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# **Preparation and study of poly(9-methylcarbazole) and poly(9-ethylcarbazole) films by electrochemical oxidation of monomers and dimers**

Abdeslam Et Taouil<sup>1,\*</sup>, Sophie Lakard<sup>1</sup>, Frédéric Dumur<sup>2</sup>, Emmanuel Contal<sup>1</sup>, Boris Lakard<sup>1</sup>

<sup>1</sup> *Université de Franche-Comté, Institut UTINAM, UMR CNRS 6213, F-25030, Besançon, France*

<sup>2</sup> *Aix Marseille Univ, CNRS, Institut de Chimie Radicalaire UMR 7273, F-13397 Marseille, France*

\* abdeslam.et\_taouil@univ-fcomte.fr

## **Abstract**

In the present study, we succeed in depositing poly(9-methylcarbazole) and poly(9-ethylcarbazole) films by electrochemical oxidation using dichloromethane as solvent. Poly(9-methylcarbazole) films obtained from 9-methyl-9*H*-carbazole are green, thick but not very rough and have a needle-like structure very different from that of carbazole, which is porous and looks like a honeycomb; whereas poly(9-methylcarbazole) films obtained from 9,9'-dimethyl-9*H*,9'*H*-3,3'-bicarbazole are rougher, more electroactive and have a structure mixing needles and nodules. Poly(9-ethylcarbazole) films can only be grown from 9-ethyl-9*H*-carbazole and are generally less homogeneous and have a more nodular structure. Finally, poly(9-alkylcarbazole) with longer chains cannot be electrochemically formed, mostly due to solubility problems.

**Keywords:** Bicarbazoles; Electropolymerization; Conducting polymers; Thin solid films.

## 1. Introduction

Carbazole is an aromatic heterocyclic organic compound with a tricyclic structure, composed of two benzene rings fused on either side of a central pyrrole ring. Carbazoles and their derivatives represent an important class of heterocycles which has become important materials for optoelectronics [1,2], medicine [3,4], energy storage [5,6], and chemical sensors [7,8]. Carbazoles can be oxidized to form polymers either chemically [9] or electrochemically [10,11]. In particular, the oxidation of 9-substituted carbazoles can lead under specific oxidative conditions to the formation of dimers or polymers through 3,3'-coupling and 6,6'-coupling of carbazoles. Indeed, the mechanism of the electrochemical polymerization of 9-substituted carbazole derivatives starts with the oxidation of the monomers at the electrode which leads to the formation of radical cations on the nitrogen atoms [9]. Then, the radicals delocalize to the C<sub>3</sub> or C<sub>6</sub> position due to the conjugated bonds and 3,3'-coupling or 6,6'-coupling occurs between two radical cations. 9,9'-coupling is not possible since the C<sub>9</sub> position is already occupied. On the other hand, coupling at the C<sub>1</sub> or C<sub>8</sub> positions is possible but the quantity of dimers formed is very low due to steric hindrance. The 9-substituted carbazoles are particularly interesting because of the possibility to add many substituents at the nitrogen of the central pyrrole ring. For example, carbazoles bearing methanol, carboxylic acid and cyanoethyl at the 9-position were electropolymerized by Pekmez *et al.* [12] when carbazoles bearing anilines at the 9-position were electropolymerized by Ak *et al.* [13]. Also, carbazoles substituted at the 9-position by inert groups such as methyl, ethyl, dimethyl [14-16], phenyl [14,17], or ether oxide groups [18] have been oxidized and led to the formation of polymers linked at the 3,6-positions since the 9-position was already occupied. These electrodeposited polycarbazole films, especially the ones synthesized from N-substituted carbazoles, exhibit electrical conductivity and optical properties that make them useful for many applications. Thus, it has been evidenced

that N-substituted polycarbazole films can be used for example as emitting materials in OLEDs leading to energy-efficient displays and lighting [19], in supercapacitors and energy storage devices due to their ability to store and release charge quickly [20], or in (bio)sensors where they serve as sensitive layer to a particular analyte [21].

Recently, our group has shown that electrochemical oxidation in acetonitrile of *N*-substituted carbazoles by vinyl, acid or ester functions leads to the formation of solid polymer films at the electrode surface [22]. On the contrary, the electrochemical oxidation of 9-substituted carbazoles by alkyl groups containing between 2 and 8 carbons did not produce polymer films. Fast electrochemistry experiments evidenced that these failures were due to the high stability of radical cations obtained by electrochemical oxidation in acetonitrile [22]. In the present work, we continue to investigate the reactivity of carbazoles and seek to develop new polymers by first synthesizing original carbazole monomers and dimers and then proceeding with their electrochemical oxidation in the hope of achieving electrodeposition. Thus, 9-alkylcarbazole monomers and dimers, with a chain length ranging from 1 to 12 carbon atoms (Scheme 1), were electrochemically oxidized in acetonitrile or dichloromethane to obtain new solid polymer films. As will be described, this strategy successfully led to the formation of poly(9-methylcarbazole) films and poly(9-ethylcarbazole) films while poly(9-alkylcarbazole) with longer chains could not be electrochemically formed, mostly due to solubility problems.

## **2. Materials and methods**

### *2.1. Reagents*

Acetonitrile (CAS: [1484-12-4]) and dichloromethane (CAS: [75-09-2]) were purchased from Fisher Scientific and used as solvent for electrochemical experiments. Tetraethylammonium tetrafluoroborate (CAS: [429-06-1]) was purchased from Alfa Aesar and used as supporting salt for electrochemical experiments. 9-Methyl-9*H*-carbazole (CAS: [1484-12-4]) and 9-ethyl-9*H*-

carbazole (CAS: [86-28-2]) were from TCI America. Other compounds including 9-butyl-9H-carbazole, 9-hexyl-9H-carbazole, 9-octyl-9H-carbazole, 9,9'-dimethyl-9H,9'H-3,3'-bicarbazole, 9,9'-diethyl-9H,9'H-3,3'-bicarbazole, 9,9'-dioctyl-9H,9'H-3,3'-bicarbazole, and 9,9'-didodecyl-9H,9'H-3,3'-bicarbazole were home-synthesized.

## 2.2. Monomer synthesis

9-Butyl-9H-carbazole, 9-hexyl-9H-carbazole and 9-octyl-9H-carbazole were synthesized as previously reported in the literature, without modification and in similar yields [22]. The other molecules were synthesized as described below. It is noticed that synthesis of these carbazole derivatives have previously been reported in literature but using other procedures. A general procedure is given below.

General procedure used for synthesis of carbazole dimers: to a suspended solution of iron(III) chloride  $\text{FeCl}_3$  (12.88 g, 79.85 mmol, Molar mass = 162.19 g/mol, 2.4 eq.) in 100 mL of dry chloroform  $\text{CHCl}_3$  under nitrogen atmosphere, a solution of carbazole (33.19 mmol, 1 eq.) in chloroform  $\text{CHCl}_3$  (50 mL) was slowly added at 25 °C. After 3 h of stirring, methanol  $\text{MeOH}$  (300 mL), and dichloromethane  $\text{CH}_2\text{Cl}_2$  (100 mL) were added, and the mixture extracted using distilled water (2×200 mL). The combined organic layers were dried over magnesium sulfate and the solution was filtered on a plug of silicagel using dichloromethane  $\text{CH}_2\text{Cl}_2$  as the eluent.

9,9'-Dimethyl-9H,9'H-3,3'-bicarbazole: starting from 9-methyl-9H-carbazole (6.01 g), 4.31 g of product were obtained (72% yield).  $^1\text{H}$  NMR (chloroform-d1  $\text{CDCl}_3$ ) : 3.86 (s, 6H), 7.24 (t, 2H,  $J = 7.9$  Hz), 7.37-7.41 (m, 2H), 7.44-7.48 (m, 4H), 7.82 (dd, 2H,  $J = 8.5$  Hz,  $J = 1.8$  Hz), 8.17 (d, 2H,  $J = 7.6$  Hz), 8.39 (d, 2H,  $J = 1.8$  Hz);  $^{13}\text{C}$  NMR (chloroform-d1  $\text{CDCl}_3$ ) : 29.2, 108.6, 108.7, 118.90, 118.91, 120.4, 123.0, 123.4, 125.6, 125.8, 133.5, 140.1, 141.5. Analyses were consistent with those previously reported in literature [23].

9,9'-Diethyl-9*H*,9'*H*-3,3'-bicarbazole: starting from 9-ethyl-9*H*-carbazole (6.48 g), 4.19 g of product were obtained (65% yield). <sup>1</sup>H NMR (chloroform-*d*<sub>1</sub>  $\text{CDCl}_3$ ): 8.45 (d, *J* = 1.4 Hz, 2H), 8.23 (d, *J* = 7.7 Hz, 2H), 7.86 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.55 – 7.49 (m, 4H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.28 (ddd, *J* = 5.3, 4.7, 1.4 Hz, 2H), 4.43 (q, *J* = 7.2 Hz, 4H), 1.50 (t, *J* = 7.2 Hz, 6H). Analyses were consistent with those previously reported in literature [24].

9,9'-Dioctyl-9*H*,9'*H*-3,3'-bicarbazole: starting from 9-octyl-9*H*-carbazole (9.27 g), 8.13 g of product were obtained (88% yield). <sup>1</sup>H NMR (chloroform-*d*<sub>3</sub>  $\text{CDCl}_3$ ): 0.92 (t, 6H, *J* = 6.9 Hz), 1.31-1.44 (m, 20H), 1.92 (qt, 4H, *J* = 7.1 Hz), 4.35 (t, 4H, *J* = 7.1 Hz), 7.29 (t, 2H, *J* = 7.8 Hz), 7.44-7.55 (m, 6H), 7.86 (dd, 2H, *J* = 8.5 Hz, *J* = 1.8 Hz), 8.23 (d, 2H, *J* = 8.5 Hz), 8.45 (d, 2H, *J* = 1.8 Hz); <sup>13</sup>C NMR (chloroform-*d*<sub>3</sub>  $\text{CDCl}_3$ ): 14.1, 22.6, 27.4, 29.2, 29.3, 29.4, 31.9, 63.3, 108.9, 113.8, 118.8, 118.9, 120.5, 123.1, 123.5, 125.6, 125.7, 133.4, 139.6, 141.0; Analyses were consistent with those previously reported in literature [25].

9*H*,9'*H*-3,3'-bicarbazole: starting from carbazole (5.55 g) 4.41 g of product were obtained (80% yield). <sup>1</sup>H NMR (dimethylsulfoxide-*d*<sub>6</sub>  $\text{DMSO-}d_6$ ): 7.17 (t, 2H, *J* = 7.1 Hz), 7.39 (t, 2H, *J* = 7.1 Hz), 7.49 (d, 2H, *J* = 8.1 Hz), 7.57 (d, 2H, *J* = 8.4 Hz), 7.79 (dd, 2H, *J* = 8.5 Hz, *J* = 1.7 Hz), 8.23 (d, 2H, *J* = 7.7 Hz), 8.49 (d, 2H, *J* = 1.5 Hz); <sup>13</sup>C NMR (dimethylsulfoxide-*d*<sub>6</sub>  $\text{DMSO-}d_6$ ): 111.0, 111.1, 118.0, 118.4, 120.3, 122.6, 123.1, 124.9, 125.5, 132.3, 138.7, 140.2; Analyses were consistent with those previously reported in literature [26].

9,9'-Didodecyl-9*H*,9'*H*-3,3'-bicarbazole : 1-Bromododecane (24.9 g, 24 mL, 100 mmol, Molar mass = 249.23 g/mol, *d* = 1.038) and potassium hydroxide (33.9 g, 605.4 mmol) were added to a solution of 9*H*,9'*H*-3,3'-bicarbazole (16.62 g, 50 mmol, Molar mass = 332.41 g/mol) in dimethyl sulfoxide  $\text{DMSO}$  (200 mL) under stirring. The reaction mixture was stirred for 24 h

at 80°C. The reaction was quenched with water. A white precipitate formed. It was filtered off, washed several times with water and pentane, and finally dried under vacuum. It was used without any further purification (27.43 g, 82% yield). <sup>1</sup>H NMR (chloroform-d<sub>3</sub> CDCl<sub>3</sub>) : 0.84 (t, 6H, *J* = 6.4 Hz), 1.15-1.44 (m, 30H), 1.85 (qt, 4H, *J* = 6.8 Hz), 4.25 (t, 4H, *J* = 7.1 Hz), 7.20 (td, 2H, *J* = 6.8 Hz, *J* = 0.8 Hz), 7.35-7.46 (m, 8H), 7.77 (dd, 2H, *J* = 8.5 Hz, *J* = 0.8 Hz), 8.15 (d, 2H, *J* = 8.5 Hz), 8.37 (d, 2H, *J* = 1.5 Hz); <sup>13</sup>C NMR (chloroform-d<sub>3</sub> CDCl<sub>3</sub>) : 14.1, 22.7, 27.3, 29.0, 29.3, 29.4, 29.43, 29.51, 29.57, 29.60, 31.9, 43.2, 108.7, 108.8, 118.6, 118.9, 120.4, 123.1, 123.4, 125.5, 125.6, 133.3, 139.5, 140.9; Analyses were consistent with those previously reported in literature [27].

### 2.3. Electrochemistry

Electrochemistry experiments were carried out using an AUTOLAB PGSTAT30 potentiostat equipped with SCAN250 and ADC10M modules. A classical three-electrode cell was used with platinum wire as counter-electrode and saturated calomel electrode (SCE) as reference electrode (a protection compartment containing the organic electrolyte was used to avoid water contamination of acetonitrile and dichloromethane solution). Working electrode was either a platinum disc (0.071 cm<sup>2</sup>) or Fluorine doped Tin Oxide (FTO) plate (1.5 cm<sup>2</sup>). The solution contained 5 mM of organic compound and 0.1 M of tetraethylammonium tetrafluoroborate (supporting salt) in acetonitrile or dichloromethane. For fast electrochemistry experiment, 1.5 mM of functionalized carbazole in tetraethylammonium tetrafluoroborate (0.5 M) acetonitrile solution was employed. A platinum microelectrode (diameter 180 ± 20 μm calibrated with ferrocene system) was used. The scan rate was 100 V/s. Electrochemical simulations were realized with DigiElch Pro software.

### 2.4. Characterization

- SEM microscopy

The morphology of the polycarbazole films was observed with a high-resolution Thermo Scientific Apreo 2 Scanning Electron Microscope with an electron beam energy of 5 keV and a working distance of 10 mm. No metallization pre-treatment was needed since the samples were conductive.

#### *- Profilometry*

The thickness and roughness of the polycarbazole films were measured using a Dektak 150 mechanical profilometer. Both thickness and roughness were obtained by scanning a fine diamond tip on the sample over a scan length of 2000  $\mu\text{m}$  at a scan speed of 50  $\mu\text{m/s}$ . 5 measurements were done at different positions for each sample.

#### *- UV/Visible absorption spectroscopy*

Absorption spectra of the monomer solutions and polycarbazole films were acquired with a SECOMAN UviLine 9400C spectrophotometer scanning a wavelength range from 190 to 1100 nm.

### **3. Results and discussion**

#### *3.1. Electrochemical deposition of poly(9-methylcarbazole)*

##### *3.1.1. Electrochemical deposition of poly(9-methylcarbazole) from oxidation of 9-methyl-9H-carbazole*

Cyclic voltammetry of 9-methyl-9H-carbazole (5 mM) is performed on platinum electrode (Fig. 1a) in acetonitrile solution containing 0.1 M of tetraethylammonium tetrafluoroborate. The signal shows an oxidation peak at +1.11 V vs. SCE, corresponding to oxidation of monomers into radical cations. As well established, these radical cations lead to dimers and oligomers through successive oxidation processes to eventually lead to formation of a polymer film on the surface. Reduction and oxidation peaks observed during following cycles at +0.72 V vs. SCE



and +0.80 V vs. SCE, respectively, result from redox activity of the formed organic film. However, no clear increase in these peaks current is observed during successive scans, meaning that no film is grown on the electrode surface. This is confirmed visually, as no polymer deposit is observed on platinum electrode. Cyclic voltammetry of the modified electrode is also carried out in monomer free solution and very poor redox activity is observed (Fig 1b), confirming electrochemically the absence of a conducting polymer film on the surface. Similar results are observed for 9-ethyl-9*H*-carbazole, 9-butyl-9*H*-carbazole, 9-hexyl-9*H*-carbazole and 9-octyl-9*H*-carbazole in acetonitrile [22]. This behavior is attributed to the good stability of electrochemically generated radical cations which do not polymerize very fast leading to short oligomer chains easily solubilized into acetonitrile solution. Fast electrochemistry experiments (Fig. 1c) reveal a dimerization rate constant for 9-methyl-9*H*-carbazole radical cations of about  $(4.3 \pm 0.1) \times 10^5 \text{ M}^{-1} \cdot \text{s}^{-1}$  which is the same value as the one found for 9-ethyl-9*H*-carbazole in previous studies [22]. This is a relatively low dimerization rate constant in comparison to bare carbazole for which radical cations dimerization rate constant was estimated at least at  $3 \times 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$  [15]. Therefore, it is confirmed that no poly(9-alkylcarbazole) films can be obtained in acetonitrile from electrochemical oxidation of 9-alkylcarbazole monomers.

As well known, the nature of solvent is very important for electropolymerization process. Acetonitrile is polar with a dipole moment of 3.45 Debye (D) and other polar solvents were tested unsuccessfully in terms of poly(9-alkylcarbazole) deposition: dimethyl sulfoxide (3.96 D) or trifluoroborate etherate (4.92 D). A much less polar solvent was therefore also tested: dichloromethane (1.14 D).

Cyclic voltammetry of 9-methyl-9*H*-carbazole (5 mM) is performed on platinum electrode (Fig. 2a) in dichloromethane solution containing 0.1 M of tetraethylammonium tetrafluoroborate. Unlike the experiment carried out in acetonitrile, a more conventional electrochemical signal is observed in dichloromethane. During the first scan, monomer oxidation is observed at +0.96 V

vs. SCE. For successive cycles, increase in electrochemical peaks indicates growing of a conducting polymer film on the surface. An adherent dark green deposit is observed on platinum electrode (Fig. 2a). Therefore, it is possible to electrochemically synthesize poly(9-methylcarbazole) from 9-methyl-9*H*-carbazole monomers in dichloromethane, which was impossible in acetonitrile. This was a surprising result. The proposed explanation would be a lower solubility of formed oligomers in dichloromethane (in comparison to acetonitrile) enabling electrochemical growing of a polymer film on the surface. Electrochemical behavior of the polymer film in monomer free dichloromethane solution is investigated. Cyclic voltammetry signal (Fig. 2b) shows unusual electrochemical activity mainly exhibiting very large reduction peak.

Polymer films are also electrodeposited on FTO electrodes by applying a voltage of +1.5 V vs. SCE during 150 s. A homogeneous dark green thick (1.7  $\mu\text{m}$ ) and smooth (roughness < 0.1  $\mu\text{m}$ ) organic film is deposited homogeneously on FTO electrode (Fig. 2c). SEM images reveal very homogeneous morphology with needle-like structures (Fig. 2c). UV/Visible absorption spectrum contains two broad peaks centered at 350 nm and 700-750 nm (Figure 2d), which is consistent since polycarbazole in the ground state has an absorption band around 350 nm while p-doped conjugated polycarbazole shows a longer absorption in the wavelength due to polarons and bipolarons [28]. ~~UV/Visible absorption spectrum contains two broad peaks centered at 350 nm and 700-750 nm (Figure 2d), which are generally observed for polycarbazole films as a result of the formation of polymer chains of different sizes with strong electronic conjugation [28].~~

### *3.1.2. Electrochemical deposition of poly(9-methylcarbazole) from oxidation of 9,9'-dimethyl-9*H*,9'*H*-3,3'-bicarbazole*

In order to deepen investigations, electrochemical behavior of dimers is also investigated to study the influence of monomer or dimer used on polymer formation. Cyclic voltammetry of 9-methyl-9*H*-carbazole dimer: 9,9'-dimethyl-9*H*,9'*H*-3,3'-bicarbazole is performed on platinum electrode (Fig. 3a) in acetonitrile solution containing 0.1 M of tetraethylammonium tetrafluoroborate. The signal exhibits two anodic peaks at +0.80 and +1.25 V vs. SCE and two cathodic peaks at +0.75 and +1.15 V vs. SCE. The first oxidation peak at about +0.80 V vs. SCE is due to oxidation of dimers into radical cations. As expected, this oxidation potential is much smaller than the one for corresponding monomer (9-methyl-9*H*-carbazole) which was around +1.11 V vs. SCE. Indeed, radical cations produced by oxidation of dimers present a higher number of mesomeric forms in comparison to the ones obtained from oxidation of monomers. This leads to an easier oxidation of dimers and a lower oxidation potential. Similar electrochemical signal is obtained from carbazole in the same solvent (not shown) with two oxidation peaks and two reduction peaks increasing with successive cycling. Therefore, it is assumed that polymerization mechanism from the dimer is the same as the one for carbazole. Ambrose *et al.* [15] investigated redox mechanisms of carbazole in acetonitrile solution and concluded to an ECE type mechanism. In this mechanism, the starting molecule is oxidized (one electron process) into its radical cationic form. After chemical coupling of these radical cations (and loss of protons), the resulting molecule is oxidized (two electrons process). The intensity of all redox peaks increases with the number of cycles, evidencing growing of a conducting polymer film on the electrode surface. The obtained film is dark green and adherent (Fig. 3a). Electrochemical activity of this polymer film is studied in monomer free solution (Fig. 3b). Reversible redox peaks show good electroactivity of the organic film. These results interestingly show that poly(9-methylcarbazole) can be electrochemically grown on platinum in acetonitrile solution from 9,9'-dimethyl-9*H*,9'*H*-3,3'-bicarbazole dimer while it is not possible from 9-methyl-9*H*-carbazole monomer. A possible explanation is that oligomers

formed from electrochemical coupling of dimers are long enough to become insoluble in acetonitrile and enable growing of a polymer film on the surface.

Polymer films are also electrodeposited by chronoamperometry (+1.5 V vs. SCE for 150 s) on FTO electrodes. A very thin brown homogeneous polymer film is visually observed on FTO surface (Figure 3c). Profilometry experiments reveal a film thickness of 0.2  $\mu\text{m}$  with a roughness of 10 nm. It is much thinner than the one obtained on platinum using cycling voltammetry, except at the air/liquid interface where it is thicker and dark green. SEM imaging are carried out on that air/liquid interface area (Fig. 3c). The observed morphology consists in clusters of globules not very uniformly deposited on the surface. Cyclic voltammetry of 9,9'-dimethyl-9*H*,9'*H*-3,3'-bicarbazole is performed on platinum electrode in dichloromethane solution containing 0.1 M of tetraethylammonium tetrafluoroborate (Fig. 4a). During the first cycle, two oxidation peaks are revealed at about +0.8 V vs. SCE and +1.2 V vs. SCE and two reduction peaks at around +0.9 V vs. SCE and +0.6 V vs. SCE. For successive cycles, the signal evolves. The second oxidation peak's current increases along cycling and its potential shifts towards anodic values. This peak becomes more and more sluggish until disappearing. Reduction peaks current also increases with potential scanning. Their potentials progressively get closer before being encompassed within the same broad reduction peak. These currents increase seems to indicate growing of a conducting deposit on the surface. Indeed, a dark green polymer film is visible on platinum electrode (Fig. 4a). This polymer presents good electroactive behavior as shown by cyclic voltammogram obtained in monomer free solution (Fig. 4b).

Polymer film is also electrodeposited by chronoamperometry (+1.8 V vs. SCE for 150 s) on FTO electrode. The deposit appears very homogeneous and covering. Profilometry experiments reveal a thickness of 1.7  $\mu\text{m}$  and a roughness of 0.5  $\mu\text{m}$ . Therefore, the polymer deposit is much thicker and rough when grown in dichloromethane in comparison to acetonitrile for which a

thickness of 0.2  $\mu\text{m}$  and a roughness of 10 nm were revealed. Finally, SEM image shows a structure composed of globules and needles (Figure 4c).

### *3.2. Electrochemical deposition of poly(9-ethylcarbazole)*

#### *3.2.1. Electrochemical deposition of poly(9-ethylcarbazole) from oxidation of 9-ethyl-9H-carbazole*

As largely discussed in previous work, poly(9-ethylcarbazole) cannot be grown from oxidation of 9-ethyl-9H-carbazole in acetonitrile [22].

Cyclic voltammetry of 9-ethyl-9H-carbazole (5 mM) is performed on platinum electrode (Fig. 5a) in dichloromethane solution containing 0.1 M of tetraethylammonium tetrafluoroborate. Oxidation of monomers is visible from +1.10 V vs. SCE on the first scan. For successive scans, four reduction peaks are visible at around +1.22 V vs. SCE, +1.13 V vs. SCE, +0.81-0.87 V vs. SCE and +0.00-0.09 V vs. SCE and one oxidation peak at about +1.00 V vs. SCE corresponding to electroactivity of grown polymer film. Indeed, these peaks currents increase along potential scanning which indicates formation and accumulation of a conductive film on the surface. An adherent green film is visible on platinum electrode. Electroactivity of the modified electrode was checked in monomer free dichloromethane solution (Fig. 5b). Three redox systems centered at about +0.75 V vs. SCE, +0.92 V vs. SCE and +1.29 V vs. SCE are observed for the organic film which is proved to be conducting. Electrodeposition is also carried out on FTO electrode at +1.8 V vs. SCE for 3 minutes. An adherent green deposit is grown (Fig. 5c). SEM images reveal nodular surface morphology with some clusters on several zones (Fig. 5c). One can note that surface morphology for poly(9-ethylcarbazole) film is much less homogeneous and much less smooth than the ones previously observed for poly(9-methylcarbazole) (Fig. 2c) deposits. The same hypothesis can be advanced to explain why poly(9-ethylcarbazole) can be electrogenerated from 9-ethyl-9H-carbazole in dichloromethane and not in acetonitrile: a lower

solubility of formed oligomers permitting formation of a polymer film on the surface of the electrode.

### *3.2.2. Electrochemical deposition of poly(9-ethylcarbazole) from oxidation of 9,9'-diethyl-9H,9'H-3,3'-bicarbazole*

Since it was shown that poly(9-methylcarbazole) can be electrochemically formed from 9,9'-dimethyl-9H,9'H-3,3'-bicarbazole oxidation, the same experiments are carried out with 9,9'-diethyl-9H,9'H-3,3'-bicarbazole.

Dissolution of 9,9'-diethyl-9H,9'H-3,3'-bicarbazole in acetonitrile is complicated and incomplete, even after vigorous stirring and ultrasonication. Cyclic voltammetry of the dimer in 0.1M tetraethylammonium tetrafluoroborate acetonitrile solution is carried out anyway (Fig. 6a). Two diffusive reversible redox systems are visible at about +0.80 V vs. SCE and +1.20 V vs. SCE. Peak separations are 62 and 69 mV, respectively, showing good reversibility of the two redox systems. Therefore, a small number of dimers is solubilized and presents good electrochemical behavior, but no polymer film is formed. The good reversibility of the signals prove that radical cations formed from oxidations of dimers are very stable.

Unlike in acetonitrile, 9,9'-diethyl-9H,9'H-3,3'-bicarbazole is very soluble in dichloromethane. Cyclic voltammetry of 9,9'-diethyl-9H,9'H-3,3'-bicarbazole (5 mM) is performed in 0.1 M tetraethylammonium tetrafluoroborate dichloromethane solution (Fig. 6b). Two diffusive reversible redox systems are visible like it was the case in acetonitrile (Fig. 6a). They are centered at about +0.8 V vs. SCE and +1.2 V vs. SCE. Peak separation is of 290 mV for both redox systems which indicate slower kinetics in comparison to the same redox systems in acetonitrile. No increase in current is observed during successive cycles. As expected from this, no polymer film is formed on platinum surface. As observed on FTO electrode, it is interesting to note that during potential scanning, a blue-green colored film is forming on the electrode

surface at anodic currents, but it is rapidly dissolved when cathodic currents are reached. When polarized anodically during chronoamperometry ( $E = +1.5$  V vs. SCE), the same observations are made: a homogeneous green organic layer is formed on the surface during anodic polarization. This layer is composed of oligomers obtained from oxidation and coupling processes, but the chains are not long enough to efficiently precipitate on the electrode surface and the formed organic layer is too easily dissolved into the solution as one can clearly see oligomers heaps leaving FTO surface and dissolving into the solution. When current is cut off, the entire organic layer is dissolved, and the electrode surface is totally cleared.

### *3.3. Electrochemical deposition of other poly(9-alkylcarbazole) compounds*

#### *3.3.1. Electrochemical deposition of poly(9-alkylcarbazole) from oxidation of corresponding 9-alkyl-9H-carbazole monomers*

Previous works showed the impossibility to form poly(9-alkylcarbazole) films from monomers oxidation in acetonitrile [22], regardless of alkyl chain length.

Cyclic voltammetry of 9-butyl-9H-carbazole, 9-hexyl-9H-carbazole and 9-octyl-9H-carbazole are carried out on platinum electrode (Fig. 7) in dichloromethane solution containing 0.1 M of tetraethylammonium tetrafluoroborate. The obtained voltammograms for all three compounds have many similarities (Fig. 7). Oxidation potentials for three monomers is nearly the same *i.e.* +1.16 V vs. SCE for 9-hexyl-9H-carbazole and +1.17 V vs. SCE for 9-butyl-9H-carbazole and 9-octyl-9H-carbazole. Beside the main oxidation peak at about +1.5 V vs. SCE, a small oxidation peak is present at +1.0 V vs. SCE and two larger reduction signals are visible at +0.85 V vs. SCE and below +0.5 V vs. SCE. The current for these peaks evolves during successive cycling. For 9-butyl-9H-carbazole, all redox signals increase with potential scanning while for 9-hexyl-9H-carbazole and 9-octyl-9H-carbazole only oxidation signal increases as reduction peaks currents decrease with potential cycling. However, in all cases, no polymer film is

visually observed on platinum electrode. Cyclic voltammetry experiments in monomer free solutions reveal no electroactivity for all modified surfaces. Electrodeposition is also unsuccessful on FTO electrodes. As with 9,9'-diethyl-9*H*,9'*H*-3,3'-bicarbazole in dichloromethane, a green colored film is forming on the electrode surface at anodic currents, but it is rapidly dissolved when cathodic currents are reached. Chronoamperometry is also used ( $E = +1.8$  V vs. SCE) and the same observations are made: a polymer film is grown on the electrode surface but it is dissolved as soon as the current is cut off. The same explanation can be advanced: a too high solubility in dichloromethane of formed oligomers. This solubility problem is not present for short carbon chains *i.e.* methyl and ethyl but becomes predominant when alkyl chain is lengthened.

*3.3.2. Electrochemical deposition of poly(9-alkylcarbazole) from oxidation of corresponding 9,9'-dialkyl-9*H*,9'*H*-3,3'-bicarbazole dimers*

9,9'-Dioctyl-9*H*,9'*H*-3,3'-bicarbazole and 9,9'-didodecyl-9*H*,9'*H*-3,3'-bicarbazole were synthesized to study electrochemical behavior of carbazole dimers functionalized with long alkyl chains. As for 9,9'-diethyl-9*H*,9'*H*-3,3'-bicarbazole, their dissolution in acetonitrile is weak. The longer the alkyl chain, the more difficult is the dissolution. This is not very surprising as acetonitrile being a polar solvent, the non-polar alkyl chain functionalization on bicarbazole *N* positions prevents good solubilization from ethyl to longer chains. Cyclic voltammetry of these dimers in 0.1 M tetraethylammonium tetrafluoroborate acetonitrile solution was carried out anyway (Fig. 8). For 9,9'-didodecyl-9*H*,9'*H*-3,3'-bicarbazole (Figure 8b): two diffusive reversible systems are visible at about +0.84 V vs. SCE and +1.16 V vs. SCE (peak separation of 54 and 51 mV, respectively). One additional irreversible peak is present at +1.36 V vs. SCE. As expected from dissolution problems, no polymer film can be grown from this case either. The signal obtained for 9,9'-dioctyl-9*H*,9'*H*-3,3'-bicarbazole (Figure 8a) is much more



sluggish. No polymer film is grown. However, two redox systems are visible at around +0.84 V vs. SCE and +1.13 V vs. SCE.

Cyclic voltammetry of 9,9'-dioctyl-9*H*,9'*H*-3,3'-bicarbazole and 9,9'-didodecyl-9*H*,9'*H*-3,3'-bicarbazole are performed in 0.1 M tetraethylammonium tetrafluoroborate dichloromethane solution (Fig. 8). Unlike in acetonitrile, these dimeric compounds are very soluble in dichloromethane. For 9,9'-dioctyl-9*H*,9'*H*-3,3'-bicarbazole (Fig. 8c), the voltammetry signal is much clearer than in acetonitrile (Fig. 8a). Two diffusive reversible redox systems are present at +0.9 V vs. SCE (peak separation 200 mV) and +1.3 V vs. SCE (peak separation 200 mV). For 9,9'-didodecyl-9*H*,9'*H*-3,3'-bicarbazole (Fig. 8d), the same electrochemical behavior as the one observed in acetonitrile (Fig. 8b) is witnessed: two reversible redox peaks (centered at +0.9 and +1.3 V vs. SCE) and one irreversible peak (+1.65 V vs. SCE). The peak separation for the two reversible systems is 230 and 250 mV: here again, electrochemical kinetics is faster in acetonitrile.

As for 9,9'-diethyl-9*H*,9'*H*-3,3'-bicarbazole, no clear increase in currents during successive cycles and no indication of organic film growing is observed on cyclic voltammetry curves. As expected from this, no polymer film is formed on platinum surface. During chronoamperometry experiments on FTO, growing of an organic layer is observed but like with 9,9'-diethyl-9*H*,9'*H*-3,3'-bicarbazole it is dissolved when current is cut off. The same explanation can be given: the formed oligomers are too soluble in dichloromethane and are dissolved into the solution after their formation on the surface.

### 3.4. UV/Visible spectroscopy

To complete our study, calculation of HOMO and LUMO energies of monomers and dimers are carried out by using UV/Visible spectra in dichloromethane and voltammograms obtained in the same solvent. Eq (1) is used to calculate the optical band gap  $E_g$  of molecules from

spectroscopic data (Figure 9). Indeed, the wavelength  $\lambda_{\text{onset}}$  can be deduced from UV/Visible spectrum of each molecule by extrapolating the intersection of the tangent with the x-axis from the peak point.

$$E_g(eV) = \frac{1240}{\lambda_{\text{onset}}(\text{nm})} \quad \text{eq (1)}$$

Then, HOMO and LUMO energy levels are calculated using eq (2) and eq (3). Indeed, values of energy levels can be deduced from molecule's first onset oxidation potential ( $E_{\text{onset}}$ ) which is visible in the first cycle of the cyclic voltammogram [29]. Then, the energy of HOMO is calculated from this experimental value and from the energy of saturated calomel reference electrode which can be found in literature (4.65 eV). The energy of LUMO is finally deduced from the energy of HOMO and the optical band gap previously calculated.

$$E_{\text{HOMO}}(eV) = -(E_{\text{onset,ox}} + 4.65)(eV) \quad \text{eq (2)}$$

$$E_{\text{LUMO}}(eV) = E_{\text{HOMO}} + E_g(eV) \quad \text{eq (3)}$$

The resulting  $\lambda_{\text{onset}}$ ,  $E_g$ ,  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  values are gathered in Table 1. They are consistent with values previously calculated for other carbazoles [30]. As expected, the molecules presenting the highest HOMO energies are the easiest to oxidize. Interestingly, one can notice that the most easily oxidizable carbazole monomers *i.e.* 9-methyl-9H-carbazole and 9-ethyl-9H-carbazole, are those that are successfully electropolymerized in dichloromethane. The same can be said for bicarbazoles, since 9,9'-dimethyl-9H,9'H-3,3'-bicarbazole, which is the only bicarbazole that can be polymerized electrochemically, has a higher HOMO energy than the other bicarbazoles.

#### 4. Conclusion

The objective of this work was to electrochemically synthesize poly(9-alkylcarbazole) films. Since it is not possible to generate them classically from monomers in acetonitrile, alternative ways were investigated.

To summarize the obtained results:

- Poly(9-methylcarbazole) was successfully electrodeposited on platinum from oxidation of 9-methyl-9*H*-carbazole monomer in dichloromethane. It could also be grown from 9,9'-dimethyl-9*H*,9'*H*-3,3'-bicarbazole dimer in acetonitrile and dichloromethane. In all cases, a dark homogeneous and conducting polymer film was obtained.
- Poly(9-ethylcarbazole) could only be grown from 9-ethyl-9*H*-carbazole monomer in dichloromethane. An adherent green film was obtained on platinum.
- All other poly(9-alkylcarbazole) films with longer alkyl chains *i.e.*, 4 to 12 carbons, could not be electrosynthesized from oxidation of corresponding monomers or dimers in acetonitrile or dichloromethane.

Therefore, poly(9-methylcarbazole) and poly(9-ethylcarbazole) are the only poly(9-alkylcarbazoles) that can be electrochemically generated from their monomers. A solvent of poor polarity such as dichloromethane needs to be used. For longer alkyl chains, the oligomers formed from monomers oxidation and coupling are too soluble in dichloromethane and no polymer film can be obtained. The impossibility to electrosynthesize poly(9-alkylcarbazole) from monomers in acetonitrile was already discussed in previous work [22].

Moreover, poly(9-methylcarbazole) can be electrogenerated from 9,9'-dimethyl-9*H*,9'*H*-3,3'-bicarbazole dimer in both acetonitrile and dichloromethane. All other dimers were not soluble enough in acetonitrile (due to non-polar alkyl chain) to enable efficient polymerization process, while their oligomers were too soluble in dichloromethane to permit growing of polymer film on the electrode surface.

This study shows the possibility to electrosynthesize poly(9-alkylcarbazole) of short alkyl chains through monomers or dimers electrochemical oxidation. Solvent of poor polarity *i.e.* dichloromethane enables wider range of possibilities. The impossibility to electrochemically generate poly(9-alkylcarbazole) of long alkyl chains was confirmed.

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