SYNTHESIS OF A MINIMALLY COLOURED CARBAZOLE AND CARBORANE BASED ELECTROACTIVE POLYMER AND ITS USE AS A COUNTER ELECTRODE IN ELECTROCHROMIC DEVICES

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I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Atilla Cihaner
Head of Department

This is to certify that we have read the thesis "Synthesis of a Minimally Coloured Carbazole and Carborane Based Electroactive Polymer and Its Use as a Counter Electrode in Electrochromic Devices" submitted by "Dhcyaa Al-Mahdawi" and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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I declare and guarantee that all data, knowledge and information in this document has been obtained, processed and presented in accordance with academic rules and ethical conduct. Based on these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

SYNTHESIS OF A MINIMALLY COLOURED CARBAZOLE AND CARBORANE BASED ELECTROACTIVE POLYMER AND ITS USE AS A COUNTER ELECTRODE IN ELECTROCHROMIC DEVICES

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M.S., Chemical Engineering and Applied Chemistry

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A novel electroactive trimeric monomer (**1**) based on carbazole and carborane units was polymerized successfully via potentiostatic and potentiodynamic methods in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate/CH_2Cl_2. Electrochemical behavior of the corresponding polymer (**P1**) was investigated by using electroanalytical methods. The polymer **P1** film firmly coated on the Pt electrode surface exhibited high robustness under ambient condition upon switching between its redox states. For example, 73% of the electroactivity of the film retained after 1000 cycles when switched between the redox states. On the other hand, spectroelectrochemical studies showed that the polymer film has no absorption band in the visible spectral region and has a band gap of 2.5 eV with a maximum wavelength at 307 nm. Upon oxidation, the polymer film (58 nm) did not show any appreciable color change. The results showed that the film is colorless and has a transparency over 90% at all redox states. Also, the polymer film exhibited a percent trasmittance change of 6.8% and a coloration efficiency of 12 cm^2/C at 555 nm when switched between neutral and oxidized states. This minimally color changing property of the polymer film makes it a promising counter electrode material in electrochromic devices. When compared to the poly(3,4-ethylenedioxythiophene) (PEDOT) film (61% at 580 nm), the device prepared based on **P1** and PEDOT films nearly exhibited similar optical behaviors, as expected. The device has a percent transmittance change of 51% at 580 nm. Also, this device exhibited high robustness, high redox and optical stability under ambient conditions since it retains 88% of its electro-optical stability even after 1000 switching cycles between various redox states.

Keywords: Electrochromic device, counter electrode, minimally color changing polymer, carbazole, carborane

ÖZ

EN AZ RENKLİ KARBAZOL VE KARBORAN ESASLI ELEKTROAKTİF BİR POLİMERİN SENTEZİ VE ELEKTROKROMİK CİHAZLARDA KARŞIT ELEKTROT OLARAK KULLANIMI

Dheyaa Al-Mahdawi
Yüksek Lisans, Kimya Mühendisliği ve Uygulamalı Kimya Bölümü
Tez Yöneticisi: Prof. Dr. Atilla Cihaner
Aralık 2015, 47 sayfa

Karbazol ve karboran birimleri esaslı yeni bir elektroaktif üçlü monomer (**1**) potentiostatik ve potentiodinamik yöntemlerle 0.1 M tetrabütilamonyum hekzaflorofosfat/CH_2Cl_2 elektrolit çözeltisi içerisinde başarılı bir şekilde polimerleştirilmiştir. İlgili polimerin (**P1**) elektrokimyasal davranımı elektroanalitik yöntemler kullanılarak incelenmiştir. Pt elektrot yüzeyine sıkıca kaplanmış **P1** polimer filmi ortam koşulları altında redoks halleri arasında anahtarlanırken yüksek dayanıklılık göstermiştir. Örneğin, polimer filmi redoks halleri arasında anahtarlanırken 1000 döngü sonrası elektroaktifliğinin %73'ünü korumuştur. Diğer bir taraftan, spektroelektrokimyasal çalışmalar göstermiştir ki polimer filminin görünür tafy bölgesinde soğurma bandı yoktur ve maksimum dalga boyu 307 nm olup 2.5 eV değerinde bir band aralığına sahiptir. Yükseltgenirken polimer filmi (58 nm) dikkate değer bir renk değişimi göstermemiştir. Sonuçlar polimer filminin renksiz ve tüm redox hallerinde %90'ın üzerinde bir geçirgenliği olduğunu göstermiştir. Ayrıca, polimer filmi nötr ve yükseltgen halleri arasında anahtarlanırken 555 nm'de % 6.8'lik bir yüzde geçirgenlik değişimi ve 12 cm^2/C'luk bir renk etkinliği göstermiştir. Polimerin bu en az renk değişimi özelliği kendisini elektrokromik cihazlarda umut verici bir karşıt elektrot malzemesi yapmıştır. Poli(3,4-etilendioksitiyofen) (PEDOT) filmi ile karşılaştırıldığında (540 nm' de %61), **P1** ve PEDOT esaslı hazırlanan cihaz benzer optiksel davranımlar göstermiştir. Cihaz 580 nm'de %51'lik bir yüzde geçirgenlik değişimine sahiptir. Buna ek olarak, cihaz ortam şartlarında yüksek dayanıklılık, yüksek redoks ve optiksel kararlılık göstermiştir, zira 1000 anahtarlanma sonrasında dahi farklı redoks hallerine anahtarlandığında elektro-optiksel kararlılığının %88'ini korumuştur.

Anahtar Kelimeler: Elektrokromik cihaz, karşıt elektrot, en az renk değiştiren polimer, karbazol, karboran.

To my family…

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INTRODUCTION

1.1 Conjugated (Conducting) Polymers

From the beginning of human history to now, materials have played an important role on the development of societies. Owing to this reason, the ages had been named as “stone age”, “bronze age” and “iron age”. In fact, these “stone”, “bronze” and “iron” were defined in terms of the materials that were used by the societies in ancient times. Now, the question is that “which age are we in?”

For the answer the asked question, it is enough to check the materials that are used in our daily life. For example, mobile phones, printers, laptops, door knockers, kitchen equipments, toys, etc. are made by “plastics”, in other word “polymers”. Actually, these materials have attracted great attention since 1920’s by Staudinger’s definition; which was “macromolecule” (polymer) [1]. Then, first nylon was synthesized by Wallace H. Carother in 1935 [2] and therefore, “polymer age” has started by Karl Ziegler and Giulio Natta because the alpha-olefins (1-alkenes) was successfully polymerized by using a specific catalyst called Ziegler-Natta catalyst.

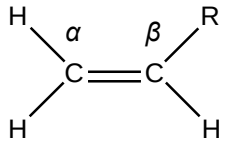


Figure 1.1 An illustration for alpha olefins (1-alkenes).

After the invention of polymers, many scientists had focused on material science and applications. As a result of this inspiration, in 1977, Alan MacDiarmid, Hideki Shirakawa and Alan Heeger had announced novel polymeric materials, "conducting (conjugated, conductive) polymers", which would have opened up a new door to science materials and applications in future. These scientists had been awarded with Nobel Prize in Chemistry in 2000 due to their pioneering studies in polymer science [3]. In fact, nowadays many scientists have focused and studied on the conducting polymers owing to their interesting properties and applications such as photovoltaic cells [4,5], organic light-emitting diodes [6,7] organic field effect transistors [8], electrochromic devices [9,10], smart windows [11], sensors [12], artificial muscles [13], and so forth. Among these applications, electrochromic devices are one of the most studied and performed fields because of interesting electro-optical behaviors of the conducting polymers under applied potentials.

1.1.1 Optical and Electronic Properties of Conducting Polymers

1.1.1.1. Band Gap Theory

Band gap energy (E_g) is the required energy of an electron to pass toward the lowest unoccupied molecular orbital (LUMO) from the highest occupied molecular orbital (HOMO). Whether any materials conducting the electricity can be defined by using E_g values of the related materials because conductor, semiconductor and insulator have different E_g values (see **Figure 1.2**).

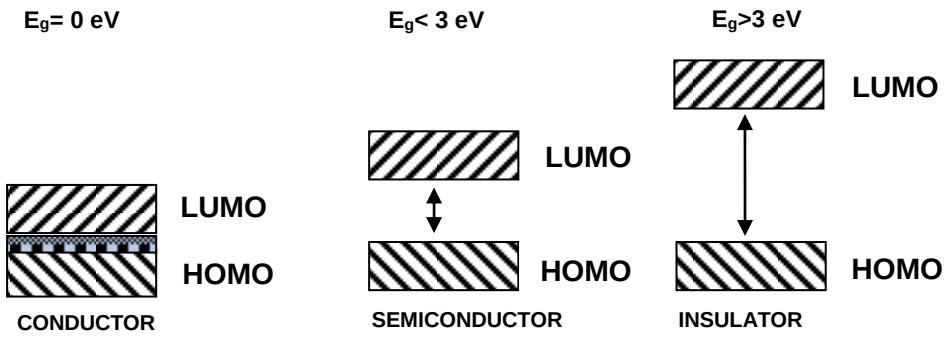


Figure 1.2 A schematic representation for band gap energy (E_g).

During the oxidation and reduction processes for an electroactive polymer, new charge carriers called polaron and bipolaron are formed on the main polymer backbone in order to create new energy levels which define the ability of conductivity (**Figure 1.3**).

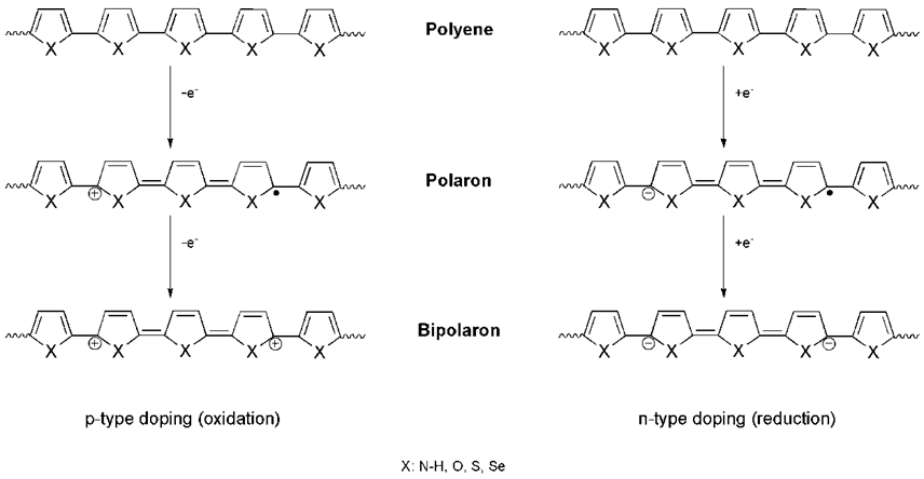


Figure 1.3 Schematic representation of the formation of polaron and bipolaron charge carriers for any polyene [16].

1.1.2 Electrochromic Polymers

Electrochromism can be defined as the reversible color change in visible, near-IR and/or IR regions under applied external potentials. The color change can be observed when the related polymer is reduced or oxidized chemically or electrochemically. In literature, there are lots of examples of the conducting polymers showing the electrochromic properties. Their colors have published at different oxidation/reduction states. Recently, most scientists have studied on missing and/or wanted colors in RGB (red-green-blue) and CMYK (cyan-magenta-yellow-key black) color pallets at different redox states. **Figure 1.4** showed some common examples of the electrochromic polymers and their colors at various redox states.

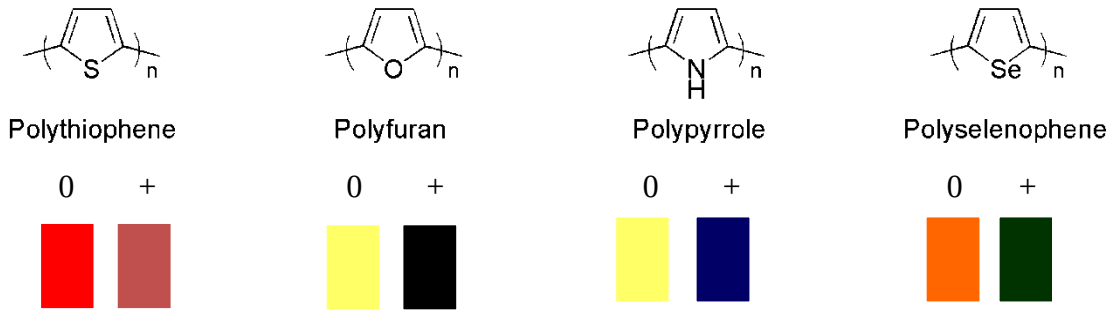


Figure 1.4 Some examples of the electrochromic polymers and their colors in their various redox states, 0: neutral state and +: oxidized state [14].

In order to investigate the electo-optical behaviours of the polymers, the corresponding polymer is coated on a conductive and transparent glass electrode called indium-tin oxide (ITO) (see **Figure 1.5**) and then the changes in optical spectra are monitored in-situ under applied potentials to perform and observe their intrinsic electrochromic properties. The related polymers may be coated electrochemically from their corresponding monomers in a suitable electrolyte solution, or their polymer films may be coated on ITO by using spray and/or spin coating techniques.

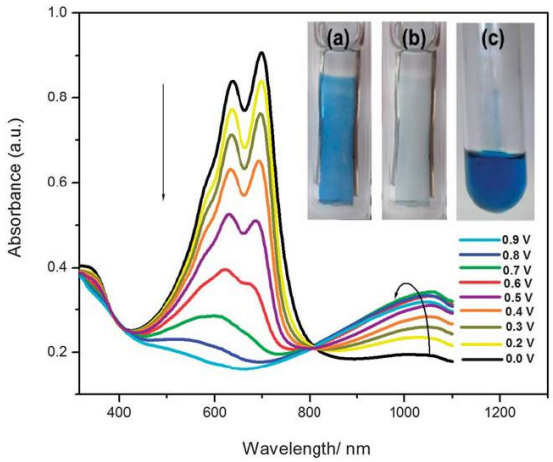


Figure 1.5 Optical absorption spectra of dialkylsubstituted poly(3,4-propylenedioxyselenophene) coated electrochemically on ITO in an electroyte solution at various applied potentials. Inset: Colors of the polymer at (a) a neutral state at 0.0 V, (b) an oxidized state at 0.9 V and (c) dissolved in dichloromethane [15].

1.1.2.1. Electrochromism

Chromism can be defined as the *color change* and the given prefix defines the related source [17]. For example, *solvato-chromism* means the color change in different type solvent medium. *Photo-chromism* means the color change when any photonic source is applied. *Electro-chromism* is the color change under external electrical current. Owing to that reason, for example, electrochromic materials have been placed in different fields such as smart mirrors, curtains, camouflages, radar systems etc. [18,19].

In literature and in our daily life, there have been lots of types of electrochromic materials but these materials are prepared based on inorganic compounds and complexes such as tungsten oxide, prussian blue, viologens etc. With the development of conducting polymers, inorganic materials have given their places to organic based polymers because the organic electrochromic materials have the following features;

- Color changes can be observed by naked eye
- Fast switching time and homogenous change
- More switchable than 10^6 times
- Stable under ambient conditions
- Non-toxic in open air
- Various color changes between its redox states

1.1.2.2. Optical Contrast

Optical contrast is the *percent transmittance change* (optical contrast, Δ%T) between colored and bleached states of the polymer film at a given wavelength. When an electroactive polymer film coated on ITO is characterized by using the spectrophotometer, its optical contrast can be discussed by using a square-wave potential method between the neutral and oxidized states (**Figure 1.6**) [20]. The percent transmittance change can be calculated by the following Equation 1.1.

$$\Delta\%T = \%T_{bleached} - \%T_{colored}$$ Equation 1.1

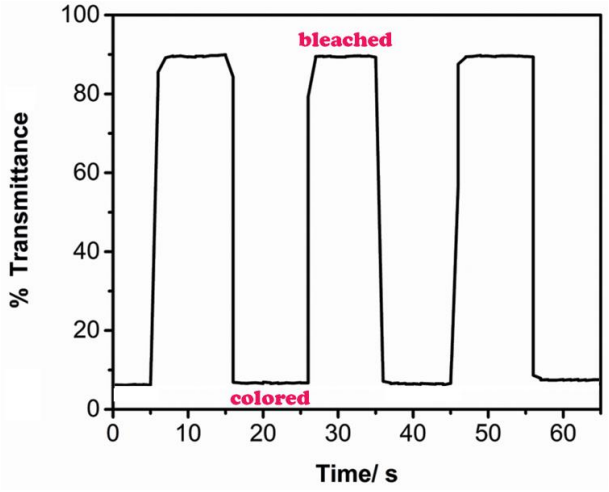


Figure 1.6 An example for the percent transmittance change (Δ%T) of any electrochromic polymer film on ITO via a square-wave potential method between its neutral and oxidized states in an electrolyte solution.

1.1.2.3. Switching Time

Switching time is the elapsed time to change the polymer's oxidized and reduced colors and vice versa. There have been some factors affecting the switching time, such as the movement ability of counter ions, the ability of diffusion of the used ionic species on the polymer backbone, and the surface morphology of the obtained polymer film. Also, 95% of the full contrast is regarded as the switching time since human eye couldn't be able to catch the last 5%.

1.1.2.4. Coloration Efficiency

Coloration efficiency (CE, η) is defined as optical density change (ΔOD) per injected and/or ejected charge density (Q_d) for an electrochromic polymer during its redox states. Equation 1.2 will be used to calculate the coloration efficiency after chronoabsorptometry experiments.

$$\eta = \Delta OD/Q_d = (T_{bleached}/T_{colored})/Q_d$$ Equation 1.2

1.1.3 Definitions for Electroanalytical Methods

Cyclic voltammetry, differential pulse voltammetry and spectroelectroanalytical methods are commonly applied techniques for the characterization of the formed conjugated polymers. The data obtained from these techniques give information about the band gap energy, the formation of charge carriers, the oxidation-reduction potentials and the stability of the polymer, etc. In order to determine these parameters, some conditions like solvent medium, supporting electrolyte, electrode, temperature and working potential range must be optimized.

1.1.3.1. Solvent Medium

At first glance, the electrochemical stability and ionic conductivity values may inform about whether the solvent is proper or not for the related electrochemical studies. First of all, the solvent should be suitable in the working range of the target monomer and its corresponding polymer [21]. For example, dichloromethane and acetonitrile are the most commonly used solvents because of their working range and dielectric constants (9 and 37, respectively). Moreover, the working potential range of acetonitrile is between -3.0 V and +3.0 V against the saturated calomel electrode (SCE). Furthermore, dichloromethane will work easily and stable above 3.0 V under ambient conditions [22]. Moreover, in terms of the dielectric constant, water is one of the best alternatives for the electrochemical studies because the dielectric constant value of water is 80. However, many electroactive compounds are not soluble in water in spite of their dielectric constants. [23,24]. The solvent list can be expanded with the common organic solvents such as dimethylformamide and dimethylsulfoxide, which are not proper for the potential above 1.0 V.

1.1.3.2. Supporting Electrolyte

Many ionizable salts and/or complexes in any solvent medium may be defined as supporting electrolyte. Like solvent choice, the mentioned electrolyte should be inactive in the applied potential range. Furthermore, the supporting electrolyte should be highly soluble in the solvent medium. For example, tetraalkylamonium salts are the widely used electrolytes because of their high solubilities and working range in organic solvents. Also, perchlorate anions (ClO_4^-) are commonly chosen electrolyte up to +1.6 V vs SCE. Moreover, tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-) salts work up to +3.0 V vs SCE [25].

1.1.3.3. Electrodes

Voltammetric studies are performed by means of using an electrochemical cell including two or three electrodes.

1.1.3.3.1. Working Electrode

Working electrode is the electrode in which an oxidation/reduction process takes place when any external potential is applied. In fact, platinum (Pt), palladium (Pd), gold (Au), silver (Ag), glassy carbon (C) and nickel (Ni) are the most known electrodes. On the other hand, indium tin oxide (ITO) electrode is widely used electrode for spectroelectrochemical studies because of its transparency. Owing to this property, electrochromic studies can be performed easily.

1.1.3.3.2. Reference Electrode

In the electrochemical cells, saturated calomel electrode (SCE), silver wire electrode (Ag), standard hydrogen electrode, and silver/silver chloride electrode (Ag/AgCl) are commonly used electrodes. Reference electrodes enable the potential between working and reference electrodes to hold stable and constant. Also, internal reference is widely used for the experiments. Ferrocene is one of the most known

internal references for the electroanalytical studies since it can be oxidized/reduced reversibly and its half wave potential is of 0.48 V vs Ag/Ag^+ in acetonitrile solution [22].

1.1.3.3.3. Counter Electrode

Counter electrode is the electrochemically inactive electrode like platinum or graphite. This electrode carries the electrons from the source to the other electrode in the electrolyte medium. Moreover, the surface area of the counter electrode should be larger than that of the working electrode to eliminate the deviations, which is additional resistance, coming from the counter electrode.

1.2 Literature Survey

1.2.1 Conjugated Polymers

After being discovered of the first type of conducting polymers, this field has got great attention of most scientists due to the unstability, insolubility and infusibility problems of the corresponding polyacetylene. Due to these deficiencies, most scientists have focused on the designing and creating of new types of monomers and their corresponding polymers, which would be called "second generation conducting polymers", such as polyfurans, polypyrroles, polythiophenes, polyanilines, polyphenylenes, poly(phenylene vinylene)s, polycarbazoles and so forth (**Figure 1.7**).

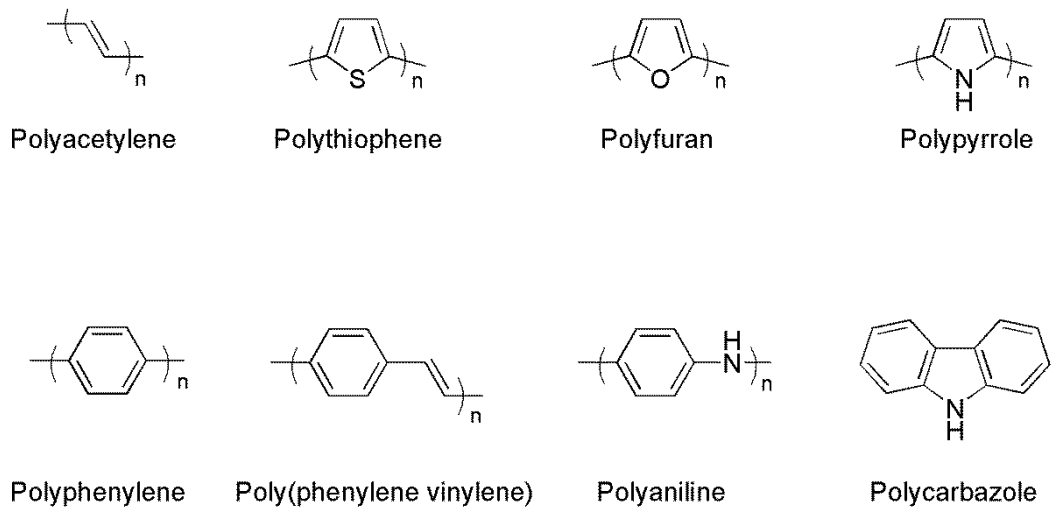


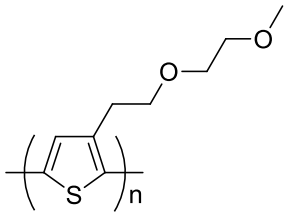
Figure 1.7 Chemical structures of some second generation type of conducting polymers.

In fact, researchers and scientists have mainly concentrated on thiophene based polymers due to their chemical, electrical, and optical features. For example, polythiophene is highly conductive polymer in its oxidized state, 500 S/cm, even under ambient conditions [26].

In time, it was believed and claimed that polythiophene should be derived to be able to get superior forms by attaching some functional groups because it has a disadvantage called as "thiophene paradox". In fact, this paradox can be summarized as the overoxidation of polymer chain during the monomer oxidation. In other words, when any potential like 2.0 V is applied to monomers to form its polymer, the corresponding polymer would be overoxidized at lower potential compared to the corresponding monomer [27,28]. In order to overcome the overoxidation and insolubility problems, thiophene ring must be modified by attaching some alkyl groups.

Poly[3-(3,6-dioxyheptyl)thiophene] (**2**) is one of the first derived conjugated polymers [29,30] (**Figure 1.8**). It was published that the polymer **2** is the Li^+ ion sensitive in the organic medium at its oxidation state. Actually, because this polymer

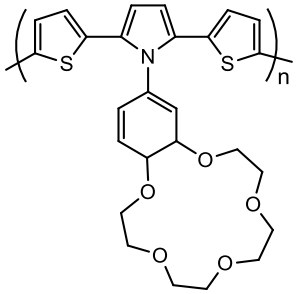
has the property of biosensor, most scientists have been inspired from the polymer **2** to synthesize different electrochemical sensors in order to sense various ions.



2

Figure 1.8 Chemical structure of the polymer **2**.

At the end of 2000s, Algi and Cihaner synthesized and characterized a novel hybrid biosensor (**3**) based on benzo-15-crown-5-ether and dithienylpyrrole units. In this study, it was explained that the corresponding polymer responsed reversibly and selectively to Li^+, Na^+, and K^+ ions [31].



3

Figure 1.9 Chemical structure of the polymer **3**.

It has been proved that the attachment of different moieties on the polymer backbone enhances the intrinsic properties; such as the fluorescence (**4** and **5**) [32], photochromism (**4-6**) [32,33] chemiluminescence (**7-9**) [34-36] etc. (**Figure 1.10**). Recently, Cihaner and Algi synthesized and characterized some derived compounds in

their studies. For example, the polymers **10**-**12** [37-39] exhibited the multichromic properties at their different oxidation states (**Figures 1.11** and **1.12**).

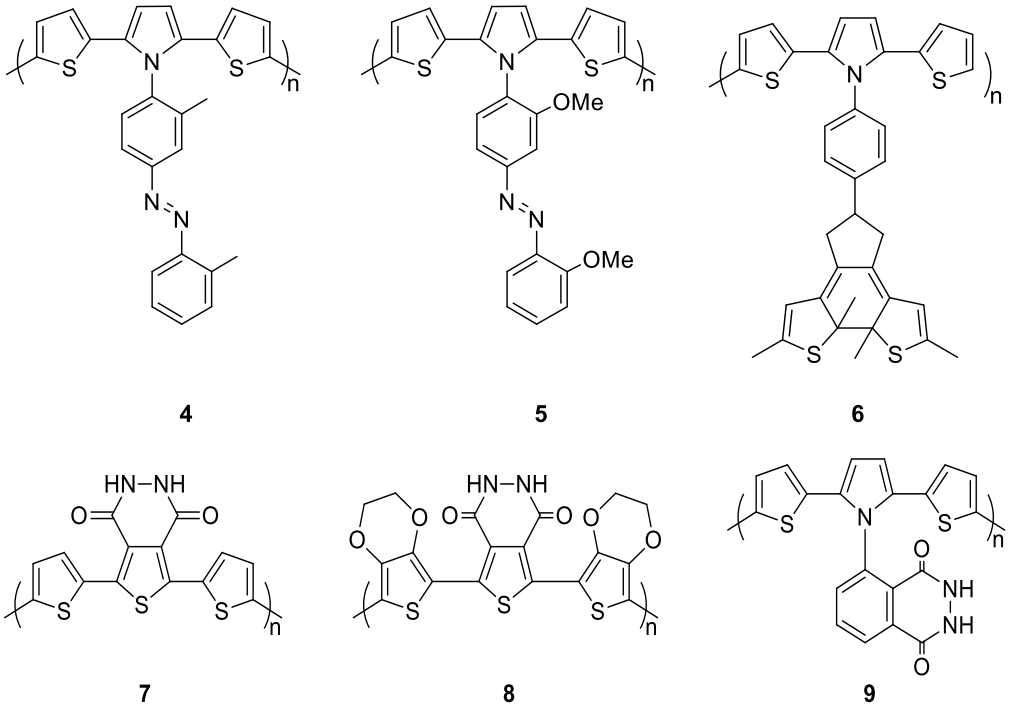


Figure 1.10 Chemical structures of functional polymers **4**-**9**.

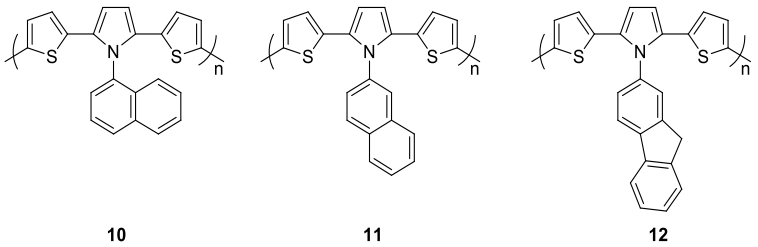


Figure 1.11 Chemical structures of the polymers **10**-**12**.

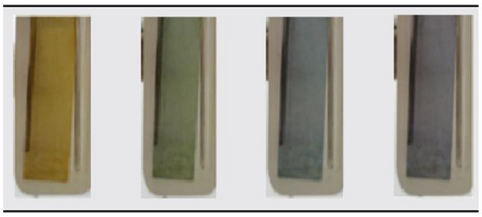


Figure 1.12 The colors of the polymer **12** upon moving from from neutral to oxidized states.

After the invention of fullerene (C_{60}) [40] and carbon nanotubes [41], nanotechnology and materials sciences have started to get great attention on these fields and related studies. For instance, novel fullerene C_{60} based trimeric monomers had been designed and synthesized, and their corresponding polymers had been characterized. According to related studies, they reported that the polymer **13** [42] had a low band gap of 0.7 eV. On the other hand, the photochemical stability of the polymer **14** [43] made it a promising candidate for solar cells (**Figure 1.13**).

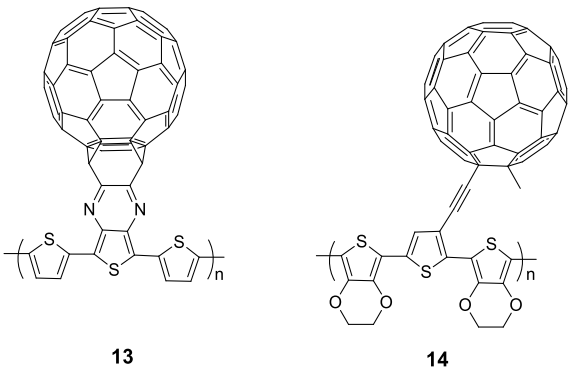


Figure 1.13 Chemical structures of the polymers **13** and **14**.

1.2.2 Carboranes

Boron (B) is the first element in group 3A. When a compound has boron atom, it can show some superior properties. One of the most popular examples is the carboranes, $C_2B_{10}H_{12}$ [44,45]. They have three different isomers in terms of attaching positions,

which are 1,2; *ortho* (*o*-), 1,7; *meta* (*m*-) or 1,12; *para* (*p*-) (**Figure 1.14**). Carboranes playing an important role on "Boron World" have lots of applications such as boron cluster in medicine, anti-crown reagent, metal ion extraction, homogenous catalysis, liquid crystal and self-assembly etc.

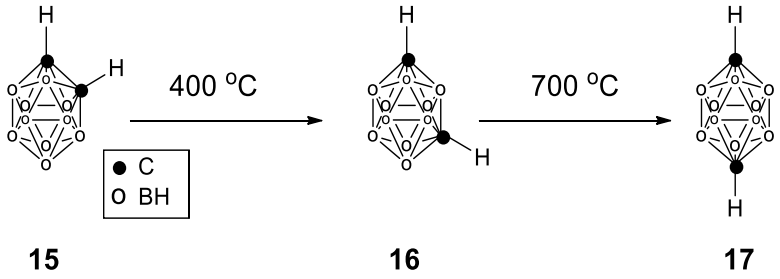


Figure 1.14 *o*-carborane (**15**), *m*-carborane (**16**) and *p*-carborane (**17**) isomers.

In 1963, the synthesis of the first o-carborane had been published by coupling acetylene with decaborane in acetonitrile medium. According to this study, *o*-carborane could be converted to their isomers at different temperatures, *m*-carborane at 400-500 ^{o}C at inert atmosphere and *p*-carborane at 600-700 ^{o}C (**Figure 1.15**) [46].

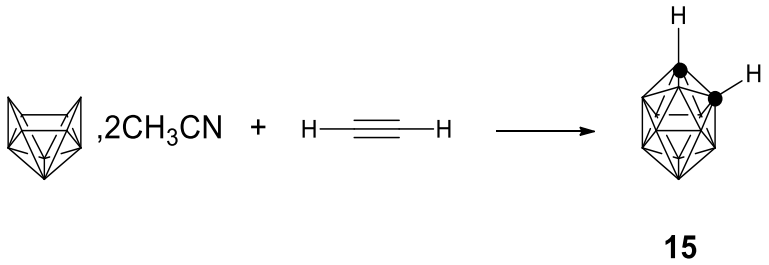


Figure 1.15 A synthetic route for the synthesis of *o*-carborane by coupling acetylene with decaborane.

1.2.2.1. Carborane Based Polymeric Materials

Carboranes can be used to enhance thermo-mechanic, thermo-optic and/or thermo-electric properties for the related polymers because of their thermal stabilities. In literature, there are some examples of carborane containing polymers where the carborane cages were used as side groups (**18-20**) or one of the main parts (**21-23**) in the polymeric backbones (**Figure 1.16**) [47-55]. Compared to the polymers containing carboranes as side groups, the polymers bearing carborane cages in the main polymer backbones exhibited higher thermal stabilities.

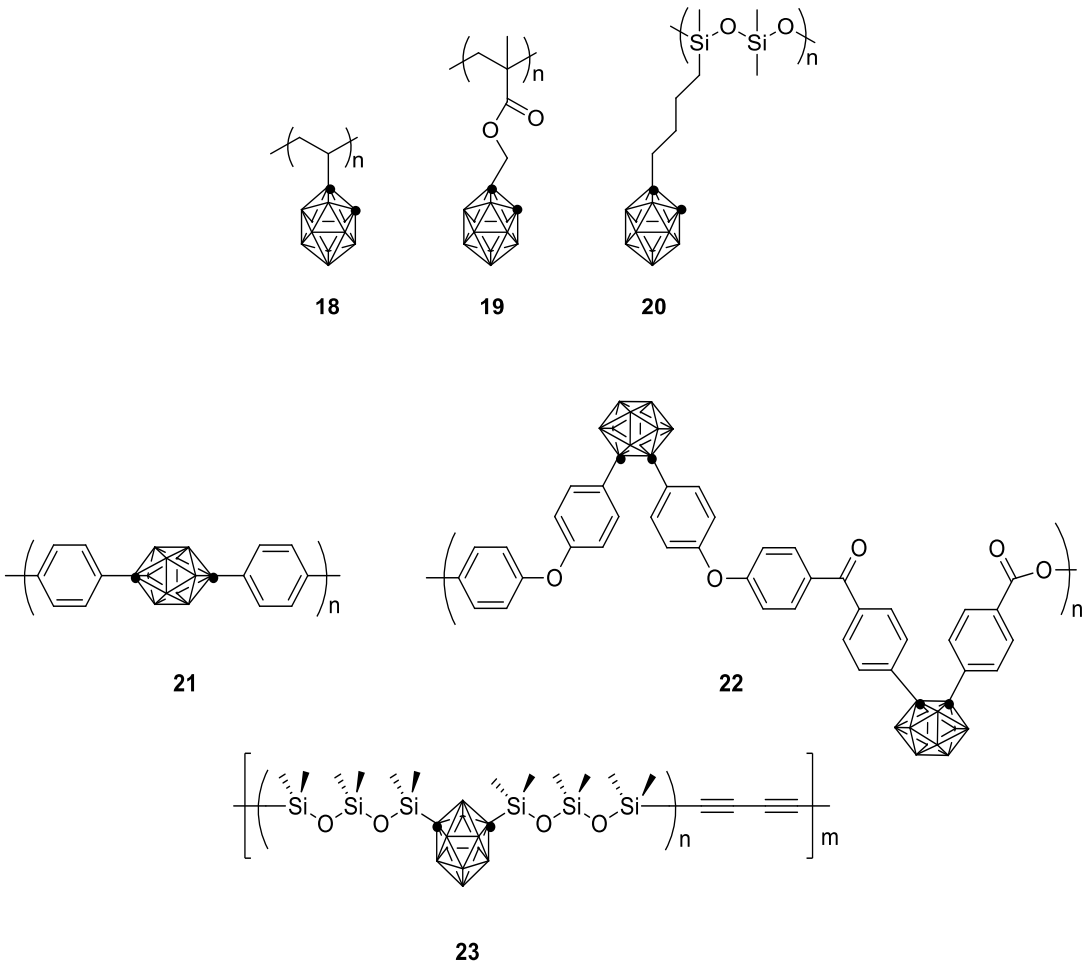


Figure 1.16 Some examples for carborane containing polymers.

1.2.2.2. Carborane Based Conjugated Polymeric Materials

The properties of both “conjugated polymers” and “carboranes” can be melted in the same pot and therefore, this approach can lead to a new member of functional electroactive polymers. As an example, Teixidor et al. reported an organometallic carborane complex (**24**), $Cs[Co(C_2B_9H_{11})_2]^-$, for the conducting polymers as a dopant and after this study novel polypyrrole (**PPy**) including carborane units were formed. When compared to the parent polypyrrole **PPy** including the dopants of Cl^- and NO_3^-, the polymer **25** having carborane dopants showed that it was highly stable against to over-oxidation up to 1.25 V (**Figure 1.17**) [56,57].

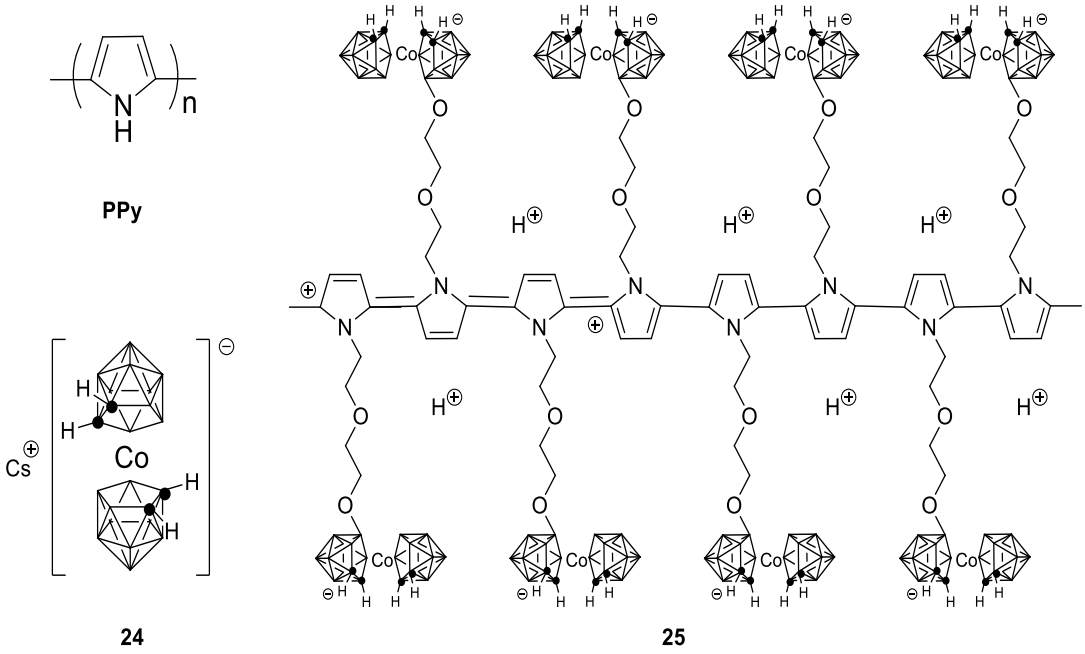


Figure 1.17 A schematic representation for PPy and PPy including carborane units.

In 2003, it was the first time that carborane units were attached to the conjugated polymer backbone via covalent bonds (**Figure 1.18**). According to the pioneering study reported by Fabre et al., the pyrrole (**26**) substituted on 3-position was electrochemically polymerized (**27**) [58]. The polymer **27** lost 10% of its electro-activity with respect to

that of the parent **PPy** (40%), because the polymer **27** was very stable under applied higher oxidation potential (1.5 V). This electrochemical stability can be explained by the hydrophobic and electron-withdrawing properties of carborane units. Therefore, the nucleophile attacks owing to OH^- ions were diminished/prevented by these cages. For this reason, the carborane based polymers have been attracted great attention in order to create new energy storage devices.

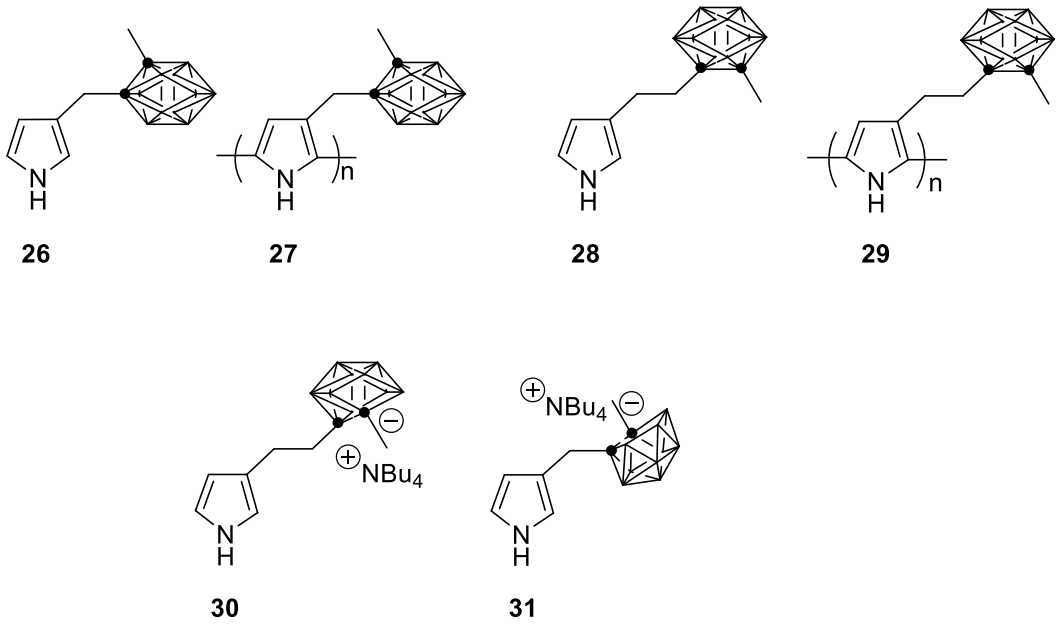


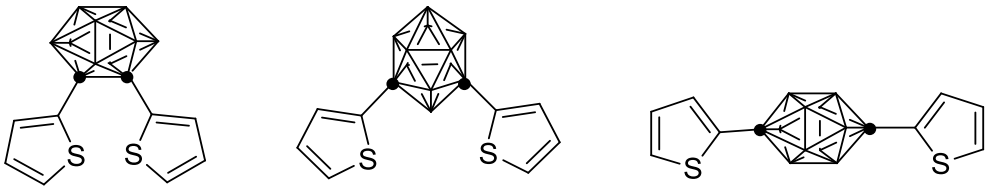
Figure 1.18 Some examples for carborane based pyrrole derivatives and their corresponding polymers.

After this pioneering study, it was reported successfully designed and characterized carborane based 3-substituted pyrroles bearing various alkyl chains between pyrrole and carborane units (**Figure 1.18**). In addition, some anionic carborane derivatives (**30** and **31**) were reported in the same study. By synthesizing of these new derivatives, the length of alkyl chains and anion effects were discussed [59].

On the other hand, while the monomers **30** and **31** could not be polymerized, the monomers **26** and **28** were polymerized successfully. In fact, it was reported that the polymer **29** exhibited the best electroactivity and conductivity when compared to its

shorter chain length. Furthermore, when **PPy** and **29** were compared to each other in terms of thermal and electrochemical stabilities, the polymer **29** exhibited superior properties. For example, while **PPy** could not be stable and robust up to 2.16 V vs. Ag/Ag^+ at which it would be over oxidized, the polymer **29** showed no appreciable change in electrical and optical properties. Moreover, while the polymer, **29** lost its only 15% of its mass at 700 ^oC, this value is 70% for **PPy.**

By the inspiration of the studies on **PPy** and carborane cages, the similar approach was applied to thiophene; therefore, thiophene and carborane cages were combined under the same umbrella. As a result, a family of trimeric monomers (**32-34**) bearing *o*-, *m*-, and *p*-carborane cages with thiophene rings were designed, synthesized and then polymerized successfully [59].



32 **33** **34**

Figure 1.19 Chemical structures of trimeric monomers (**32-34**) bearing carborane cages and thiophene units.

The properties of the corresponding polymers of the trimeric monomers (**32-34**) were studied systematically and the results showed that the polymers were more stable than their polythiophene analogue (**PTh**). Also, the decomposed amounts of mass are 10% and 80% for the poylmer **35** and **PTh**, respectively (**Figure 1.20**).

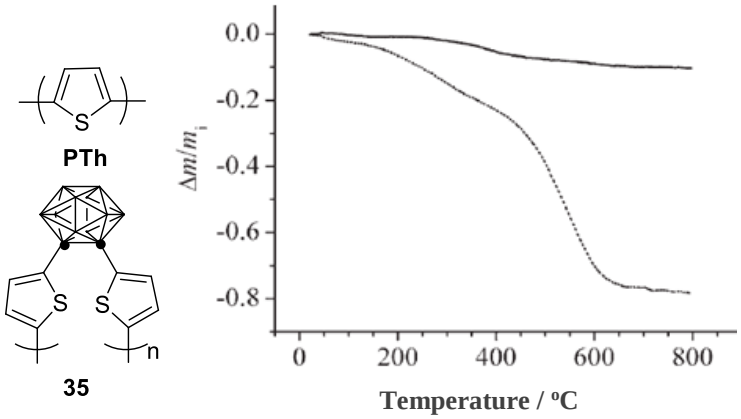
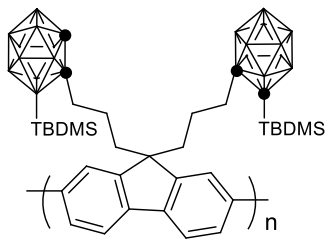


Figure 1.20 TGA results for both **35** (line) and **PTh** (dashed line) [59].

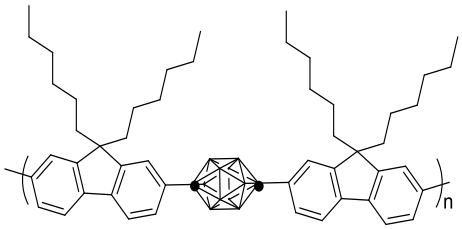
9,9-disubstituted polyfluorenes are the suitable materials that emit blue light for optoelectronic applications. They can be derived from 9-position by various length of alkyl chains in order to tune quantum yield and to get soluble and processable polymers. Unfortunately, these attached alkyl groups can result in thermal and electronic instabilities during the annealing process of polymers. In order to overcome this problem, Peterson et al. reported novel carborane based conjugated polymers in 2009 to enhance the performance of light emitting diodes [60]. For example, the polymer **36** had high thermal and color stabilities owing to the presence of carborane units as pendant group on the polymer backbone (**Figure 1.21**). When compared to its polyfluorene analogue shifting its emission from blue to green at high temperature, the polymer **36** did not show any color change in emission after 3 hours at 160 °C. Actually, it can be explained by the presence of carborane units.



36

Figure 1.21 Chemical structure of the polymer **36**. TBDMS: *tert*-Butyldimethylsilanyl.

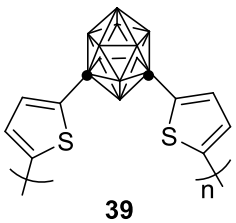
Also, Peterson et al. reported the effect of the presence of carborane cages as a main part of polymer backbone instead of a pendant group (**38**) (**Figure 1.22**) [61]. They reported similar results reported in their previous work [60]. The presence of carborane cage in the polymer backbone resulted in superior color, thermal and chemical properties under ambient conditions when compared to its dialkyl substituted polyfluorene analogue.



38

Figure 1.22 Chemical structure of the polymer **38**.

Recently, Cihaner and his colleague [62] reported the electrochromic properties of a trimeric monomer (**33**) consisting of two thiophene units and one m-carborane cages synthesized previously in literature (**Figure 1.23**) [59]. They reported successfully the first electrochromic device application of a conjugated polymer containing carborane cage. The corresponding polymer **39** exhibited an ambipolar character and has an optical band gap of 1.95 eV (**Figure 1.23**). Also, the polymer film showed multicolor behaviors under applied external potentials: orange, yellowish-green, faded-green, greenish-blue, and blue upon moving from neutral state to oxidized state (**Figure 1.24**).



39

Figure 1.23 Chemical structure of the polymer **39**.

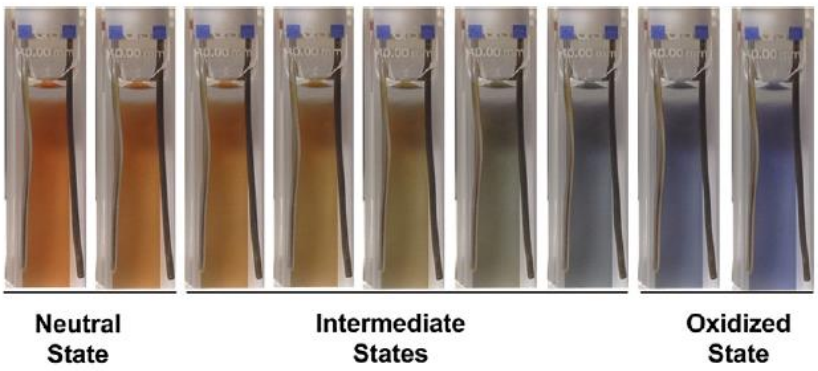


Figure 1.24 Colors of the polymer film **39** on ITO between its various redox states on ITO electrode in 0.1 M TBAH/CH_2Cl_2 between -0.20 and 1.20 V vs Ag-wire [61].

Also, the same group reported new copolymers of **33** with EDOT units [63]. When compared to their homopolymers **39** and PEDOT, the corresponding copolymer films expectedly exhibited different electro-optical properties. The copolymer films have electrochromic properties and the band gaps (from 1.69 to 1.82 eV) of the films can be tuned by changing the feed ratio of the starting co-monomers (**Figure 1.25**).

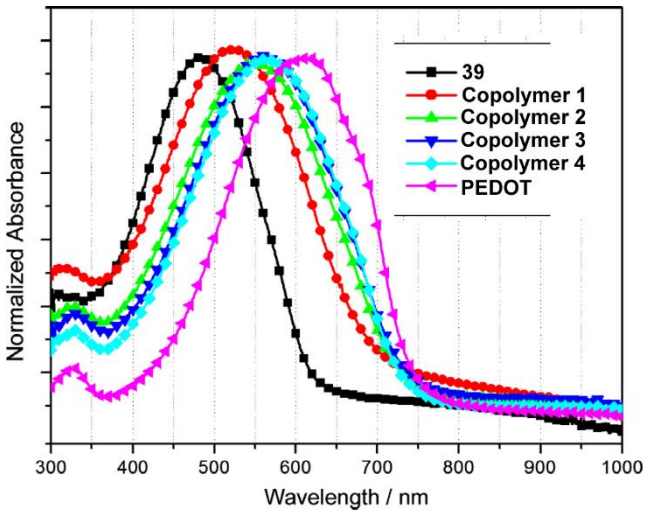
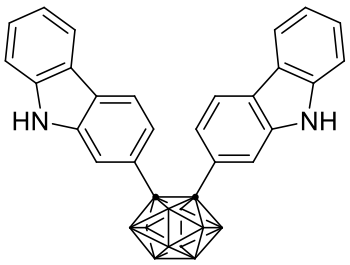


Figure 1.25 Absorption spectra of the neutral state copolymers on ITO electrode [63].

Aim of the Study

In this study, carbazole and carborane units will be tried to combine under the same roof (**Figure 1.26**). The corresponding trimeric monomer called 2-(2-(9H-carbazol-7-yl)carborane)-9H-carbazole (**1**) will be polymerized electrochemically. The electrochemical and optical properties of the polymer (**P1**) will be investigated by using electrochemical methods and spectroscopic techniques. In order to investigate the electro-optical properties, the polymer **P1** will be coated on ITO and spectral change will be monitored in situ under applied external potentials. After electrochemical stability tests under ambient conditions, the polymer **P1** film will be used as a counter electrode in electrochromic devices. Finally, electro-optical stability test will be performed for the device by using a square wave potential method between the related redox states.



1

Figure 1.26 Chemical structure of the monomer **1**.

CHAPTER 2

MATERIALS AND METHODS

2.1 Materials

All chemicals were purchased from Sigma-Aldrich Chemical and used as received unless otherwise noted. For electrochemical and chemical experiments, dichloromethane and toluene were freshly distilled over CaH_2 under N_2 atmosphere.

2.2 General Methods

Photographs of the polymer films were taken using a Nikon (D600) digital camera. Colorimetric measurements were recorded on Specord S600 (standard illuminator D65, field of width 10^o observer) and color space was given by the International Commission of Illumination with luminance (L), hue (a), and intensity (b). Platinum cobalt DIN ISO 621, iodine DIN EN 1557, and Gardner DIN ISO 6430 are the references of colorimetric measurements. The polymer thicknesses were measured by using Horiba AUTO Spectroscopic Ellipsometer.

2.3 Electroanalytical Studies

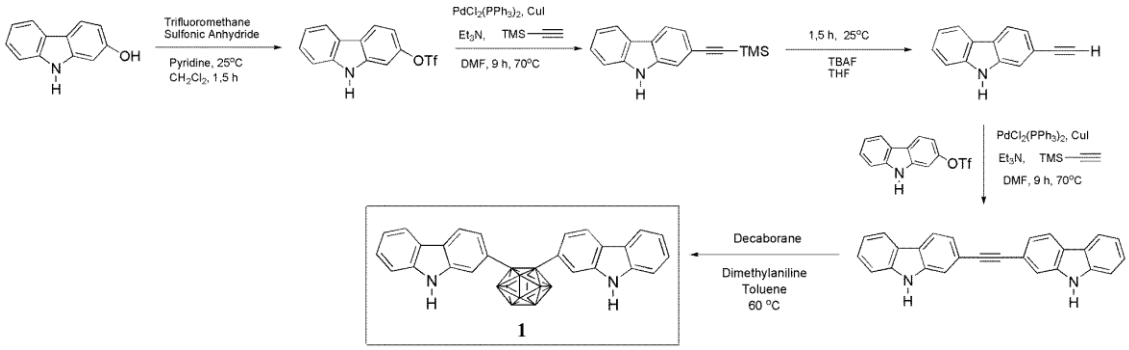
Cyclic voltammetry and electrolysis experiments were performed by using a Gamry PCI4/300 and Gamry Reference 600 potentiostat–galvanostat. The electro-optical spectra were monitored on a Specord S600 Spectrometer. The optoelectrochemical spectra of the films were recorded in-situ under applied different potentials. Also, a square wave potential method was used to investigate the ability of switching of the polymer film between its neutral and doped states. Tetrabutylammonium

hexafluorophosphate (TBAH) was used as an electrolyte. Redox behaviour and polymerization were performed in an electrolyte solution of 0.1 M TBAH dissolved in dichloromethane. Electrochemical and optical properties of the polymers were also studied in CH_2Cl_2 containing 0.1 M TBAH. In three-electrode system, a platinum disc (0.03 cm^2) and a platinum wire electrode were used as working and counter electrodes, respectively. A Ag/AgCl electrode in 3 M NaCl(aq) solution was used as a reference electrode calibrated externally using 0.53 mM solution of ferrocene/ferrocenium couple in 0.1 M TBAH/CH_2Cl_2 solution. The oxidation onset potential of ferrocene was found as 0.54 V vs Ag/AgCl. Electrochemically obtained polymer films were synthesized both by repetitive cycling and constant potential electrolysis. After electropolymerization, the polymer coated working electrode was washed with CH_2Cl_2 to remove the unreacted monomers and oligomeric species. Then, the polymer film was switched in several times between its redox states to get repeatable results in electrochemical and optical studies. Optical properties were investigated in situ by using an indium-tin oxide (ITO, Delta. Tech. 8–12 Ω, 0.7 x 5.0 cm^2) electrode as a working electrode in a UV cuvette. A platinum wire and a Ag wire were used as a counter electrode and a pseudo-reference electrode, respectively.

2.4 Synthesis of Chemicals

2-(2-(9H-carbazol-7-yl)ethynyl)-9H-carbazole and the monomer **1** have been synthesized according to the previous studies [61,64] (**Scheme 2.1**). The final compound was obtained from the study of Aykut Yoldaş's Master Thesis [63].

2.4.1 Synthesis of 2-(2-(9H-carbazol-7-yl)carborane)-9H-carbazole (1)



Scheme 2.1 A synthetic route for the monomer **1** [63].

2.5 Electrochromic Device Fabrication

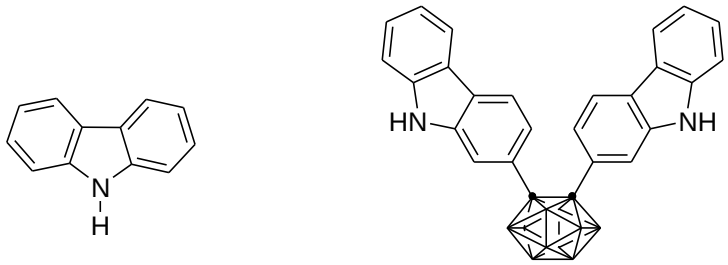
In order to construct an electrochromic device, two electrodes, ITO, should be coated by the corresponding polymer (**P1**) of the monomer **1** and PEDOT. This process has been performed via coulometry in TBAH/CH_2Cl_2 electrolyte/solvent couple. After being coated, these two electrodes have been adhered to each other by using a gel electrolyte, which has ability of conductivity and adhesive. To reach the target gel, 3: 70: 7: 20 (weight percentage) TBAH/ acetonitrile / poly(methylmetacrylate) / propylene carbonate have been used [65]. After poly(methylmetacrylate) was added in propylene carbonate, TBAH/acetonitrile mixture has been added to the initial mixture. Finally, the faces of coated electrodes have been adhered by using the gel electrolyte and left on a safety place to dry well.

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 Optical and Electrochemical Properties of Monomer 1

In order to understand the effect of the combination of carbazole units with carborane unit on the optical and electrochemical properties, the corresponding monomer **1** was compared to its parent monomer carbazole (**Scheme 3.1**).



Carbazole **1**

Scheme 3. 1 Chemical structures of carbazole and the monomer **1**.

As shown in **Figure 3.1(a)**, the absorption band at 292 nm observed for carbazole, as expected, shifted to a longer and broad wavelength for the monomer **1** (300 nm) due to its more electron rich nature.

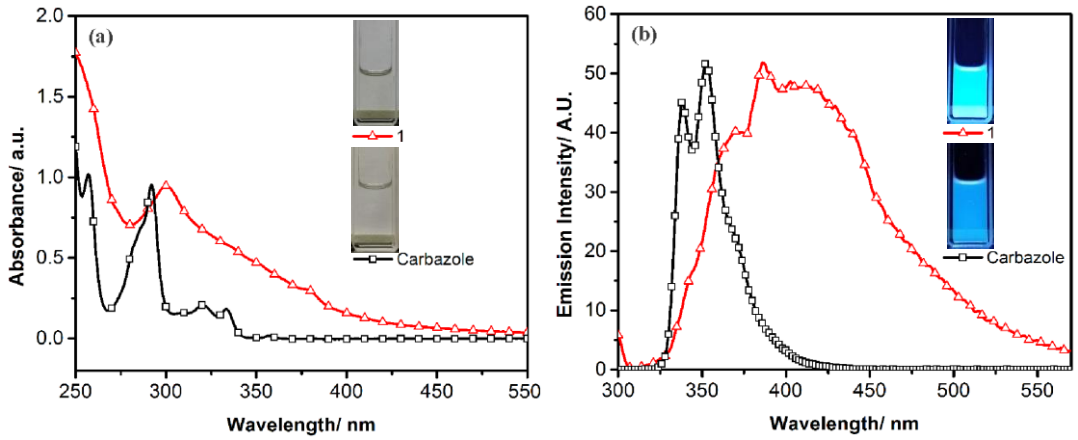


Figure 3.1 (a) Absorption and (b) emission spectra of carbazole (λ_{exc}= 290 nm) and the monomer **1** (λ_{exc}= 290 nm) in toluene.

On the other hand, both compounds carbazole and **1** emitted blue light when they were excited at 290 nm in spite of their various fluorescence spectra (**Figure 3.1(b)**). The emission spectrum of carbazole was observed in a narrow range of 320-425 nm, whereas the monomer **1** represented an emission in a broad range of 320-575 nm.

Also, the electrochemical properties of the compounds were studied by using cyclic voltammetry in an electrolyte solution of 0.1 M TBAH dissolved in CH_2Cl_2. As shown in **Figure 3.2**, unexpectedly, the maximum oxidation of the trimeric unit (**1**, beyond 1.6 V) has more positive potential when compared to carbazole (1.35 V), which can be due to the incompatibility among the HOMO and LUMO energy levels of carbazole and carborane units when they were combined under the same roof to get the monomer **1**. On the other hand, keep in mind that the monomer **1** started to oxidize easily before carbazole, which represented an interaction among the enegy levels of the parent units (carbazole and carborane) and the monomer **1** has one irreversible oxidation peak, which is responsible from the electropolymerization to get an electroactive film on the surface of the working electrode. In addition, there is no any reduction peak for the monomer **1** when the cathodic scan was performed between 0.0 V and -2.0 V.

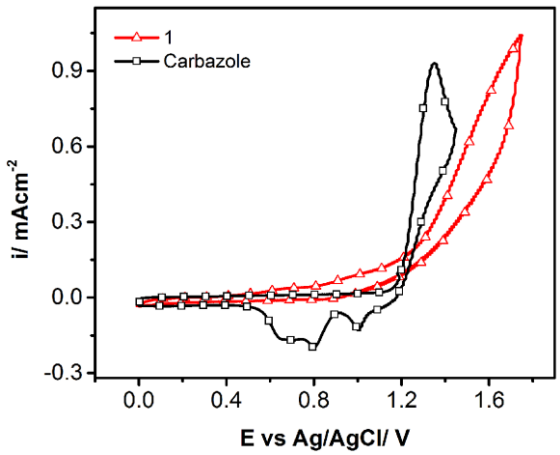
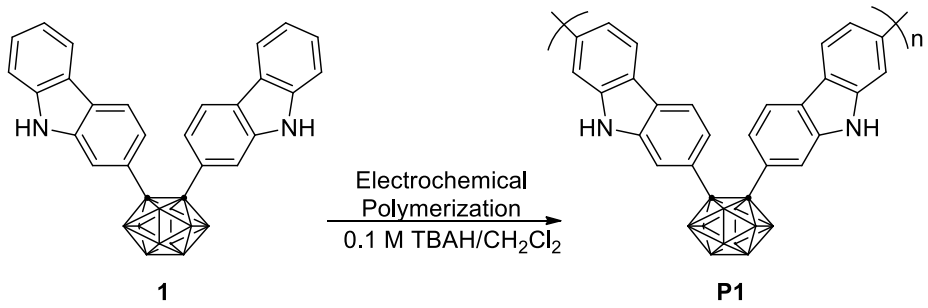


Figure 3.2 Cyclic voltammograms of the monomer **1** and carbazole in an electrolyte solution of 0.1 M TBAH/CH_2Cl_2 at a scan rate of 100 mV/s.

As seen in **Figure 3.3**, an electroactive polymer film can be formed on a Pt working electrode via repetive cyclic voltammetry between 0.4 V and 1.7 V at a scan rate of 100 mV/s (see **Scheme 3.2**). After first cycle, a new oxidation/reduction redox couple started to appear between 0.6 V and 1.3 V and the intensity of this redox couple increased systematically after each successive cycle. It can be easily concluded that an electroactive polymer film called **P1** was formed on the electrode surface potentiodynamically and its film thickness can be increased as a function of scan numbers.



Scheme 3.2 Chemical structures of the monomer **1** and its polymer **P1** after getting electropolymerization.

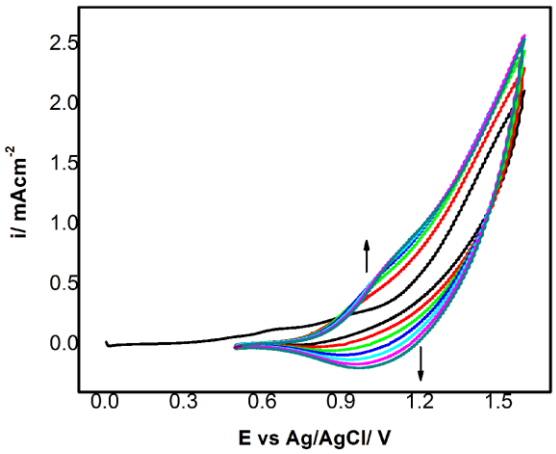


Figure 3.3 Electropolymerization of 0.01 M of the monomer **1** on a Pt electrode in an electrolyte solution of 0.1 M TBAH/CH_2Cl_2 at a scan rate of 100 mV/s between 0.0 V and 1.7 V by using repetitive cyclic voltammetry (11 cycles).

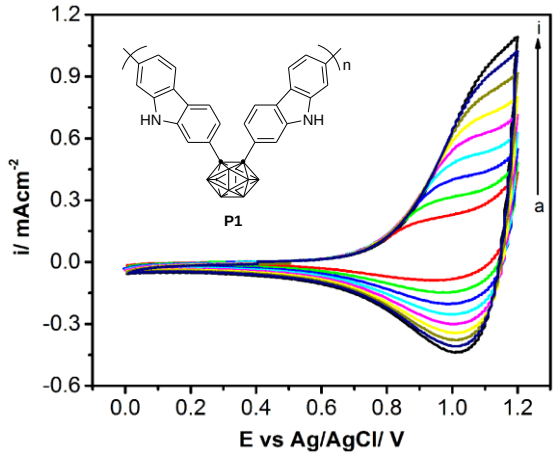


Figure 3.4 Cyclic voltammograms of the polymer **P1** film on the Pt electrode in a monomer free electrolyte solution of 0.1 M TBAH/CH_2Cl_2 between 0.0 V and 1.2 V at different scan rates between 40 mV/s and 200 mV/s with 20 mV/s increments (mV/s): (a) 40; (b) 60; (c) 80; (d) 100; (e) 120; (f) 140; (g) 160; (h) 180; (i) 200.

In order to investigate the electrochemical properties of the polymer **P1** film, the polymer film coated on the Pt electrode by cyclic voltammetry was washed with CH_2Cl_2 to remove unreacted monomers and oligomeric species. The study was performed in a monomer free electrolyte solution containing 0.1 M TBAH dissolved in CH_2Cl_2 solvent. The **P1** film has a reversible redox couple with a half wave potential of 1.05 V during anodic scan (**Figure 3.4**). The name of this process is p-doping and the intensity of the couple increased as a function of scan rate. Also, the peak current intensity increased linearly as a function of scan rate (**Figure 3.5**), which confirmed that the redox process is non-diffusional and the film was coated firmly on the electrode surface.

The amount of charge and discharge values at different scan rates were determined by measuring the area under the redox couple peaks. As shown in **Figure 3.6**, the polymer **P1** film exhibited the similar amount of charge and discharge values, which confirmed that the rate of diffusion of the ions in doping/dedoping (charge/discharge) processes in the polymer film are as fast as the electron transfer occuring between the polymer **P1** and the working electrode surface even at high scan rates.

Stability is one of the most important parameters for electroactive polymers for their application in industrial areas. The polymer **P1** has high electrochemical stability under ambient conditions; for example, 73% of its electroactivity remains after one thousand cycles (**Figure 3.7**).

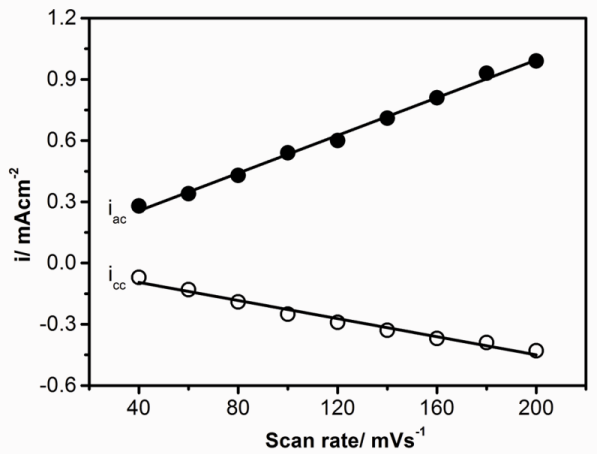


Figure 3.5 The relationship of anodic (i_{ac}) and cathodic (i_{cc}) current peaks as a function of scan rates for the neutral and oxidized **P1** films on the Pt electrode in 0.1 M TBAH/CH_2Cl_2 electrolyte solution vs Ag/AgCl reference electrode.

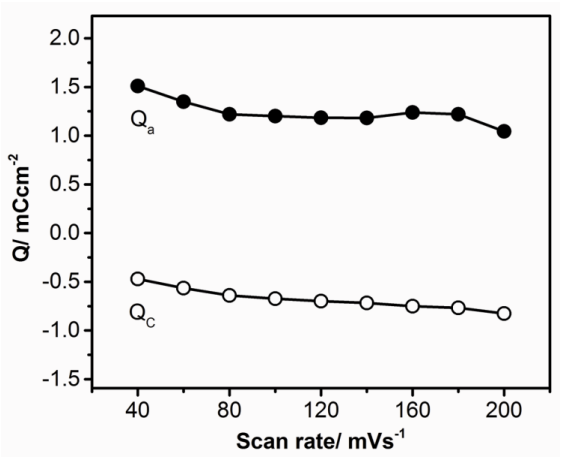


Figure 3.6 Relationship of charge (Q_a) and discharge (Q_c) values as a function of scan rate between 0.0 V and 1.2 V for the **P1** film in 0.1 M TBAH/CH_2Cl_2 electrolyte solution vs Ag/AgCl reference electrode.

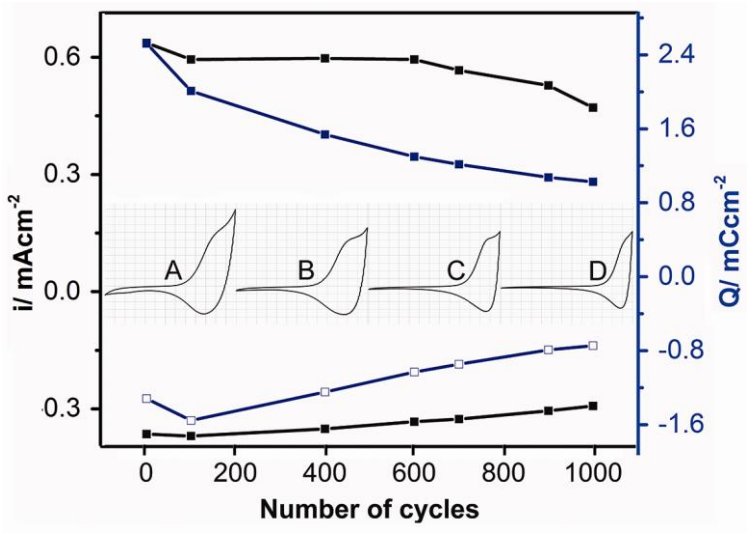


Figure 3.7 Optical stability of **P1** under external potentials at 0.0 V and 1.2 V with 10 s intervals. A: 1st cycle, B:100th cycle, C:500th cycle and D:1000th cycle.

3.2 Spectroelectrochemistry of the Polymer P1

In order to investigate the electro-optical properties of the polymer **P1**, the corresponding polymer was obtained via constant potential electrolysis at 1.7 V vs Ag wire in an electrolyte solution of 0.1 M TBAH/CH_2Cl_2. After electropolymerization, the **P1** film coated on ITO electrode was washed with CH_2Cl_2 and put into a monomer free electrolyte solution. The film was break in by cycling between 0.0 V and 1.2 V to get repeatable results for optical studies.

Then, the film was tried to neutralize fully at an applied potential of 0.0 V. As shown in **Figure 3.8**, the **P1** film has maximum wavelength at 307 nm with a shoulder at 340 nm attributed to the π- π* transition band. Also, the polymer film nearly has no absorption band after 450 nm, which confirmed the transparent state of the film in its neutral state. It is well-known that the human naked eye is very sensitive to the visible region between 400 nm and 700 nm [66].

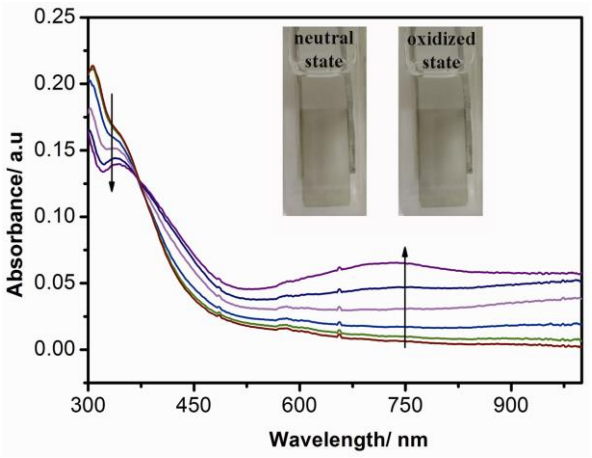


Figure 3.8 Absorption spectra of the **P1** films (58 nm) on ITO in 0.1 M TBAH/acetonitrile at various applied potentials between 0.0 V and 1.2 V vs Ag wire. Inset: Colors of the polymer **P1** on ITO at various redox states.

Based on the cyclic voltammogram of the film given in **Figure 3.8**, the polymer film was oxidized step by step from 0.0 V to 1.2 V at a scan rate of 40 mV/s. During oxidation, the intensity of the π- π* transition band started to decrease with a concomitant increase beyond 525 nm attributed to the formation of charge carriers. Upon further oxidation, the π-π* transition band lost its intensity and the band responsible from charge carriers received a maximum intensity level. During p-doping process, the film preserved its transparency and no appreciable change in polymer film color was observed. The observed La*b* values are 98, -0.68, 3.31 for the neutral **P1** film and 95, -2.17, 3.13 for the oxidized **P1** film (58 nm), respectively (**Figure 3.8, inset**).

In other words, the polymer film was not only electroactive but also transparent in different redox states. This behavior can also be confirmed by La*b* values measured at different potentials. As shown in **Figure 3.9**, the L values of the film retained nearly the same as a function of applied potential.

It is well-known that the intensity of the color depends on the thickness of the polymer film. Therefore, the **P1** films with different polymer thicknesses were coated

on ITO electrode with various amounts of the charge. As shown in **Figure 3.10**, the intensity of the π-π* transition band increased as a function of film thicknesses, whereas there is somewhat change in the intensity of the absorbance beyond 400 nm. Based on this observation, it can be easily concluded that the electroactive polymer film is transmissive even at high polymer film thicknesses. The coloration efficiency was found to be as 12 cm^2/C at 555 nm, at which human eye is very sensitive.

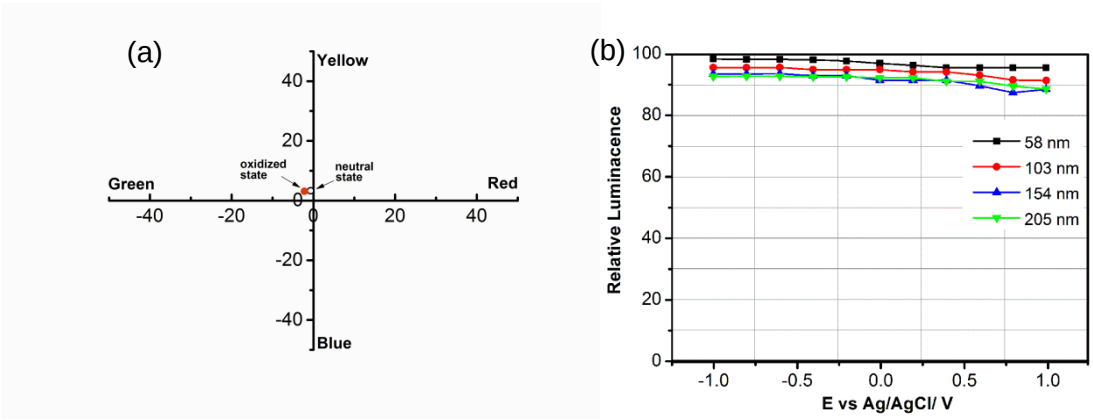


Figure 3.9 (a) CIE 1976 a*b* values for **P1** at its neutral and oxidized states. (b) Relative luminance as a function of increasing applied potential for **P1** film.

Table 3.1 L, a*, b* values for the polymer **P1** (58 nm) at different applied potentials.

E (V)	L	a*	b*
0.0	98.4	-0.68	3.31
0.1	98.4	-0.67	3.27
0.2	98.4	-0.68	3.29
0.4	98.2	-0.75	3.27
0.6	97.8	-0.95	3.37
0.8	97.1	-1.38	3.86
1.0	96.4	-1.81	3.81
1.2	95.6	-2.17	3.13

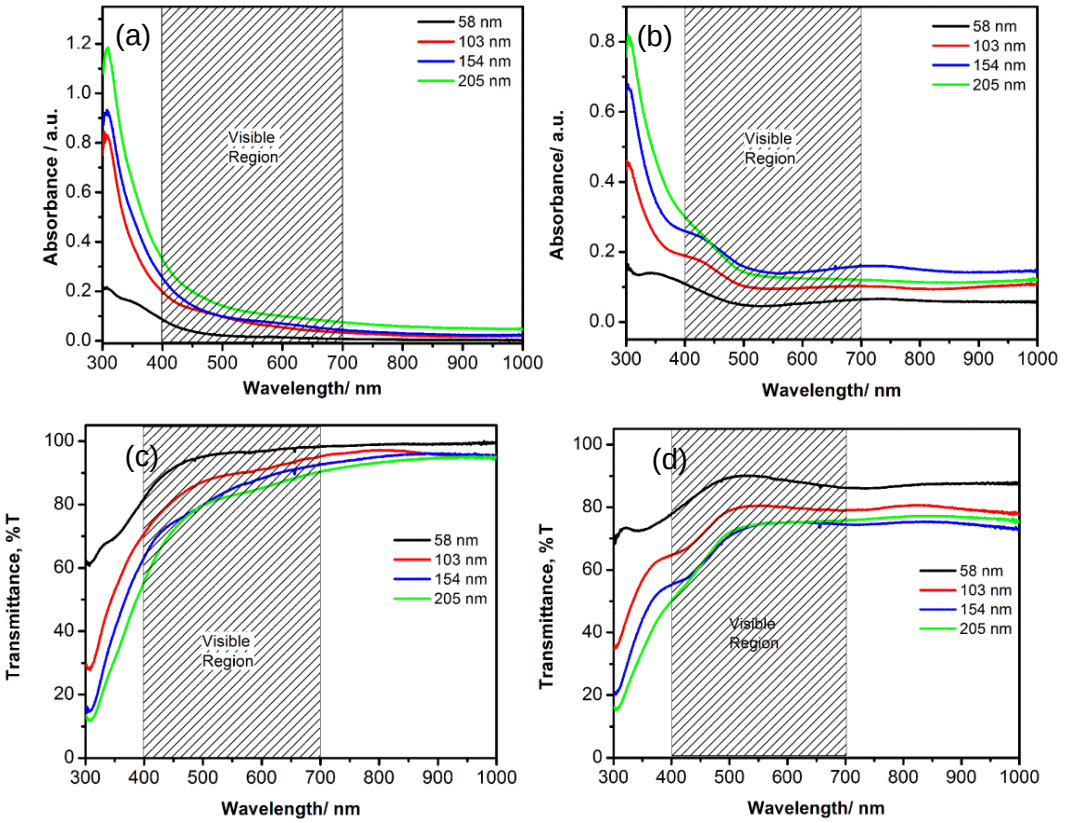


Figure 3.10 Absorption spectra of the neutral **P1** films on ITO electrode coated with various amount of charges in 0.1 M TBAH/acetonitrile.

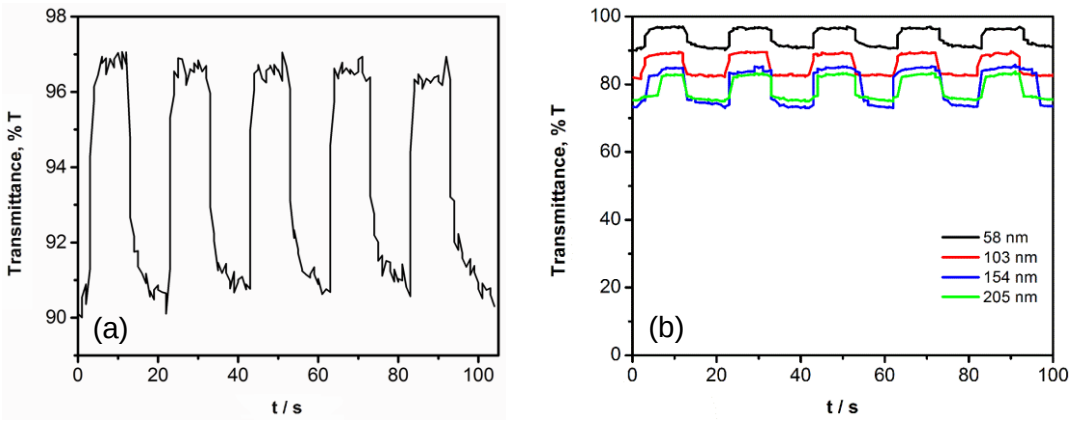


Figure 3.11 Chronoabsorptometry experiments for the **P1** film (58 nm) at 306 nm and on ITO in 0.1 M TBAH/CH_2Cl_2 while the polymer film was switched between 0.0 V and 1.2 V vs Ag wire.

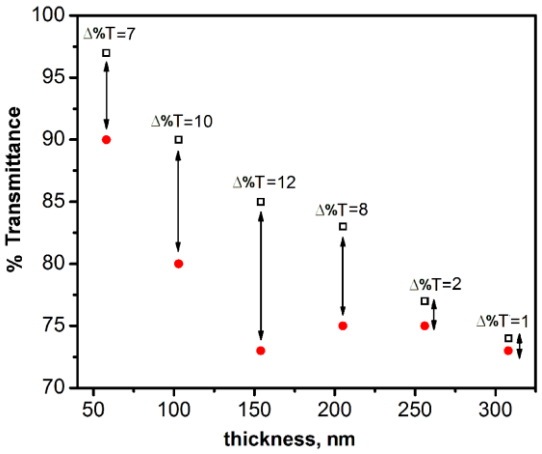
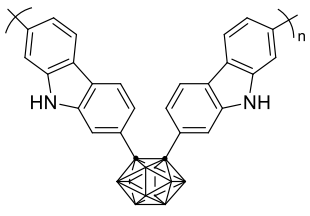
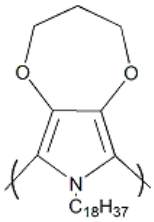
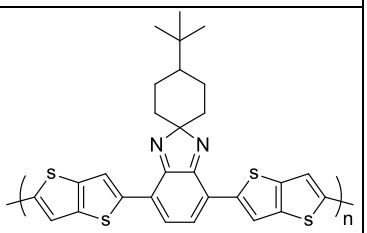


Figure 3.12 A graph for %Transmittance change vs thickness of **P1** films (●: neutral state, ◘: oxidized state)

The **P1** film has a high optical transparency in all redox states and its percent transmittance change in visible and NIR regions is about 1-12 Δ%T. There are few studies in literature for minimally color changing electroactive polymers [67,68] and this property makes this polymer a promising candidate as a counter electrode material in electrochromic devices.

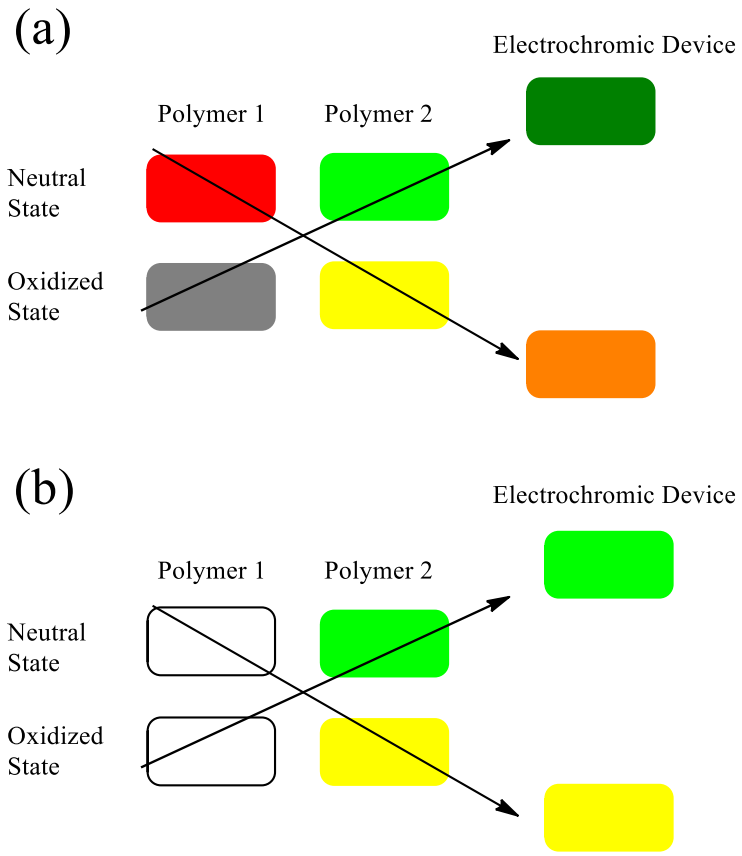
Table 3.2 Optical and electrochemical properties of minimally colored electrochromic polymers.

Polymer	P1	PProDOP [67]	PTTBI [68]
Structure			
E_g (eV)	2.5	2.96	1.60
HOMO (eV)	3.57	-	-5.73
LUMO (eV)	-1.07	-	-3.79
λ_{max} (nm)	307	350	-
CE (cm^2/C)	12	35	7.1

PEDOT/P1 Based Electrochromic Device

It is well known that a counter electrode used as a charge balance material with high transparency at all redox states becomes a promising electrode since the working electrode coated with electrochromic polymer can show absolutely its color changes at all redox states under applied external potentials. In literature, the used electrochromic polymers mostly exhibit multichromic properties at various redox states or they change their colors cathodicaly or anodicaly and the device based on these polymers represents a mixing color of the electrodes.

Based on this information, it can be concluded that the polymer **P1** has a very valuable property due to its high transparency/colorless at various redox states with a low redox potential. There are few examples of high transparent/colorless electroactive polymers at their various redox states in literature [67,68]. This property makes the polymer **P1** a promising candidate for use in the electrochromic devices as a counter electrode material. Therefore, the electrochromic device absolutely exhibits the color changes of the electrochromic polymer under external potentials when used as an anode electrode. **Scheme 3.3** showed the advantage of a minimally colored polymer as a cathode electrode in an electrochromic device.



Scheme 3.3 Expected colors from an electrochromic device under different external potentials (a) the electrodes have various colors at different redox states and (b) the cathode electrode is nearly colorless at different redox states and the anode electrode has a multichromic property.

By inspiration of this property, in order to test the utilisation of the polymer as a charge balancing counter electrode, an electrochromic device was prepared based on the polymer **P1** and PEDOT. It is well known that PEDOT is dark blue/violet at its neutral state and transmissive sky blue at its oxidized state. Based on the foregoing result, the similar colors were expected from the constructed electrochromic device. Polymer **P1** and PEDOT were used as cathode and anode electrodes, respectively. Before spectroelectrochemical studies, the redox behaviour of the device was investigated.

The electrochromic device is dark blue (L= 85.2, a*= -4.31, b*= -0.03) at the neutral state and transmissive sky blue at the oxidized state (L= 57.0, a*= 7.85, b*= -29.0) (**Figure 3.13a**). The device has a broad absorption band at 581 nm attributed the neutral PEDOT film used as the anode electrode. Upon oxidation, the band at 581 nm started to lost its intensity and disappeared with a concomitant increase at 891 nm due to the formation of charge carriers in PEDOT backbones. As expected, the spectroelectrochemical behaviour of the device looks like that of PEDOT film under applied external potentials in **Figure 3.13b**. The percent transmittance change of the device was calculated as 51% at 580 nm (**Figure 3.13a**). The response time for the device is 3 s for the 95% of the full optical switch.

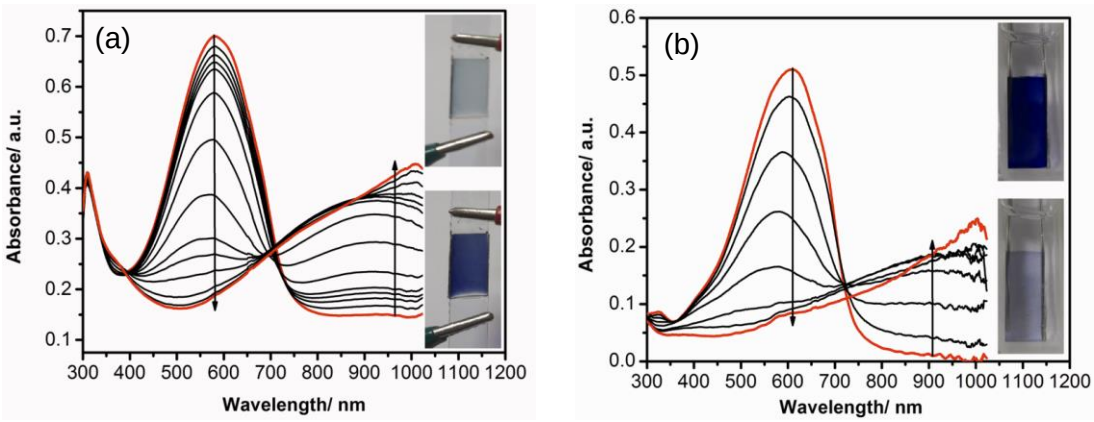


Figure 3.13 The change in the optical spectra of (a) **P1**-PEDOT based electrochromic device between -2.0 V and 2.1 V. Inset: The colors of the device at the neutral and oxidized states. (b) PEDOT film on ITO in 0.1 M TBAH/CH_2Cl_2 electrolyte solution between -1.0 V and 1.0 V. Inset: The colors of the PEDOT film at the neutral and oxidized states.

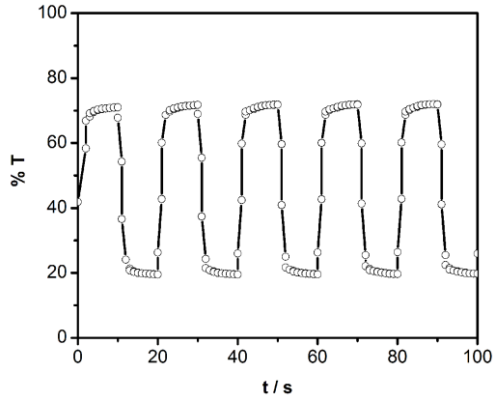


Figure 3.14 Chronoabsorbtometry experiments for the **P1**/PEDOT electrochromic device at a maximum wavelength of 680 nm under an applied square voltage signal between -2.0 V and 2.1 V with the potential steps of 10 s.

One of the important parameters in the electrochromic device is the long cycle life. In order to test the optical stability of the device, the switching was performed by applying potential steps of 10 s between -2.0 V and 2.1 V. After a certain number of switching, electro-optical behavior of the device was also checked with the potential steps of 10 s bewteen its redox states. Device keeps working and 88% of its optical activity retains after 1000 switching cycles (see **Figure 3.15**). This result indicated the high robustness, high redox and optical stability of the device under ambient conditions.

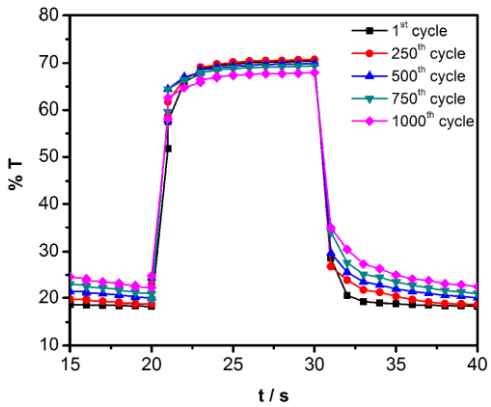


Figure 3.15 Optical stability experiment for the **P1**/PEDOT electrochromic device at a maximum wavelength of 581 nm under an applied square voltage signal between -2.0 V and 2.1 V.

CHAPTER 4

CONCLUSION

A novel carbazole and carborane based electroactive polymer called **P1** was synthesized successfully via potentiostatic and potentiodynamic methods in an electrolyte solution of 0.1 M TBAH/CH_2Cl_2. Its electrochemical behavior was investigated by using cyclic voltammetry technique. The results showed that the corresponding polymer film was firmly coated on the Pt electrode surface and the film exhibited high robustness under ambient condition. After 1000 cycles between the redox states, the film retains 73% of its electroactivity. Spectroelectrochemical studies showed that the polymer film has a band gap of 2.5 eV with a maximum wavelength at 307 nm. Upon oxidation or reduction, the polymer film with a thickness of 58 nm did not show any appreciable color change. It is colorless and has a transparency over 90% at all redox states. Also, the polymer film exhibited a percent trasmittance change of 6.8% and a coloration efficiency of 12 cm^2/C at 555 nm. This minimally color changing polymer film at all redox states makes it a promising counter electrode material in electrochromic devices. The device prepared based on **P1** and PEDOT films nearly exhibited similar optical behavior of the PEDOT, as expected. The device has a percent transmittance change of 51% at 580 nm and this value is 61% for PEDOT film. Also, this device exhibited high robustness, high redox and optical stability under ambient conditions since it retains 88% of its electro-optical stability after 1000 switching cycles.

These prominent features make **P1** an excellent candidate as a counter electrode in electrochromic device applications. Furthermore, this work opens up the door for the engineering of new molecules. The next step will be to synthesize soluble and processable polymer films by the modification of carbazole unit in **P1** polymer with long or branch alkyl chains.

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