Polymers as Sensors

Green as it Gets; Donor-Acceptor type Polymers as the Key to Realization of RGB Based Polymer Display Devices

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Summary: Polymers that have one of the three complementary colors (red, green, and blue, RGB) in the neutral state and high transmissivity in the oxidized state are the key materials towards use in electrochromic devices and displays. Although many neutral state red and blue polymers have been reported up to date, green polymers with highly transmissive oxidized states, high optical contrasts, fast switching times, and advanced long-term switching stabilities were essentially missing in the literature. This paper reviews our previous efforts towards realization of neutral state green polymers with highly transmissive oxidized state. The key to this problem was found to be the synthesis of donor-acceptor polymers bearing benzothiadiazole or quinoxaline derivatives as the acceptor and electron rich 3,4-ethylenedioxythiophene unit as the donor component. Green neutral state polymeric materials with highly transmissive oxidized state with excellent electrochromic properties have been realized with the design and synthesis of these types of materials. A solution processable green polymeric material has also been realized via chemical polymerization that has shown all superior properties of the electrochemically synthesized counterparts.

Keywords: donor-acceptor polymers; green polymers; processable electrochromics; RGB based display devices

Introduction

The only possible way for realization of RGB based full-color display devices is the syntheses of polymeric materials that have the primary colors in their neutral state[1]. The research in syntheses of electrochromic polymers have been fruitful over the last 20 years but the polymers generally reflected blue or red color in their neutral state.[2] This is due to one wavelength dependence of the most of the colors, especially blue and red. A neutral state green polymeric material had to be realized for the completion of RGB color space to generate all the colors in the visible spectrum. It took over 20 years for the synthesis and characterization of first neutral state green polymeric material, PDDTP, poly(2,3-di(thien-3-yl)-5,7-di(thien-2-yl)thieno[3,4-b]pyrazine).[1] Sonmez et. al. successfully described the synthesis and all electrochemical and electrochromic properties of this highly promising material. The polymer can be classified as a breakthrough in the era since it had a green color in neutral state, had very fast switching times and an outstanding stability of 10 000 cycles. Unfortunately, as Sonmez et. al described in his following paper,[3] that there was a significant drawback which obstruct the use of this material in commercial applications; the residual brown color in the oxidized state. In addition to the need of primary colors in

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the neutral state towards realization of RGB base polymeric display devices the polymeric materials should possess a highly transmissive oxidized state. For a polymer to reveal green color there should be two absorption bands in certain regions of the visible spectrum. Additionally, these absorption bands should be simultaneously depleted upon oxidation to create a transparent state. Research over the last years clearly pointed out that donor-acceptor type polymers can satisfy the above conditions.[4] Donor-acceptor type polymers commonly reveal two absorption bands due to the transitions from the valence band (thiophene-based units) to the antibonding orbital, and between the valence band and the narrow conduction band (localized mainly on the donor substituents).[5] Moreover, these absorption bands tend to deplete simultaneously upon oxidation. Furthermore, donor-acceptor polymers lead to a narrower bandgap due to the resonances that enable a stronger double bond character between the donor and acceptor moieties.[6] If we take into account that the first green polymeric material was also a donor-acceptor type polymer, the starting point for the design of new green polymeric materials with transmissive oxidized states should be the synthesis of different donor-acceptor systems. The ultimate goal is the synthesis of a polymeric material with a neutral state green color with highly transmissive oxidized state, very high optical contrasts, fast switching times and significant switching stability. The paper highlights our previous efforts for the synthesis and characterization of neutral state green polymers with transmissive oxidized states.

Results and Discussion

The first polymeric materials designed and synthesized towards the goal was GS. The same acceptor moiety of DDTP has been chosen but instead of thiophene, EDOT units have been utilized. (Figure 1)

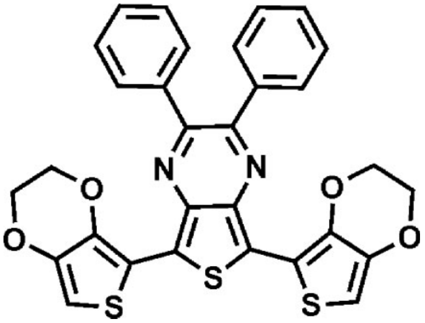


Figure 1.
5,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-diphenylthieno[3,4-b]pyrazine (GS).

Although the polymer revealed two absorption bands, the higher wavelength band was in the NIR region and had no contribution to the color of the polymer. This resulted in a red colored polymer in neutral state which upon oxidation becomes highly transmissive[7] (Figure 2). Although the neutral state color did not meet the expectations, we realized that the introduction of EDOT units as the donor moieties enhanced the transmissivity in the oxidized state and revealed a polymer with a substantially lower band gap. The factor that determines the position of absorptions band in the visible region is the match between donor and acceptor moieties. At this point we concluded that the EDOT units' donor capacity was a higher match for thienopyrazine to realize the green color, hence a stronger acceptor group had been replaced with the thienopyrazine unit which is benzothiadiazole. Although the target molecule has been synthesized in the literature, the electrochromic properties were not examined[8].

The monomer was synthesized according to the literature methods and the electrochemical and electrochromic properties were investigated. Spectroelectrochemistry studies revealed fruitful results.[9]

The corresponding polymer PBDT had a saturated green color in the neutral state. Upon oxidation both absorption bands depleted to reveal a highly transmissive light blue oxidized state (Figure 4). The kinetic studies showed substantial increase in optical contrasts compared to PDDTP (37% at 428 nm and 23% at 755 nm versus

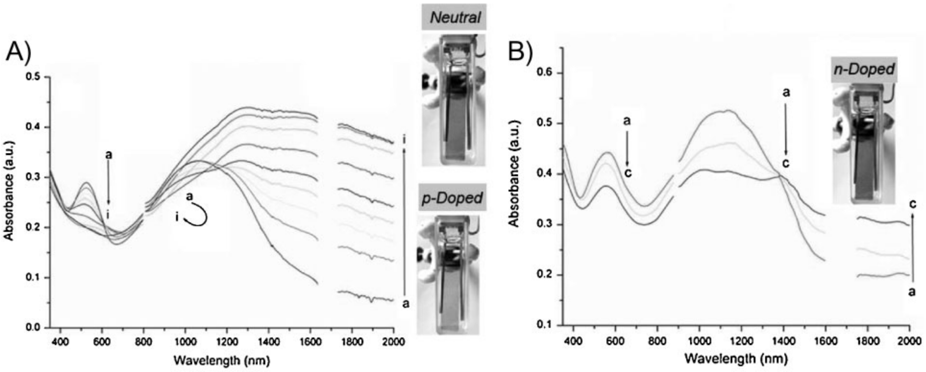


Figure 2.
Spectroelectrochemistry of PGS film on an ITO coated glass slide in monomer-free 0.1M TBAPF6/ACN electrolyte solution. (A) p-type doping at applied potentials: (a) -0.8, (b) -0.6, (c) -0.5, (d) -0.4, (e) -0.3, (f) -0.1, (g) 0.2, (h) 0.5, (i) 0.8. vs Ag/Ag$^+$. (B) n-type doping at applied potentials: (a) -1.7, (b) -2.0, (c) -2.2 V vs Ag/Ag$^+$.

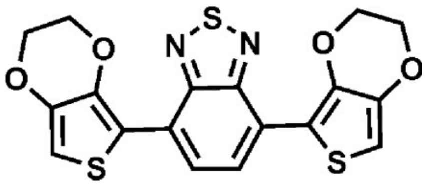


Figure 3.
4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo-[c][1,2,5]thiadiazole (BDT).

23% at 370 nm and 12% at 725 nm) without any significant increase in switching times(ca. 1 second). PBDT is highly stable, no significant charge loss was observed even after 5000 consecutive cycles.

Although PBDT is the first green polymeric electrochromic with a highly transmissive oxidized state there was still room for improvement in optical contrast. Additionally the benzothiadiazole unit is

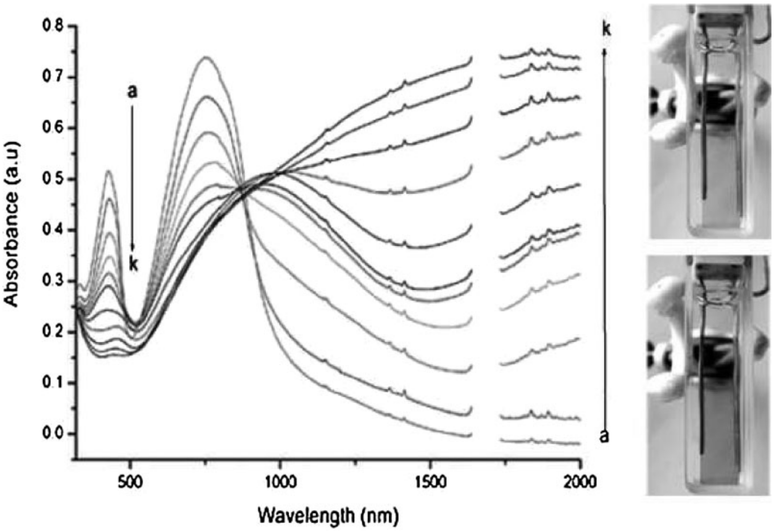
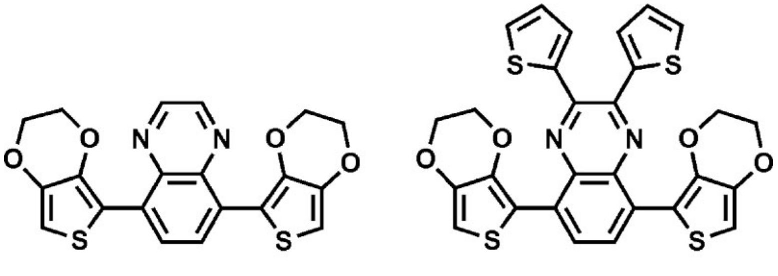


Figure 4.
Spectroelectrochemistry of PBDT film on an ITO coated glass slide in monomer-free, 0.1 M TBAPF6–MeCN electrolyte–solvent couple at applied potentials; (a) -0.8, (b) -0.5, (c) -0.2, (d) -0.15, (e) 0.0, (f) 0.1 (g) 0.3, (h) 0.5, (i) 0.7, (j) 0.9, (k) 1.1 V.



DEQ **DETQ**

Figure 5.
5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3 diphenylquinoxaline (DEQ) and 2,3-bis(4-tert-butylphenyl)-5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline (DETQ).

not convenient for further modifications towards the synthesis of a processable green polymeric material. Hence quinoxaline was chosen as the acceptor unit since it has similar acceptor capacity with benzothiadiazole and can be modified easily for fine tuning of the color and solubility. The unsubstituted quinoxaline was chosen as the starting point.[10] Dibromoquinoxaline was prepared according to literature procedures and Stille coupling was performed with stannylated EDOT to give the title monomer in good yield. The monomer was highly electroactive and quickly polymerized to give PDEQ.

The spectroelectrochemistry studies revealed a bluish green color in the neutral state and a highly transmissive blue color in the oxidized state (Figure 6). At this point it has been realized that the acceptor capacity of quinoxaline was not strong enough since the polymer revealed similar characteristics with those of PEDOT. To increase the acceptor capacity, a quinoxaline unit with an extended conjugation was proposed. Two thiophene units were introduced on the quinoxaline moiety and used as the acceptor unit(DETQ). The results were fruitful. Spectroelectrochemistry results revealed a saturated green color in the

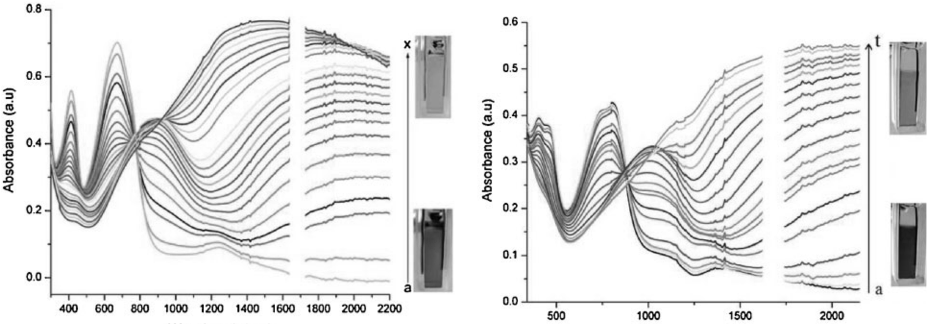


Figure 6.
Left. Spectroelectrochemistry of PDETQ film on an ITO coated glass slide in monomer-free, 0.1 M TBAPF6/ACN electrolyte-solvent couple at applied potentials (V): (a) -1.0, (b) -0.8, (c) -0.5, (d) -0.4, (e) -0.3, (f) -0.25, (g) -0.2, (h) -0.15, (i) -0.1, (j) -0.05, (k) 0, (l) 0.1, (m) 0.2, (n) 0.3, (o) 0.4, (p) 0.5, (q) 0.6, (r) 0.7, (s) 0.9, and (t) 1.0. Right. Spectroelectrochemistry of PDEQ film on an ITO coated glass slide in monomer-free, 0.1 M TBAPF6/ACN electrolyte-solvent couple at applied potentials (V): (a) -1.0, (b) -0.6, (c) -0.5, (d) 0.0, (e) 0.05, (f) 0.1, (g) 0.15, (h) 0.2, (i) 0.25, (j) 0.3, (k) 0.35, (l) 0.4, (m) 0.45, (n) 0.5, (o)0.55, (p) 0.6, (q) 0.65, (r) 0.7, (s) 0.75, (t) 0.8, (u) 0.85, (v) 0.9, (w) 0.95, and (x) 1.0.

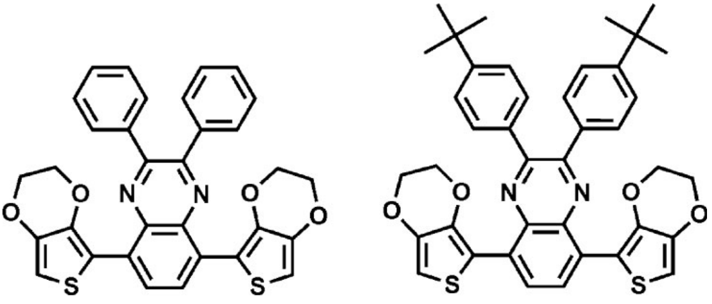
neutral state and highly transmissive oxidized state (Figure 6).

The kinetic studies showed that, the polymer revealed an optical contrast of 30% at 780 nm and 20% at 405 nm which are significantly better that PDDTP. PBDT had better characteristics than this polymer but quinoxaline unit enabled us the flexibility for the fine tuning of the structure. Massive changes in both electrochemical and electrochromic properties were observed when hydrogens in quinoxaline exchanged with thiophene units.

Since the green color has been successfully attained with PDETQ, we believed that minor modifications are reasonable for fine tuning of the color and to improve electrochromic properties. To do so, thiophene units were replaced with benzene units and the corresponding monomer was synthesized via Stille coupling.[11] The monomer had very limited solubility in either chloroform or DMSO which caused difficulties in its characterization. Only ^{1}H-NMR spectrum has been successfully recorded. t-Butyl groups were introduced on the para position of pendant phenyl rings to increase the solubility.

The resulting monomer had very good solubility in common organic solvents and full characterization of the monomer was achieved. The electrochemical and electrochromic properties of both monomers and corresponding polymers have been studied extensively. Both monomers were highly electroactive and easily polymerized on ITO and spectroelectrochemistry studies were performed. Both polymers revealed two distinct absorption bands, which is a necessity to have neutral state green conducting polymers. Even though having two absorption bands is crucial for generation of green color, absorption wavelengths are the decisive values for green color to be observed.

The absorption maxima of PTBPEQ are centered at 452 and 711 nm whereas for PDPEQ they are at 448 and 732 nm. These values are the accurate absorption maxima values for neutral state green polymers. T-butyl groups affected the monomer oxidation and the polymer redox couple potentials, additionally the maximum absorption wavelengths were shifted significantly. This behavior can be attributed to the different corresponding electronic structures of the polymers, which signifies the different acceptor capacities of the quinoxaline derivatives and the unique donor–acceptor matches with EDOT moieties. The kinetic studies were even more interesting. Although the t-butyl groups were only introduced to induce solubility, they had also a significant effect on the optical contrasts. PDPEQ showed a 35% at 448 nm and % 29 optical contrasts at 732 nm. PTBPEQ had a very similar optical contrast of 33% at 452 nm but a very high optical contrast increase (14%) was observed at 711 nm (% 43). Hence,



DPEQ **TBPEQ**

Figure 7.
5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-diphenylquinoxaline (DPEQ) and 2,3-bis(4-tert-butylphenyl)-5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline (TBPEQ).

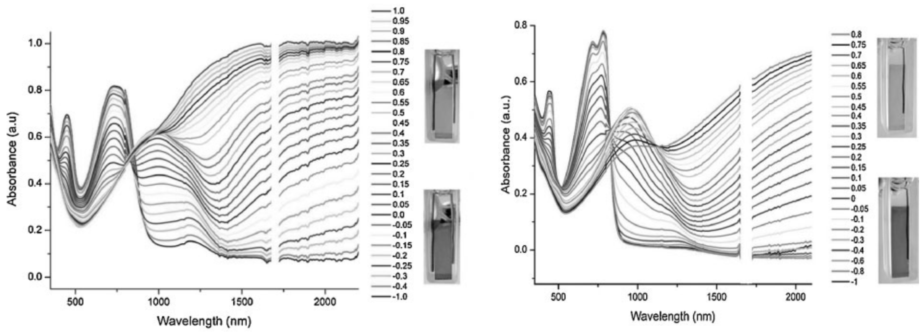
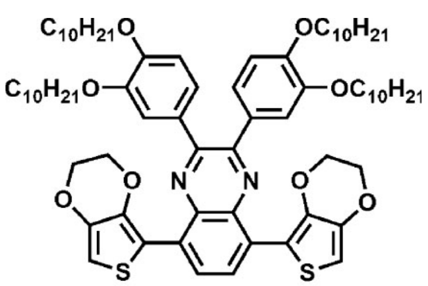


Figure 8.
Spectroelectrochemistry of PDPEQ film on an ITO coated glass slide in monomer free, 0.1 M TBAPF6/ACN electrolyte-solvent couple at applied potentials between -1.0 to 1.0 V and Spectroelectrochemistry of a PTBPEQ film on an ITO-coated glass slide in monomer-free, 0.1M TBAPF6/ACN electrolyte–solvent couple at applied potentials between −1.0 V and 0.8 V.

PTBPEQ had a 76% optical contrast change in the visible region which resulted in a very saturated green color in the neutral and extremely high transmissivity in the oxidized state (Figure 8).

This value nearly doubles the optical contrast value of the first example of green polymeric material, PDDTP. At this point, we believe that there is no need for further modification in the structure since all optical contrast values, switching times and long-term stabilities were highly satisfactory. PTBPEQ can satisfy all the requirements for completing the 3rd leg of the RGB color space towards realization of electrochromic display devices. However, for commercial applications the ease of monomer synthesis and solution processibility of the polymer is crucial.



DOPEQ

Figure 9.
2,3-bis(3,4-bis(decyloxy)phenyl)-5,8-bis(2,3-dihydrothieno[3,4-b][1,4] dioxin-5-yl)quinoxaline.

Although we know the fact that alkyl groups on the para position of the phenyl rings result in appropriate acceptor capacity, introduction of long alkyl chains on the pendant phenyl rings are not trivial. It is a fact that t-butyl groups are more electron-donating than hydrogens. This motivated us to introduce long alkoxy chains on the phenyl rings since increased electron density will be in favor of fine tuning of the color and introduction of alkoxy chains are trivial.[12] The diketone synthesis could not be achieved by simple benzoin condensation due to the electron donating ability of the alkoxy chains. Hence, a simple Friedel-Craft acylation reaction was performed to synthesize the diketone. The alkoxy substituted quinoxaline unit was prepared and the corresponding monomer was also realized by Stille coupling reaction.

The monomer was both electrochemically and chemically polymerized (PDOPEQ). Spectroelectrochemistry studies clearly revealed that PDOPEQ has a highly saturated green color in the neutral state whereas it is highly transmissive in the oxidized state. These results imply the synthesis and characterization of the first solution processable green polymeric material with a transmissive oxidized state in the literature.

The electrochemically synthesized polymer showed a remarkable optical contrast of 42% at 690 nm and 29% at 415 nm. The

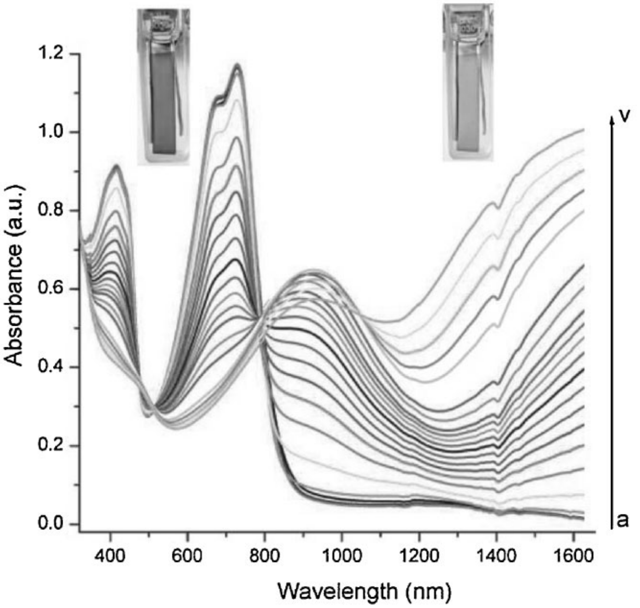


Figure 10.
Colors of PDOPEQ film on an ITO-coated glass slide at neutral and oxidized states and spectroelectrochemistry of an PDOPEQ film on an ITO-coated glass slide in a monomer-free 0.1M TBAPF6/ACN electrolyte–solvent couple at applied potentials: (a) - 0.6, (b) - 0.15, (c) 0 (d) 0.05, (e) 0.075, (f) 0.1 (g) 0.15, (h) 0.175, (i) 0.2, (j) 0.225, (k) 0.25, (l) 0.275, (m) 0.3, (n) 0.35, (o) 0.4, (p) 0.45, (q)0.5, (r) 0.55, (s) 0.6, (t) 0.65, (u) 0.7, (v) 0.8 V.

polymer had switching times around 1 second for both absorption maxima and revealed excellent long term stability. The polymer retained 90% of its activity even after 5000 repetitive cycles. The polymer has been prepared by a simple $FeCl_3$ catalysis and has revealed all superior properties of the chemically synthesized polymer.

Conclusion

In conclusion, donor-acceptor type polymers with careful design and synthesis were proven to be the key materials for tuning the desired electrochemical and electrochromic properties. The donor-acceptor type polymer, PBDT, was shown to be the first neutral state green polymeric material with a transmissive oxidized state, fast switching time and long term stability. PTBPEQ showed that the electrochromic properties were highly improved by the introduction of phenyl substituted quinoxaline units, especially with a t-butyl group on the para position. The substantial effect of t-butyl groups was remarkable. PDOPEQ added the most important characteristic towards commercial applications, solubility, to all the superior properties of PBDT and PTBPEQ and proven to be first proccesable green polymeric material with a transmissive oxidized state.

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