



# Electrochemical Synthesis of Polycarbazole Film in Nonacidic Medium and its Electrochromic Properties

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Başvuru/Received: 08/08/2022

Kabul / Accepted: 11/10/2022

Çevrimiçi Basım / Published Online: 31/12/2022

Son Versiyon/Final Version: 31/12/2022

## Abstract

This study is about the electrochemical polymerization of carbazole in nonacidic medium. Although anodic polymerization of it is very common in the literature, the numbers of studies related electrochromic properties for polycarbazole is limited. In literature, there are three different classes (nonacidic, acidic and ionic liquid) of polymerization medium for carbazole. Basically, most of the scientists try to make experiments in nonacidic medium since the new structures obtained by derivatization of the aromatic structure are polymerized in this typed of medium. However, sometimes the polymerization of the monomer becomes difficult or the resulting polymer does not exhibit electrochemical and optical stability. In this case, medium solutions with acidic or ionic liquids are preferred. Although the polymers obtained in the ionic liquid and the acidic medium are stable electrochemically and fully adhered to the electrode surface, it is clear that these solutions also have some disadvantages, such as, the high cost of ionic liquid and the fact that the polymer obtained in an acidic medium may contain contamination particles at the end of polymerization. In this study, the electrochemical and optical properties of the obtained polymer were investigated by polymerizing the carbazole monomer on the electrode surface in a nonacidic medium. For this purpose, polycarbazole was coated on both glassy carbon and indium tin oxide (ITO) glass electrodes in 0.1 M tetrabutylammonium hexafluorophosphate /dichloromethane (TBAPF<sub>6</sub>/ DCM) medium using electroanalytical techniques. The polymer film synthesized showed reversible electrochemical oxidation process properties as well as electrochromic properties. Different colors of the polymer film were achieved under different applied potentials. In the neutral state, polycarbazole exhibits transparent color at -0.3 V. Upon oxidation its colors turns green and bluish green at 0.3 V and 1.3 V, respectively. The maximum difference of the UV-vis absorption of the film was found about 22 % at 390 nm and 15 % at 800 nm optical contrast ratio (for the first cycles). Considering that this study will form a basis for other studies, it is thought that the evaluation of carbazole polymer in terms of its electrochromic properties will provide a great deal to the literature.

## Key Words

“Carbazole; polycarbazole; electrochromism; conjugated polymer”

## 1. Introduction

There is probably no one who does not know the importance of conductive polymers in the field of materials, energy, technological and innovative medical science in our age and that they are open to development in every field (Shi et al.2015; Baughman et al. 1996). Conductive polymers have become materials that have the feature of a remedy, sometimes in the field where energy efficiency is needed, sometimes in the application area, where the materials used should be cheaper, flexible, lighter and more economical (Omar et al. 2019; Grancaric et al. 2018; Margolis et al. 2012) Especially alternative to inorganic materials, less waste, more environmentally friendly and recyclable polymers continue to attract the attention of scientists with all their features (Phan et al. 2019). It is very crucial to optimize and modify the optical and electronic properties of conjugated polymers and to modify the chemical structure of the material as a conductive polymer engineer. By designing the electronic and optical properties of conjugated polymers, conductive polymers can be used in organic light-emitting diodes (Carbas et al. 2014), capacitors (Carbas et al. 2018), dye-sensitized solar cells (Carbas et al. 2017), biological photovoltaic solar cells (Cevik et al. 2018), transistors (Sirringhaus et al. 2010), electrochromic (Carbas et al. 2022) and sensor (Azak et al. 2018), which enable the development of technological and engineering practice. Among these applications, electrochromic applications are the most remarkable and the application can be considered quite simple (Beaujuge et al. 2010). Electrochromism is a reversible color change of a polymer or other material by applying electrical energy (Rosseinsky et al. 2001). Electrochromic polymers are used for a variety of applications such as smart windows (Rauh et al. 1999), memory elements (Sonmez et al. 2006), electrochromic displays (Mortimer et al. 2006) and camouflage materials (Beaupré et al. 2009).Conductive polymers are a very large family and different derivatives of new conductive polymers are encountered day by day (Kumar et al. 1998). If conjugated monomers that can polymerize electrochemically are thought of as the root of a tree, there will be many new tree branches and leaves derived from this root. These conjugated monomers are generally thiophene, pyrrole, furan, fluorene, carbazole and indoles are just a few of them (Carbas et al. 2022, Cansu-Ergun et al. 2019). In its simplest form, this conjugated monomer can be homopolymerized in its bare state or functionalized from its active ends. Sometimes it can be combined with another structure (for example, various donor groups or processable units such as 3,4-ethylene dioxythiophene (EDOT), propylene dioxythiophene (Prodot), thiophene, carbazole and fluorene, etc.) with various sequences to make copolymers (Verheyen et al. 2017, Ergun et al. 2022, Bingol et al. 2017).

**Table 1.** A literature summary of polycarbazole film formations in different conditions

Reference	WE	Electropolymerization medium	Acidity	Electrochromism
Ambrose et al. 1968	a large Pt gauze	0.1 M TEAClO <sub>4</sub> /ACN	nonacidic	-
Desbene-Monverna et al. 1981-7	Pt/Au	BTPA/ACN or TMATFB /ACN	nonacidic	<i>dark green deposit</i>
O'Brien et al. 1985-4	Au plated glass disc electrode	0.1 M TBAClO <sub>4</sub> /DMF	nonacidic	-
Abe et al. 2002	SnO <sub>2</sub> coated glass substrate	0.1 M LiClO <sub>4</sub> /ACN	nonacidic	-
Ates et al. 2008-9	single carbon fiber microelectrode	0.1 M LiClO <sub>4</sub> /ACN	nonacidic	-
Taoudi et al. 2001-5	SnO <sub>2</sub> coated glass substrate	0.1 M TEAClO <sub>4</sub> / ACN:H <sub>2</sub> O (1:2) (by volume)	nonacidic	-
Taoudi et al. 1997-3	SnO <sub>2</sub> coated glass substrate	0.1 M TEAClO <sub>4</sub> / ACN:H <sub>2</sub> O (1:2) (by volume)	nonacidic	-
Mengoli et al. 1988-8	Au disc	CH <sub>3</sub> OH (75 vol.%) 5 M HClO <sub>4</sub> , in H <sub>2</sub> O (25 vol.%).	acidic	<i>transparent colorless (neutral) dark green (oxidized)</i>
Verghese, 1996	ITO	CH <sub>3</sub> OH (75%) 5M HClO <sub>4</sub> , in H <sub>2</sub> O (25%) (by volume)	acidic	<i>pale yellow (neutral) green (oxidized)</i>
Hua-Ming et al. 2008-6	ITO	CH <sub>3</sub> COOH containing 26% BFEE , 5% PEG400 (by volume)	acidic	<i>transparent colorless (neutral) dark green (oxidized)</i>
Zhuang, 2009	ITO	BMI-PF <sub>6</sub> BMP-TFSI	Ionic liquid	<i>pale green (neutral) deep green (oxidized) for (BMI-PF<sub>6</sub>), transparent green (neutral) dark green (oxidized) for (BMP-TFSI)</i>
Sezai Sarac et al. 2006-10	ITO	<i>No details</i>	nonacidic	<i>transparent colorless (neutral) dark green (oxidized)</i>
This work	GC and ITO	0.1 M TBAPF <sub>6</sub> /DCM	nonacidic	<i>transparent colorless (neutral) dark green (intermediate) bluish color (oxidized)</i>

(WE: working electrode, acetonitrile (ACN), tetraethylammonium perchlorate (TEAClO<sub>4</sub>), dimethylformamide (DMF), tetra-n-butyl ammonium perchlorate (TBAClO<sub>4</sub>), 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF<sub>6</sub>), N-butyl-N-methylpyrrolidinium bis((trifluoromethyl)sulfonyl)imide (BMP-TFSI), tetramethylammonium tetrafluoroborate (TMATFB), Benzyltrimethylammonium perchlorate (BTPA), boron trifluoride diethyl etherate (BFEE))

Polymers containing carbazole in the main or side chain are of great interest today with their photoconductivity, electroluminescence and electrochromic properties (Yi et al. 2007, Carbas et al. 2016). Carbazoles can generally be electropolymerized at 3, 6 positions. The first studies related with the electrochemical oxidation of carbazole belong to Ambrose and Nelson (Ambrose et al. 1968). They electrochemically synthesized polycarbazole and discussed anodic oxidation pathways of carbazole during polymerization. There are also many publications in the literature on the electrochemical polymerization of carbazole monomer (Abe et al. 2002; Diamant et al. 2005; Zhuang et al. 2009; Miao et al. 2008; Ates et al. 2008; Desbene-Monverna et al. 1981; Hua-Ming et al. 2008; Mengoli et al. 1988; O'Brien et al. 1985; Sezai Sarac et al. 2006; Taoudi et al. 2001; Taoudi et al. 1997; Verghese et al. 1997). Synthesizing the polymer of carbazole via electrochemical method is quite challenging. Coating on a conductive substrate or forming a free standing film on the electrode substrate is not easy. Different electropolymerization solvent/electrolyte medium and working electrodes were used in order to get qualified polymer films on the electrode. Therefore, studies on different electropolymerization medium and different types of electrodes have still been ongoing by scientists (**Table 1**). Three types of medium were used in order to get polycarbazole films (nonacidic, acidic and ionic liquid medium) during electropolymerization. In nonacidic medium of electrolyte/solvent mixture for electropolymerization, related studies generally used tetra alkyl ammonium salts and some other organic salts. Among them, Desbene-Monverna et al. used Pt or Au working electrode in the medium of benzyltrimethylammonium perchlorate (BTPA) /ACN or tetramethylammonium tetrafluoroborate (TMATFB) /ACN in order to get polycarbazole. Experiments showed that the film inhomogeneously coated on the electrode surface and poorly adherent to the electrode surface (Desbene-Monverna et al. 1981). Sezai Sarac et al. also studied electropolymerized polycarbazole and used different nonacidic solution medium for polymerization. However they didn't give the details of polymerization medium and mention any other electrochromic properties apart from its color in the reduced and oxidized state of polymer. Acidic and ionic liquids electropolymerization media were also chosen for most of the studies in order to get more stable qualified polycarbazole films as seen in **Table 1**. Although ionic liquids are nonvolatile solvents, they, unfortunately suffer from toxicity, preparation and high cost during process (Shamsuri et al. 2010). Zhuang et al. studied with ionic liquids (1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF<sub>6</sub>), N-butyl-N-methylpyrrolidinium bis((trifluoromethyl)sulfonyl)imide (BMP-TFSI)) in order to obtain electrochromic polycarbazole film. They showed electrochromic colors of each polymer film and did not give detailed information. Acidic media are most preferable ones for electropolymerization but they may have also some drawbacks, such as partly or non conjugated chains or contaminated particles in the chain (Sadki et al. 2000). Protic medium was first used by Mengoli in 1988 to electrochemically polymerize carbazole on Au disc (Mengoli et al., 1988). But the results showed that the film was fair conductivity and stability. Moreover it shows electrochromism between colorless (in the neutral state) and green color (in the oxidized state). The same medium for electropolymerization was used by Verghese et al. (Verghese et al. 1997) and it was written that polycarbazole was coated on the ITO surface in different acidic solution and changed color to yellow in the reduced state and green in the oxidized state. This study was the first study related with electrochromic polycarbazole in acidic medium. However they could not get one level higher about their studies because they could not get desired reversibility for various supporting electrolytes and postponed their work to a later date for better results. BFEE, the magic electrolyte and solvent of the conductive polymer world, came to mind to improve the unstable states of the polycarbazole film was used by Hua-Ming et al. They managed to get high quality film by mixing it with acetic acid (Hua-Ming et al. 2008). However, BFEE is a toxic, volatile material and not economical. Furthermore, they didn't mention too much detail in their work related electrochromic properties of polycarbazole film.

The electrochemical and optical properties of polycarbazole and its derivatives attract attention by the scientific world. The electrochromic behavior of conjugated polymer films containing carbazole and the contribution of the carbazole structure to the chain in this respect still arouses curiosity. Carbazole-containing polymer films are generally electrochemically polymerized in nonacidic medium. For this reason, it is more meaningful to compare the properties of films with electropolymerized structures in organic solvent and salt medium (non acidic medium). In the light of this information, the electrochromic behavior of polycarbazole synthesized in a nonacidic medium may be a reference when comparing the electrochromic properties of carbazole-containing conjugated polymers to be synthesized in the future. In this study, carbazole monomer was electropolymerized in the medium of 0.1 M TBAPF<sub>6</sub>/DCM. Electrochemical and spectroelectrochemical properties of its corresponding polymer were investigated in monomer free medium. Moreover, the electrochromic properties of polycarbazole have been tried to be detailed.

## 2. Experimental section

### 2.1. Materials and instrumentation

All chemicals were purchased from Sigma Aldrich without further purification. Carbazole as and tetrabutylammonium hexafluoro phosphate (TBAPF<sub>6</sub>) as organic electrolyte was dissolved in dichloromethane (DCM) and electrolyte medium was prepared for electropolymerization. As a potentiostat, an Ivium CompactStat brand device was used during electrochemical and spectroelectrochemical studies. For spectroelectrochemical studies, a Specord S600 spectrometer was used. The color space given by the International Commission of Illumination with luminance (L), hue (a), and intensity (b) was also analyzed. FTIR spectra were carried out with Bruker Equinox 55 with an attenuated total reflectance (ATR).

### 2.2. Electrochemical polymerization

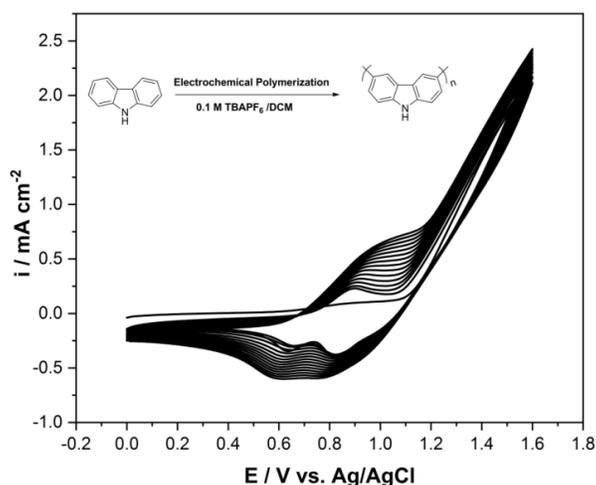
3.5 mM monomer and 0.1 M TBAPF<sub>6</sub> electrolyte were dissolved in 3 ml DCM during electropolymerization. Three electrode systems, which consists of working electrode (Glassy carbon electrode (GC) (area 0.07 cm<sup>2</sup>), Indium tin oxide glassy electrode (ITO)), reference electrode (Ag/AgCl in 3 M NaCl solution, Ag wire) and counter electrode (Pt wire) were used. These electrodes were placed in a round Teflon wheel, which has three holes. This cape was put on a cyclic voltammetry (CV) cell, which contains polymerization medium or monomer free medium for electrochemical characterization experiments. For spectroelectrochemical experiments, a UV cuvette were

used as solution container. Again a square teflon cape with three holes on which three electrodes can be placed, was placed on this container together with the electrodes. CV and constant potential electrolysis methods were used during electrochemical polymerization and both electrochemical and spectroelectrochemical characterization. For kinetic spectroelectrochemical studies, transients at constant potential as an electroanalytical method was used and electrochromic polymer was switched. For FTIR analysis, ITO was coated with carbazole monomer until the total charge comes until 3C.

### 3. Results and Discussion

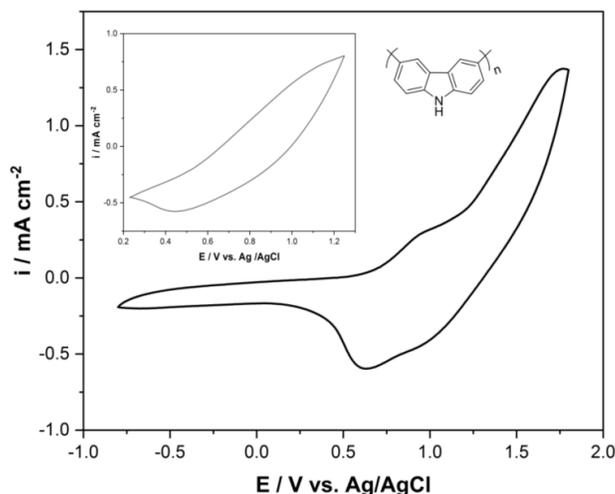
#### 3.1. Electrochemical polymerization of carbazole and characterization of its polymer

Electrochemical behavior of carbazole (3.5 mM) was investigated in the medium of 0.1 M TBAPF<sub>6</sub> / DCM solution. Monomer had an onset (1.10 V vs. Ag/AgCl) and maximum (1.40 V vs. Ag/AgCl) oxidation potential. As seen from **Figure 1**, repetitive cyclic voltammogram experiment for monomer was performed in order to see whether monomer was electropolymerized or not on GC electrode. The potential range between 0.0 V and 1.6 V with a scan rate of 200 mV s<sup>-1</sup> was chosen for electropolymerization process of carbazole monomer in the medium of 0.1 M TBAPF<sub>6</sub> / DCM. The results show that a new oxidation and reduction couple peaks were observed at about 1.0 V and 0.7 V, respectively during second and following cycles. Current density and charge of each cycles also increased when cycle number increase. This is a proof for a conductive coated polymer on working electrode.



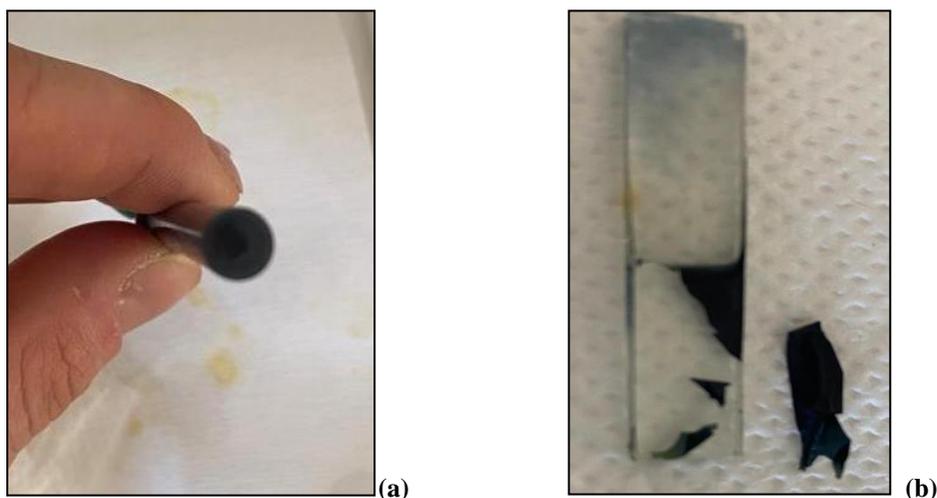
**Figure 1.** Repetitive cyclic voltammogram of carbazole in the medium of 3.5 mM monomer and 0.1 M TBAPF<sub>6</sub> / DCM solution

GC coated (15 cycled) with polycarbazole film was taken out and washed with fresh DCM solvent in order to remove oligomeric and monomeric species. Electrochemical behavior of polycarbazole film was investigated in the monomer free medium with a scan rate of 200 mV s<sup>-1</sup>. Polymer has reversible two redox couple at about 0.95 V and 1.60 V vs. Ag/AgCl, indicating the formation of charge carriers on the main chain backbone. Two redox couple was observed during the scan the potentials between -0.7 V and 1.7 V as seen in **Figure 2**. The polymer was scanned between 0.2 V and 1.3 V in order to see the first redox couple as seen in the inset of **Figure 2**.



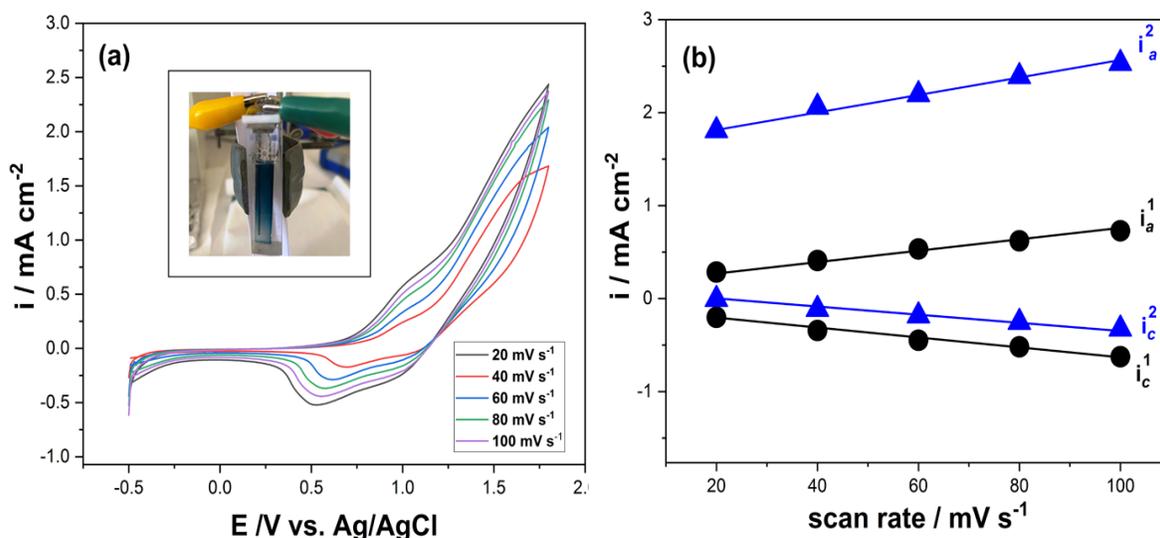
**Figure 2.** Electrochemical behavior of polycarbazole on GC electrode in the medium of 0.1 M TBAPF<sub>6</sub>/DCM solution via CV technique. (Figure inset: polymer was scanned the potentials between 0.2 V and 1.3 V with a scan rate of 200 mVs<sup>-1</sup>)

The polymer film was successfully coated on the GC electrode surface as seen in **Figure 3a**. Polymer film coated on the ITO electrode in a thicker thickness was used for FTIR analysis (**Figure 3b**). The film adhered very well to the ITO surface and was self-peeled from the electrode surface after the drying step.



**Figure 3.** The photos of polycarbazole film coated on (a) GC electrode (b) ITO electrode

After these preliminary studies, the polymer film was coated on ITO as the electrochromic properties of polycarbazole were to be investigated (the inset of **Figure 4a**). After the polymer film was washed in DCM solvent, the polymer film the behavior was examined in monomer free medium at different scan rates (from  $20 \text{ mV s}^{-1}$  to  $100 \text{ mV s}^{-1}$ ) via CV method (**Figure 4a**). The current density data depending on scan rates were depicted in **Figure 4b**. A linear increase in the peak currents as a function of the scan rates confirmed well-adhered electroactive polymer films on the electrode surface as well as a nondiffusional redox process

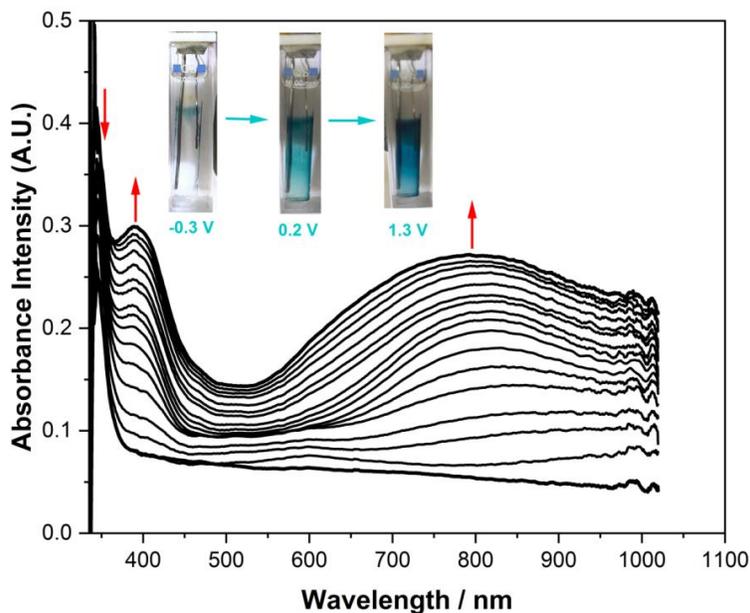


**Figure 4.** (a) Electrochemical behavior of polycarbazole on ITO electrode in the medium of  $0.1 \text{ M TBAPF}_6/\text{DCM}$  solution via CV technique at different scan rates. (Figure inset: the photo of polymer carbazole on ITO electrode) (b) The relationship of anodic ( $i_a^1$ ) and ( $i_a^2$ ) and cathodic ( $i_c^1$ ) and ( $i_c^2$ ) current peaks at various scan rates in  $0.1 \text{ M TBAPF}_6/\text{DCM}$  solution. (anodic ( $i_a^1$ ) and cathodic ( $i_c^1$ ) current for the first redox process; anodic ( $i_a^2$ ) and cathodic ( $i_c^2$ ) current for the second redox process.)

### 3.2. Spectroelectrochemical characterization of polycarbazole

In order to investigate spectroelectrochemical behavior of polycarbazole, carbazole was electropolymerized on ITO electrode at constant potential ( $1.4 \text{ V}$ ). As seen in the inset of **Figure 5**, a thin-film thick film was coated for easy color change detection. After electropolymerization procedure, ITO coated polymer film was cleaned with DCM solvent and a clean electrolyte medium were prepared in order to get electrochemical properties together with spectroelectrochemical properties. CV technique was used for this and polymer film was scanned between  $-0.3 \text{ V}$  to  $1.3 \text{ V}$ . As soon as the polymer film was scanned via CV method, UV-vis spectra of

film were taken and noted. Since ITO electrode in DCM solution has a cut off value at lower than 330 nm, the neutral polymer film has a  $\pi-\pi^*$  transition at lower than this value. The spectra of polycarbazole showed an absorption onset at about 360 nm. The optical band gap of polymer film was calculated from its low energy absorption edge and it was found as 3.41 eV. Upon oxidation at about 0.1 V, the absorption intensity of  $\pi-\pi^*$  transition decreases the polymer film showed new charge carriers at about 390 nm and 800 nm because the absorption intensities increase at these maximum wavelengths.



**Figure 5.** Spectroelectrochemical behavior of polymer film coated (with a thickness of 75  $\text{mC}/\text{cm}^2$ ) on ITO electrode in the medium of 0.1 M TBAPF<sub>6</sub> / DCM solution. (Figure 5 inset: electrochromic colors of ITO coated polymer films at applied potentials)

### 3.3. Electrochromic behavior of polycarbazole

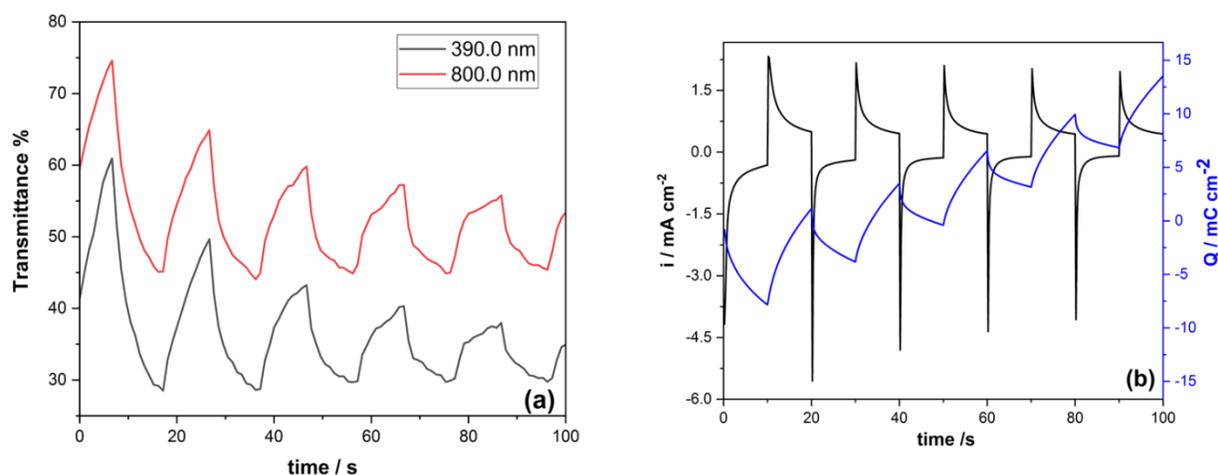
**Table 2.** Colorimetric values summary of polycarbazole ( Lab color analysis were done with respect to D65 and 10°) (with a thickness of 75  $\text{mC}/\text{cm}^2$  coated polymer film).

Applied Potetial	-0.3 V	0.2 V	0.8 V	1.0 V	1.3 V
<b>Color</b> (polycarbazole coated on ITO)					
<b>Color</b> (calculated from Lab data)					
<b>L</b>	97.87	89.0	85.28	81.88	79.55
<b>a</b>	-0.09	-9.72	-13.3	-15.2	-16.4
<b>b</b>	0.144	2.95	3.40	2.04	2.66

Polycarbazole shows different colors at different applied potentials as seen in the inset of **Figure 4** and **Table 2**. In the neutral state, polycarbazole exhibits transparent color (at -0.3 V). Green and bluish green colors were observed at 0.3 V and 1.3 V, respectively. The experimental studies showed that the bluish green color after the polymer film was coated becomes transparent over time when -0.3 V was applied, but it did not turn green again when higher potentials are applied than this potential. Most likely, the polymer film loses its electroactivity when this potential is reached. However, the polymer film exhibits reversible electrochromic properties when switched between 0.3 V and 1.3 V. The Lab values of the electrochromic properties of the polymer film and the corresponding colors are given in **Table 2**.

It is very important to switch an electrochromic film with a very fast response. Data regarding the keying property of the electrochromic polymer between 0.2 V and 1.3 V are given in **Figure 6a** (chronoabsortimetry data at 390 nm and 800 nm) and **Figure 6b** (current-time and charge-current data). Accordingly, the polymer film has 22 % at 390 nm and 15 % at 800 nm optical contrast ratio (for the

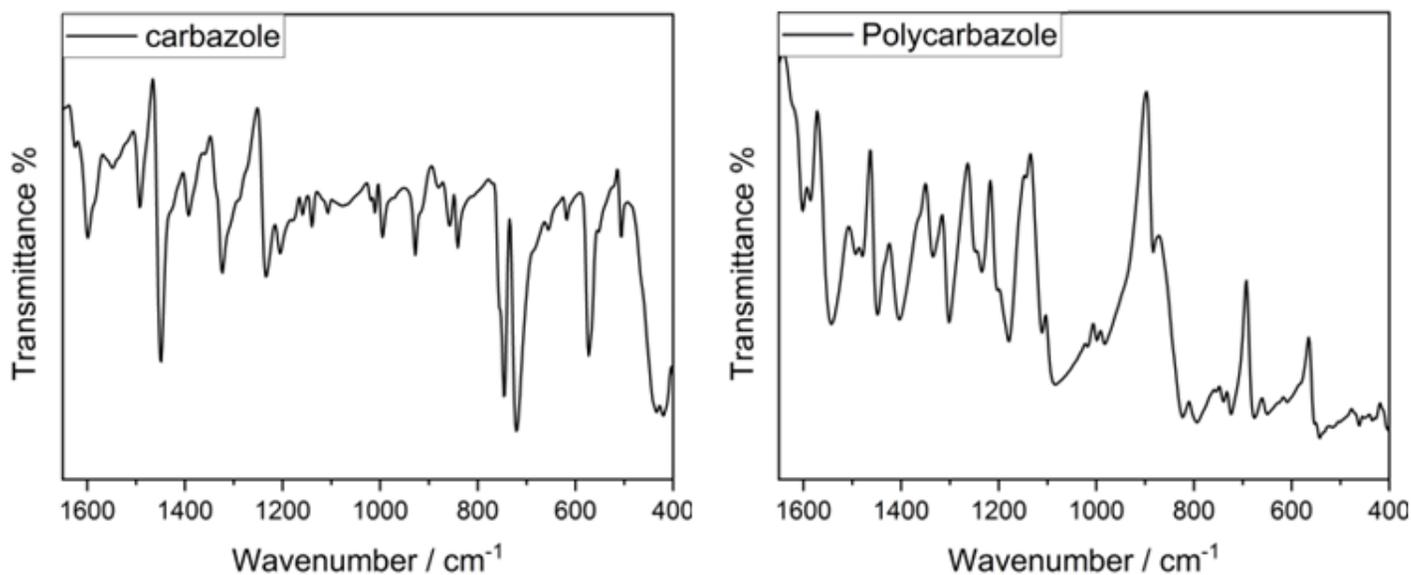
first switching data cycle received). However, as can be seen in the **Figure 6a**, polycarbazole film did not show a stable switching property. Because the percent transmittance difference ( $\% \Delta T$ ) decreased as the switching cycle increased. Looking at the electrochromic property of the polymer film in **Figure 6a**, it can be said that the response time is very slow. This is why many studies have worked with many scientists to improve its electrochromic properties by adding functional groups to various carbazole monomers or making it a copolymer (Cansu-Ergun et al. 2018, Hai et al. 2016).



**Figure 6.** (a) Electrochromic switching and optical absorbance change monitored during switching at 390 nm and 800 nm (b) chronoamperometry experiments for polycarbazole in 0.1 M TBAPF<sub>6</sub> / DCM (with a thickness of 75 mC/cm<sup>2</sup> coated polymer film).

### 3.4. FTIR analysis of carbazole and polycarbazole

The chemical structures of carbazole and polycarbazole were analyzed by means of FTIR spectra (**Figure 7**). The band at around 3500 cm<sup>-1</sup> for both structures was the stretching bond of -NH. The bands at 3022 cm<sup>-1</sup> can be ascribed to the C-H stretching vibration of benzene ring. The two strong bond at 1590 and 1495 cm<sup>-1</sup> were related with the stretching vibrations of the C=C bands and an absorption peak at 1230 cm<sup>-1</sup> were due to the C-N bond stretching. When both spectrums were compared, the peak at 746 cm<sup>-1</sup> for spectrum of carbazole does not appear in the FTIR spectrum of polymer. This indicates polymerization. The peaks between 800 and 830 cm<sup>-1</sup> in FTIR spectrum of polycarbazole are due to 1, 2 and 4 tri substituted benzene rings, which indicates polymerization proceeding from 3,6 position of carbazole ring (Zhou et al. 1999 ; Sezer et al. 1999).



**Figure 7.** FTIR spectra of carbazole and polycarbazole

#### 4. Conclusion

In this study, the electrochromic behavior of polycarbazole film, which is generally stated in the literature to be transparent in the reduced state and green in the oxidized state, has been investigated in detail. This study, which is considered as a building block for carbazole-based polymers with electrochromic properties, will form a basis for future studies. Moreover, in this study, the electrochemical behavior of the carbazole film synthesized in nonacidic medium was analyzed by first coating it on the GC electrode and then on the ITO working electrodes. Experimental studies have shown that the polymer film has two reversible redox couples and adheres well to the electrode surface. The polymer film was characterized by CV and FTIR techniques in order to prove polymer formation. Spectroelectrochemical experiments revealed that polycarbazole has electrochromic property (transparent color at -0.3 V, green color at 0.2 V and bluish color at 1.3 V) with moderate  $\Delta T$  values (22 % at 390 nm and 15 % at 800 nm) with low stability. Furthermore, polycarbazole has a large band gap of 3.41 eV. It is thought that it will serve as a reference for the scientific world when analyzing the behavior of new carbazole-based electrochromic polymers.

#### Acknowledgment

This study has been evaluated within the scope of the special issue of engineering sciences research and development applications.

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