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Electrochemistry of two novel conjugated conducting polymers containing phenothiazine moieties in main chain

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Abstract

The electrochemical behaviour of two novel conjugated polymers (*m*-Polymer and *Ph*-Polymer) containing phenothiazine moieties in main chain were studied in DMF with 0.1M TBAP by means of cyclic voltammetry (CV) and differential pulse voltammetry (DPV) on the glassy carbon electrode (GCE). The results show that *m*-Polymer has a stable oxidative peak at 1.084V and a reductive peak at –1.546V. However, *Ph*-Polymer has two oxidative peaks at 0.852V and 1.155V and two reductive peaks at –1.682V and –2.044V respectively. By some electrochemical techniques, the electrode reaction processes were investigated in detail and their dynamic parameters were obtained. In addition, the electrode reaction mechanism was deduced and the energy levels of the frontier orbits of the two polymers were calculated using CV and UV.

Keywords

Conjugated polymers; Electrochemistry; Dynamic parameters; Reaction mechanism; The energy levels.

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INTRODUCTION

Conventional polymers, plastics, have been used traditionally because of their attractive chemical, mechanical, and electrically insulating properties, but not for their electronic properties. Conjugated polymers as electronic materials[1,2] in molecular-based electronics, although known for many years, did not draw significant research attention till the mid 1970s. In 1977 Heeger, MacDiarmid and Shirakawa showed that poly(acetylene), which was the simplest polyconjugated system, could be rendered conductive by the reaction with bromine or iodine vapors[1]. Since the discovery of conducting polyacetylene, conjugated polymers have successively been served as the active component in organic conducting materials, light-emitting diodes (LEDs)[3-6], solid-state lasers[7-9], photovoltaic cells (PVs)[10,11], biosensors[12], and transistors[13,14]. Especially, organic light-emitting diode (OLED) has been the subjects of intensive investigation because of their application in full-color displays[15,16] since the first OLED was reported by Tang and Vanslyke in 1987[17]. At present, the OLED has been applied in a variety of products such as electronic and optoelectric commercial products. However, there is still a large potential for the exploration of new organic semiconductors. For example, the efficiency and color purity of organic semiconductor materials for blue and red OLEDs need particularly to be improved, which is currently to be resolved in the development of a satisfactory full color display based on OLEDs[15,16]. The polymers currently applied to OLEDs are mainly poly(phenylene vinylene)s, polyfluorenes, poly(triphenylamine)s, polythiophenes, polycarbazoles, etc. While, few conjugated polymers containing phenothiazine moieties in the main chain have been reported up to now[18-22].

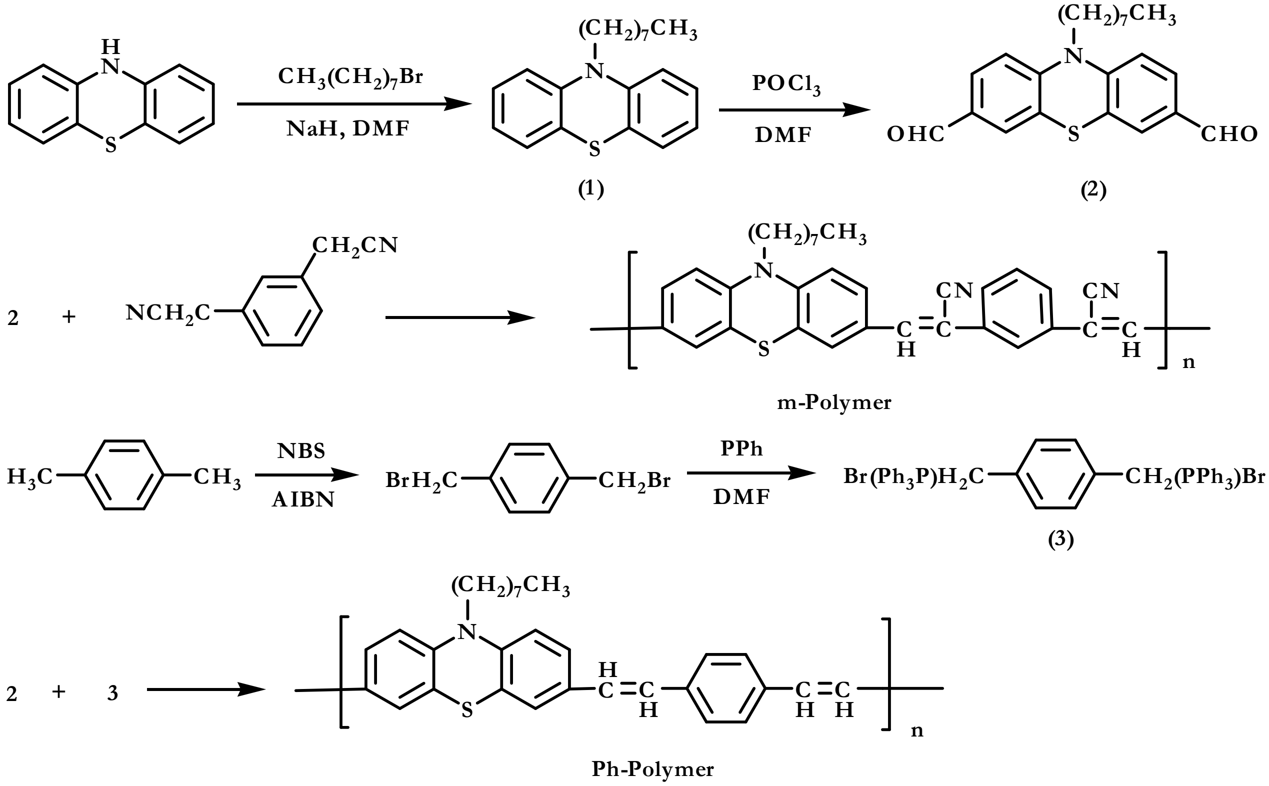
However, the electronic structure of the emitting materials is of vital importance to the characteristics of OLEDs. For example, the energy gap is defined by the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and the energy levels are required to match the work function of corresponding electrodes. The measurement of electrochemical redox properties provides a basis for estimating and assessing the electronic structure of the “-conjugated molecules[23]. However, the studies in the field is restricted.

In this paper, we present the detailed electrochemical characterisation of two new conjugated polymers containing phenothiazine moieties in main chain, which were synthesized by Knovenagel or Wittig condensations and would be good candidate materials for OLEDs[24]. Especially, it is notably that an OLED fabricated with the Ph-polymer (Scheme 1) as an active layer, can emit a pure yellow light[24]. This will be very interesting for OLEDs.

EXPERIMENT

Materials and instruments

The synthetic procedures for the two polymers are shown in Scheme 1. Compounds 1 and 2 were synthesized following literature procedures[25] with some modifications. Compound 3 was prepared by bromination of *p*-dimethylbenzene. *m*-Polymer was synthesized by the polycondensation of compound 2 with *m*-phenylene diacetonitrile. *Ph*-Polymer was synthesized by Wittig condensation with compound 2 and compound 3. The polymers were identified and characterized by measurements of ^{1}H-NMR, IR, GPC (gel permeation chromatography), TG (thermogravimetric), UV-vis and FL (Fluorescent spectra). The results on the synthesis and measurements have been reported previously[24].



Scheme 1 : Synthetic route for intermediates and polymers

The electrochemical properties of the two polymers were performed on a CHI 650A electrochemistry workstation (CHI instrument Co, USA) with a three-electrode system. The glass carbon disk electrode (Φ=4mm), Pt wire electrode and saturated calomel electrode (SCE) were used as the working electrode, counter electrode and reference electrode respectively. Redox processes of the polymers in DMF were observed using 0.1M tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte. TBAP was prepared according to the literature[26].

RESULTS AND DISCUSSION

The electrochemical behavior of *m*-Polymer and *Ph*-Polymer at GC electrode

Cyclic voltammetry (CV) was performed in a standard electrochemical cell with a three -electrode system. Figure 1 shows the voltammogram of *m*-Polymer and *Ph*-Polymer in DMF with TBAP. The results indicate that two polymers show redox peaks between potential range of –2.4~1.6V. The CV curve of *m*-Polymer (dot line in Figure 1 a) shows us that it has a well-defined oxidative peak at 1.084V(I_{pa}') and a stable reductive peak at –1.546V(I_{pc}'). However, *Ph*-Polymer (solid line in Figure 1 a) shows us that it has another oxidative peak at 1.155V (II_{pa}) and reductive peak at –2.044V(II_{pc}) besides the oxidative peak at 0.852V (I_{pa}) and the reductive peak at –1.682V(I_{pc}). The results of CV are showed in TABLE 1.

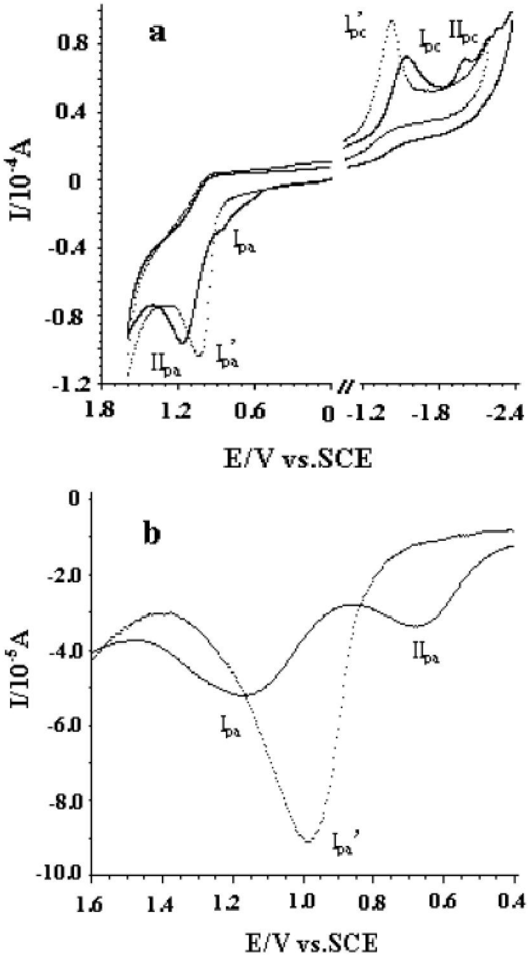


Figure 1 : CV (a) and DPV (b) curves of 5x10^{-3}mol/L *Ph*-Polymer (solid line), *m*-Polymer (dot line) in DMF+0.1M TBAP with scan rates 0.1V/s

TABLE 1 : Electrochemical date (E_p, n and α) of two polymers

Electrochemical data	*m*-Polymer		*Ph*-Polymer			
	I_{pa}'	I_{pc}'	I_{pa}	II_{pa}	I_{pc}	II_{pc}
E_p(V)	1.084	-1.546	0.852	1.155	-1.682	-2.044
N	1.34	0.68	0.80	1.12	1.18	1.07
A	0.382	0.264	0.239	0.164	0.293	0.597

Figure 1b shows us the differential pulse voltammetry (DPV) of two polymers in DMF with TBAP between potential range of 0.4~1.6V. *Ph*-Polymer (solid line in Figure 1 b) shows two distinct oxidative peak compared with singly oxidative peak of *m*-Polymer (dot line in Figure 1 b). The results are consistent with the behavior of CV.

These results mean that the oxidation of *m*-Polymer becomes more difficult when the two H atoms at the two ends of vinylene-substituted phenylene are substituted by –CN. It can be speculated that the electronic cloud is dispersed with the increase in electron-withdrawing ability of the substituents. The decrease of the electronic cloud density in the middle part of the molecule makes it difficult to lose electrons and ease to gain them, so as to raise the oxidative potential and reduce the reductive potential.

In addition, it was found that the peak current of two polymers increased and the peak potential shifted to more positive values (oxidation peaks) or negative values (reductive peaks) with increasing scan rate. Figure 2 shows the relationship between peak current I_{pa} and the square root of scan rate $v^{1/2}$. From Figure 2, we know that both I_{pa} are linearly proportional to $v^{1/2}$, confirming the irreversible diffusion-controlled process for two polymers electrochemical system.

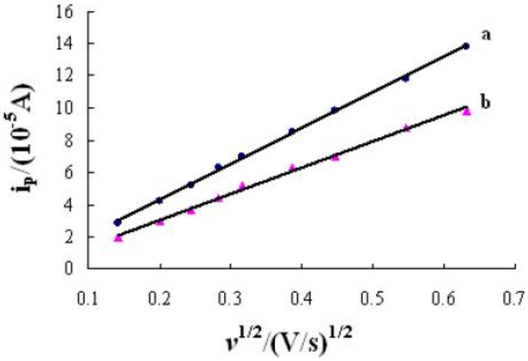


Figure 2 : The relationship between anodic peak current I_{pa} (I_{pa}') and the square root of scan rate $v^{1/2}$ of *m*-Polymer (a) and *Ph*-Polymer (b).

Determination of the electron transfer number (n) and the transfer coefficients (α)

The electron transfer number (n) was calculated using the normal pulse voltammetry (NPV):

$$E = E_{1/2} + 2.303\frac{RT}{nF}\lg\frac{i_l - i}{i} \qquad (1)$$

where E and $E_{1/2}$ are separately the potential and the half wave potential (V); n is the number of electron transferred, i represents the electrical current (A); and i_l expresses the limited electrical current (A). At 25 °C, the RT value becomes 2480 $J\cdot mol^{-1}$ and the Faraday constant is $F=96487\ C\cdot mol^{-1}$. The results are showed in TABLE 1.

According to the relationship between peak potential (E_p) and scan rate (υ) of irreversible redox process, the transfer coefficients (α) was calculated with linear sweep voltammetry using following electrochemical equation[27]:

$$E_p = E_i - \frac{RT}{\alpha nF}(0.780 + 0.51\ln\frac{\alpha n_\alpha DF\nu}{RT} - \ln k_s) \qquad (2)$$

Where D is the diffusion coefficient ; k_s denotes electrochemical reaction rate constant ; and E_i and E_p are the standard peak potential and peak potential, separately; α is the transfer coefficients which need to be calculated, and v expresses scan rate ($V\cdot s^{-1}$). Figure 3 shows the relationship of E_p~ln$v$ of the each peak. From the slope of E_p~ln$v$, we can deduced the transfer coefficients (α). The results are listed in TABLE 1.

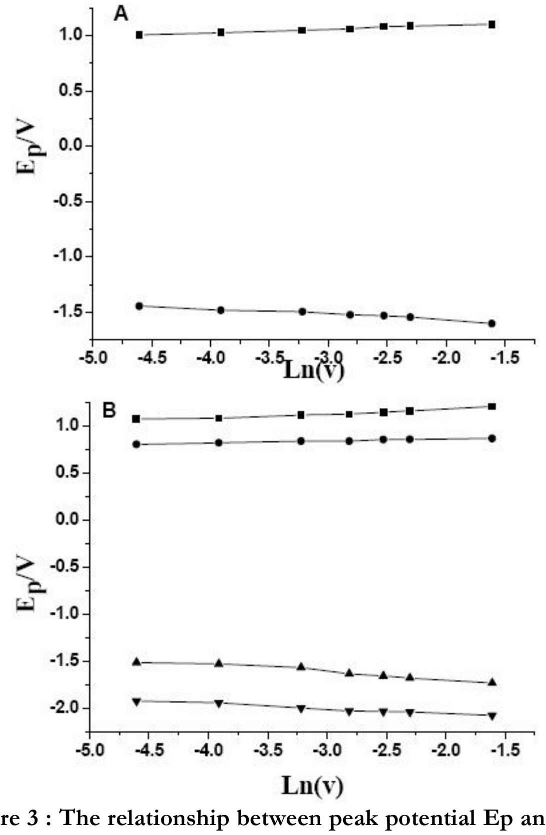


Figure 3 : The relationship between peak potential Ep and the natural logarithm of scan rate Ln(υ) of two polymers.

Determination of the diffusion coefficient (D) and electrochemical reaction rate constant (k_s)

The potential step chronoamperometry (CA) and chronocoulometry (CC) method are widely used for the determination of the diffusion coefficients based on the theoretical derivation presented initially by Wen et al.[28] for diffusion controlled electrode processes.

In this present, the diffusion coefficient (D) was determined by CA and CC. The potential steps from 0.8V to 1.3V (*m*-Polymer) and from 0.9V to 1.5V (*Ph*-Polymer) were inflicted on the electrode and maintained for 1s. According to the Cottrell relationships[29] (Eq. (3)), and using the values of slope of Cottrell i-$t^{-1/2}$ and Q - $t^{1/2}$ plots, the diffusion coefficient D can be calculated.

$$i(t) = \frac{nFAD^{1/2}c}{(\pi t)^{1/2}} + i_c \quad Q(t) = \frac{2nFAD^{1/2}ct^{1/2}}{\pi^{1/2}} + Q_{dl} \qquad (3)$$

where A denotes the electrode surface area (cm^{-2}); c represents the analyte concentration ($mol\cdot cm^{”3}$), t is the elapsed time from the beginning of the step (s), and other parameters have either been discussed above or have their usual significance. The diffusion coefficient, D, in units of cms^{-1} can be calculated from Eq. (3) and summarized in TABLE 2.

TABLE 2 : Electrochemical kinetics data of *m*-Polymer and *Ph*-Polymer

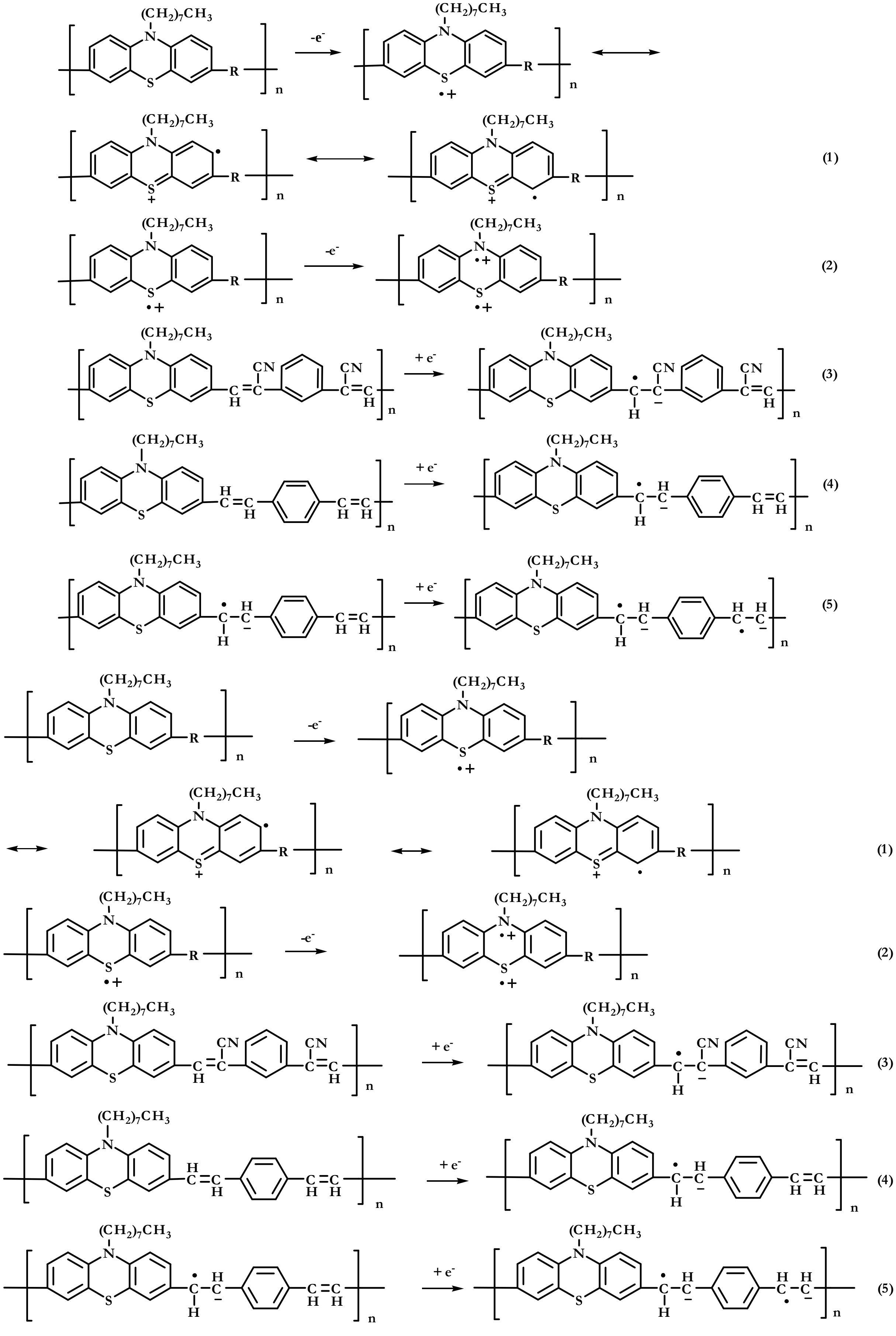
Polymer	$D\times10^5/(cm^2/s)$		$k_s\times10^4/(cm/s)$
	CA	CC	
m-Polymer	0.491	0.762	1.160
Ph-Polymer	1.696	1.536	3.838

The resulting values of diffusion coefficient obtained by the two methods are almost agreements. In addition, for *Ph*-Polymer, the values of the diffusion coefficient obtained are bigger than that of *m*-Polymer, which agree with this concept of that D usually decreases with the increase of the molecular weight and the size of a molecule.

According to the relationship between peak potential (E_p) and scan rate (υ) of irreversible redox process (Eq. (2)), the k_s values were calculated with the intercept of E_p ˆ ÿlnυand listed in TABLE 2. The results reveal that electrochemical reaction rate constant (k_s) of *m*-Polymer is smaller than that of *Ph*-Polymer after the introduction of the substitute -CN. This is agreement with the phenomenon of diffusion coefficient (D).

The possible electrochemical reaction mechanism

Base on the literature[30], the oxidation peak I_{pa} and I_{pa}’ were caused by the phenothiazine group of the polymers according to the reaction (1) in Scheme 2. There is only one electron transfer in the reaction process owing to the neutral molecule of the polymers in nonaqueous



Scheme 2 : The possible electrode reaction mechanism of the two polymers.

medium. This is different from the literature[30]. Also, for *Ph*-Polymer, there are no strong electron-withdrawing group, thus the electronic cloud density is large, so it can continue to lose another electron when the potential shifted to more positive values, which is corresponding to the peak II_{pa}.

In addition, based on the literature[31], the reductive peak I_{pc}' was caused by cyanoisophthalylidene according to the reaction (3) in Scheme 2. Also, for *Ph*-Polymer, although there is no strong electron-withdrawing group, the introduction of *p*-phenylene decrease the steric hindrance compared with that of *m*-phenylene. Therefore, *Ph*-Polymer continued to gain another electron when the potential shifted to more negative values, which is corresponding to the peak II_{pc}. At the same time, the vinylene-substituted *p*-phenylene is changed a twin-electron species. The possible electrode reaction mechanisms of the two polymers are shown in Scheme 2.

The evaluation of the energy level (HOMO and LUMO)

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are two energy parameters that establish the positions of the frontier orbital. Extensive previous studies have illustrated that the energy parameters HOMO and LUMO are related to the measured redox potentials. In this work, the HOMO and LUMO levels of two polymers were calculated with formula of $E_{HOMO} = -|E_{ox}+4.74|$ eV and $E_{LUMO} = -|E_{red}+4.74|$ eV[32,33], where E_{red} and E_{ox} are respectively the reductive potential (peak potential I_{pc} and I_{pc}') and the oxidative potential (peak potential I_{pa} and I_{pa}') in volts versus the SCE. The energy gap E_g is the separation between the HOMO and LUMO level, thus $E_g = E_{LUMO} - E_{HOMO.}$ In addition, the energy gaps (E_g) are also evaluated by utilizing the optical absorption edge[34], which are calculated from λ_{onset}/nm (the onset absorption wavelength). All the results are showed in TABLE 3. There exist some differences between the optical E_g^{opt} and electrochemical E_g^{el}. The value difference calculated from two methods is estimated to be less than 0.5 eV.

TABLE 3 : The energy levels of two polymers

Polymer	E_{red} (V)	E_{ox} (V)	HOMO (eV)	LUMO (eV)	E_g^{el} (eV)	E_g^{opt} (eV)
m-Polymer	-1.546	1.084	-5.824	-3.194	2.630	2.318
Ph-Polymer	-1.682	0.852	-5.592	-3.058	2.534	2.431

CONCLUSIONS

In this paper, we investigated the electrochemical property of two novel conjugated conducting polymers (*m*-Polymer and *Ph*-Polymer) in detail. *m*-Polymer has one oxidative peak and one reductive peak in potential –2.4~1.6V. However, *Ph*-Polymer has two oxidative peaks and two reductive peaks in the above potential range. It was caused by different electron-withdrawing ability and steic hindrance. At the same time, we estimated the energy level from CV and UV. The results show that *m*-Polymer and *Ph*-Polymer are excellent semiconductor materials. In addition, the dynamic parameters of the polymers are gained using different electrochemical methods.

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