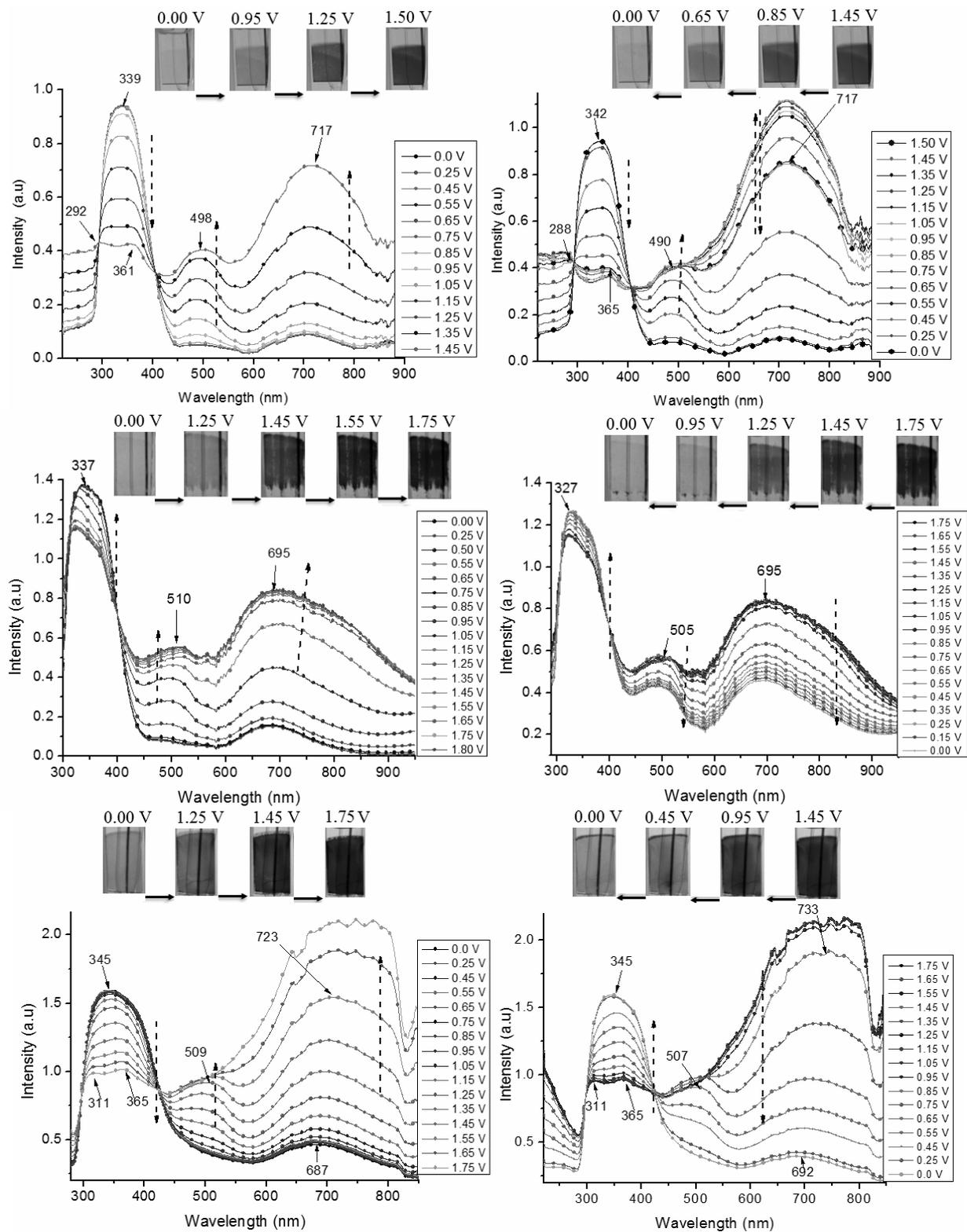


Fig. 4 – Electronic absorption spectral change for a) polyL, b) polyS1, c) polyS2 recorded during the potential sweeping between 0.00 – 1.80 V: oxidation process (left hand) and 1.8 – 0.0 V: reduction process (right hand) with 50 mVs^{-1} scan rate and at room temperature. The inset Fig.s represent the photographic images of the films during the applied potentials.

Electrochromic behavior

Electrochromic switching studies were performed to detect the changes in transmittance with time at the wavelength corresponding to the maximum optical contrast of the polymers between reduced and oxidized states. For these measurements, double step chronoamperometry technique was used to investigate the switching ability of polymer films (coated area is 0.96 or 0.97 cm²) between their neutral and full doped state (Fig. 5). The measurements were carried out by switching the applied potential between 0.00 V and 1.45 V. The transmittance intensity was measured for 338 nm, 497 nm and 717 nm bands for polyL, 500 nm and 700 nm for polyS1 and 344 nm, 503 nm and 709 nm for polyS2. The transmittance difference between the redox states, named as optical contrast ($\Delta T\%$), is an important characteristic for electrochromic materials. As it is shown in Fig. 5, the optical contrast for

polymer polyL is 85.03 % recorded for 717 nm, which is much higher than for other two polymers, 50.71 % for polyS2 (709 nm) and 33.52 % for polyS1 (700 nm). In case of polyL, the optical activity was retained by 94 % even after 35 cycles of operations, and for polyS2 the optical activity was retained by 90.6% even after 45 cycles of operations, which is in accordance with the electrochemical stability. Another important parameter is the response time defined as time required for reaching 95 % of full optical switch after the switching of the potential. The optical response time from the neutral state to the oxidized state was found to be 20 s for polyL, 18 s for polyS1 and 11 s for polyS2. The coloration efficiency (CE) is another important parameter and this is calculated by using $CE = (\Delta OD / \Delta Q)$, where $\Delta OD = \log (T_{\text{neutral}} / T_{\text{oxidized}})$ and ΔQ represents the injected/ejected charge between neutral and oxidized states, respectively.

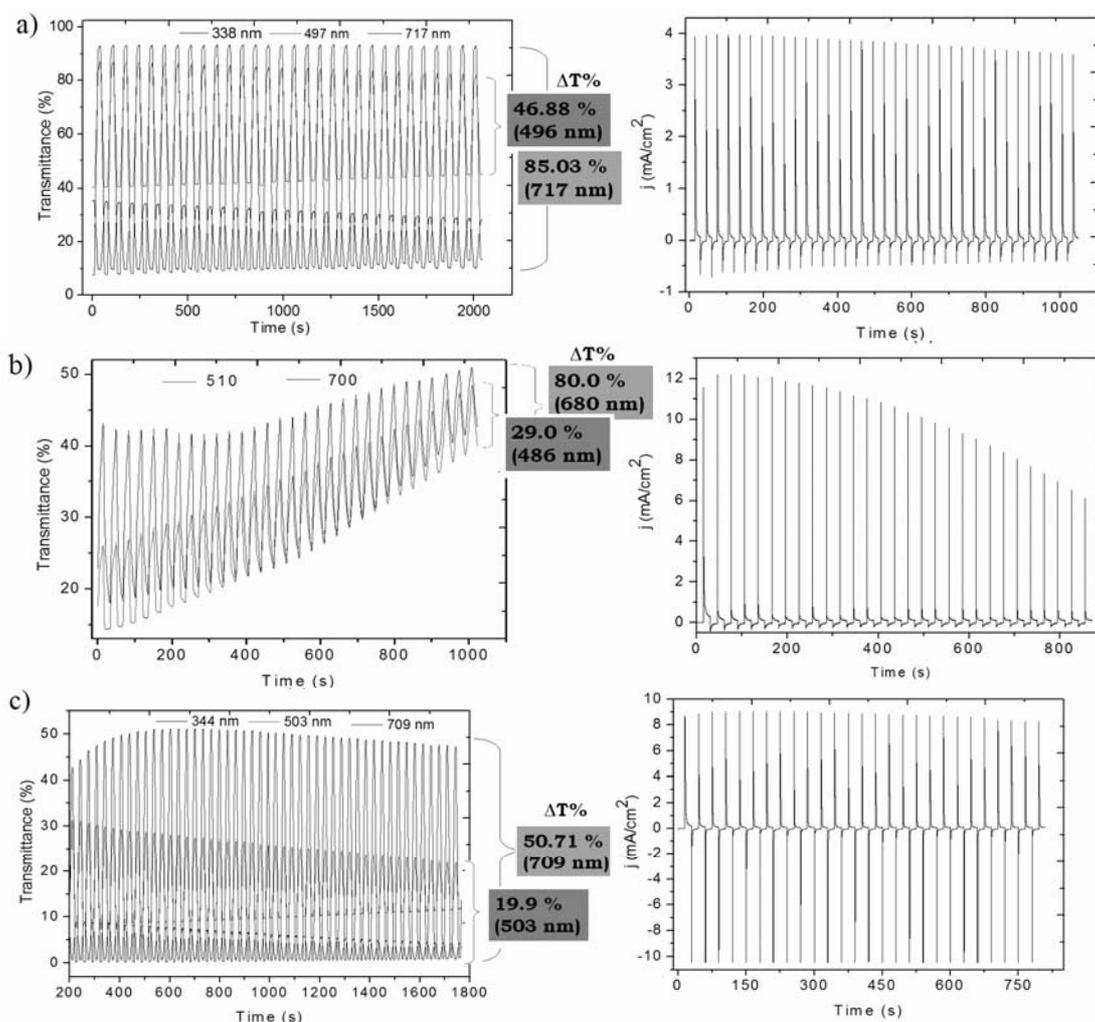


Fig. 5 – Electrochromic switching of polymers a) polyL, b) polyS1 and c) polyS2 films monitored between 0.00 V and 1.45 V potentials switching values.

Using these equations, CE measured for the electrogenerating polymers were $268 \text{ cm}^2\text{C}^{-1}$, $132.23 \text{ cm}^2\text{C}^{-1}$, $246 \text{ cm}^2\text{C}^{-1}$ for polyL, polyS1 and polyS2, respectively. Having a contrast ratio of 85.03 % on the IR region is an advantage of polyL for NIR electrochromic applications.

EXPERIMENTAL

Materials

The synthesis and chemical characterization of triphenylamine-based oligomers L, S1 and S2, were published elsewhere.²³⁻²⁵ Tetrabutylammonium perchlorate (TBAP) purchased from Aldrich was used as supporting electrolyte in electrochemical and spectroelectrochemical studies. Dichloromethane (CH_2Cl_2), chloroform (CHCl_3) and acetonitrile (ACN) (all from Aldrich) were used as solvents in electrochemical and electrochromic studies.

Characterization

Electrochemical polymerization of oligomers was carried out by cyclic voltammetry with a BASi 100B/W electrochemical workstation, by using an electrochemical cell equipped with an ITO/glass as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. Electrodepositions of polymers were performed by cycling the potential of working electrode immersed in the CH_2Cl_2 solution of oligomers ($c = 10^{-3} \text{ M}$) containing 0.1 M TBAP. The electrodeposited polymers films were then raising them with CH_2Cl_2 solvent and dried, were immersed in ACN solutions containing 0.1 M TBAP in order to investigate the electrochemical stability and electrochromic characteristics. Prior to each experiment the solutions with supporting electrolyte were deoxygenated by passing dry argon gas for 10 min, and the measurements were performed at room temperature. All potential values in this study are expressed relative to the ferrocene/ferrocenium redox couple ($E_{1/2(\text{Fc}^+/\text{Fc})} = 0.45 \text{ V vs Ag/AgCl}$). *In situ* UV-Vis spectroelectrochemistry measurements were performed on SEC2000 Spectrophotometer connected to the BASi 100B/W Potentiostat, and using a 1.0 cm width quartz cell, which contains Ag/AgCl reference electrode and platinum wire as auxiliary electrode, respectively. The ITO/glass plates (rectangular with 2.5 cm x 0.7 cm area, and surface resistance, Ω) were chosen as transparent working electrodes. Before each experiment, the ITO/glass plates were sonicated for 5 min, in a mixture of detergent, acetone and methanol, and then rinsed with isopropyl alcohol, and dried. The UV-Vis/CV measurements were carried out in anhydrous acetonitrile containing 0.1 M TBAP, supporting electrolyte.

CONCLUSIONS

Three oligomers containing triphenylamine units as end groups and triphenylamine or benzene groups as cores linked by vinylene segments and having linear and star-shape architectures were successfully electropolymerized by cycling the

electrode potential on positive domain. The polymers were deposited as pale yellow or pale green thin films on the ITO/glass working electrode surface, being visible with naked eyes. These films are insoluble in methylene chloride and acetone. The polymers films exhibit good electrochemical activity and stability, displaying different colors associated to oxidation states that undergo the polymeric structures. The surface morphology of the films was analyzed by AFM, and the results show that the films were uniformly deposited on the electrode surface, have a smooth surface without grains for polyL or boundary surface for polyS2, and their surface roughness is related directly to the molecular structure of electrogenerated polymers. The polyL and polyS2 films present very good electrochromic properties, they retained their electrochromic parameters and optical activity even after a number of 45 continuous cycles operations. It can be anticipated that all three oligomers/polymers can find applications in electrochromic devices, optical displays, and smart windows.

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