Electrogenerated networks from poly[4-(diphenylamino)benzyl methacrylate] and their electrochromic properties

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Received 24 February 2014; accepted in revised form 28 April 2014

Abstract. Poly[4-(diphenylamino)benzyl methacrylate] with well-defined molecular weight and low polydispersity was prepared by atom transfer radical polymerization (ATRP) using 4-(diphenylamino) benzyl 2-bromo-2-methyl-propanoate as initiator and CuBr/2,2'-bipyridine as catalytic complex. Electrochemical behavior and optical properties of the polymers were investigated by cyclic voltammetry and UV-Vis and fluorescence spectroscopy. Cyclic votammetric studies revealed that the redox processes were accompanied by dimerization of triphenylamine pendant groups. The initial polymer was post-modified, in solution or bulk, by electrochemical oxidation leading to a crosslinked and insoluble network with electrochromic properties, accompanied by strong color changes with high coloration efficiency. The crosslinking reaction took place between triphenylamine groups through *para* free positions leading to tetraphenylbenzidine bridges. The structure of polymers was confirmed by Fourier transform infrared (FT-IR) spectroscopy and ^1H and ^{13}C -nuclear magnetic resonance spectroscopy. Morphology studies of the cross-linked film have evidenced a smooth and continuous aspect without any pin-holes or defects.

Keywords: polymer synthesis, triphenylamine-based polymers, crosslinking, electrochromic networks

1. Introduction

Conjugated polymers have been extensively investigated in the last decades and continue to attract scientific interest due to their wide range of applications. Among the large variety of conjugated polymers, triphenylamine-based oligomers and polymers have received much attention because they have good hole-transporting properties, high light-emitting efficiencies, photoconductivity and photorefractivity, large two-photon absorption cross-section, being attractive materials for optoelectronic applications [1–3]. Responsible for all these properties is triphenylamine, a well-known molecule that possesses interesting functions such as redox activity, fluorescence, high oxidability of nitro-

gen center and good hole-transporting properties via radical-cation species [4]. Thus, oligomers and polymers containing triphenylamine group in the main or side chain have found applications as photoconducting materials in xerography, organic field-effect transistors, photorefractive systems, light emitting diodes [5–7], solar cells [8, 9] or electrochromic materials [10, 11].

Electrochromic materials have ability to change reversible their absorption and transmittance upon electrochemical oxidation or reduction. For electrochromic applications these materials have to possess good film-forming properties, long-term stability, high coloration efficiency and fast switching of color. To increase the long-term stability an efficient

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route is to use cross-linked materials. Electrochromic networks can be obtained as films with fine control of the layer thickness from vinyl polymers containing carbazole or triphenylamine substituents by anodic oxidation [12–14]. Generally, vinyl polymers that contain pendant chromophore groups (carbazole, triphenylamine, etc.) have greater solubility than rigid-rod conjugated polymers, facilitating thus their processing as thin films from solution. In the class of carbazole-based polymers, an important place is taken by poly (N-vinylcarbazole) (PVK) because it is easily synthesized and soluble in common organic solvents [15]. The controlled radical polymerizations of N-vinyl carbazole (VK) monomers are considered to be difficult because radical precursors are highly reactive due to the nature and strong electron donating pendant groups [16, 17]. Nevertheless, several attempts to synthesize PVK using various controlled radical polymerization systems have been reported in the literature. Polymerization *via* reversible addition-fragmentation chain transfer (RAFT) can be only readily mediated using xanthates or dithiocarbamate as the chains transfer agent [16, 18–21] or nitroxide-mediated polymerization (NMP) [22] and by atom transfer radical polymerization (ATRP) [23, 24].

Several attempts for synthesis of vinyl polymers having triphenylamine as pendant groups, using controlled radical polymerization (NMP [25–28] and RAFT [29–32]) or living anionic route [33–40] have been recently reported. However, the controlled radical polymerization of triphenylamine-based (meth)acrylate monomers was less studied until now, only a paper revealing the group transfer polymerization of 4-(dimethylamino)benzyl methacrylate was published [41]. As a continuation of our previous studies regarding controlled radical polymerization of arylamine-based vinyl monomers [19, 42, 43], in this paper we have reported the synthesis and characterization of poly [4-(diphenylamino) benzyl methacrylate] employing the atom transfer radical polymerization method. This polymer was used in the next step in order to obtain electrochromic networks by electrochemical crosslinking of triphenylamine pendant sites.

2. Experimental

2.1. Materials

Methacryloyl chloride (97%), triethylamine (99,5%), copper (I) bromide (CuBr, 99,99%), 2,2-bipyridine

(bpy) (98%) and tetrabutylammonium tetrafluoroborate (TBABF₄) were purchased from Aldrich (Steinheim, Germany) and used without further purification. Solvents (Aldrich) were dried by usual methods or used as received. 4-(diphenylamino) benzyl alcohol and 4-(diphenylamino) benzyl 2-bromo-2-methylpropanoate, were synthesized according to the reported methods [42].

2.2. Measurements

The infrared spectra of the polymers were recorded on FT-IR Bruker Vertex 70 Spectrophotometer in transmission mode using KBr pellets (Ettlingen, Germany). UV-Vis absorption and fluorescence spectra of polymers were recorded with a Specord 200 spectrophotometer (Analytik Jena AG, Jena, Germany) and Perkin Elmer LS 55 apparatus (United Kingdom), respectively, by using diluted polymer solutions and very thin films deposited on quartz plates by drop-cast technique. ¹H and ¹³C-NMR spectra were recorded on a Bruker NMR spectrometer, Avance DRX 400 MHz (Rheinstetten, Germany), using deuterated chloroform (CDCl₃) and tetramethylsilane as an internal standard. Gel permeation chromatography (GPC) analyses were carried out on PL-EMD 950 Evaporative light Detector instrument using chloroform (CHCl₃) as an eluent phase and standard polystyrene sample for calibration. Samples were filtered through 0.45 µm syringe. The surface investigation was performed using atomic force microscopy (AFM) solver PRO-M (NT-MDT, Russia). Thin film of the cross-linked polymer was deposited upon ITO coated. Differential scanning calorimetry (DSC) measurements were conducted on a Pyris Diamond DSC, Perkin Elmer (USA), in nitrogen with a heating and cooling rate of 10°C/min. The glass transition temperatures (*T_g*) were determined from the second heating run.

Electrochemical studies were carried out with a Bio-analytical System, Potentiostat–Galvanostat (BASi 100B/W, SUA, Indiana, West Lafayette). All the experiments were performed in a one-compartment cell using a standard three-electrode cell arrangement with a working platinum electrode, an auxiliary electrode (platinum wire), and a reference electrode (consisted of a silver wire coated with AgCl). Before each experiment, the Pt working electrode was cleaned by polishing it successively with 0.3 and 0.05 µm Al₂O₃ slurry on emery paper to a mirror finish, and then washed with methanol and bi-dis-

tilled water. The electrochemical studies were carried out both in solution and film deposited on platinum electrode and tetrabutylammonium tetrafluoroborate (TBABF₄) as supporting electrolyte.

Electro-optical properties were investigated using an indium tin oxide (ITO, Adrich Sigma Aldrich with an active area of 1.1 cm×0.8 cm) electrode as well as a platinum wire as counter electrode and an AgCl reference electrode. A film of the cross-linked polymer was deposited upon ITO coated glass electrode by electrochemical polymerization using a solution of polymer in acetonitrile/toluene (1:1) and TBABF₄ as electrolyte. The film was prepared by sweeping the potential between 0 and +1.8 V for 14 scan cycles and after deposition, the ITO/polymer film was rinsed with distilled water and further used as working electrode in a standard spectroelectrochemical cell (a quartz cuvette of 1cm×1cm dimensions) filled with supporting electrolyte (TBABF₄, solution 0.1M in acetonitrile/toluene, 1:1). The electrodes were connected to a BASi Potentiostat–Galvanostat and spectroelectrochemical spectra were recorded using an SEC-2000-UV/VIS-type spectrophotometer (Tokyo, Japan).

2.3. Synthesis of 4-(diphenylamino) benzyl methacrylate

Monomer was prepared according to the modified method described in the literature [44]. To a mixture of 4-(diphenylamino) benzyl alcohol (7.00 g, 25.42 mmol) and triethylamine (3.08 g, 4.05 mL, 30.5 mmol) in dry toluene (150 mL), methacryloyl chloride (3.18 g, 2.95 mL, 30.5 mmol) was slowly added at 0°C under argon atmosphere. The reaction mixture was then stirred for 24 h, at room temperature. The Et₃N·HCl was separated by filtration and

the toluene solution was washed successively with Na₂CO₃ solution, water and finally dried on CaCl₂. After toluene evaporation in vacuum, monomer was purified by column chromatography (silica gel as stationary layer and a mixture of hexane: CH₂Cl₂ as eluent), giving 5.85 g (83%) as viscous oil. ¹H-NMR (CDCl₃, δ, ppm): 1.96 (s, 3H, –CH₃), 5.12 (s, 2H, –CH₂–O), 5.56 and 6.14 (s, 2H, =CH₂), 6.95–7.30 (m, 14H, aromatic protons). ¹³C-NMR (CDCl₃, δ, ppm): 18.35, 66.17, 122.99, 123.91, 124.72, 125.68, 129.40, 129.80, 136.30, 147.58, 167.30.

2.4. Synthesis of poly [4-(diphenylamino) benzyl methacrylate]

An example for ATRP polymerization was as follows (entry 2 in Table 1): In a two neck round bottom flask equipped with magnetic stirrer and nitrogen inlet-outlet, vacuumed and back-filled with nitrogen for several times, CuBr (8.48 mg, 0.059 mmol), 2,2-bipyridine (18.48 mg, 0.118 mmol), and the ATRP initiator (25.1 mg, 0.059 mmol) were added to a solution of monomer (1.01 g, 2.95 mmol) in 3 mL toluene. The reaction mixture was degassed by nitrogen for 60 min. The polymerization was carried out by immersing the flask into an oil bath thermostated at 103°C, for 24 hours. Then, the reaction mixture was precipitated twice in a large amount of cold hexane from dichloromethane. The polymer was filtered and dried at 40°C in vacuum. Yield = 33.1%. GPC measurements: *M_n* [g/mol] = 5370, *M_w*/*M_n* = 1.13.

3. Results and discussion

3.1. Synthesis

The atom transfer radical polymerization of 4-(diphenylamino)benzyl methacrylate monomer was

Table 1. Results and experimental conditions of polymerization of 4-(diphenylamino) benzyl methacrylate) using 4-(diphenylamino) benzyl 2-bromo-2-methylpropanoate as initiator in the presence of catalytic complex CuBr/bpy at 103°C

Sample	[Monomer] ₀ : [I] ₀ : [CuBr] ₀ : [bpy] ₀	<i>M_n</i> th. ^(a) [g/mol]	<i>M_n</i> ^(b) [g/mol]	<i>M_w</i> / <i>M_n</i> ^(b)	Yield [%]	<i>T_g</i> [°C]
P1	30:1:1:2	4330	4100	1.08	38.3	160
P2	50:1:1:2	6080	5370	1.13	33.1	161
P3	75:1:1:2	9400	8045	1.13	35.2	162
P4	150:1:1:2	9680	8920	1.18	18.6	162

^{a)}The theoretical number-average molecular weight is defined as follows:

$$\overline{M}_n(\text{theor.}) = \frac{[\text{Monomer}]_0}{[I]_0} \cdot M_{\text{Monomer}} \cdot \text{Conv.} + M_I$$

where: *M_I* and *M_{Monomer}* are the molecular weights of initiator (424) and of the monomer (343), and [Monomer]₀ and [I]₀ are the initial concentrations of the monomer and I, respectively. Conversion was determined by gravimetry.

^{b)}Number average molecular weight (*M_n*) and molecular weight distribution (*M_w*/*M_n*) are measured by gel permeation chromatography (GPC) using polystyrene as a standard in DMF.

carried out in dry toluene at 103°C temperature, in the presence of 4-(diphenylamino) benzyl 2-bromo-2-methylpropanoate as initiator and CuBr/bipyridyl as catalyst (Figure 1). This TPA-based initiator was previously used in ATRP polymerization of styrene to obtain triphenylamine end-functionalized polystyrenes with well-defined molecular weights and narrow polydispersities. The electrochemical and chemical oxidative polymerizations of these macromonomers led to soluble polytriphenylamine hairy-rod polymers having oligostyrene segments as grafts in every hairy structural unit [42]. On the other hand, this initiator was also used as monomer for interfacial and microemulsion chemical oxidative polymerization in the presence of ammonium peroxodisulfate as the oxidizing agent, obtaining functional polytriphenylamines [43]. In this paper, 4-(diphenylamino) benzyl 2-bromo-2-methylpropanoate was used as an ATRP initiator in controlled radical polymerization of methacrylate monomer containing triphenylamine moiety, (4-(diphenylamino)benzyl methacrylate) (TPMA) to get macromonomers with controlled molecular weight and narrow polydispersity index (Table 1). At the end of the polymerization reaction, the polymers were precipitated in hexane. They are completely soluble in organic solvents such as THF, DMF and in chlorinated solvents and have a well-defined molecular weight and narrow polydispersity. The polymers were purified by dissolution in a small amount of THF to which was added few drops of ammonium hydroxide (to prevent oxidation of nitrogen of the triphenylamine unit) and precipitated in hexane.

The molecular weight of the polymers was controlled by varying the $[\text{monomer}]_0/[\text{initiator}]_0$ ratios and these ratios were fixed in the range of 30 to 150, while all other experimental conditions were set to be the same. The M_n values proportionally increase by increasing the feed ratio and the polydispersity indices (M_w/M_n) for all samples are less than 1.2. In all cases, the molecular weights measured by GPC in DMF, were lower than the theoreti-

Figure 1. ATRP polymerization of 4-(diphenylamino)benzyl methacrylate

cal values calculated from the monomer/initiator molar ratio and conversion of the monomer. The molecular weights obtained by conventional GPC using polystyrene calibration are just apparent values; moreover the conversion was approximated by gravimetry. The synthesized polymers have glass transition temperatures (T_g), determined by DSC at a heating rate of 10°C/min, in nitrogen atmosphere, after the second heating scan ranged between 160–162°C.

3.2. FT-IR and NMR spectra

The chemical structure of the polymer was proved by ^1H and ^{13}C -NMR and FT-IR measurements. In Figure 2 is shown the ^1H -NMR spectrum of poly [4-(diphenylamino) benzyl methacrylate] recorded in CDCl_3 . By comparing both the ^1H -NMR spectrum for the monomer and polymer, in the last one it was observed the disappearance of the signals assigned to vinyl protons that in case of monomer spectra are located at 5.56 and 6.14 ppm region. At the same time, new signals emerge around 0.8 to 2.2 ppm, associated with the protons of poly [4-(diphenylamino) benzyl methacrylate] backbone, while the signals located at 4.85 ppm are assigned to methylene protons from the $-\text{CH}_2-\text{O}-$ polymer segments. All other peaks are readily assigned on the pendant triphenylamine groups. Due to the structural similarity of both initiator and monomer, it was not possible to calculate the polymer molecular weight by using ^1H -NMR spectroscopy data. The ^{13}C -NMR spectral analysis of polymer, recorded in CDCl_3 shows the following signals: the region from 16.80 to 18.85 ppm is assigned to signals of methyl carbons (Ca), while the methylene carbon signals (Cb) are visible in 22.66 to 30.32 ppm region (Figure 3).

Figure 2. ^1H -NMR (CDCl_3) spectra of polymer

Figure 3. ^{13}C -NMR (CDCl_3) spectra of polymer

Quaternary carbons (Ci) show the signals in 40.69 to 44.18 ppm region, and the methylene carbons Cc are located at 66.64 ppm. Aromatic carbons located in the region 123.02 to 124.48 ppm are attributed to the carbon, Cf and Ch, while Cd, Cg, Ck are located in the region 128.86 to 129.77 ppm, and carbons Cl and Cm are located at 147, 95 and 147.60 ppm, respectively. The signals at 176.29 and 177.25 ppm are assigned to the Cj carbonyl carbon.

In Figure 4 is shown the FT-IR spectrum of the polymer. The bands assigned to the (H-C=) aromatic deformation vibrations are located at 3059 and 3033 cm^{-1} . The 2961 cm^{-1} band is characteristic to deformation vibration of the aliphatic (C-H) linkages. The band at 1729 cm^{-1} is attributed to the valence vibration of C=O bond while the bands located at 1140 and 1173 cm^{-1} are due to stretching vibrations of C-O-C bond. The bands at 1589 and 1492 cm^{-1} correspond to in-plane deformations of

Figure 4. FT-IR spectrum (KBr) of polymer

aromatic rings. The bands at 1110 and 1028 cm^{-1} are assigned to the deformation vibration of the methyl and methylene groups. The spectrum shows a band of 1325–1273 cm^{-1} corresponding to the vibration of the C-N bond from the triphenylamine, and the bands at 753 and 695 cm^{-1} correspond to the out-of-plane deformation of the C-H monosubstituted benzene rings, while the band located at 806 cm^{-1} can be assigned to the C-H bond out-of-plane deformation from the 1,4-disubstituted benzene rings.

3.3. Optical properties

Absorption and emission spectra of polymer were recorded for polymers solution in dilute CHCl_3 ($\sim 10^{-5}$ M) and for thin film made from CHCl_3 solution (Figure 5). Absorption spectra for the polymer shows a single absorption band at 306 nm attributed to π - π^* transitions of the triphenylamine pendant

Figure 5. UV-Vis a) and fluorescence b) spectra of polymer recorded at an excitation wavelength of 306 nm. Sample/ CHCl_3 = 0.100 mg/10 mL.

moiety. The polymer film cast from CHCl_3 exhibit main absorption maximum at 334 nm, which was found to be bathochromically shifted with 28 nm compared to the absorption of the polymer in solution state. The emission spectrum shows a single emission band at 370 nm for polymer solution and 448 nm for film, at an excitation wavelength of 306 nm. An identical red shift phenomenon was also observed for the emission spectra of polymer in solid state compared to polymer solution due to the intermolecular aggregation.

3.4. Electrochemical behavior

Electrochemical characteristics of polymer were investigated by running cyclic voltammogram. Thus, polymer (P2) was investigated by recording current intensity vs applied potential curves, for both solution state (using CH_2Cl_2 as solvent and $3.5 \cdot 10^{-3}$ M polymer concentration) and in film deposited on platinum electrode (using acetonitrile/toluene 1:1 solvent mixture). The working electrode potential was swept on the 0.0 to 1.8 V with $50 \text{ mV} \cdot \text{s}^{-1}$ scan rate, for 14 cycles. The multiple cyclic voltammograms of polymer are shown in Figure 6. As it can be seen, in the first scan recorded for the polymer in solution, the voltammogram shows two anodic peaks located at $E_{\text{ox1}} = 0.981 \text{ V}$ and $E_{\text{ox2}} = 1.299 \text{ V}$ and on the reverse scanning, two cathodic peaks located at $E_{\text{red1}} = 0.861 \text{ V}$ and $E_{\text{red2}} = 0.743 \text{ V}$ appeared. The anodic peaks correspond to the oxidation processes of the triphenylamine units from the polymer structure. The first anodic peak is attrib-

uted to one electron removal from the nitrogen atom of triphenylamine, leading to formation of the radical-cation. Being unstable, chemical coupling processes of the radical cations occurred in the next step with the loss of two protons, leading to neutral tetraphenylbenzidine (TPB) dimer formation [45–48]. Starting with the second scan, the peaks current intensities associated with tetraphenylbenzidine oxidation processes increase, while the oxidation peaks are overlapping.

The increase of the current peaks intensities with each running cycle is correlated with the progress of dimerization reaction and formation of a green colored electroactive polymer film on the electrode surface. The shift of the oxidation potential at higher values is due to the increase of the electrical resistance of the polymer film when over-potential was needed to overcome the resistance. The polymer film in the undoped state was washed with CH_2Cl_2 , removed mechanically, and then was characterized by FT-IR spectroscopy (Figure 7).

The electrochemical behavior of the polymer P2 as thin film deposited on the Pt electrode surface by drop-cast from CH_2Cl_2 solution was also investigated. For this, it was recorded the cyclic voltammogram in acetonitrile/toluene (1:1) mixture solution containing TBABF_4 (10^{-1} M) as supporting electrolyte (Figure 6b). The first cycle shows one large reversible anodic peak located in the 0.852 and 1.446 V, which seems to be composed of two overlapping anodic peaks, corresponding to two successive oxidation processes of triphenylamine units,

Figure 6. Multiple cyclic voltammograms (14 cycles) recorded for: a) polymer as CH_2Cl_2 solution, containing TBABF_4 (0.1 M) as supporting electrolyte, using Pt as working electrode (disk, diameter = 1.6 mm) and right b) the polymer film deposited on Pt electrode surface and in acetonitrile/toluene (1:1) solvent mixture containing TBABF_4 (0.1 M) as supporting electrolyte; scan rate was $50 \text{ mV} \cdot \text{s}^{-1}$

Table 2. The electrochemical data of polymer (P2)

Polymer	E_{ox}^{onset} [V]	E_{ox1} [V]	E_{ox2} [V]	E_{red}^{onset} [V]	E_{red1} [V]	E_{red2} [V]
CH ₂ Cl ₂ -solution	0.745	0.981	1.299	1.193	0.861	0.743
Film deposited on Pt	0.852	–	1.336	1.059	–	0.705

Figure 7. FT-IR spectra (KBr, cm⁻¹) of cross-linked polymer by electropolymerization in solution

while on the reverse scan only one cathodic peak appear at $E_{red} = 0.705$ V which is assigned to reduction process of the oxidized species. The large anodic peak can be due to a more reduced mobility of the electroactive sites in the solid state. At the end of 14 cycles, it was observed that the intensities of anodic and cathodic peaks currents decreased and this can be explained by the fact that during the electropolymerization process the triphenylamine units are consumed forming a cross-linking network. Comparing the onset oxidation potential values from both cases, it can be noted that the polymer is more easily oxidized as CH₂Cl₂-solution than as film (Table 2).

By comparing the FT-IR spectra of parent polymer (Figure 4) and cross-linked material (Figure 7) obtained by electropolymerization in solution, some differences can be evidenced:

- the disappearance of the characteristic bands 3059 and 3033 cm⁻¹ assigned to the deformation vibrations of the (C–H) aromatic;
- the disappearance of the bands at 753 and 695 cm⁻¹ assigned to the deformation vibrations of mono-substituted benzene ring.

3.5. Electrochromic properties of polymer films

Depending on the oxidation states, the electrochromic material shows different colors, and usually conjugated electrochromic polymers allow fast color changes when different potentials are applied. The

applications of the electrochromic conjugated polymers are quite different due to advantages owned by these materials, because the oxidation states of the polymers are stable and ‘resistant over time’ [12]. It was observed that the film obtained by electropolymerization of polymer upon transparent ITO electrode surface shows different colors depending on the applied potential. For a more detailed study, in-situ UV-Vis spectroelectrochemistry was further employed, using a polymer film deposited on a transparent ITO/glass working electrode and cyclic voltammetry technique coupled with UV-Vis absorbance measurements. This procedure allowed simultaneous recording of the electronic absorption spectra in the range of 300–900 nm and the current intensity versus applied potential. The experiments were carried out in acetonitrile/toluene (1:1) solvent mixture containing TBABF₄ (0.1 M) as supporting electrolyte. Varying the applied potential in range of 0.0–(+1.5) V and then to 0.0 V, the film shows absorption bands in the range of 300–900 nm, which corresponds to the different oxidation states. In the neutral state of polymer (at 0 V), the film is transparent in the visible region. By increasing the applied potential value two absorption bands with maxima at 486 and 680 nm, were observed (Figure 8). The intensity of absorption bands increase simultaneously and gradually when the potential values reaches to 1.5 V. During the oxidation process, the polymer film switches its color from colorless, brown, and green to blue, respectively. During the reduction process, the intensities of absorption bands located at 486 and 680 nm, decrease and a third band at 396 nm can be observed, which is attributed to π - π^* transitions due to expansion of the conjugations (Figure 8).

The potential of the working electrode have been applied to a range of positive values such as 0.0, 1.0, 1.2, 1.3 and 1.5 V for 3 minutes (Figure 9), and the polymer switches its color, like in previous case. Spectroelectrochemistry data presented above confirm the presence of the tetraphenylbenzidine (TPB) dimer, which is oxidized at about 0.65 V forming the TPB^{•+} radical-cations which shows a maximum

Figure 8. Absorption spectra of P2 as film deposited on ITO/glass electrode, recorded during the electropolymerization process at different applied potentials: a) during the oxidation and b) during the reduction process

absorption band at 480 nm. The dication formation is observed at potentials more anodic and shows an absorption band at about 678 nm (Figure 10).

Figure 9. Evolution of the color of the polymer film from neutral to oxidized states

The color switching times were estimated by applying a potentials step and the transmittance profiles were followed. The switching time was defined as the time that was required to reach 95% of the full change in transmittance after switching potential. The ITO/P2 film oxidation state was switched by stepping the potential between 0.0 and 1.5 V, with time intervals of 15 s and the current and transmittance at 486 and 680 nm was monitored versus time. The film color changed from transparent to blue with high contrast of optical transmittance change ($\Delta T\%$) of 80% for 680 nm and only 29% for 486 nm. Moreover, the response time of the polymer film was found to be 10 s at 1.5 V from color switching and 5 s for bleaching (Figure 11). The amount of charge (Q_d) in each current curve for both processes was very similar and reveals a stable anodic electrochemical characteristic of P2 film. On the other hand, coloration efficiency (η) of the polymer film at 680 nm was also calculated to be $670 \text{ cm}^2/\text{C}$, using the equation $\eta = \Delta OD/Q_d = \log[T_{\text{neut}}/T_{\text{oxi}}]/Q_d [\text{cm}^2/\text{C}]$, where Q_d is the injected charge per unit electrode

Figure 10. The proposed mechanism for the crosslinking process and the change of color with the applied potential

Figure 11. ITO/P2 electrochromic switching between 0 and 1.5 V (vs Ag/AgCl) applied to the electrodeposited film of P2 in CH₃CN/toluene with 0.1 M TBABF₄ with a cycle time of 15 s, the current (a) and optical (b) response. Absorption was recorded at 486 nm (red) and 680 nm (blue)

area during a redox step, and T_{neut} and T_{oxi} are the bleached and colored transmittance values, respectively [13].

After 17 continuous cycles the polymer film exhibited excellent stability of electrochromic characteristics. Considering these results it can be stated that the electropolymerized P2 film can be considered a promising materials for application in optoelectronic devices.

3.6. Surface morphology of polymer films

Atomic force microscopy (AFM) investigations were conducted to investigate the surface morphology of the polymer deposited on ITO/glass after electropolymerization. The micrographs recorded show that the film appears smooth and continuous over the whole image, without pinholes or defects and is characterized by morphology consisted of many crowded spheres with a mean diameter of 110 nm and root mean square (RMS) roughness of 2.75 nm (Figure 12).

4. Conclusions

Polymers based on triphenylamine with well-defined structure and characteristics, were successfully synthesized by atom transfer radical polymerization reactions. The optical properties of poly [4-(diphenylamino)benzyl methacrylate] were investigated by UV-Vis and fluorescence spectroscopy. The electrochemical properties of the synthesized polymers with triphenylamine pendant units were investigated using cyclic voltammetry technique. The synthesized polymers undergo cross-linking processes leading to a conductive film with electrochromic properties and stable color changes with coloration efficiency and high contrast of optical transmittance. The electrochemical cross-linking reaction was possible because the polymers contain in their structure triphenylamine as pendant groups with two free *para*-positions for direct coupling. The morphology of the resulting film with cross-linked structure was examined by AFM microscopy, the

Figure 12. The AFM images of film deposited by electropolymerization process (after 14 scan cycles)

film appears smooth and continuous without any pinholes or defects being formed from crowded spheres with a mean diameter of 110 nm.

Acknowledgements

The authors thank to the Romanian National Authority for Scientific Research (UEFISCDI) for financial support (Grant PN-II-ID-PCE-2011-3-0274, Contract 148/2011)

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