Polymer 51 (2010) 1663–1669

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

A new imine coupled pyrrole–carbazole–pyrrole polymer: Electro-optical properties and electrochromism

Ozde Deniz Is [a], Fatma Baycan Koyuncu [a], Sermet Koyuncu [b,*], Eyup Ozdemir [a,**]

[a] *Department of Chemistry, Faculty of Sciences and Arts, Çanakkale Onsekiz Mart University, 17020 Canakkale, Turkey*
[b] *Çan Vocational School, Çanakkale Onsekiz Mart University, 17400 Çanakkale, Turkey*

ARTICLE INFO

Article history:
Received 8 December 2009
Received in revised form
5 February 2010
Accepted 10 February 2010
Available online 16 February 2010

Keywords:
Carbazole
Pyrrole
Imine polymers

ABSTRACT

In this study, imine bond coupled pyrrole–carbazole–pyrrole monomers were synthesized in four steps and then directly polymerized onto ITO/glass surface via potentiodynamic electrochemical process. Electrochemical and optical bad gap of these monomers and polymers were calculated by using cyclic voltammetry and UV–Vis absorption spectroscopy. Conductivity of the polymers with different alkyl side-chain was determined by using four point probe technique. Length of the side-alkyl chain influence iodine doping and also conductivity of polymers. As a result of the spectroelectrochemical measurements, the orange color of film changed to green color with applied potential and the polymer was found to be suitable material for electrochromic applications.

1. Introduction

In comparison to the inorganic semiconductors, conducting polymers containing conjugated double bonds along the backbone are useful materials because of their flexibility, lightness of weight, ease of fabrication and chemical inertness. Due to these useful properties, they have been investigated as the materials of electronics, optoelectronics, and photonics. These polymers are also potential candidates for a wide variety of commercial applications ranging from catalysts for photo-electrochemical processes, electrode materials, microelectronic devices, and organic batteries to electrochromic display devices [1].

Due to the –CH=N– group isoelectronic with the –CH=CH– group, imine polymers incorporated of nitrogen atoms into the conjugated system have another approach to form classes of materials with equally interesting electronic and optical properties [2,3]. These polymers have industrial applicability such as light emitting diodes, thin film transistors, electrochromic devices and photovoltaic cells because of useful semiconducting and optoelectronic properties as well as high thermal stability and good mechanical strength [3–8]. Aromatic polyazomethines are usually synthesized via both polycondensation of an aromatic diamine and a dialdehyde [9,10] and oxidative polymerization of imine monomers with electron rich terminal heterocycle such as thiophene [7,11], carbazole [12] and pyrrole [6,13] etc.

Thanks to carbazole can be easily functionalized on the 3,6- [14], 2,7- [15], or N-positions [16], it is covalently linked into polymeric systems, both in the main chain [17] as building blocks and in a side-chain as pendant group [18], and its good hole transporting ability, high thermal and photo-electrochemical stabilities, carbazole containing polymers have played a very important role in organic photo-electronic technology products such as organic light emitting diodes [19,20], organic photovoltaic cells [21,22] and electrochromic devices [23,24] etc. Besides, like carbazole, polypyrrole is one of the most stable among known conducting polymers, and its thin and plastic film has many possible applications such as capacitors, electrochromic devices, anti-corrosive coatings, batteries, actuators and sensors [25]. Due to the ease of formation of relatively stable radical cations (polarons), pyrrole readily polymerizes at oxidative polymerization process both chemically [26] and electrochemically [27]. Since polypyrrole was first electrochemically synthesized about three decades ago by Diaz et al. [28], its properties and applications have been intensively investigated by now.

Although, some of pyrrole–imine polymers were prepared via electrochemically [6] and chemically [13,29] oxidative process in the literature before, this is the first study about imine polymers having pyrrole and carbazole as second electroactive moiety in the main chain, and also electrochemical, optical and electrochromic properties of these polymers having different side-alkyl chain were

---

* Corresponding author. Tel./fax: +90 286 4167706.
** Corresponding author. Tel.: +90 286 2180018; fax: +90 286 2180533.
E-mail addresses: sermetkoyuncu@hotmail.com, skoyuncu@comu.edu.tr (S. Koyuncu), eozdemir@comu.edu.tr (E. Ozdemir).

0032-3861/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2010.02.020

intensively investigated. Further conductivity was measured by using a four point probe technique. It is observed that conductivity was changed by length of the side-alkyl chain and iodine doping.

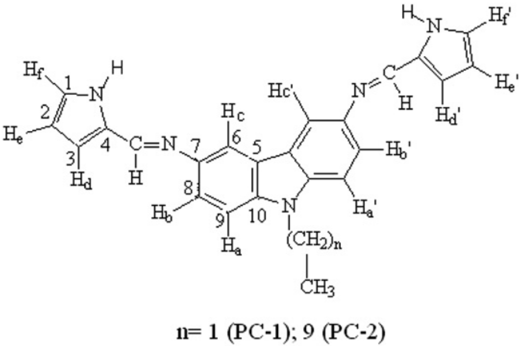
2. Experimental

2.1. Materials

All chemicals was purchased from Aldrich, Alfa Aesar and Merck and used without further purification. The syntheses and characterizations of 9*H*-*N*-alkylcarbazole (**1**), 3,6-dinitro-9*H*-*N*-alkylcarbazole (**2**) and 3,6-diamino-9*H*-*N*-alkylcarbazole (**3**) were prepared according to published procedure by Koyuncu et al. [7].

2.2. General procedure for synthesis of 9-alkyl-N,N′-bis-(1H-pyrrole-2-yl-methylene)-9H-carbazole-3,6-diamine (PCs)

9-Alkyl-*N*,*N*′-bis-(1H-pyrrole-2-yl-methylene)-9H-carbazole-3,6-diamine (PC) were prepared from the condensation of 2-pyrrolecarboxaldehyde (20 mmol) with 3,6-diamino-9-*N*-alkylcarbazole (10 mmol) in methanol (20 mL) achieved by boiling the mixture under reflux for 3 h at 70 °C. The precipitate was collected by filtration, re-crystallized from *n*-heptane and then dried in vacuum desiccator. Yield: PK-1: 76%; PK-2: 72%.



Scheme 1.

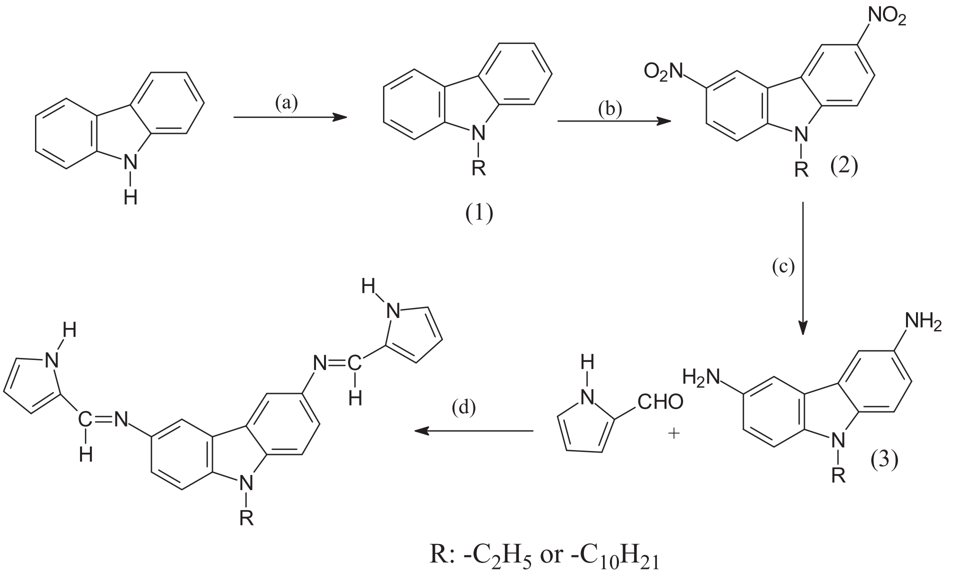
UV−Vis (λ_{max}) ($CHCl_3$): 252, 284, 312 and 352 nm. FT-IR (cm^{-1}): (N−H amine) 3432; (C−H aromatic) 3068, 3022; (C−H aliphatic) 2916, 2850; (−CH=N−, imine), 1620; (C=C phenyl) 1605, 1578, 1423. ^{1}H NMR ($CHCl_3$-*d*): δ ppm, 8.48 (s, 2H, −CH=N−); 6.72 (d, 2H, Ar−H_{aa}′); 6.93 (d, 2H, Ar−H_{cc}′); 7.42 (d, 2H,Ar−H_{ff}′); 6.33 (t, 2H, Ar−H_{bb}′); 7.99 (d, 2H, H_{dd}′); 7.42 (t, 2H, H_{ee}′); 4.33 (t, 2H, −N−CH_2−); 1.96−1.30 (C−H aliphatic; for *N*-decyl-Carb (PC-2)); 1.38 (t, 3H, R−CH_3; for *N*-ethyl-carb); 1.00 (t, 3H, R−CH_3; for *N*-decyl-Carb). ^{13}C NMR ($CHCl_3$-*d*): δ ppm, 148 (−$\underline{C}$H=N−), 124, (C1); 110, (C2); 120, (C3); 131, (C4); 144, (C5); 116, ($\underline{C}$6); 109, (C7); 140, (C8); 112, (C9); 123, (C10); 43, (N−$\underline{C}H_2$); 34−21, (N−CH_2−($\underline{C}H_2)_n$); 14, (CH_2−$\underline{C}H_3$) (Scheme 1 and 2).

2.3. Electrochemical polymerization of 9-alkyl-N,N′-bis-(1H-pyrrole-2-yl-methylene)-9H-carbazole-3,6-diamine (poly-PC-1)

Electrochemical measurements were performed using a CHI660B electrochemical workstation from CH Instruments (Austin, TX, U.S.A.). Monomer of PC-1 or 2 (2×10^{-3} M) and pyrrole (2×10^{-3} M) were covered on Pt and ITO/glass electrode surfaces by applying potentials ranging between −0.5 V and +1.5 V in 0.1 M $NaClO_4$/$LiClO_4$ as supporting electrolyte at 100 mV/s as scan rate by electrochemical method (Schemes 3 and 4). Polymer film of PCs on ITO/glass surface was also dedoped electrochemically in monomer free-electrolyte solution. Further, to investigation of the UV−Vis and CV measurements, the polymers can be partly dissolved in CH_2Cl_2 by using ultrasonic bath.

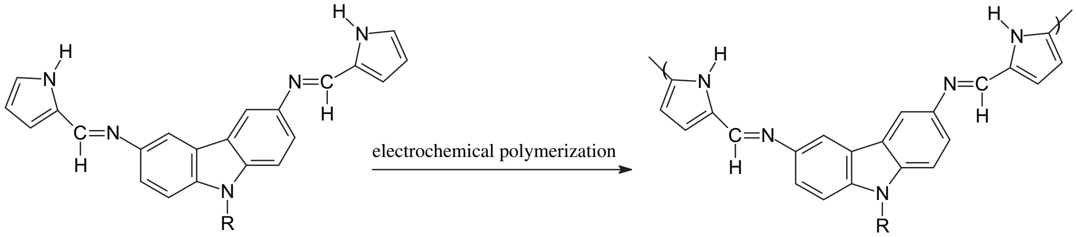
2.4. Instrumentation

FT-IR spectra were recorded by a Perkin Elmer FT-IR Spectrum One by using ATR system (4000−650 cm^{-1}). ^{1}H and ^{13}C NMR (Bruker Avance DPX-400) data recorded at 25 °C by using $CHCl_3$-*d* as solvent and TMS as internal standard. Electrochemical

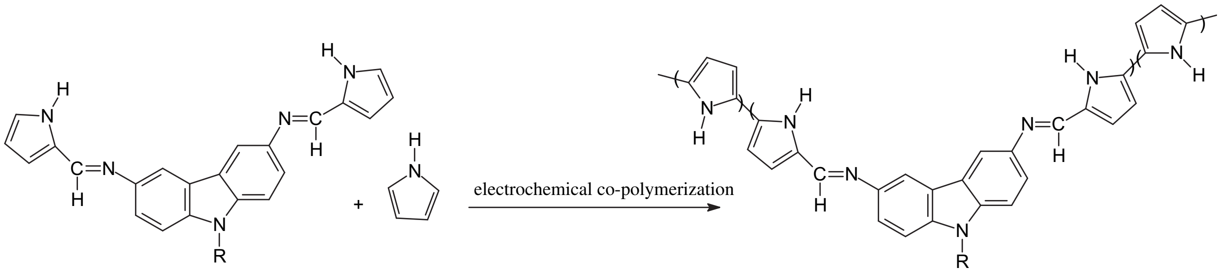


a) R-Br, 18-Crown-6, KOH, toluene, 110 °C, 10 h reflux, (b) $Cu(NO_3)_2$. 2.5 H_2O, acetic acid-acetic anhydride, 1 h, r.t. (c) Pd/C, N_2H_4OH, EtOH, 24 h reflux (d) MeOH, 3 h reflux,

Scheme 2.



Scheme 3.



Scheme 4.

measurements were carried out by CH instruments 660B cyclic voltammetry. The electrochemical cell consists of an Ag wire as reference electrode (RE), Pt wire as counter electrode (CE) and platinum as working electrode (WE) immersed in 0.1 M $TBAPF_6$ as the supporting electrolyte. All measurements were carried out under argon atmosphere. The potentials were calibrated to the ferrocene redox couple $E(Fc/Fc^+) = +0.41$ V. The electrochemical HOMO–LUMO energy level of synthesized monomer and polymer were calculated from their oxidation and reduction onset values [30].

UV–Vis absorption spectra were measured by Jena Speedcord S-600 diode-array spectrophotometer. The absorption spectra of these compounds were recorded in both $CHCl_3$ (liquid phase) and ITO/glass transparent film (solid phase). The optical band gaps (E_g) of PC monomers and polymers were calculated from their absorption edges [31]. We used the data obtained from UV–Vis spectra and cyclic voltammetry for spectroelectrochemical measurements of poly-PC-1 on ITO/glass transparent film. These measurements were carried out to consider absorption spectra of this polymer film under applied voltage and 0.1 M $NaClO_4/LiClO_4$ in CH_3CN was used as supporting electrolyte. The spectroelectrochemical cell includes a quartz cuvette, an Ag wire (RE), Pt wire counter electrode (CE) and ITO/glass as transparent working electrode (WE). Conductivity was measured on the ITO/glass surface coated PC polymers and carried out by using a Keithley 2400 electrometer. Iodine doping was carried out by exposure of the films to iodine vapor at atmospheric pressure and room temperature in a desiccator.

3. Results and discussion

3.1. Synthesis and characterization

The initial compounds (**1**, **2**, **3**) were synthesized and fully characterized by Koyuncu et al. in the previous studies [7]. The final products, imine monomers containing pyrrole and *N*-alkylcarbazole (PC-1, PC-2) moieties, synthesized by the condensation reaction of 3,6-diamino-9-*N*-alkylcarbazole (**3**) compounds and 2-pyrrolecarboxaldehyde. Synthesized compounds were purified by column chromatography and re-crystallization from *n*-heptane. Structure of final product was also fully identified by using FT-IR, ^1H NMR and compiled in the Experimental section. Finally, these results indicate that all reactions were completed successfully.

3.2. Optical and electrochemical properties

The UV–Vis spectra were recorded in $CHCl_3$ solution (Fig. 1). These compounds showed multi absorption peak attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition of the pyrrole, carbazole and imine moieties. Due to enlargement of $\pi \rightarrow \pi$ conjugation, the red shift is observed at the end of the polymerization. Absorption maximum (λ_{max}) of poly-PC-2 at 378 nm exhibits about a 20 nm red shift as compared to PC-2. This shift was also observed in the poly-PC-1. On the other hand, McCullough claimed that the length of the alkyl substituents affects on the absorption maximum and bang gap due to solvation is promoted with increase in the length of the alkyl side-chain, leading to expanded chain structure with longer π conjugation [32,33]. Because of this effect, about 3–5 nm red shift were observed on the absorption maximum and bang gap with the increasing the alkyl side-chain.

The electrochemical properties of PC monomer and the polymers were investigated by cyclic voltammetry (CV). Due to having the same electroactive units in their structure, all PC monomers and polymers show similar electrochemical behavior. As a result of CV

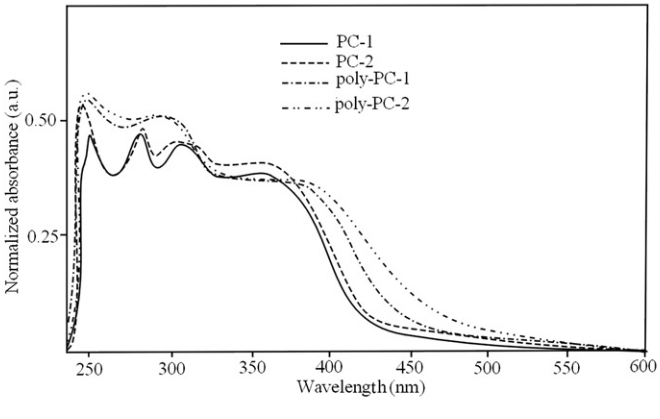


Fig. 1. UV–Vis spectra of synthesized monomers and polymers.

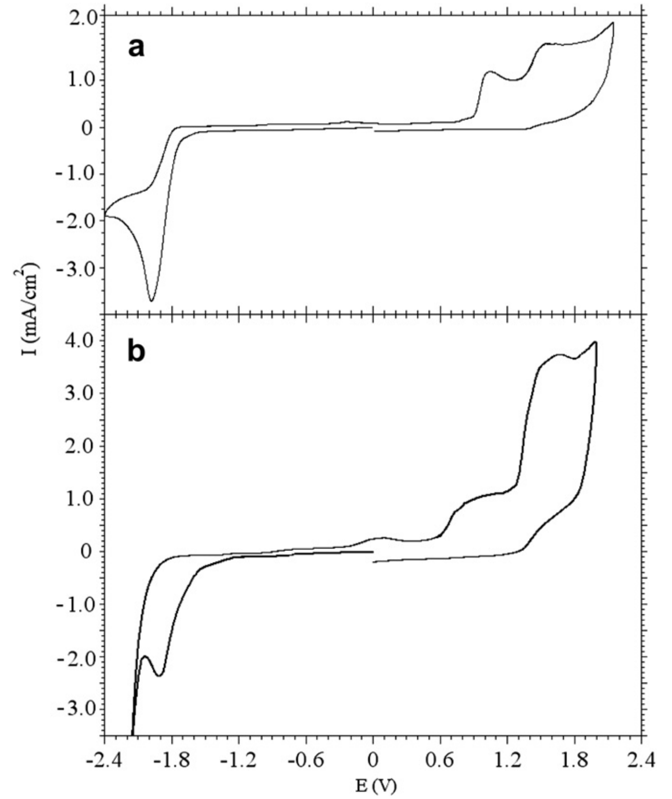


Fig. 2. Cyclic voltammogram of (a) PC-2 and (b) poly-PC-2 in the TBAPF$_6$–acetonitrile, scan rate 100 mV/s, Ag–AgCl.

measurements (Fig. 2), in the negative regime, the irreversible peak which reflect the reduction of imine (–CH=N–) with peak potential of −1.98 and −1.90 were observed for radical anion formation of PC-2 and poly-PC-2, respectively. Due to PC-2 polymer have not uniform structure than that of PC-2 monomer, the imine reduction peak of the polymer was broadened and slightly shifted to positively. The same effect was observed between PC-1 and poly-PC-1. On the other hand, during anodic scan, two irreversible oxidation peaks of PC-2 were observed attributed to pyrrole at 1.01 V and carbazole at 1.51 V, respectively. Besides, solvation is promoted with increase in the length of the alkyl side-chain, leading to expanded chain structure with longer π conjugation Because of enlargement of π conjugation, oxidation of poly-PC-2 was observed at lower potentials compared to PC-1. Thus, oxidation of poly-PC-2 was observed at lower potential than that of poly-PC-1. Finally, HOMO–LUMO energy levels, electrochemical and optical band gap values of the PC monomers and polymers were calculated. It is concluded that synthesized polymer oxidized at significantly lower potentials than that of imine polymer of thiophene–carbazole derivative [6] and thus having lower HOMO–LUMO band gap. As seen from Table 1, in comparison to electrochemical and optical band gap of all monomers and their polymers, the values are not agreement. This is resulted that the electroactive centers and photoactive centers behave independent from each other for synthesized molecules.

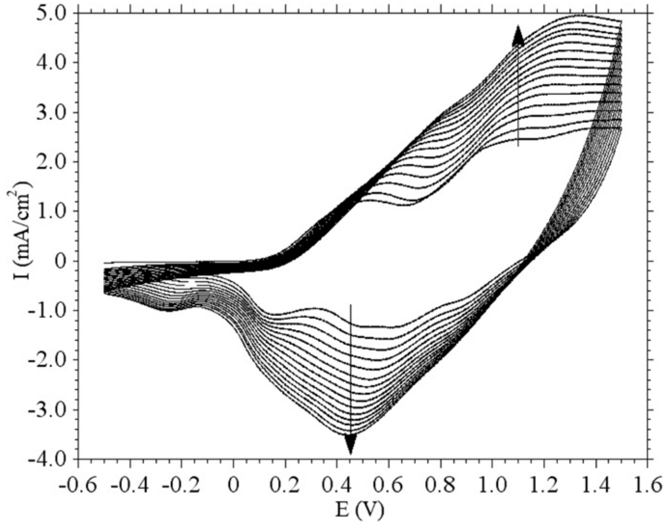


Fig. 3. Repeated potential scan of PC-1-pyrrole between 0 and 1.6 V in 0.1 M LiClO$_4$–NaClO$_4$–acetonitrile, scan rate 100 mV/s.

3.3. Electrochemical polymerization and electrochromic properties

Conjugated aromatic molecules such as pyrrole, thiophene, furan, etc. can be easily oxidized and deposited as electroactive polymer films onto the ITO/glass surface by repeated anodic scans [34]. Pyrrole–imine compounds have a low oxidation potential (≈0.8 eV against Ag/Ag$^+$ electrode) than that of thiophene or furan imine derivatives, so that they can be easily polymerized by the electrochemical process. Because of having low oxidation potential, pyrrole–imine compounds don't need a co-monomer except from the others. In this study, when the co-monomer wasn't utilized, PC monomers were polymerized on the ITO/glass surface but didn't show any reversible redox behavior and electrochromic effect. For the electrochromic applications, pyrrole was used as the co-monomer for electro polymerization of PC-1. By the repeated anodic scan, the constant increase of the peak current indicates that the monomers become more repeated in the polymer backbone and a regular amount of polymer is coated on the electrode after each new sweep. Due to aromatic conjugation becomes more pronounced, these peaks broadened and slightly shifted to lower potential at the end of the polymerization. Electro polymerization of PC-1 in the presence of pyrrole was presented in Fig. 3 and Scheme 4.

Spectroelectrochemical measurements investigate the changes in optical properties of conducting polymers upon applied voltage. These measurements showing the formation of polaronic species of poly-PC-1 molecule on the ITO/glass surface were studied by

Table 1
HOMO and LUMO energy levels, electrochemical ($E_g^{'}$) and optical band gaps (E_g) values of PC monomers and polymers.

Compounds	Reduced groups and peak potentials (V)	Oxidized groups and peak potentials (V)		HOMO (eV)	LUMO (eV)	($E_g^{'}$), Electrochemical band gap (eV)	(E_g), Optical band gap (eV)
	–HC=N– (imine)	Pyrrole (Ring)	Carbazole (Ring)				
PC-1	−1.99	+1.02	+1.50	−5.28	−2.67	2.62	2.90
PC-2	−1.98	+1.01	+1.51	−5.28	−2.67	2.61	2.87
poly-PC-1	−1.92	+0.84	+1.51	−5.01	−2.77	2.24	2.76
poly-PC-2	−1.90	+0.81	+1.50	−4.98	−2.81	2.17	2.69

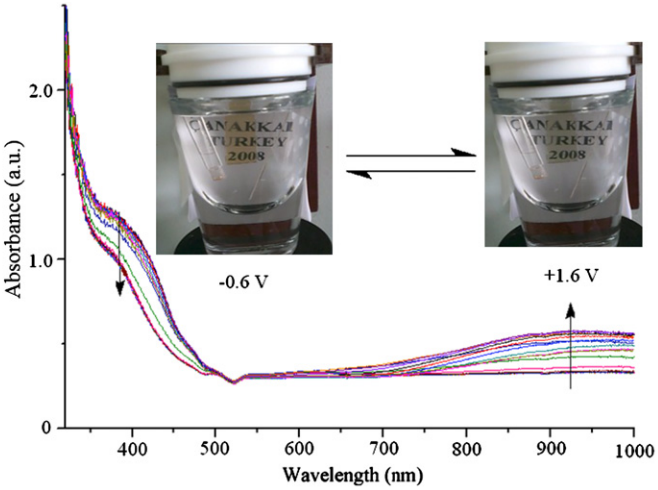


Fig. 4. Spectroelectrochemical measurements of poly-(PC-1-pyrrole) film.

applying potentials ranging between −0.6 V and 1.6 V in monomer free acetonitrile/$LiClO_4$–$NaClO_4$ (0.1 M) medium. The appearance of broad band around 950 nm could be attributed to the evolution of polaronic species. As can be seen from Fig. 4, the orange color of film at neutral state was changed to green by the oxidation.

Electrochromic parameters of poly-PC-1 film were analyzed by changes that occurred in the transmittance (increments and decrements of the absorption band at 950 nm with respect to time) while switching the potential step wisely between neutral (−0.6 V) and oxidized states (+1.6 V) with a residence time of 10 s. Double potential step chronoamperometry was carried out to estimate the response time of the polymer film. During the experiment, the 12% transmittance at the wavelength of maximum contrast was measured by using a UV–Vis spectrophotometer. The oxidation and reduction response times were calculated as about 3 s. Optical activity of the film was retained by 74.6% even after 1000 cycles of operation, signifying reasonable redox stability. Despite having a relatively slow response and low contrast ratio, co-polymer of poly-PC-1 with pyrrole shows reversible redox behavior, resistance to over oxidation and thus it can be useful for electrochromic applications (Fig. 5).

3.4. Conductivity

Conductivity is related to both intermolecular and intramolecular electron transfer on the polymer backbone. Therefore these results have shown that the dopant interacts with the double bond in the polymer backbone and forms a polaronic state (radical cation) as an electron is transferred from the double bond to the dopant creating a hole or a positive carrier at the double bond site. These holes or positive carriers are responsible for the electrical conduction in these materials [35]. Conductivity measurements of poly-PC's were carried out with an electrometer using a four point probe technique. Fig. 6 shows the electrical conductivity behavior results of poly-PC-1 and poly-PC-2 molecules under iodine doping in varying periods at 25 °C. First of all, conductivities of PC-1 and PC-2 polymers were found to be approximately 10^{-7}–10^{-8} S/cm and then an increase were observed after iodine doping. Conductivity measurements carried out at the end of each doping period. Despite the polymers have same electroactive moiety (pyrrole and carbazole), poly-PC-1 showed lower conductivity than that of poly-PC-2. These differences are assumed to be caused by the different side-alkyl chain substituted on the carbozyl nitrogen. While poly-PC-1 reached maximum conductivity value within 2 days, poly-PC-2 reached within 4 days. This result explains that steric effect of poly-PC-1 is less than poly-PC-2. Also, these alkyl groups hinder the coordination of I_3^- with nitrogen, because of the steric effect exerted by them. Since nitrogen is a very electronegative element and is capable of coordinating with the I_3^-, Diaz et al. suggested a conductivity mechanism of imine (–CH=N–) polymers when

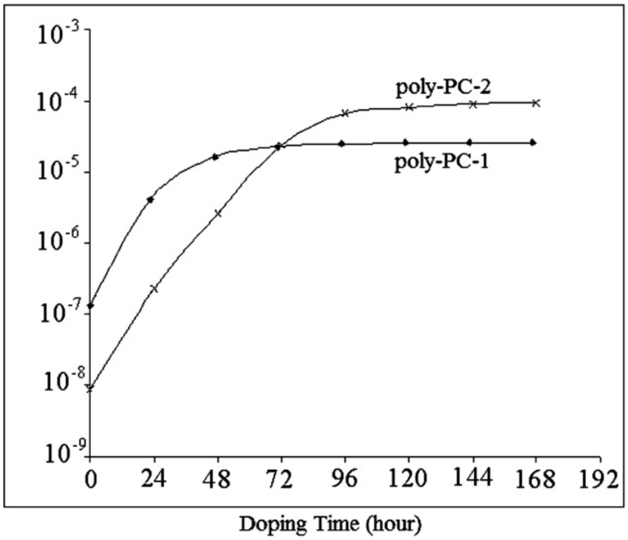


Fig. 6. Change in the electrical conductivities of PC polymers during the process of iodine doping (done at atmospheric pressure and 25 °C).

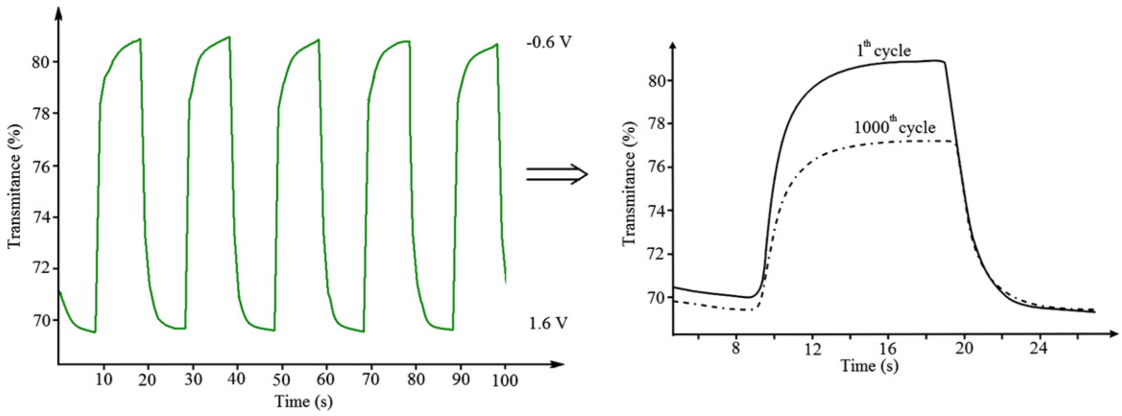
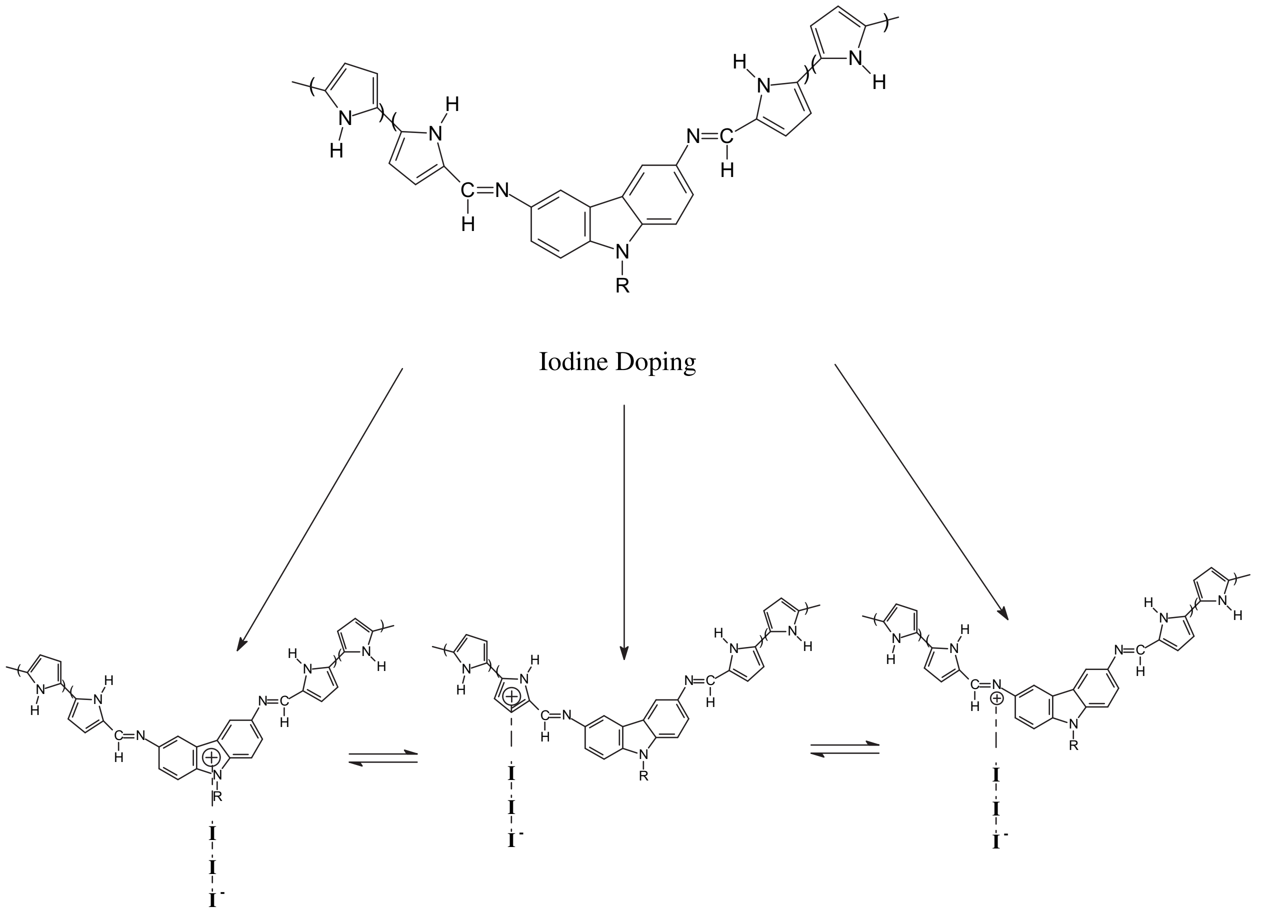


Fig. 5. Electrochromic switching, optical absorbance monitored for poly-(PC-1-pyrrole) film at 950 nm (0.6–1.6 V).



Scheme 5.

doped with iodine [36]. Furthermore, it is believed that iodine doping occurs not only on the nitrogen atoms but also on the pyrrole or carbazole rings. The conductivity mechanism over the polymer backbone can be proposed as Scheme 5.

4. Conclusion

The synthesis and electrochemical polymerization of a two imine coupled PC monomers with different side-alkyl chain is reported. Due to the same electroactive moiety, these molecules show similar electrochemical and optical behaviors but different conductivities. It is observed that length of the side-alkyl chain influenced the oxidation–reduction potential and absorption maximum of the PC polymers. As a result of spectroelectrochemical investigation, the orange color of the film on the ITO/glass surface prepared via electro-oxidative polymerization changed into green color during the *p*- doping process. In addition, kinetic study exhibited that poly-(PC-1-pyrrole) has reasonable stability on transparent ITO/glass surface. Owing to the stable electrochromism and reversible color changes, the PC polymers can be candidate for design of organic electrochromic devices (OECD).

Acknowledgement

We gratefully acknowledge the supports from Çanakkale Onsekiz Mart University Grants Commission (Project Number: 2009/18).

References

[1] Wallace GG, Spinks GM, Kane-Maguire LAP, Teasdale PR. Conductive electroactive polymers: intelligent materials systems. CRC Press; 2003.
[2] Grigoras M, Antonoaia NC. Polym Int 2005;54:1641.
[3] Yang CJ, Jenekhe SA. Chem Mater 1991;3:878.
[4] Yang CJ, Jenekhe SA. Macromolecules 1995;28:1180.
[5] J-Cho S, Kimoto A, Higuchi M, Yamamoto K. Macromol Chem Phys 2005;206:635.
[6] Tarkuc S, Sahin E, Toppare L, Colak D, Cianga I, Yagci Y. Polymer 2006;47:2001.
[7] Koyuncu S, Kaya İ, Baycan Koyuncu F, Ozdemir E. Synth Met 2009;159:1034.
[8] Koyuncu S, Kus M, Demic S, Kaya İ, Ozdemir E, Icli S. J Polym Sci Part A Polym Chem 2008;46:1974.
[9] Grigoras M, Catanescu CO. J Macromol Sci Part C Polym Rev 2004;C44:131.
[10] Iwan A, Sek D. Prog Polym Sci 2008;33:289.
[11] Zotti G, Randi A, Destri S, Porzio W, Schiavon G. Chem Mater 2002;14:4550.
[12] Grigoras M, Antonia MC. Eur Polym J 2005;41:1079.
[13] Simuonescu CI, Grigoras M, Cianga I, Olaru N. Eur Polym J 1998;34:891.
[14] Han F, Chi L, Liang X, Ji S, Liu S, Zhou F, et al. J Org Chem 2009;74:1333.
[15] Bloudin N, Leclerc M. Acc Chem Res 2008;41:1110.
[16] Watanabe M, Nishiyama M, Yamamoto T, Koie Y. Tetrahedron Lett 2000;41:481.
[17] Chen JP, Natansohn A. Macromolecules 1999;32:3171.
[18] Bubniene G, Malinauskas T, Getautis V, Stanisauskaite A, Jankauskas V, Sidaravicus J. Synth Met 2006;158:670.
[19] Michinobu T, Kumazawa H, Otsuki E, Usui H, Shigehara K. J Polym Sci Part A Polym Chem 2009;47:3880.
[20] Lin S-L, Chan L-H, Lee R-H, Yen M-Y, Kuo W-J, Chen C-T, et al. Adv Mater 2008;20:3947.
[21] Li J, Dierschke F, Wu J, Grimsdale AC, Müllen K. J Mater Chem 2006;16:96.
[22] Wang ZS, Koumura N, Cui Y, Takahashi M, Seguchi H, Mori A, et al. Chem Mater 2008;20:3993.
[23] Beaupre S, Breton A-C, Dumas J, Leclerc M. Chem Mater 2009;21:1504.
[24] Koyuncu S, Gultekin B, Zafer C, Bilgili H, Can M, Demic S, et al. Electrochim Acta 2009;54:5694.
[25] Soloducho J. Synth Met 1999;99:181.

[26] Pickup PG, Osteryoung RA. J Am Chem Soc 1984;106:2294.
[27] Khulbe KC, Mann RS, Khulbe CP. J Polym Sci Part A Polym Chem 1982;20:1089.
[28] Diaz AF, Kanazawa KK, Gardini GP. J Chem Soc Chem Commun 1979;14:635.
[29] Simionescu CI, Cianga I, Ivanoiu M, Airinei A, Grigoras M, Radu I. Eur Polym J 1999;35:1895.
[30] Wudl F, Kobayashi M, Colaneri N, Noysel M, Heeger AJ. Mol Cryst Liq Cryst 1985;118:199.
[31] Bredas JL. J Chem Phys 1985;82:3808.
[32] McCullough RD. Adv Mater 1998;10:93.
[33] Shin C-K, Lee H. Synth Met 2004;140:177.
[34] Satoh M, Imanishi K, Yoshino K. J Electroanal Chem 1991;317:139.
[35] Shirakawa H, Louis EJ, Macdiarmid AG, Chiang CK, Heeger AJ. J Chem Soc Chem Commun; 1977:579.
[36] Diaz FR, Moreno J, Tagle LH, East GA, Radic D. Synth Met 1999;100:187.