Synthesis and electro-optical properties of a new copolymer based on EDOT and carbazole

M. Akbayrak, E. G. Cansu-Ergun & A. M. Önal

To cite this article: M. Akbayrak, E. G. Cansu-Ergun & A. M. Önal (2016) Synthesis and electro-optical properties of a new copolymer based on EDOT and carbazole, Designed Monomers and Polymers, 19:7, 679-687, DOI: 10.1080/15685551.2016.1209627

To link to this article: https://doi.org/10.1080/15685551.2016.1209627

Published online: 14 Jul 2016.

Submit your article to this journal

Article views: 718

View related articles

View Crossmark data

Citing articles: 5 View citing articles
Synthesis and electro-optical properties of a new copolymer based on EDOT and carbazole

M. Akbayrak, E. G. Cansu-Ergun and A. M. Önala

ABSTRACT
A new copolymer of 3,4-ethylenedioxythiophene (EDOT) and 5-(2-ethylhexyl)-1,3-bis(9-methyl-9H-carbazol-3-yl)-5H-thieno[3,4-c]pyrrole-4,6-dione (CzPDICz) was electrochemically synthesized using different monomer feed ratios. The resulting copolymer films were investigated in terms of their electrochemical and electro-optical behaviors. Properties of the obtained copolymer films through different monomer feed ratios were compared to each other and to individual poly(ethylenedioxythiophene; PEDOT) and homopolymer of CzPDICz in order to observe the differences in the properties with respect to PEDOT and P(CzPDICz). Copolymers exhibited well adherence on the electrode surface with having non-diffusional redox process. The monomer feed ratios were prepared as 9:1; 4:1, and 1:1 (EDOT:CzPDICz) and changes in the electrochemical and spectroelectrochemical behavior were noted with increasing CzPDICz ratio in the monomer mixture. Although no appreciable change in the optical band gap values of the copolymers was noted as compared to PEDOT, the neutral blue copolymers exhibited grayish color in their semi-oxidized states and transparent green in their fully oxidized states.

1. Introduction
Conjugated polymers (CPs) have been one of the most popular topics over the past decades [1,2] since they have opened a huge gate through the next generation electronics such as solar cells,[3–6] light emitting diodes,[7,8] electronic displays,[9–11] electrochromic devices [12,13], and biosensors.[14,15] These applications depend on the properties of CPs which can be tuned via modifications of the molecular structure.[16,17] Since the band gap energy is one of the most crucial properties of conjugated polymers in above-mentioned applications, there has been extensive research on band gap tuning. Among them, alternating sequence of the appropriate donor (D) and acceptor (A) units is widely used which induces a reduction in the band gap energy.[18–21] Copolymerization is another way to adjust the properties of CPs which leads materials with intermediate properties between two homo-polymers,[22–24] thus allowing modification of the physical properties of the conducting polymers.

3,4-Ethylenedioxythiophene (EDOT) is a commonly used polythiophene derivative for copolymer synthesis via electrochemical methods since this monomer can be electropolymerized at reasonable anodic potentials with having good adherence on the electrode surface. [25] Moreover, high conductivity and stability of PEDOT make this monomer useful in CP studies.[26] There are various investigations about electrochemically prepared copolymers from novel conjugated molecules and EDOT in the literature.[27–29] Carbazole derivatives, on the other hand, are one of the attractive conjugated molecules for electronic applications due to its ease of functionalization not only at the nitrogen atom but also at 2,7- and 3,6- positions. In several studies, nitrogen atom of the carbazole units was functionalized with various alky groups for enhancing the solubility of the resulting polymer.[30] On the other hand, introducing acceptor units on the nitrogen atom was found to be effective on tuning the electrochromic properties.[31–33] There are also several studies reporting copolymerization of carbazole derivatives with various donor units including thiophene and EDOT.[34,35] Recently, Ateş et al. reported the electrochemical properties and capacitive behavior of a copolymer which is prepared from 4-vinylbenzyl 9H-carbazole-9-carbodithioate and EDOT as co-monomers.[36] In the light of the above considerations, we have successfully synthesized a new carbazole derivative, 5-(2-ethylhexyl)-1,3-bis(9-methyl-9H-carbazol-3-yl)-5H-thieno[3,4-c]pyrrole-4,6-dione (CzPDICz), including thienopyrroledione unit as a strong acceptor and methyl substituted carbazole as a donor.
After the synthesis of CzPDICz, it was electropolymerized to obtain its corresponding polymer P(CzPDICz). Since the band gap of obtained polymer was found to be much larger than that of PEDOT, copolymers of EDOT and CzPDICz monomers were prepared using different monomer feed ratios by repetitive potential cycling in order to investigate its effect on band gap tuning. Changes in the properties of the copolymers and homopolymers were comparatively investigated in terms of their electrochemical and electro-optical properties. To the best of our knowledge, there have been no reports about the electrochemical copolymerization of CzPDICz with EDOT so far.

2. Experimental

2.1. Materials

All chemicals were purchased from Sigma Aldrich Chemicals and used as received unless otherwise noted. Electrochemical studies were performed using platinum (Pt) disk as a working electrode (WE), Pt wire as a counter electrode (CE) and silver–silver chloride (Ag/AgCl; in 3 M NaCl (aq) solution) as a reference (RE) electrode. The cyclic voltammograms (CVs) were recorded with Gamry Reference 300 model potentiostat-galvanostat. Electropolymerizations of co-monomers and electrochemical studies were performed in dichloromethane (DCM) containing 0.1 M TBABF$_4$ as a supporting electrolyte. Acetonitrile (ACN) was used as a solvent for spectroelectrochemical studies of the polymer films.

Spectroelectrochemical measurements were performed using a Cary 60 model UV–Vis spectrometer combined with Gamry PC14/300 potentiostat–galvanostat. Indium tin oxide (ITO, Delta Tech. 8–12 Ω, 0.7 cm × 5 cm) coated glass, Pt wire, and Ag wire were used as WE, CE, and pseudo RE, respectively. Fluorescence measurements were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer.

Structural characterization of monomer was revealed by using $^1$H and $^{13}$C NMR spectra, recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer. All measurements were performed at room temperature and ambient conditions.

2.2. Synthesis of CzPDICz

Monomer (CzPDICz) synthesis was achieved via Suzuki coupling reaction as shown in Scheme 1.[37]

2.2.1. General procedure for the monomer synthesis

1,3-dibromo-5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (0.3 mmol), 9-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (0.6 mmol), and 5% of Pd (0) were dissolved in freshly distilled tetrahydrofuran (THF; 20 ml) and stirred under nitrogen gas (N$_2$) for 15 min. Potassium carbonate (K$_2$CO$_3$; 10 mmol) was dissolved in 5 ml distilled water and degassed for 10 min. Then, 1 ml of aqueous K$_2$CO$_3$ solution was added to the reaction mixture. The mixture was purged with N$_2$ for 30 min and refluxed for 50 h at 73 °C. At the end of reaction, the crude product was washed with DCM and water. The collected organic phase was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. Further purification was done using silica gel column chromatography (3 DCM: 1 Hexane). Final product was obtained as yellow solid (120 mg, 64%).

$^1$H NMR (CDCl$_3$) d: 8.9 ppm (s, 1H), 8.4 ppm (dd, 1H), 8.23 ppm (d, 1H), 7.5 ppm (t, 1H), 7.42 ppm (t, 2H), 7.3 ppm (t, 1H), 5.29 ppm (s, 3H), 3.61 ppm (d, 2H), 1.92 ppm (m, 1H), 1.32 ppm (m, 8H), 0.9 ppm (dt, 6H).

$^{13}$C NMR (CDCl$_3$) d: 163.73, 145.7, 141.71, 141.56, 128.45, 126.33, 126.25, 123.09, 122.87, 122.130, 120.80, 120.40, 119.64, 108.768, 108.58, 53.40, 38.24, 31.6, 29.24, 23.97, 22.65, 14.1, 10.6 ppm.

2.3. Copolymer synthesis

EDOT and CzPDICz were dissolved in DCM separately to prepare 0.025 M stock solutions of each monomer. Then the monomer solutions were mixed in the ratio of 9:1, 4:1, and 1:1 (EDOT:CzPDICz; v:v) in separate vials. Copolymerization of CzPDICz with EDOT was achieved via potential cycling between −0.8 and +1.5 V vs. Ag/AgCl in DCM–TBABF$_4$ electrolytic medium as shown in Scheme 2. For spectroelectrochemical investigations, copolymers were deposited on ITO working electrode (50 mC cm$^{-2}$) by constant potential electrolysis at 1.5 V vs. Ag wire.

Scheme 1. Synthesis route of monomer CzPDICz.
3. Results and discussion

3.1. Electrochemical and optical properties of CzPDICz

Before the copolymerization studies, electrochemical and optical properties of the monomer, CzPDICz, were investigated. CV of the monomer recorded in DCM–TbABF₄ electrolytic medium is given in Figure 1(a). As seen from the figure, CzPDICz exhibits two reversible oxidation peaks at 1.20 and 1.47 V. However, no reduction peak was observed during the cathodic scan. Electronic absorption spectrum of CzPDICz in DCM shows one major absorption band at 397 nm (Figure 1(b)) and the monomer solution exhibits yellow and fluorescent yellow colors under daylight and UV light, respectively. Emission spectrum of CzPDICz is given in Figure 1(c). Comparison of absorption and emission maxima of the monomer solution reveals 71 nm Stokes shift indicating the conformational changes of the molecules upon excitation.[38]

After electrochemical and optical characterization of the monomer is completed, its electrochemical polymerization was monitored via potentiodynamic and potentiostatic methods in DCM–TbABF₄ electrolytic medium. However, no sign of polymerization was observed when the potential was cycled repetitively between 0.0 and +1.20 V (first oxidation potential of the monomer). When
Figure 3. CVs of EDOT (a) and EDOT/CzPDICz monomer feed ratios of 9:1 (b); 4:1 (c) and 1:1 (d) during electropolymerization on Pt WE between −0.8 and 1.5 V in 0.1 M DCM-TBA BF$_4$ with a scan rate of 100 mV s$^{-1}$. The second (e) and the last (f) CVs of the electropolymerization cycles, (g) CVs of PEDOT and resulting copolymers in monomer free solution containing 0.1 M TBABF$_4$ in ACN.
It is important to note that, when the monomer feed ratio reaches to 1, the problem observed during homopolymerization of CzPDICz was also noted; causing loss of some part of polymer film from the electrode surface into the electrolytic solution. However, the remaining polymer film on the surface was still enough to reflect a different behavior from PEDOT (See Figure 3(f) and (g)).

The copolymer films were scanned with increasing scan rates between −1.0 and 1.0 V in order to observe their scan rate dependancy. The copolymers exhibited a linear increase in current densities with increasing scan rates indicating well adhering electrocative polymer film on the electrode surface and the non-diffusional redox behavior even at high scan rates. The scan rate dependence of the copolymer (4:1) was demonstrated in Figure 4 as a representative example.

### 3.2. Synthesis and the electrochemical properties of the copolymers

Prior to copolymerization studies, CV and differential pulse voltammograms (DPV) of CzPDICz and EDOT were recorded in DCM–TBABF₄ electrolytic medium and the results are given in Figures 2(a) and 3(b), respectively. As seen from the figure, the oxidation potentials of CzPDICz and EDOT are compatible to obtain a copolymer via electrochemical techniques.

Copolymers were prepared utilizing CV technique by applying 20 repetitive cycles between a certain potential range of −0.8 and 1.5 V in an electrolytic solution of 0.1 M DCM–TBABF₄ (Figure 3). As seen from the Figure 3(a)–(d), after the first anodic scan, a new redox couple starts to intensify upon successive cycling in the case of EDOT and co-monomer mixtures with different feed ratios which indicates polymer deposition on the working electrode surface. When the second and last cycles recorded during electropolymerizations were compared (Figure 3(e) and (f), respectively), a decrease in the current densities were noted with increasing CzPDICz/EDOT ratio (i.e. from 1:9 to 1:1) due to decreasing electroactivity of copolymer as compared to PEDOT. The characteristic anodic and cathodic peaks (1.2 and 1.0 V, respectively) of CzPDICz becomes clearly noticeable in the co-monomer mixture and their intensities increase with increasing CzPDICz/EDOT ratio (Figure 3(e)). Appearance of these characteristic anodic–cathodic peaks of CzPDICz in the CVs of polymer films indicates incorporation of CzPDICz in to polymer matrix. The decrease in the current density by increasing the CzPDICz in the monomer feed ratio further proves the copolymer formation during repetitive potential cycling.

After completion of electropolymerization (20 repetitive cycles) monomeric or oligomeric parts were removed by washing the polymer films with DCM and the CVs of PEDOT and copolymer films were recorded in monomer free solution between −1.0 and 1.0 V (Figure 3(g)). Although current density decreases with decreasing EDOT in the feed ratio, characteristic capacitive behavior of PEDOT was still observable in the copolymer films.

It is important to note that, when the monomer feed ratio reaches to 1, the problem observed during homopolymerization of CzPDICz was also noted; causing loss of some part of polymer film from the electrode surface into the electrolytic solution. However, the remaining polymer film on the surface was still enough to reflect a different behavior from PEDOT (See Figure 3(f) and (g)).

The copolymer films were scanned with increasing scan rates between −1.0 and 1.0 V in order to observe their scan rate dependancy. The copolymers exhibited a linear increase in current densities with increasing scan rates indicating well adhering electrocative polymer film on the electrode surface and the non-diffusional redox behavior even at high scan rates. The scan rate dependence of the copolymer (4:1) was demonstrated in Figure 4 as a representative example.
sake, EDOT and CzPDICz homopolymers (PEDOT and PCzPDICz) were also prepared on the ITO working electrode surface. After washing with DCM, polymer film-coated electrodes were dipped into monomer free electrolytic solution and were brought into their neutral form by applying −1.0 V potential for 60 s. Electronic absorption spectra of

3.2. Spectrochemical properties of the copolymers

The copolymer films were also investigated in terms of their optical behaviors. The copolymers were obtained on ITO working electrode surface via constant potential electrolysis by applying 1.5 V potential until the same amount of charge of 50 mC cm⁻² passed through the system. For comparison

Figure 6. Collected electronic absorption spectra of PEDOT (a); PCzPDICz (b); copolymers of 9:1, 4:1, 1:1 (c, d, e, respectively) during potential scanning from −1.0 to 1.0 V in 0.1 M ACN-TBABF₄ monomer free solution with scan rate of 20 mV s⁻¹ and colors of homopolymers and copolymers in their neutral and oxidized states (f). (For PCzPDICz, potential scanning range is between −0.5 and 1.2 V).
The percent transmittance values ($T\%$) of the copolymer films at their low lying energy bands were calculated as 27, 32, and 43% for P(9:1), P(4:1), and P(1:1), respectively and $T\%$ of the PEDOT film was calculated as 35%. As seen from the transmittance data, the copolymer formation results with higher $T\%$ values with increasing CzPDICz ratio in the co-monomer mixture.[42] However, the inverse trend was observed for their high energy bands. At their high energy bands, the transmittance percents were found as 15, 14, and 11% for P(9:1), P(4:1), and P(1:1), respectively, further indicating the increasing amount of CzPDICz contribution in the copolymers.

To get insight into morphological differences between homopolymer and copolymer (feed ratio 9:1) films, scanning electron microscopy (SEM) images were taken and are shown in Figure 8. As seen from the figure, both 410 and 595 nm bands lose their intensities during oxidation of the copolymer films which is accompanied by the appearance of new intensifying band located at 850 nm due to formation of charge carriers (i.e. polarons). Upon further oxidation, another band beyond 1000 nm was also noted indicating the bipolaron formation (Figure 6). These changes in the electronic absorption spectra were also accompanied by a color change from blue to transparent blue for PEDOT,[29] yellow to deep yellow for P(CzPDICz), and blue to transparent green for the copolymer films in their neutral and oxidized states, respectively. The different colors of PEDOT (transparent blue) and copolymer films (transparent green) in their oxidized states can be explained in terms of differences in their electronic absorption spectra. A close inspection of Figure 6(e) reveals that the copolymer films absorb visible light in two regions, a band around 410 nm and another one beyond 700 nm, which are essential values for the appearance of green color.[41] Moreover, a grayish color was observed in semi-oxidized states of copolymers which were not observed during oxidation of the homopolymers (Figure 6(f)).

CVs recorded during in-situ spectroelectrochemical studies are also given in Figure 7. As seen from the figure, the intensity in current decreases by the increasing amount of CzPDICz in monomer feed ratio. Moreover, onset oxidation potentials of copolymer films approach to that of CzPDICz homopolymer (0.51 V) with increasing concentration of CzPDICz in the electrolytic solution.

Optical band gap values of the copolymers and homopolymers were calculated from the onsets of $\pi-\pi^*$ transition bands in their neutral absorption spectra and the results are depicted in Table 1. The band gap energies of the copolymers did not show appreciable difference from that of PEDOT albeit they became much lower when compared to band gap of CzPDICz homopolymer (see Table 1).

The percent transmittance values (7%) of the copolymer films at their low lying energy bands were calculated as 27, 32, and 43% for P(9:1), P(4:1), and P(1:1), respectively and 7% of the PEDOT film was calculated as 35%. As seen from the transmittance data, the copolymer formation results with higher 7% values with increasing CzPDICz ratio in the co-monomer mixture.[42] However, the inverse trend was observed for their high energy bands. At their high energy bands, the transmittance percents were found as 15, 14, and 11% for P(9:1), P(4:1), and P(1:1), respectively, further indicating the increasing amount of CzPDICz contribution in the copolymers.

To get insight into morphological differences between homopolymer and copolymer (feed ratio 9:1) films, scanning electron microscopy (SEM) images were taken and are shown in Figure 8. As seen from the figure, the morphology of PEDOT is quite regular with a growth of long curved shapes (Figure 8, left) and the image of P(CzPDICz) is appeared as pollen flowers (Figure 8, right). On the other hand, the morphology of the copolymer film exhibited a smoother surface pattern than that of both homopolymer film surfaces which can be used as a further support for the copolymer formation.
4. Conclusion

In this study, synthesis of a new carbazole (CzPDICz) derivative bearing a strong acceptor unit, and its electrochemical copolymerization with EDOT was reported. The changes in the electrochemical and optical behavior of the copolymer films were investigated with respect to PEDOT and P(CzPDICz) using different monomer feed ratios. The lowest oxidation potential and optimum film formation with well adherence on the electrode surface were obtained from 4:1 EDOT/CzPDICz feed ratio. The copolymer demonstrates blue color in its neutral form as in PEDOT, but transparent green in its oxidized form different from PEDOT (transparent blue). Although copolymer formation lowered both onset oxidation potential (from 0.51 to −0.41 V) and band gap values (from 2.64 to 1.67 eV) as compared to homopolymer of CzPDICz, these values did not exhibit any appreciable difference from that of PEDOT. In summary, the new copolymers exhibited lower band gap values as compared to P(CzPDICz) and different electrochromic response as compared to PEDOT. The copolymers exhibit blue and green colors in their neutral and oxidized states and grayish color in semi-oxidized state which makes them a potential candidate for electrochromic device applications.

Disclosure statement

No potential conflict of interest was reported by the authors.

References

[1] Nalwa HS. Handbook of organic conductive molecules and polymers. Vol. 4. Chichester: Wiley; 1997.
[2] Feast WJ, Tsibouklis J, Pouwer KL, et al. Synthesis, processing and material properties of conjugated polymers. Polymer. 1996;37:5017–5047.
[3] Liscio A, De Luca G, Nolde F, et al. Photovoltaic charge generation visualized at the nanoscale: a proof of principle. J. Am. Chem. Soc. 2008;130:780–781.
[4] Liang Y, Wu Y, Feng D, et al. Development of new semiconducting polymers for high performance solar cells. J. Am. Chem. Soc. 2009;131:56–57.
[5] Song S, Park SH, Jin Y, et al. Synthesis and characterization of low-bandgap copolymers based on dihexyl-2H-benzimidazole and terthiophene. Synth. Met. 2010;160:2618–2622.
[6] Zhou H, Yang L, Stuart AC, et al. Development of fluorinated benzothiadiazole as a structural unit for a polymer solar cell of 7% efficiency. Angew. Chem. 2011;123:3051–3054.
[7] Jin Y, Kang JH, Song S, et al. Poly(p-phenylenevinylene) derivatives containing a new electron-withdrawing CF3F4 phenyl group for LEDs. Bull. Korean Chem. Soc. 2008;29:139–147.
[8] Song S, Jin Y, Kim SH, et al. Synthesis and characterization of polyfluorenevinylene with cyano group and carbazole unit. J. Polym. Sci., Part A: Polym. Chem. 2009;47:6540–6551.
[9] Mortimer RJ, Dyer AL, Reynolds JR. Electrochromic organic and polymeric materials for display applications. Displays. 2006;27:2–18.
[10] Beaujuge PM, Reynolds JR. Color control in Pi-conjugated organic polymers for use in electrochromic devices. Chem. Rev. 2010;110:268–320.
[11] Kelly FM, Meunier L, Cochrane C, et al. Polyaniiline: application as solid state electrochromic in a flexible textile display. Displays. 2013;34:1–7.
[12] Sonmez G, Shen CKF, Rubin Y, et al. A red, green and blue (RGB) polymeric electrochromic device (PECD): the dawning of the PECD era. Angew. Chem. Int. Ed. 2004;43:1498–1502.
[13] Sonmez G, Sonmez HB, Shen CKF, et al. A processable green polymeric electrochrome. Macromolecules. 2005;38:669–675.
[14] Gerard M, Chaubey A, Malhotra BD. Application of conducting polymers to biosensors. Biosens. Bioelectron. 2002;17:345–359.
[15] Arshak K, Velusamy V, Korostynska O, et al. Conducting polymers and their applications to biosensors: emphasizing on foodborne pathogen detection. IEEE Sens. J. 2009;9:1942–1951.
[16] Chochos CL, Choulis SA. How the structural deviations on the backbone of conjugated polymers influence their optoelectronic properties and photovoltaic performance. Prog. Polym. Sci. 2011;36:1326–1414.
[17] Sonmez G. Polymeric electrochromics. Chem. Commun. 2005;14:5251–5259.
[18] Arbizzani C, Mastragostino M, Soavi F. Polythiophene s,s dioxides: an investigation on electrochemical doping. Electrochim. Acta. 2000;45:2273–2278.
[19] Granqvist CG. Electrochromic tungsten oxide films: review of progress 1993–1998. Sol. Energy Mater. Sol. Cells. 2000;60:201–262.
[20] Granqvist CG, Avendano E, Azens A. Electrochromic coatings and devices: survey of some recent advances. Thin Solid Films. 2003;442:201–211.
[21] Avendano E, Berggren L, Niklasson GA, et al. Electrochromic materials and devices: brief survey and new data on optical absorption in tungsten oxide and nickel oxide films. Thin Solid Films. 2006;496:30–36.
[22] Oliver R, Munoz A, Ocampo C, et al. Electrochemical characterisation of copolymers electrochemically synthesised from N-methylpyrrole and 3,4-ethylenedioxythiophene on steel electrodes: comparison with homopolymers. Chem. Phys. 2006;328:299–306.
[23] Zhang Y, Mu S, Zhai J. Nanostructured poly(aniline-co-2,4-diaminophenol) synthesized via chemical copolymerization and the properties of the resulting copolymer. Synth. Met. 2009;159:1844–1851.
[24] Yue R, Yao Z, Geng J, et al. Facile electrochemical synthesis of a conducting copolymer from 5-aminooindole and EDOT and its use as Pt catalyst support for formic acid electrooxidation. J. Solid State Electrochem. 2013;17:751–760.
[25] Wang F, Wilson MS, Rauh RD, et al. Electrochromic linear and star branched poly(3,4-ethylenedioxythiophene-2,6-diuridloxybenzene) polymers. Macromolecules. 2000;33:2083–2091.
[26] Dodabalapur A, Torsi L, Katz HE, et al. Organic heterostructure field-effect transistors. Science. 1995;269:1560–1562.
[27] Sun H, Lu B, Duan X, et al. Electroosynthesis and characterization of a new conducting copolymer from 2′-aminomethyl-3,4-ethylenedioxythiophene and 3,4-ethylenedioxythiophene. Int. J. Electrochem. Sci. 2015;10:3236–3249.
[28] Nie G, Qu L, Xu J, et al. Electroosyses and characterizations of a new soluble conducting copolymer of 5-cyanooindole and 3,4-ethylenedioxythiophene. Electrochim. Acta. 2008;53:8351–8358.
[29] Cansu-Ergun EG, Cihaner A. A new carborane based polymeric electrolyte. J. Electroanal. Chem. 2013;707:78–84.
[30] Cheng YJ, Yang SH, Hsu CS. Synthesis of conjugated polymers for organic solar cell applications. Chem. Rev. 2009;109:5868–5923.
[31] Hu B, Zhang YJ, Lv XJ, et al. Electrochemical and electrochromic properties of two novel polymers containing carbazole and phenyl-methanone units. J. Electroanal. Chem. 2013;689:291–296.
[32] Hu B, Lv XJ, Sun JW, et al. Effects on the electrochemical and electrochromic properties of 3,6 linked polycarbazole derivative by the introduction of different acceptor groups and copolymerization. Org. Electron. 2013;14:1521–1530.
[33] Hu B, Luo W, Jin J, et al. Electrochemical and spectroelectrochemical properties of poly(carbazole-EDOT)s derivatives functionalized with benzonitrile and phthalonitrile units. ECS J. Solid State Sci. Technol. 2016;5: P21–P26.
[34] Aydın A, Kaya I. Synthesis and characterization of yellow and green light emitting novel polymers containing carbazole and electroactive moieties. Electrochim. Acta. 2012;65:104–114.
[35] Aydın A, Kaya I. Syntheses of novel copolymers containing carbazole and their electrochromic properties. J. Electroanal. Chem. 2013;691:1–12.
[36] Ates M, Uludag N, Arican F. Copolymer formation of 4-vinylbenzyl-9H-carbazole-9-carbodithioate and ethylenedioxythiophene and capacitive behavior. High Perform. Polym. 2014;26:587–597.
[37] Jayakannan M, Van Hal PA, Janssen RAJ. Synthesis and structure–property relationship of new donor–acceptor type conjugated monomers and polymers on the basis of thiophene and benzothiadiazole. J. Polym. Sci., Part A: Polym. Chem. 2002;40:251–261.
[38] Yasutania Y, Honsho A, Saekia A, et al. Polycarbazoles: relationship between intra- and intermolecular charge carrier transports. Synth. Met. 2012;162:1713–1721.
[39] Dhanalakshmi K, Saraswathi R. Electrochemical preparation and characterization of conducting copolymers: poly(pyrrrole-co-indole). J. Mater. Sci. 2001;36:4107–4115.
[40] Sonmez G, Schwendeman SL, Schottland P, et al. N-substituted poly(3,4-propylenedioxyxrypyrrole): high gap and low redox potential switching electroactive and electrochromic polymers. Macromolecules. 2003;36:639–647.
[41] Hongtao Y, Shan S, Lijia Y, et al. Side-chain engineering of green color electrochromic polymer materials: toward adaptive camouflage application. J. Mater. Chem. C, 2016;4: 2269–2273.
[42] Varis S, Ak M, Akhmedov IM, et al. A novel multi electrochromic copolymer based on 1-(4-nitrophenyl)-2,5-di(2-thienyl)-1H-pyrrrole and EDOT. J. Electroanal. Chem. 2007;603:8–14.