

Synthesis, chemically and electrochemically polymerization of *N*-substituted pyrrole containing azo chromophore and its copolymerization with pyrrole

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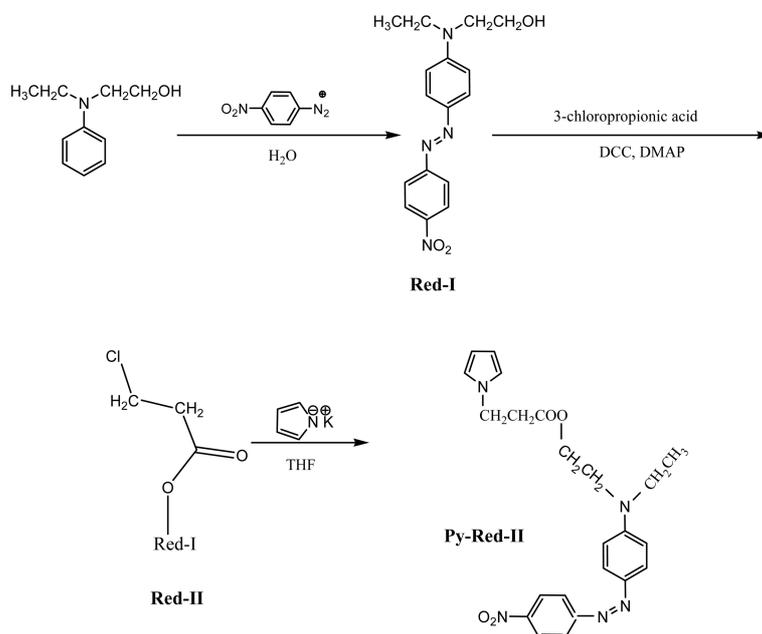
Abstract. This article describes the synthesis of a novel *N*-substituted pyrrole monomer containing an azobenzene group. The 2-[*N*-ethyl-*N*-[4-[(4-nitrophenyl) azo]-phenyl] amino] ethyl-3-chloropropionate (RedII) compound was synthesized via reaction of 4-nitro-4'-[*N*-ethyl-*N*-(2-hydroxyethyl)-amino] azobenzene (RedI) and 3-chloropropionic acid. RedII was reacted with the potassium salt of pyrrole then 2-[*N*-ethyl-*N*-[4-[(nitro phenyl) azo] phenyl] amino] ethyl-*N*-pyrrolyl propionate (Py-RedII) was prepared. Chemical polymerization of Py-RedII and copolymerization of Py-RedII with pyrrole carried out using FeCl₃. Poly (2-[*N*-ethyl-*N*-[4-[(nitro phenyl) azo] phenyl] amino] ethyl-*N*-pyrrolyl propionate) (PPy-RedII) was characterized by UV, IR, ¹HNMR, ¹³CNMR spectroscopies. Electropolymerization of Py-RedII and electroco-polymerization of Py-RedII and pyrrole were studied using conventional three electrodes system, Ag/AgCl reference electrode, platinum counter electrode and GC disk working electrode. Scanning electron microscopy (SEM), thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) were used for thermal and rheological studies. The TGA curve of PPy-RedII demonstrated a high thermal stability up to 200°C and its DSC thermogram showed two endothermic peaks at 88 and 122°C. The glass transition temperature of the polymer was found to be above the room temperature. Electrical conductivities of PPy-RedII and its copolymer with pyrrole (PPy-RedII-co-Py) were studied by the four-probe method and produced conductivities of 7.5×10⁻⁴ and 6.5×10⁻³ S cm⁻¹, respectively.

Keywords: azo polymers; conductivity; liquid crystals polymers; polypyrroles

1. Introduction

Intrinsically conducting polymers have high conductivities, which can be compared with pure metal (Pron *et al.* 2003). They are beginning to find applications in the fields of battery materials (Cai *et al.* 2004) electrochromic displays (Arslan *et al.* 2007), electromagnetic shielding (Hosseini *et al.* 2011, 2012), sensor technology (Haynes *et al.* 2008), non-linear optics (Salaneck 1991) and molecular electronics (Bradly 1991). Also conducting polymers based on cyclic monomers, are belonged to compounds with a high environmental stability to oxygen and water. Electrodeposition of freestanding films of polypyrrole as sensor (Ansari *et al.* 2012) opened the way to intensive research into polyheterocyclic and polyaromatic conducting polymers (Hosseini *et al.* 2003). The electrochemical

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Scheme I Synthesis scheme of Red-I, Red-II and Py-Red-II

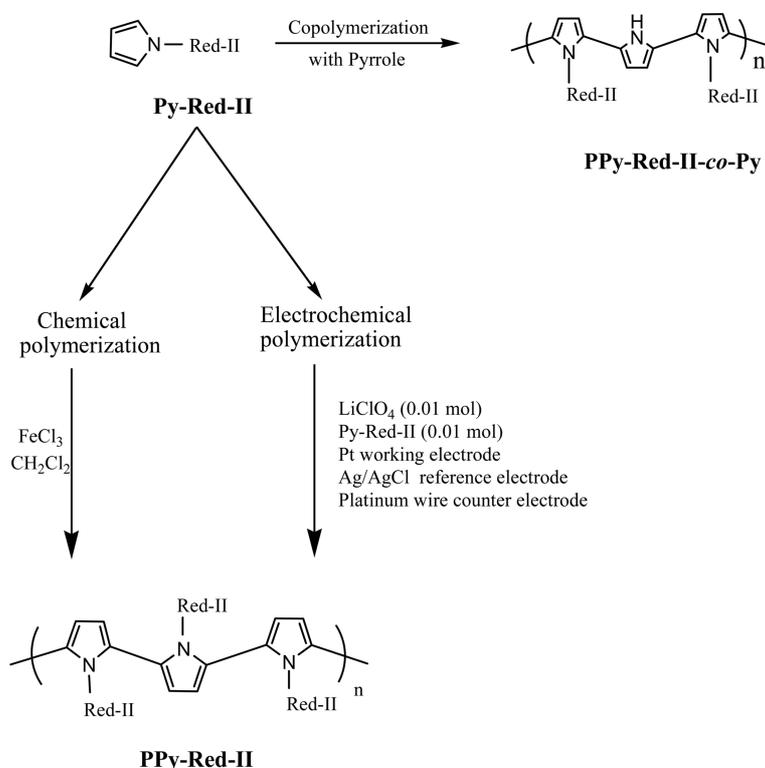
oxidation of these resonance - stabilized aromatic molecules have become one of the principal methods for preparing conjugated, electronically conducting polymers. Since the first reports of the oxidation of pyrrole, many other aromatic systems have been found undergo electro polymerization to produce conducting polymers (Hosseini *et al.* 2003, 2005). This includes, thiophene (Kiani *et al.* 2008), aniline (Munñoz *et al.* 2007), azulene (Campbell *et al.* 2007), as well as many substituted, multi-ring and polynuclear aromatic hydrocarbon systems. All the resulting polymers have a conjugated backbone, which is required for electro activity. Many studies have been carried out on the polymerization of derivatives of pyrrole and thiophene. Methods of substitution for thiophenes are well established and attachment of a simple alkyl chain to the 3-position is known to increase the solubility and fusibility of the polymers (Hosseini *et al.* 2000, 2001). 3-Substitued pyrroles and thiophenes are nonsymmetrical molecules and may be considered as having a head and a tail but *N*-substitued pyrroles are essentially symmetrical molecules. Under mild oxidizing conditions, order and planarity of the polymer backbone are increased. In this research, we have reported preparation of polypyrrole functionalized with azobenzene type chromophore. Such materials are very interesting for several reasons:

1. Azobenzene derivatives are photochromic compounds. Moreover, these photo chromic properties retain to a large extent in azobenzene derivatives grafted to the polypyrrole backbone as demonstrated by Levesque and Leclerc (Levesque *et al.* 1997).

2. Azobenzene chromophore substituted polypyrroles should exhibit very interesting electrochemical behavior, because of combination of the electroactivity of the conjugated backbone and the side chain.

3. The materials containing azobenzene group may have liquid crystalline properties that will be study in the future research.

In the previous works, we synthesized a new liquid single crystal (Yousefi *et al.* 2008,



Scheme II Schematic of chemical and electrochemical polymerization of Py-Red-II and its copolymerization with pyrrole

Zakerhamidi *et al.* 2010) and reported liquid crystalline polymer based *N*-substituted pyrrole (Hosseini *et al.* 2009). This polymer exhibit liquid crystalline and electrically conductivity properties, as well. In this research we have prepared a novel chromophore for functionalization of pyrrole, namely, 2-[*N*-ethyl-*N*-[4-[(4-nitrophenyl) azo]-phenyl] amino] ethyl-3-chloro propionate (RedII), (Scheme I). In addition, we have focused on the chemical and electrochemical polymerization of resulting monomer (Py-RedII) and its copolymerization with pyrrole and investigation of their spectroelectrochemical and thermal properties (Scheme II).

2. Experimental

2.1 Reagents and materials

Pyrrole (Fluka 96%) was distilled prior to use. Methanol (Fluka) and tetrahydrofuran (Merck) were distilled and dried with molecular sieves (4Å) prior to use. Methylene chloride (CH_2Cl_2) was distilled and dried with CaCl_2 prior to use. The chemicals were as follow: Iron (III) chloride (Merck 99%), 4-nitroaniline (Merck 98%), dicyclohexyl carbodiimide (DCC) (Merck 98%), 4-(dimethylamino) pyridine (DMAP) (Merck 99%), 3-chloropropionic acid (Merck 98%), Sodium nitrite (NaNO_2) (Merck 99%), 2-(*N*-ethyl aniline) ethanol (Merck 99%)

2.2 Instruments

Conductivity changes were measured with four-probe device (home made). A Fourier transform infrared spectrometer (8101 M-Shimadzu) was used. Band intensities were assigned as weak (*w*), medium (*m*), short (*sh*), strong (*s*) and broad (*br*). Cyclic voltammetries and electrochemical polymerization were carried out using digital potentiostat otolab-30. Proton and carbon nuclear magnetic resonance (^1H & ^{13}C NMR) spectra were recorded at 250 MHz on a Bruker. UV-Visible spectra were obtained by Perkin Elmer Lambda 15 spectrophotometer. The Perkin-Elmer (DSC-4) and Perkin-Elmer pyris-1 were used for thermal analyzes and the PHILIPSLX30 was used for scanning electron microscopy (SEM).

2.3 Preparation of 2-[N-ethyl-N-[4-[(4-nitrophenyl) azo]-phenyl] amino] ethyl (RedI)

A total of *p*-nitro aniline (7 gr, 0.05 mol) was dissolved in HCl (10%) (50 ml) as solvent. The mixture was heated to 30°C for 15 min and then, allowed to be cooled. In the next step 3.6 gr of NaNO_2 (0.05 mol) in H_2O (5 ml) was added and stirred for 30 min. A solution of *N*-ethyl-*N*-hydroxy ethyl aniline (10 gr, 0.03 mol) in HCl (10%) was prepared in the other container at 0°C simultaneously. The latter was added dropwise to the initial solution. The reaction was stirred for 30 min and then, neutralized by NaOH (10% *w/v*). Finally, filtration was followed by evaporation of the solvent and afforded a red solid which recrystallised with isopropanol. (yield 85%, red crystals). UV (ethanol); $\lambda_{\text{max}} = 470 \text{ nm}$ (1.25 intensity). FT-IR (KBr): 3250, 3100, 2979, 1594, 1512, 1469, 1320, 780, 650 cm^{-1} . ^1H NMR (CDCl_3): 1.26 (3H, *t*), 1.75 (1H, *s*), 3.56 (2H, *q*), 3.62 (2H, *t*), 3.90 (2H, *t*), 6.81 (2H, *d*), 7.88 (2H, *d*), 7.92 (2H, *d*), 8.32 (2H, *d*) ppm. ^{13}C NMR (CDCl_3): 12.1, 25.8, 46.4, 61.1, 112.3, 122.5, 124.7, 126.6, 143.8, 145.6, 151.6, 155.7 ppm.

2.4 Preparation of 2-[N-ethyl-N-[4-[94-nitrophenyl] azo]-phenyl] amino] ethyl-3-chloro propionate (RedII)

3-Chloropropionic acid (1.52 gr, 0.014 mol) and RedI (3.77 gr, 0.012 mol) (crystallized in isopropyl alcohol) were dissolved in 80 ml of dry CH_2Cl_2 . Then 2.59 gr (0.013 mol) of dicyclohexyl carbodiimide (DCC) and 0.22 gr (0.0018 mol) of 4-(dimethylamino) pyridine (DMAP) were added to the vigorously stirred solution. The stirring was continued for 24 h. The mixture was then filtered and the solvent was evaporated in *vacuo*. The product was purified by column chromatography eluting with hexane–EtOAc. (yield 50%, red crystals, m.p: 83.5°C). UV (ethanol); $\lambda_{\text{max}} = 475.5 \text{ nm}$ (1.23 intensity). FT-IR (KBr): 3126, 2979, 1728, 1603, 1515, 1464, 1340, 1141 cm^{-1} . ^1H NMR (DMSO): 1.16 (3H, *t*), 2.82 (2H, *t*), 3.55 (2H, *q*), 3.73 (2H, *t*), 3.73 (2H, *t*), 4.29 (2H, *t*), 6.91 (2H, *d*), 7.84 (2H, *d*), 7.99 (2H, *d*), 8.35 (2H, *d*) ppm. ^{13}C NMR (DMSO): 11.9, 13.8, 36.9, 44.9, 48.1, 61.8, 111.6, 122.4, 124.9, 126, 142.8, 146.8, 151.5, 156.1, 170. ppm.

2.5 Preparation 2-[N-ethyl-N- [4-[(nitro phenyl) azo] phenyl] amino] ethyl-N-pyrrolyl propionate (Py-RedII)

A sample of solid potassium (0.8 gr, 0.02 mol) was added to a solution of pyrrole (14 ml, 0.02 mol) in dry THF (30 ml). The mixture was refluxed under nitrogen atmosphere for 2 h until the

formation of yellow pyrrole salt. Subsequently RedII (1.6 gr, 0.004 mol) in dry THF (10 mL) was added dropwise over a period of 10 min at room temperature and allowed to be stirred for 24 h. The solvent was removed under vacuum. (yield 45%, red crystal, mp: 100°C). UV (ethanol); λ_{\max} = 483.5 nm (1.854 intensity), 361.5 nm (0.154 intensity), 322.0 nm (0.323 intensity). FT-IR (KBr): 3126, 2979, 1728, 1603, 1515, 1464, 1340, 1141, 1096, 858 cm^{-1} . ^1H NMR (CDCl_3); 1.23 (3H, *t*), 2.75 (2H, *t*), 3.47 (2H, *q*), 3.63 (2H, *t*), 4.18 (2H, *t*), 4.30 (2H, *t*), 6.13 (4H, 6.12-6.64, *m*), 6.78 (2H, *d*), 7.92 (2H, *d*), 7.92 (2H, *d*), 8.32 (2H, *d*) ppm. ^{13}C NMR (CDCl_3); 12.3, 36.5, 44.9, 45.9, 48.9, 61.6, 108.6, 112.0, 120.6, 122.5, 124.8, 127.0, 143.6, 147.5, 151.7, 155.96, 171.0 ppm.

2.6 Chemical polymerization of Py-RedII using iron chloride

The Py-RedII monomer (0.01 mol) in methylene chloride (5 ml) was added dropwise to a suspension of anhydrous FeCl_3 (0.1 mol) in methylene chloride (50 ml) under nitrogen atmosphere. The mixture was stirred at room temperature for 24 h. The polymer in solution was precipitated by addition of excess methanol. The precipitate was extracted using boiling absolute ethanol and dried under vacuum.

UV (DMSO); λ_{\max} = 680 nm (0.072 intensity), 487 nm (0.183 intensity), 322 nm (0.11 intensity). FT-IR (KBr): 3110, 2963, 2924, 1722, 1595, 1516, 1447, 1338, 1137, 1104, 860 cm^{-1} . ^1H NMR (DMSO); 1.17 (3H, *t*), 2.37 (2H, *t*), 3.53 (2H, *q*), 3.61 (2H, *t*), 4.01 (2H, *t*), 6.87 (2H, *d*), 7.37-7.55 (2H, *m*), 7.82 (2H, *d*), 7.91 (2H, *d*), 8.35 (2H, *d*) ppm. ^{13}C NMR (DMSO); 170.1, 155.6, 151.2, 146.0, 141.8, 133.2-132.8, 127.2, 125.4-125.5, 124.2, 121.8-121.7, 119.6, 110.8, 106.5, 57.5, 51.2, 45.6, 44.6, 11.2 ppm.

2.7 Electrochemical polymerization of Py-RedII

Electrochemical polymerization of Py-Red-II (1 mmol) and its copolymerization with pyrrole (0.5 mmol) were performed using a conventional three electrode system with Ag/AgCl reference electrode (0.01 mol L^{-1}) platinum wire counter electrode and GC disk working electrode. All solutions for electrochemical polymerization were freshly prepared. Acetonitrile was distilled in presence of calcium hydride and kept over molecular sieves. In the solution of lithium perchlorate (0.1 M) in acetonitrile, dry nitrogen gas was bubbled for 20 minutes before each polymerization.

3. Results and discussion

3.1 Cyclic voltammetry studies

Fig. 1 shows the traces obtained from successive cyclic voltammetry (CV) of the Py-RedII. The peaks of the cyclic voltammogram of the sample appear at potentials (versus Ag/AgCl) of 1.25 and 1.80 V, together with a shoulder on the latter at 1.57 V.

The peaks at 1.57 and 1.75 V are attributed to oxidation of pyrrole ring and mesogenic unit. The two reduction peaks at 1.40 and 1.60 V correspond to azobenzene group according to those reported in literature (Langley *et al.* 1997).

The different peak potentials at the more anodic voltages for the *N*-substituted pyrroles can be related to different chemical processes. Under these conditions, a polymer film was deposited on the

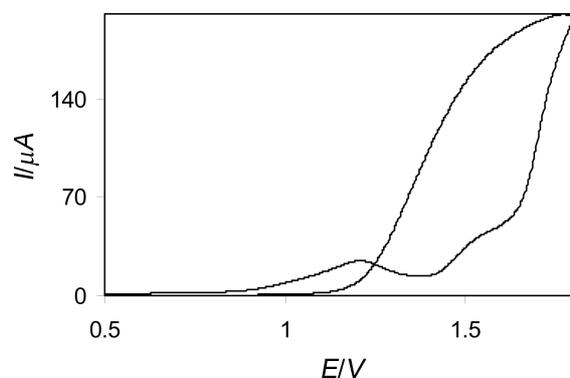


Fig. 1 Cyclic voltammogram of Py-Red-II (1 mmol) on a GC disk electrode vs. Ag/AgCl reference electrode and LiClO_4 (0.1 M) in 20 mL acetonitrile, $\nu = 50 \text{ mVs}^{-1}$

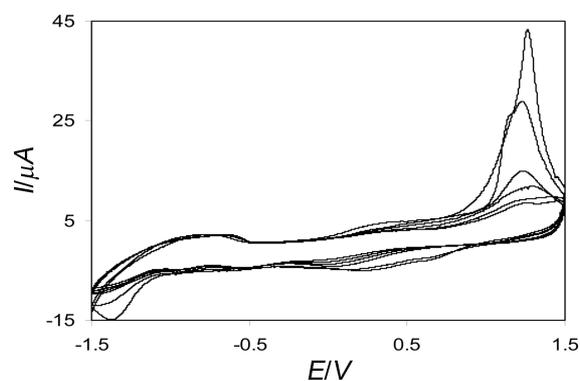


Fig. 2 Cyclic voltammograms of PPy-Red-II-co-Py formation [(Py-Red-II (1 mmol) and Pyrrole (0.5 mmol)], LiClO_4 (0.1 M) in 20 mL acetonitrile on GC disk electrode vs. Ag/AgCl reference electrode, $\nu = 50 \text{ mVs}^{-1}$ (10 cycles)

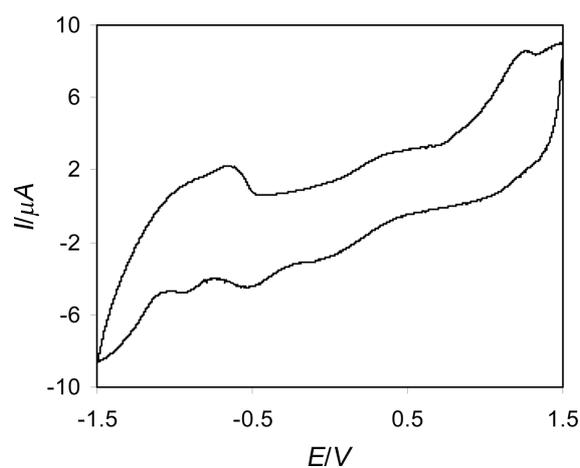
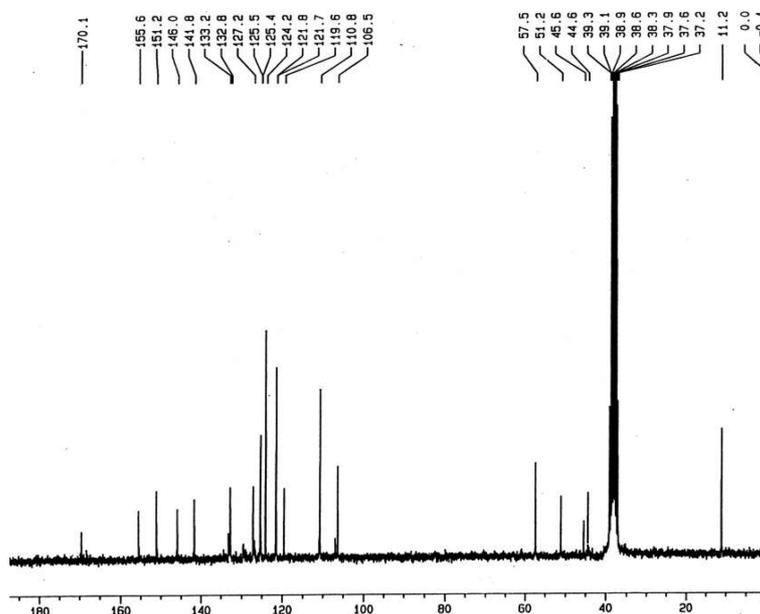


Fig. 3 Cyclic voltammogram of PPy-Red-II-co-Py on a GC disk electrode vs. Ag/AgCl reference electrode in LiClO_4 (0.1 M) in 20 mL acetonitrile, $\nu = 50 \text{ mVs}^{-1}$

Fig. 4 ^{13}C -NMR Spectrum of PPy-Red-II

electrode. The colour of this film was found to vary with potential. A reddish suspension was formed at the anode; this appeared to stream away and dissolved in the bulk solution. This is presumably due to the formation of soluble oligomeric products, such as those observed from 3-alkylthiophenes (Bryce *et al.* 1988).

Figs. 2 and 3 show electrocopolymerization of pyrrole and Py-RedII, and also the blank of PPy-RedII-co-Py respectively. Features appear at potentials (versus Ag/AgCl) of 1.4 and 0.5 can be related to oxidation of mesogenic group and pyrrole ring respectively. The features appeared at lower than -0.5 and -1.45 V; can be related to oxidation and reduction of pyrrole ring in copolymer, respectively.

3.2 NMR Spectroscopy (Kurihara *et al.* 2002)

Based on the comparison of Py-RedII and PPy-RedII, the following signals are assigned to the protons of the chromophore: 1.17 (-CH₃), 2.37 (-CH₂-COO-), 3.53 (-CH₂-CH₃), 3.61 (-CH₂-N), 4.01 (-O-CH₂-), 6.87, 7.82, 7.91 and 8.35 ppm (protons of phenylene groups). The aromatic protons of the pyrrole ring are at 7.37-7.55 ppm.

The ^{13}C NMR spectrum of the PPy-RedII is presented in Fig. 4. Based on the comparison with the spectrum of Py-RedII, the following assignments are proposed:

1. The signal at the lowest field (170.1 ppm) corresponds to the carbon of the ester group.
2. The signals at 155.6, 151.2, 146.0, 141.8, 127.2, 124.2, 121.8-121.7, 119.6, 110.8 and 106.5 ppm are assigned to the aromatic carbons in the RedII moiety.
3. The remaining four signals at 133.2-132.8 and 125.4-125.5 ppm from the correspond to the pyrrole ring and can be related to 2,2' and 3,3' respectively.
4. In the aliphatic part, the signals of low intensity at 11.2, 44.6, 45.6, 51.2 and 57.5 ppm

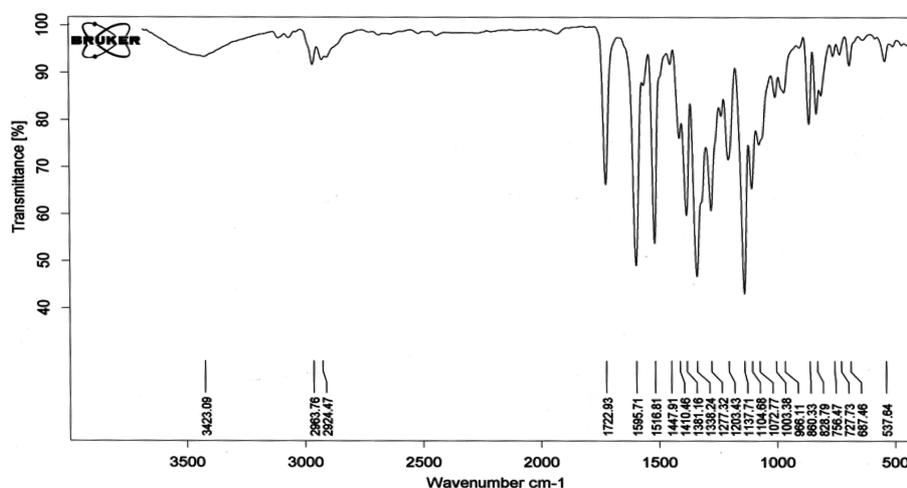


Fig. 5 FTIR Spectrum of PPy-Red-II

correspond to the RedII substituent. Therefore, the peak of 36.8 ppm probably overlapped with peaks of ^{13}C -DMSO solvent (36-41 ppm).

3.3 UV-Visible

UV-Visible spectrum of the polymer showed a peak in the visible region, characteristic of a conjugated polymer system; these spectral data indicated that the polymer has a conjugated backbone system having liquid crystalline moieties. The photochemical properties of the monomer (Py-RedII) were evaluated in DMSO as a solvent. Photoisomerization behavior of azobenzene chromophores between trans-isomer and cis-isomer upon light irradiation has been well discussed in literature (Hosseini *et al.* 2009, Mohr *et al.* 2004). It is well known that the more stable trans-isomer can be converted to the less stable cis-isomer by UV light irradiation by exciting the π - π^* electronic transition, and the reverse change can be carried out by visible light irradiation exciting the n - π^* electronic transition or by heating. In our study UV irradiation induced trans-cis isomerization leading to absorption bands centered near 322.0 and 487.5 nm, respectively. The first absorption band is related to the π - π^* transition while the latter is associated to the n - π^* transition. The polymer (PPy-RedII) exhibits a broad absorption band centered at 680 nm which can be related to the π - π^* transition of the highly conjugated poly-pyrrole units. In addition, the absorption spectrum of the PPy-RedII gives a red shift of about 10 nm with respect to the same spectrum of the monomer.

3.4 FTIR Spectroscopy

The FTIR spectrum of PPy-RedII is shown in Fig. 5. In this figure, polymer did not show the amine N - H bond stretching (3400 cm^{-1}) frequency. Instead, the $C=C$ stretching peak of conjugated polymer backbone at 1595 cm^{-1} is presented. The C - H aromatic and aliphatic, $C=O$ and $N=N$ stretching frequency peaks at 3130, 2963, 1722 and 1516 cm^{-1} are related to pyrrole and azobenzene moieties, respectively.

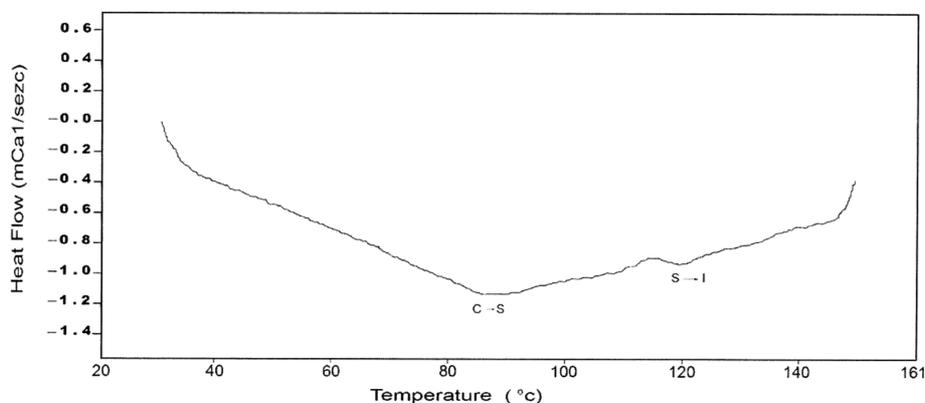


Fig. 6 DSC Thermogram of PPy-Red-II; the traces were obtained on heating from the crystalline to smectic phase ($C \rightarrow S$) and smectic to isotropic phase ($S \rightarrow I$) at the heating rate 10 min^{-1}

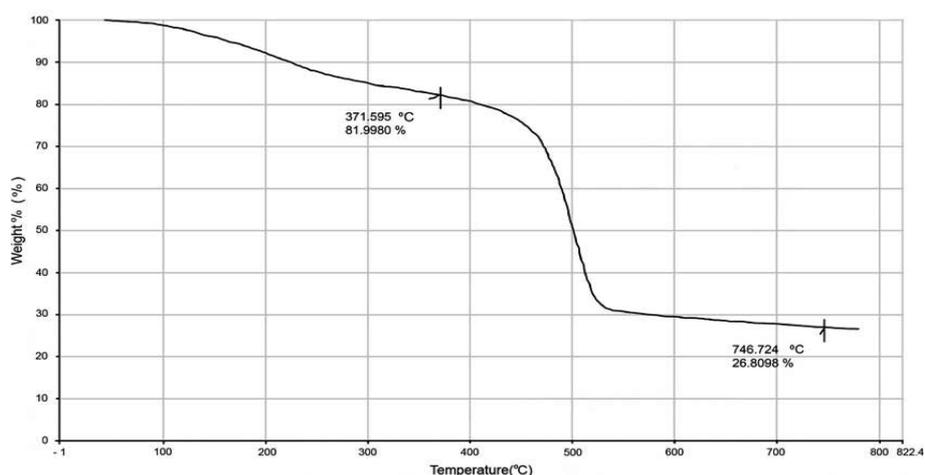


Fig. 7 TGA Thermograms of PPy-Red-II

3.5 Thermal analysis

The thermal properties of the PPy-RedII were analyzed by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) under a nitrogen atmosphere. The DSC trace obtained with a small sample of the PPy-RedII at the rate of $5^\circ\text{C}/\text{min}$. The DSC thermogram of the PPy-RedII (Fig. 6) shows two endothermic peaks that appear at 88 and 122°C . Crystalline phase changed to smectic phase ($C \rightarrow S$) at 88°C and the transition phase from smectic to isotropic phase ($S \rightarrow I$) occurred at 122°C . The TGA of the polymer shows that it has thermal resistance lower than poly-pyrrole (Hosseini *et al.* 2009, Liu *et al.* 2003).

A typical TGA curve (Fig. 7) demonstrates a high thermal stability with a heating rate of $20^\circ\text{C}/\text{min}$. The thermogravimetry scan of the PPy-RedII, reveals a remarkable weight loss at 371°C . Only 30% of the polymer remains after 550°C . This curve exhibits a softening temperature in 130°C and degradation initiation at more than 200°C . Heating was initiated from 40°C ; it approximately lost

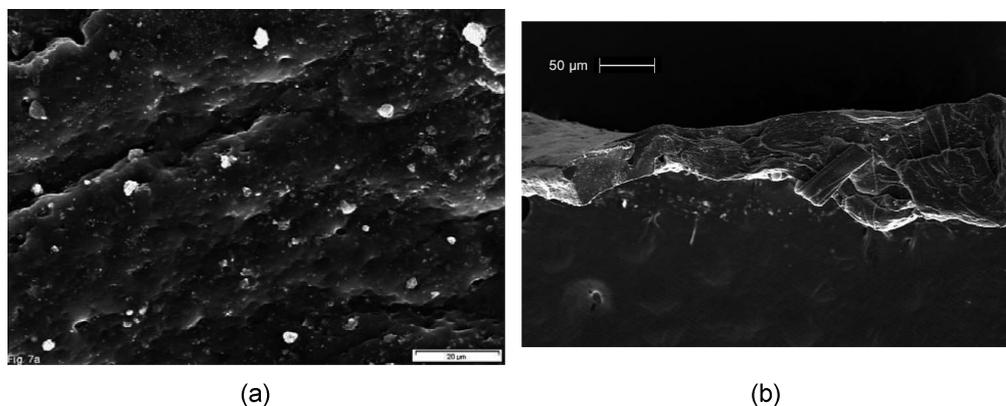


Fig. 8 SEM Micrographs of PPy-Red-II: (a) surface and (b) cross section images

5% of the weight up to 200°C that is due to the humidity and existence of solvent in the polymer chain. PPy-RedII was stable below 200°C and in the range of 200-371°C approximately lost 19% of its weight, which is due to the degradation of the azobenzene moiety (RedII). The polymer was started to completely decompose over 400°C. In addition the TGA curve of PPy-RedII illustrates initial decomposition temperature (IDT), polymer decomposition temperature (PDT) and the maximum polymer decomposition temperature (PDT_{max}) in 200°C, 400°C and 550°C, respectively. The residual weight (γ_c) of the polymer is 26.8% at 746.5°C.

3.6 Scanning electron micrograph (SEM)

The scanning electron micrographs of PPy-RedII film which had been prepared by chemical method (casting method) is presented in Figs. 8(a) and (b). The SEM micrographs clearly show that poly-pyrrole is in the form of sphere shape and homogenous texture. Having a homogenous and single-phase polymer is good evidence for successful polymer synthesis.

3.7 Electrical conductivity

Electrical conductivity of PPy-RedII and its copolymer with pyrrole (PPy-RedII-co-Py) were studied by the four-probe method. The conductivities obtained were 7.5×10^{-4} and $6.5 \times 10^{-3} \text{ Scm}^{-1}$, respectively. These values are several times lower than conductivity of polypyrrole. The highest amount of the conductivity of polypyrrole has been reported about 10^2 Scm^{-1} (Hosseini *et al.* 2009, Carrasco *et al.* 2006). These low conductivities can be related to the introducing azobenzene moiety in the polymer chain. The introduction of RedII in to the polymer tends to decrease the average conjugation length in the polymer backbone.

4. Conclusion

We have presented a simple synthetic route for *N*-substituted pyrrole containing azo dye side. This new monomer (Py-RedII) can be chemically polymerized in the presence of oxidative agents. PPy-

Red-II and its copolymer with pyrrole (PPy-RedII-co-Py) were synthesized by cyclic voltammetry and chemical polymerization methods. In spite of low processability of polypyrrole we could synthesize a kind of polypyrrole containing an azo dye side group with excellent solubility (PPy-RedII). The polymer was soluble in common organic solvents such as CH₃Cl, DMF and DMSO and processible into a homogeneous thin film, this property cause to an extensive application of polypyrrole in biological means and various industries. This new polymer contains electrochemical and spectroelectrochemical properties of the polypyrrole conjugated chain and the chromophore.

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