

# Chapter 2

## Conducting Polymers

Yongfang Li

In general, conducting polymers include electronically conducting polymers and ionically conducting polymers. Ionically conducting polymers are usually called polymer electrolytes. Electronically conducting polymers can also include conjugated conducting polymers and the insulating polymers blending with conducting materials. In this chapter, the conducting polymers are limited to conjugated conducting polymers, unless otherwise stated.

Traditionally, polymers are thought of as insulators. However, in 1977 a discovery by Alan G. MacDiarmid, Hideki Shirakawa, and Alan J. Heeger et al. changed the traditional concept. They found that conductivity of polyacetylene—after doping with electron-withdrawing  $\text{AsF}_5$ —increased ninefold, reaching the order of  $10^3$  S/cm [1, 2]. Soon after this discovery, a series of stable conducting polymers, including polypyrrole (PPy), polyaniline (PAn), and polythiophene (PTh), were reported from the end of the 1970s to the beginning of the 1980s, which greatly promoted the research on conducting polymers. Actually, the conductivity of almost all conjugated polymers can reach the order of  $10^{-3}$ – $10^3$  S/cm after doping. Now we can expand the class of conducting polymers to include all the doped conjugated polymers.

In 1990, Friends et al. found the electroluminescent properties of poly(*p*-phenylene vinylene) (PPV) [3] and opened up a new field of polymer light-emitting diodes (PLEDs) with semiconducting intrinsic conjugated polymers as the active light-emitting layer. In 1995, Heeger et al. reported bulk-heterojunction polymer solar cells (PSCs) with a conjugated polymer MEH-PPV as donor and a fullerene derivative PCBM as acceptor [4], which further extended the research on conjugated polymers to the field of organic photovoltaics. Since then, conjugated polymer

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optoelectronic materials and devices including PLEDs and PSCs have attracted great attention all over the world and have developed into hot research fields. Because of the importance of conjugated polymers, Heeger, MacDiarmid, and Shirakawa were awarded the Nobel Prize in Chemistry in 2000, in recognition of their great contributions to the discovery and developments of conducting polymers.

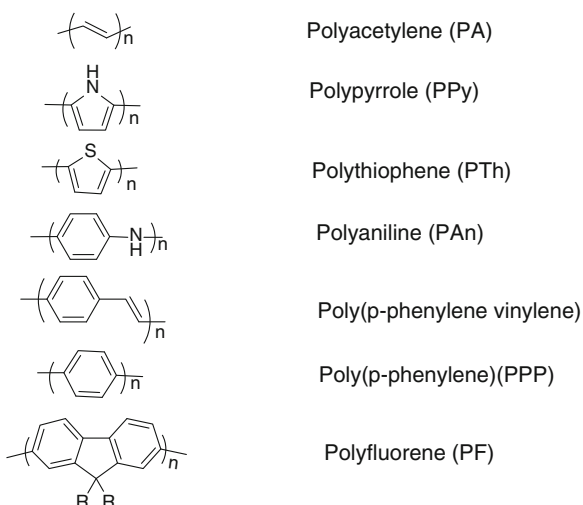
The main advantages of conducting polymers are that they possess not only the electronic and optical properties of metals and inorganic semiconductors, but also the flexible mechanics and processability of polymers. In addition, there is special electrochemical redox activity with conducting polymers. Obviously, conducting polymers, including doped conducting polymers and intrinsic semiconducting conjugated polymers, will play a key role in the future development of organic optoelectronic and electrochemical devices.

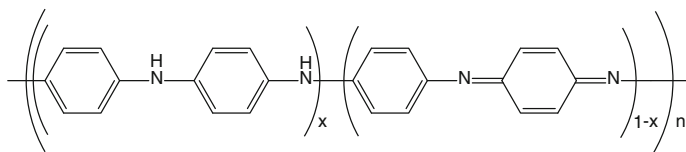
## 2.1 Molecular Structure of Conducting Polymers

The unique characteristic of conducting polymers is the conjugated molecular structure of the polymer main chain where the  $\pi$ -electrons delocalize over the whole polymer chain. Conjugated polymers become conducting polymers after doping. Figure 2.1 shows the main chain structures of representative conjugated polymers, including polyacetylene (PA), polypyrrole (PPy), polyaniline (PAn or PANi), polythiophene (PT or PTh), poly(*p*-phenylene vinylene) (PPV), poly(*p*-phenylene) (PPP), and polyfluorene (PF).

In the conjugated polymers, polyacetylene shows the simplest main chain structure composed of an alternate single bond and double bond carbon chain. According to the locations of the hydrogen atoms on the double bond carbons, there are two kinds of structures: *trans*-polyacetylene with the two hydrogen atoms on

**Fig. 2.1** Main chain structures of several representative conjugated polymers





**Fig. 2.2** Main chain structure of polyaniline

opposite sides of the double bond carbons and *cis*-polyacetylene with the two hydrogen atoms located on the same side of the double bond. *trans*-Polyacetylene is a degenerate conjugated polymer which possesses an equivalent structure after exchanging its double bond and single bond. *cis*-Polyacetylene and other conjugated polymers are nondegenerate conjugated polymers which have non-equivalent structures after exchanging their double and single bonds.

Among the various conjugated polymers, the main chain structure of polyaniline (PAn) is a little complicated. Figure 2.2 shows the conjugated main chain structure of PAn. Commonly, there exist three structure forms: leucoemeraldine (PAn-I) where  $x = 1$ , emeraldine base (EB, PAn-II) where  $x = 0.5$ , and pernigraniline (PAn-III) where  $x = 0$ . The molecular structure of PAn in Fig. 2.1 is leucoemeraldine. Actually, the structure of emeraldine base (EB) is the most important structure for conducting polyaniline, because proton-acid doping of the EB structure (Fig. 2.4) turns it into conducting PAn.

### 2.1.1 Electronic Structure of Intrinsic Conjugated Polymers

Conjugated polymers possess delocalized  $\pi$ -electron structures, including the band structure of  $\pi$ -valence band and  $\pi^*$ -conduction band. In the basic state of the intrinsic conjugated polymers, all the valence bands are filled by electrons and the conduction bands are all empty. The difference between the top of the valence band (the highest occupied molecular orbital, HOMO) and the bottom of the conduction band (the lowest unoccupied molecular orbital, LUMO) is called the bandgap ( $E_g$ ) of the conjugated polymers. The  $E_g$  values of most conjugated polymers are in the range 1.5–3.0 eV. Therefore, the intrinsic conjugated polymers are organic semiconductors.

The  $E_g$  values of conjugated polymers can be measured by absorption spectroscopy of the conjugated polymer films. From the absorption edge wavelength ( $\lambda_{\text{edge}}$ ) of the absorption spectra,  $E_g$  can be calculated according to the following equation:

$$E_g = \frac{1240}{\lambda_{\text{edge}}} \text{ (eV)}$$

where the unit of  $\lambda_{\text{edge}}$  is nm.

HOMO and LUMO energy levels of conjugated polymers can be estimated from onset oxidation and onset reduction potentials measured by electrochemical cyclic voltammetry [5]. The detailed measurement method is described in Sect. 2.6.4. The difference between the HOMO and LUMO energy levels of the conjugated polymers also corresponds to  $E_g$  values.

When the conjugated polymers were used as electroluminescent materials in PLEDs, the bandgap  $E_g$  of the conjugated polymer determines the emitted color of the PLEDs, and the HOMO and LUMO energy levels of the polymer influence the holes and electrons injection efficiency in the devices. Chapter 5 gives a more detailed discussion of the electroluminescent characteristics of conjugated polymers. For the use of conjugated polymers as donor materials in the active layer of PSCs, the  $E_g$  value of the conjugated polymer determines the absorption wavelength range of the devices, and the HOMO and LUMO energy levels influence the exciton dissociation efficiency at the donor/acceptor interface and the open circuit voltage of the PSCs. Therefore, it is very important to understand the effect of the molecular structure on the energy bandgap and electronic energy levels of the conjugated polymers.

The factors influencing the electronic structure and  $E_g$  values of the conjugated polymers are as follows:

1. For the degenerate *trans*-polyacetylene,  $E_g$  values decrease on decreasing the difference between the alternating single bond length and double bond length.
2. For the conjugated polymers formed by connecting the aromatic rings with single bonds, such as polypyrrole, polythiophene, and poly(*p*-phenylene), the deviation of the conjugated main chain from planar structure between the two neighboring aromatic rings will result in the increase of the  $E_g$  values. The larger the angle between the two neighboring aromatic rings in the main chain of the conjugated polymer, the smaller the overlap between the two molecular orbitals of the conjugated ring units and the higher the  $E_g$  values of the conjugated polymer.
3. The nature of the substituents on the main chain also influences the electronic structure of the conjugated polymers. The electron-donating substituents up-shift the LUMO and HOMO energy levels and reduce the  $E_g$  of the conjugated polymers (the up-shift of the HOMO is more than that of the LUMO). The electron-withdrawing substituents down-shift the LUMO and HOMO energy levels and also reduce the  $E_g$  of the conjugated polymers (the down-shift of the LUMO is more than that of the HOMO).
4. Copolymerization of conjugated electron-donating (D) unit and electron-accepting (A) unit results in lower bandgap conjugated D-A copolymers, and the HOMO and LUMO energy levels can be tuned by selecting suitable donor and acceptor units in the copolymers. The absorption spectra of the D-A copolymers are broadened and red-shifted because of the intramolecular charge transfer between the donor and acceptor units.
5. The existence of quinone structure in the polymer main chain can decrease the  $E_g$  values of the conjugated polymers.

6. The aggregation of the polymer main chains in the solid state also influences the  $E_g$  and electronic energy levels of the conjugated polymers. The strong intermolecular interaction in the planar main chain decreases the  $E_g$  of the conjugated polymers.

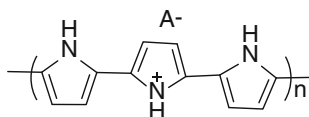
### 2.1.2 Doping Structures of Conducting Polymers

The distinguished characteristic of conducting polymers is the p-doped and n-doped states of the conjugated polymer main chains. In the p-doped state, the main chain of the conducting polymer is oxidized with counteranion doping for keeping the electron neutrality of the whole molecule. There are holes in the main chains (lost electrons) which make the conducting polymer p-type conducting. In the n-doped state, the main chain of the conducting polymer is reduced with counteranion doping for keeping the electron neutrality of the whole molecule. There are electrons in the main chains which make the conducting polymer n-type conductive.

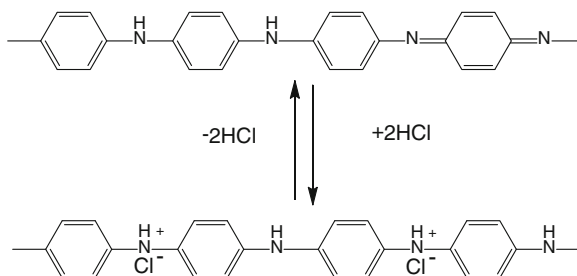
Figure 2.3 shows the p-doped structure of conducting PPy. The positive charge is delocalized on the PPy main chain.  $A^-$  represents counteranions such as  $NO_3^-$ ,  $ClO_4^-$ ,  $Cl^-$ ,  $TsO^-$ .

The number of counteranions per monomer unit of the conducting polymer (or the concentration of the charge carrier in the conjugated main chain of the conducting polymer) is called doping degree of the conducting polymer. The maximum doping degree is related to the main chain structure of the conducting polymers. For example, the doping degree for polyacetylene is usually 0.1–0.2, it is 0.25–0.35 for polypyrrole, 0.4–0.5 for polyaniline, and ca. 0.3–0.4 for polythiophene. For the p-doped polypyrrole, the doping degree of 0.25–0.35 implies that the conjugated chain including 3–4 pyrrole units can be doped with 1 counteranion (or there is a hole within the polypyrrole main chain containing 3–4 pyrrole units), as shown in Fig. 2.3.

The doping processes of conducting polyaniline are related to its structures of conjugated polyaniline. For leucoemeraldine (PAn-I), the doping process is similar to polypyrrole, i.e., it can be p-doped by oxidation. The EB, PAn-II can be doped by protonation, as shown in Fig. 2.4. In the protonation process of the PAn-II, the positive charge on the proton delocalizes on the whole conjugated main chain of polyaniline, becoming the positive charge carrier (hole) of the conducting



**Fig. 2.3** p-Doped structure of conducting PPy



**Fig. 2.4** Proton-acid doping of emeraldine base polyaniline (EB) and its proton acid doping structure

polyaniline. At the same time, the anion of the proton acid becomes the counter-anion of the conducting polyaniline.

It should be mentioned that the nature of the doping in conducting polymers is different from that of the doping in inorganic semiconductors. In inorganic semiconductors with crystalline structures, doping is realized by replacing some bulk atoms (such as Si) with outer shell electrons one more or one less than Si to achieve n-doping or p-doping. The doping concentration is very low. Although the doping of conjugated polymers with amorphous structure needs charge injection by oxidation or reduction of its conjugated main chain, counterions doping is required for keeping the charge neutrality. The doping degree is much higher in conducting polymers where the charge carrier concentration reaches  $10^{21}/\text{cm}^3$ , which is several orders higher than that of the inorganic semiconductors. In addition, the doping in conducting polymers also results in volume expansion and morphology changes because of the counteranion doping.

### 2.1.3 Charge Carriers in Conducting Polymers

Novel structures lead to novel charge carriers in conducting polymers. For *trans*-polyacetylene with the degenerate basic state, the charge carriers are solitons and polarons. However, for the basic state nondegenerate *cis*-polyacetylene, polypyrrole, polythiophene, polyaniline, etc. the charge carriers are polarons and bipolarons [6]. The *soliton* (S) is an unpaired  $\pi$ -electron resembling the charge on free radicals, which can be delocalized on a long conjugated polymer main chain (*trans*-polyacetylene main chain). The neutral soliton can be oxidized to lose an electron and form a positive soliton, or it can be reduced to gain an electron and become a negative soliton. The soliton possesses a spin of  $1/2$ , whereas there is no spin for the positive and negative solitons. The electronic energy level of the soliton is located at the middle of the bandgap of the *trans*-polyacetylene. There is no electron or there are a couple of electrons on the soliton energy levels for the positive soliton and negative soliton, respectively.

*Polarons* are the major charge-carriers in conducting polymers including basic state degenerate *trans*-polyacetylene and the basic state non-degenerate conjugated polymers. The positive polaron with positive charge and the negative polaron with negative charge are denoted as  $\mathbf{P}^+$  and  $\mathbf{P}^-$ , respectively.  $\mathbf{P}^+$  is formed after oxidation of the conjugated polymer main chain and  $\mathbf{P}^-$  is formed after reduction of the conjugated polymer main chain. The appearance of the polarons produces two new polaron energy levels in the bandgap of the conjugated polymers.  $\mathbf{P}^+$  and  $\mathbf{P}^-$  possess spin of 1/2.

The *bipolaron* is the charge carrier that possesses double charges by coupling of two  $\mathbf{P}^+$  or two  $\mathbf{P}^-$  on a conjugated polymer main chain. The bipolaron has no spin, and it can be formed when the concentration of polarons are high in the conjugated polymer main chains. The positive bipolaron and negative bipolaron correspond to the hole pair or the electron pair.

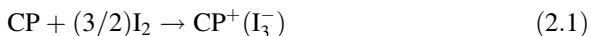
## 2.2 Doping Characteristics

As mentioned above, the doping of conducting polymers is natively different from that in inorganic semiconductors. Doping of conducting polymers can be realized chemically or electrochemically by oxidation or reduction of the conjugated polymers.

### 2.2.1 Chemical Doping

Conducting polyacetylene was discovered by chemical doping [1, 2]. The chemical doping includes p-type doping and n-type doping.

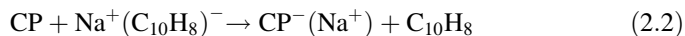
*p-Doping* is also called oxidation doping, which refers to the oxidation process of the conjugated polymer main chain to form polarons. The oxidants  $\text{I}_2$ ,  $\text{Br}_2$ ,  $\text{AsF}_5$ , etc. can be used as p-dopants. After p-doping, the conjugated polymer is oxidized and loses electron to form p-doped conjugated polymer chain, and the dopant gains an electron to become the counteranion. The following reaction is an example of the p-doping process:



where CP denotes conducting polymers.

*n-Doping* is also called reduction doping, which refers to the reduction process of the conjugated polymer main chain to form negative charge carriers. Some strong reductants, such as alkali metal vapor,  $\text{Na}^+(\text{C}_{10}\text{H}_8)^-$ , etc., can be used as n-type dopants. After n-doping, the conjugated polymer is reduced and gains electrons to

form an n-doped conjugated polymer main chain, whereas the dopant loses an electron to become the counteranion. The following reaction is an example of the n-doping process:

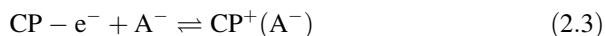


Proton acid doping of polyaniline (see Fig. 2.4) is one kind of chemical doping.

### 2.2.2 Electrochemical Doping

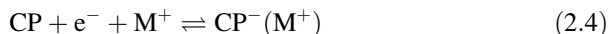
Electrochemical doping is realized by electrochemical oxidation or reduction of the conjugated polymers on an electrode.

For electrochemical p-doping, the conjugated polymer main chain is oxidized to lose an electron (gain a hole) accompanying the doping of counteranions from electrolyte solution:



where  $\text{A}^-$  denotes the solution anion,  $\text{CP}^+(\text{A}^-)$  represents the conducting polymer with the main chain oxidized and counteranion doped.

For electrochemical n-doping, the conjugated polymer main chain is reduced to gain an electron accompanying the doping of counteranions from electrolyte solution:



## 2.3 Conductivity Characteristics

Conductivity is the most important property of conducting polymers. The conductivity of common doped conducting polymers is in the range of  $10^{-3}$ – $10^3$  S/cm, whereas that of the intrinsic conjugated polymers without doping is in the range of  $10^{-9}$ – $10^{-6}$  S/cm. After doping, conductivity of conjugated polymers increases by six to ninefold. The highest conductivity reported in the literature is  $10^5$  S/cm for drawing-extended ordering conducting polyacetylene film [7].

Conducting polymers usually have an amorphous structure, in some cases with ordered domains. The charge-transporting mechanism in conducting polymers is different from that in the crystalline conducting materials where there exist conduction bands and valence bands and the charge carriers can move freely in the energy bands. In conducting polymers the charge carriers are located in the local doping energy levels (limited length of conjugated polymer chain) or in a very narrow doping energy band in the case of ordered domains. The charge carriers can



move easily on the conjugated polymer main chain, but the charges have to hop for the transportation between the conjugated polymer chains. The activation energy for the hopping of the charge carriers is much higher than that of the charge transportation within the conjugated polymer main chains. Obviously, the charge transportation in conducting polymers is limited by the hopping between the conjugated polymer chains. Therefore, the conductivity of conducting polymers shows characteristics of hopping transportation.

The conductivity of conducting polymers shows a temperature dependence similar to that of semiconductors, and it obeys the Mott Variable Range Hopping (VRH) model:

$$\sigma(T) = \sigma_0 \exp[-(T_0/T)^{1/(n+1)}] \quad (2.5)$$

where  $\sigma_0$  is a factor weakly related to temperature,  $n$  is the dimension number,  $n = 1, 2, 3$  indicate that it is one-dimension, two-dimension, and three-dimension VRH transportation. For the common three dimension system, the conductivity equation is [8]

$$\sigma(T) = \sigma_0^{3d} \exp[-(T_0^{3d}/T)^{1/4}] \quad (2.6)$$

where

$$T_0^{3d} = c/[k_B N(E_F) L^3] \quad (2.7)$$

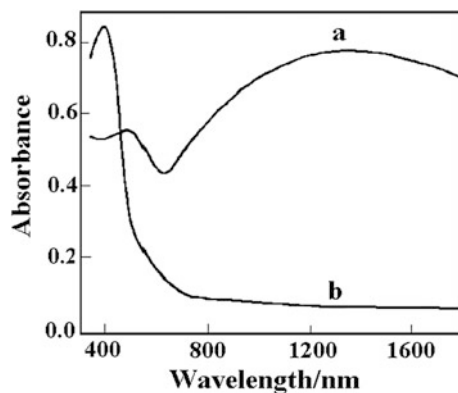
In (2.7),  $c$  is a constant,  $k_B$  is the Boltzmann constant,  $L$  is the localization length (effective conjugated chain length), and  $N(E_F)$  is the state density at the Fermi energy level.

The conductivity of conducting polymers is closely related to the doping degree and the degree of ordering of the polymer main chain in the solid film. The doping degree relates to the charge carrier concentration on the conjugated polymer main chain. In the low doping degree region (far lower than the saturated doping degree), the conductivity of the conjugated polymers increases linearly with increasing the doping degree of the conjugated polymers.

## 2.4 Absorption Spectra

Intrinsic conjugated polymers and doped conducting polymers can be distinguished by absorption spectra. There is a strong absorption peak in the near-infrared (NIR) region for doped conducting polymers, caused by the existence of the polaron and bipolaron energy levels within the bandgap of the conjugated polymers. The NIR absorption disappears after dedoping for the intrinsic conjugated polymers. Figure 2.5 shows the absorption spectra of doped and dedoped polypyrrole films,

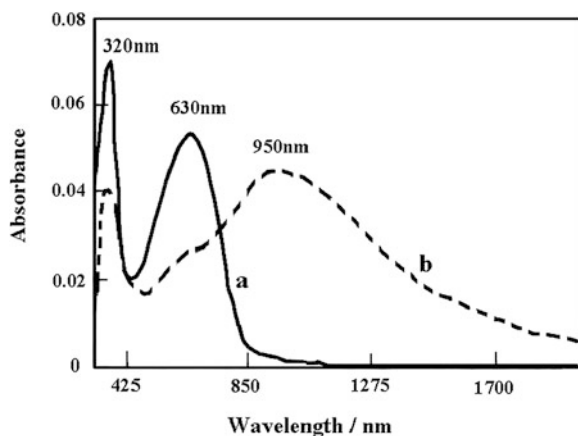
**Fig. 2.5** Absorption spectra of polypyrrole. **a** Doped state. **b** Intrinsic state



which represents the typical characteristic absorption spectra of the doped conducting polymer and the dedoped intrinsic conjugated polymer. There is an absorption peak at ca. 400 nm for the dedoped intrinsic polypyrrole film, which corresponds to the  $\pi$ - $\pi^*$  transition absorption of the conjugated polypyrrole main chain. After doping, a strong and broad absorption peak appears in the NIR region from 700 nm to ca. 2,000 nm, which corresponds to the polaron and bipolaron energy levels.

The absorption spectra of doped and intrinsic polyaniline are more complicated in comparison with those of polypyrrole because of the three structure change of polyaniline. Figure 2.6 shows the absorption spectra of polyaniline in different doping states. The absorption spectrum of doped (proton-acid doping or electrochemical doping) conducting polyaniline is similar to that of the doped conducting polypyrrole: there is a strong and broad absorption peak in the NIR region (peaked at ca. 950 nm) which corresponds to the polaron and bipolaron absorption, and an absorption peak at ca. 320 nm corresponding to the  $\pi$ - $\pi^*$  transition absorption of the

**Fig. 2.6** Absorption spectra of polyaniline.  
**a** Pernigraniline (PAn-III).  
**b** Proton-acid-doped conducting polyaniline

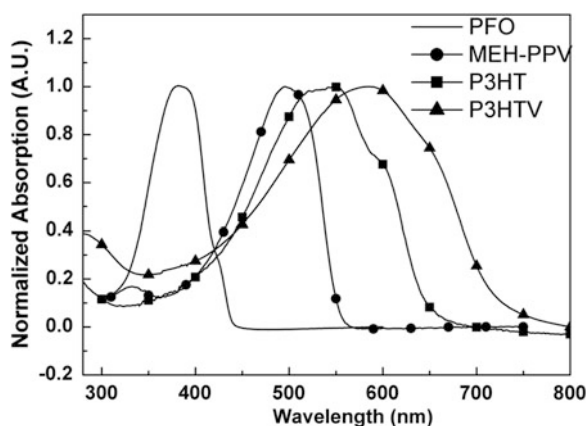


conjugated polyaniline main chain. With the reduction (dedoping) of the conducting polyaniline, the NIR absorption is weakened and finally disappears when it is reduced to its intrinsic conjugated state. Conducting polyaniline can be proton-acid dedoped to become a pernigraniline (PAN-III) which shows an absorption spectra with two strong absorption peaks at ca. 320 and 630 nm, respectively. The absorption peak at ca. 320 nm corresponds to the  $\pi$ - $\pi^*$  absorption of the conjugated polyaniline main chain, whereas the absorption peak at ca. 630 nm can be ascribed to the electron transition between the HOMO of the benzo-structure and the LUMO of the quinone-structure of PAN-III.

Figure 2.7 shows the absorption spectra of several representative intrinsic conjugated polymers including polyfluorene (PFO), MEH-PPV, poly(3-hexylthiophene) (P3HT), and poly(3-hexylthienylene-vinylene) (P3HTV). All the spectra correspond to the  $\pi$ - $\pi^*$  absorption of the conjugated polymer main chains. The bandgap ( $E_g$ ) of the conjugated polymers can be calculated from its absorption edge. It can be seen from Fig. 2.7 that the absorption edges of PFO, MEH-PPV, P3HT, and P3HTV are 443, 568, 669, and 749 nm, respectively. From the absorption edge wavelength, the bandgaps of PFO, MEH-PPV, P3HT, and P3HTV can be calculated to be 2.8, 2.18, 1.85, and 1.66 eV, respectively. The results indicate that inserting a carbon-carbon double bond between the benzene or thiophene rings in the polymer main chain can reduce the bandgap and red-shift the absorption spectra of the conjugated polymers significantly.

The characteristics of the absorption spectra of conjugated polymers play a crucial role in the applications of PSCs. Broad and strong absorption in the visible and NIR regions is pursued for the high performance polymer photovoltaic materials to harvest solar light efficiently.

**Fig. 2.7** Absorption spectra of the intrinsic PFO, MEH-PPV, P3HT, and P3HTV films



## 2.5 Solubility

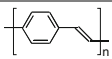
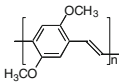
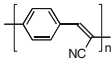
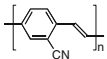
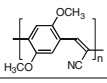
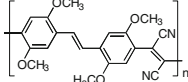
Conducting polymers are usually insoluble and infusible because of their rigid conjugated main chain, which limits their application. There are several strategies to solve the problems as discussed in the following. In 1992, Cao et al. [9] from UNIAx company prepared soluble conducting polyaniline (by counteranion induced solubility) and solved the difficulty of processing of conducting polymers, which paved the way for large-scale application of conducting polymers.

### 2.5.1 *Effect of Substituents on Solubility of Conjugated Polymers*

Conjugated polymers without substituents are all insoluble. Attaching appropriate flexible side chains (substituents) can make the conjugated polymers soluble in organic solvents. For example, polythiophene without substituents is insoluble in any solvent, whereas the hexyl-substituted polythiophene derivative P3HT is soluble in organic solvents such as toluene, chlorobenzene, dichlorobenzene, etc. In addition, for application as electroluminescent polymers or photovoltaic polymers, the side chains can also tune the bandgap and electronic energy levels (HOMO and LUMO energy levels) of the conjugated polymers. The bandgap determines the color of the PLEDs with the conjugated polymer as active layer, and it influences the photovoltaic properties of the conjugated polymers in PSCs. The HOMO and LUMO energy levels are very important for improving the optoelectronic performance of conjugated polymers.

Bredas et al. [10] studied the effect of electron-donating or electron-accepting ability of the substituents on the electronic energy levels of PPV derivatives by quantum chemistry calculation with the VEH method. They calculated the energy bandgap ( $E_g$ ), ionization potential (IP) (which corresponds to the HOMO energy level with  $IP = -HOMO$ ), and electron affinity (EA) (which corresponds to the LUMO energy level with  $EA = -LUMO$ ) of the PPV derivatives. The calculation results are listed in Table 2.1. The  $E_g$  values calculated are in good agreement with those obtained from the absorption edges of their absorption spectra, indicating that the theoretical calculation results are quite reliable. It can be seen from Table 2.1 that IP and EA values of the PPV derivatives substituted by electron-donating alkoxy groups decreased in comparison with those of PPV without substituents, with more decrease of IP than EA. IP and EA values of the PPV derivatives substituted by electron-withdrawing cyano groups increased in comparison with those of PPV without substituents, with more increase of EA than IP. Irrespective of the electron-donating or electron-withdrawing substitution, the  $E_g$  values of the PPV derivatives are reduced to some extent.

**Table 2.1** Electronic properties of PPV and its derivatives calculated by the VEH method

PPV and its derivatives	$E_g/\text{eV}$	IP/eV	EA/eV
	2.32	5.05	2.73
	2.07	4.72	2.65
	2.17	5.27	3.10
	2.24	5.15	2.91
	1.97	5.12	3.15
	1.74	5.08	3.34

### 2.5.2 Effect of Substitution on the Conductivity of Conducting Polymers

Actually, for doped conducting polymers, substitution by flexible side chains is not a good method for solving their solubility, because it usually results in a conductivity decrease in the conducting polymers. For example, the conducting polypyrrole with a long alkyl substituent on the 3- or 4-position or the *N*-position of its pyrrole ring is soluble in organic solvents, but conductivity of the conducting polypyrrole is decreased significantly to ca. 0.001 S/cm. The reason for the conductivity decrease is that introducing a substituent on the conducting polymer main chain results in distortion of the conjugated main chain, thereby decreasing the conjugation degree and the conductivity of the conducting polymers.

The best way to make conducting polymers soluble is the counteranion induced method proposed by Yong Cao et al. [9]—using proton acid and acid containing anions with flexible side chain [such as dodecyl-benzene sulfonic acid (DBSA)] to make the doped polyaniline soluble. This is the most successful method, and polyaniline film prepared from conducting polyaniline solution possesses high conductivity. Yong Cao et al. prepared conducting polyaniline film from polyaniline solution, and the conductivity of the conducting polyaniline film reached  $10^2$  S/cm [9], which is higher than that of conducting polyaniline films prepared by electrochemical polymerization or other methods.

## 2.6 Electrochemical Properties

Electrochemical doping/dedoping property is one of the most important properties of conducting polymers, because many applications of conducting polymers, including electrode materials for batteries, electrochromic materials, modified electrodes, and enzyme electrodes, etc., are based on the electrochemical properties. Studies on the electrochemical properties of conducting polymers are mainly focused on the electrochemical redox potentials, reversibility, and reaction mechanism of the doping/dedoping processes.

Electrochemical studies of conducting polymers are commonly carried out for the conducting polymer films on the working electrode. The electrochemical redox processes of conducting (or conjugated) polymers are quite complicated in comparison with common organic and inorganic molecules. Electrochemical oxidation of conjugated polymers is accompanied by the intercalation (or doping) of counteranions from electrolyte solution, so that the oxidation process of the conjugated polymers is often called oxidation doping (or p-doping). The electrochemical reduction of conjugated polymers is accompanied by the intercalation (or doping) of counteranions from electrolyte solution, so the reduction process of the conjugated polymers is often called reduction doping (or n-doping). In addition to the common electron transfer on the electrode/electrolyte interface, there are both diffusion of counterions in the conjugated polymer films and expansion of the conjugated polymer films because of the intercalation of the counterions.

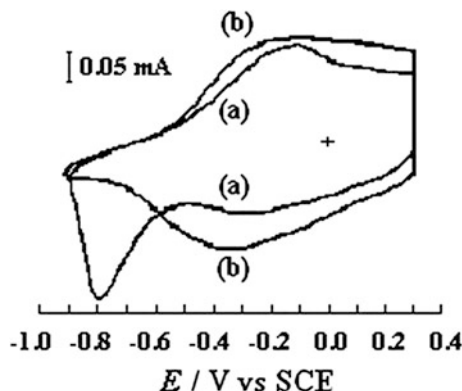
### 2.6.1 Electrochemical Properties of Conducting Polypyrrole

Polypyrrole (PPy) is a typical p-type conjugated polymer with a very low oxidation potential in the range of ca.  $-0.6$  to  $0.3$  V versus SCE, which makes the p-doped conducting PPy stable, and the neutral PPy is very easily oxidized into its p-doped state. The electrochemical properties of conducting PPy are therefore usually inferred from the reduction (dedoping)/re-oxidation (doping) of the p-doped PPy. Generally, the electrochemical reaction of conducting PPy can be expressed as follows:



where  $\text{PPy}^+(\text{A}^-)$  denotes the oxidation-doped conducting PPy doped with counteranion  $\text{A}^-$  (p-doped PPy),  $\text{PPy}^0$  denotes the neutral (intrinsic) PPy.

The electrochemical reduction/re-oxidation (dedoping/doping) processes of conducting PPy (p-doped PPy) in aqueous solution are closely related to counteranions of the electrolyte and the pH values of the aqueous solution. Figure 2.8 shows cyclic voltammograms of nitrate-doped conducting PPy film in neutral and weakly acidic  $\text{NaNO}_3$  aqueous solutions [11]. In weak acidic pH 3 solution, there are

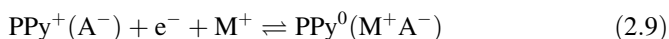


**Fig. 2.8** Electrochemical cyclic voltammograms of  $\text{PPy}(\text{NO}_3^-)$  in 0.5 mol/L  $\text{NaNO}_3$  aqueous solution at potential scan rate of 20 mV/s: **a** neutral (pH 7) aqueous solution; **b** acidic (pH 3) aqueous solution

a couple of reversible reduction/re-oxidation peaks in the potential range of 0.3 to  $-0.8$  V versus SCE (Fig. 2.8b). The reaction processes can be expressed as that in reaction (2.8). In neutral (pH 7) aqueous solution there are two reduction peaks in the potential range of 0.3 to  $-0.8$  V versus SCE (Fig. 2.8a), which corresponds to the two doping structures (oxidation doping structure and proton-acid doping structure) of conducting PPy [12]. Actually, the electrochemical reduction of conducting PPy in acidic solutions also involves two reduction processes, the two reduction peaks in the acidic solutions being mixed together to show a broad reduction peak in the cyclic voltammogram. The in situ absorption spectra at different reduction potentials of conducting PPy in a pH 3  $\text{NaNO}_3$  aqueous solution clearly indicate the two reduction processes in the potential ranges of 0.3 to  $-0.3$  V and  $-0.3$  to  $-0.8$  V versus SCE [11]. For the re-oxidation of the reduced PPy (neutral PPy), it is reversible if the upper-limited potential is lower than 0.3 V versus SCE. However, if the oxidation potential is higher than 0.5 V versus SCE, some overoxidation of the p-doped PPy takes place. The potential value where the overoxidation starts to occur is closely related to the pH value of the aqueous electrolyte solution—the higher the pH value, the lower the potential [13]. That is, PPy is more easily overoxidized in an alkaline aqueous solution than in an acidic solution.

The electrochemical reduction and re-oxidation processes of conducting PPy are closely related to the nature of the counteranions in the polymer films and the anions in the electrolyte solutions [14]. When the anions are small and spherically shaped such as  $\text{NO}_3^-$  and  $\text{Cl}^-$  etc., the reversible reduction/re-oxidation peaks can be observed in the cyclic voltammograms of the conducting PPy, as mentioned above. However, if the counteranions in the polymer film are large surfactant anions such as  $\text{TsO}^-$ , the reduction peak appears at a much lower potential because of the difficulty of dedoping the large counteranions, and the solution cations dope into the

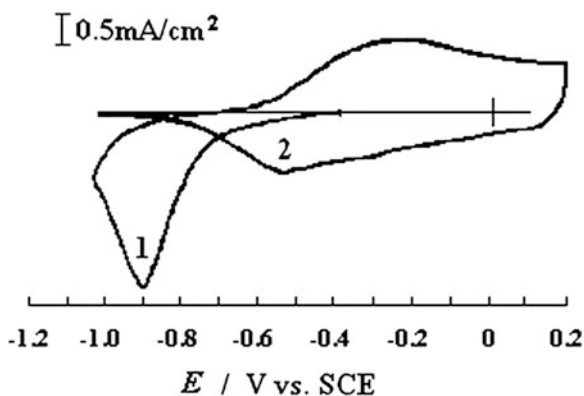
conducting PPy instead of the anions dedoping [11]. The reaction mechanism of the conducting PPy film with large counteranions such as  $\text{TsO}^-$  can be expressed as follows:



On the other hand, if the cyclic voltammetry is performed in an aqueous solution containing the electrolyte salt with large anions such as  $\text{TsO}^-$ , the first reduction of  $\text{PPy}(\text{NO}_3^-)$  is the dedoping of  $\text{NO}_3^-$  counteranions, but the re-oxidation process is irreversible because of the difficulty of  $\text{TsO}^-$  doping [14]. In a weak alkaline aqueous solution, the original counteranions in the conducting polypyrrole are exchanged with strong nucleophilic  $\text{OH}^-$  anions [15]. Then the reduction and re-oxidation of the PPy film are accompanied with the dedoping and redoping of  $\text{OH}^-$  [15, 16]. In a strongly alkaline aqueous solution, the doping structure of conducting PPy is unstable and the conjugated polymer chain of PPy can be degraded and destroyed, which results in the loss of conductivity and electrochemical properties of PPy [13].

For the PPy film prepared from an organic electrolyte, an abnormal cyclic voltammogram of the PPy film can be observed in an organic electrolyte solution. There is a high overpotential for the first reduction process of the PPy, and no reduction current until  $-0.6$  V versus SCE, as shown in Fig. 2.9. The reoxidation and the redox processes from the second cycle resumes to normal cyclic voltammograms of PPy in weakly acidic aqueous solutions [17]. This phenomenon can be explained as follows. The diffusion coefficient of the counteranions during the first reduction of PPy in organic electrolyte solution is very small and the solvation energy of the counteranions with organic solvent molecules is also very small, so it is very difficult for the counteranions to dedope from PPy into the organic solution. Then the solvated cations with organic solvent molecules dope into PPy when the potential reaches a very low value (negative potential), which increases the diffusion coefficient of the counteranions in PPy and makes the following redox reaction reversible [17].

**Fig. 2.9** Cyclic voltammograms of PPy ( $\text{ClO}_4^-$ ) in 0.5 mol/L  $\text{NaClO}_4$  PC solution. The numbers in the figure indicate the sequence of the cyclic potential scan





### 2.6.2 Electrochemical Properties of Conducting Polyaniline

Polyaniline (PAn) is another important and well studied conducting polymer. There are many potential applications (such as electrode materials for batteries and supercapacitors, anti-corrosion materials, modified electrodes and biosensors, etc.) for PAn based on its electrochemical properties. Therefore, understanding the electrochemical properties is of great importance for the applications of PAn.

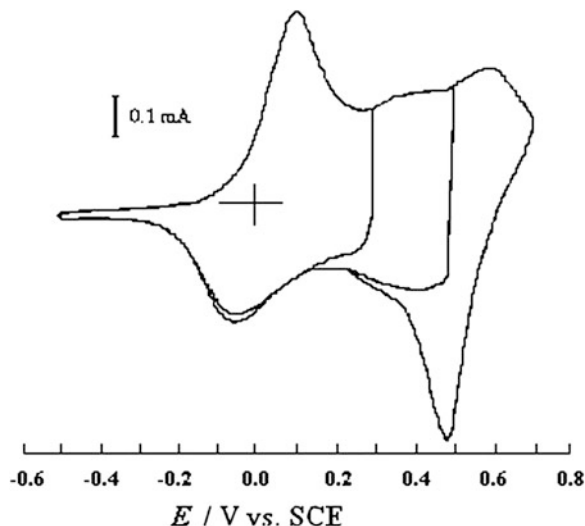
The most important characteristic of PAn, in comparison with other conducting polymers such as PPy, etc., is its proton-acid doping. The proton-acid doping benefits the preparation of conducting PAn solutions by counteranions induced proton-acid doping [9], but it also makes the doped PAn unstable in basic and neutral aqueous solutions. The doped PAn is easily dedoped by removing proton-acid in the basic and neutral solutions. PAn becomes an insulator and loses its electrochemical activity after the dedoping. Therefore, the doped PAn is stable only in acidic solutions and the electrochemical properties of PAn are mainly studied in acidic electrolyte solution.

There are two reversible redox processes for PAn in an acidic aqueous solution in the potential range of  $-0.5$  to  $0.7$  V versus SCE. Figure 2.10 shows cyclic voltammograms of polyaniline doped with  $\text{NO}_3^-$  counteranions ( $\text{PAn}(\text{NO}_3^-)$ ) in an acidic (pH 1.5)  $1 \text{ mol/L NaNO}_3$  aqueous solution [18]. Based on the in situ absorption spectra at different redox potentials, the redox processes in the potential range of  $0.3$  to  $-0.5$  V versus SCE are similar to that for PPy in acidic solution [see reaction (2.8)], the reduction peak and reoxidation peak corresponding to the dedoping and redoping of conducting polyaniline. From  $0.3$  to  $0.7$  V versus SCE, there is another unique redox processes for PAn; the doped PAn is further oxidized into the completely oxidized polyaniline pernigraniline ( $\text{PAn-III}$ ) (see Fig. 2.2) which loses conductivity. In addition, weak redox peaks often appear in the potential range of  $0.3$ – $0.5$  V versus SCE, as shown in Fig. 2.10. These weak middle redox peaks are related to an overoxidation structure of PAn. If the electropolymerization potential during the preparation of PAn is higher than  $0.8$  V, or the upper-limit potential during cyclic voltammetry is higher than  $0.8$  V versus SCE, the middle redox peaks appear in the cyclic voltammograms [19].

### 2.6.3 Electrochemical Properties of Polythiophene and Other Conjugated Polymers

In comparison with polypyrrole and polyaniline, polythiophene (PTh) possesses a narrower bandgap and a higher oxidation doping potential, which indicates that polythiophene can be both p-doped by oxidation and n-doped by reduction. The higher oxidation doping potential results in lower stability of the p-doped conducting polythiophene in comparison with conducting polypyrrole and polyaniline [20]. Nevertheless, it makes the neutral polythiophene stable which guarantees the optoelectronic applications of polythiophene as semiconducting polymers.

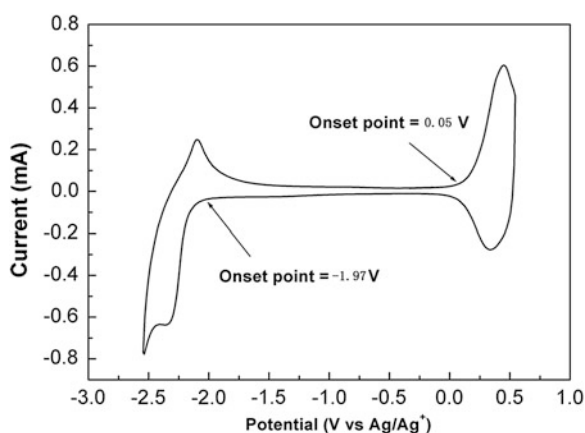
**Fig. 2.10** Cyclic voltammograms of PAn ( $\text{NO}_3^-$ ) in pH 1.5, 1 mol/L  $\text{NaNO}_3$  aqueous solution with a potential scan rate of 40 mV/s



Organic solutions are used in the measurement of the electrochemical properties of polythiophene, because of the high oxidation potential for p-doping and lower reduction potential for n-doping of polythiophene. Figure 2.11 shows the cyclic voltammogram of poly(3-hexylthiophene) (P3HT) in 0.1 mol/L  $\text{Bu}_4\text{NPF}_6$  acetonitrile solution. It can be seen that there are a couple of redox peaks in the higher potential range (0–0.6 V vs.  $\text{Ag}/\text{Ag}^+$ ) corresponding to the p-doping/dedoping of polythiophene, and a couple of redox peaks in the negative potential range (–1.8 to –2.6 V vs.  $\text{Ag}/\text{Ag}^+$ ) corresponding to the n-doping/dedoping of polythiophene.

For other semiconducting conjugated polymers used in optoelectronic devices, such as PLEDs or PSCs, their electrochemical properties are similar to those of polythiophene mentioned above. Usually, there are a couple of redox peaks in a

**Fig. 2.11** Cyclic voltammogram of poly(3-hexylthiophene) (P3HT) in 0.1 mol/L  $\text{Bu}_4\text{NPF}_6$  acetonitrile solution



higher positive potential range and a couple of redox peaks in the negative lower potential range, the only difference being their different onset oxidation/reduction potentials or their redox peak potentials in their cyclic voltammograms.

#### ***2.6.4 Electrochemical Measurement of HOMO and LUMO Energy Levels of Conjugated Polymers***

As mentioned above, in the cyclic voltammograms of polythiophene and other optoelectronic conjugated polymers, there are a couple of redox peaks in the higher potential range corresponding to their p-doping/dedoping and a couple of redox peaks in the lower (negative) potential range corresponding to their n-doping/dedoping (see Fig. 2.11). Actually, the onset p-doping (oxidation) potential corresponds to the HOMO energy level and the onset n-doping (reduction) potential corresponds to the LUMO energy level of the conjugated polymers. Therefore, cyclic voltammetry has commonly been used to measure the HOMO and LUMO energy levels of the conjugated polymers [5, 21, 22]. The HOMO and LUMO energy levels of the conjugated polymers can be calculated from the following equations:

$$\text{HOMO} = -e (E_{\text{ox}} + C)(\text{eV}); \quad \text{LUMO} = -e (E_{\text{red}} + C)(\text{eV})$$

where  $E_{\text{ox}}$  and  $E_{\text{red}}$  denote the onset oxidation and onset reduction potentials with the unit of V respectively, and C is a constant related to the reference electrode (RE) used in the measurement of onset redox potentials. C usually takes the value of 4.4 for the RE of SCE, 4.8 for the RE of  $\text{Fc}/\text{Fc}^+$  (Fc denotes ferrocene), and 4.71 for the RE of  $\text{Ag}/\text{Ag}^+$  [21, 22]. If silver wire was used as the RE, C could be 4.39 [5] (it should be calibrated with the ferrocene).

### **2.7 Optoelectronic Properties of Conjugated Polymers**

Since the discovery of PLEDs by Friend et al. in 1990, [3] the optoelectronic properties of conjugated polymers have drawn great attention. There are detailed descriptions for the optoelectronic properties and their applications in PLEDs, PSCs, and organic field effect transistors for various conjugated polymers and conjugated organic molecules in Chaps. 3, 5, and 7 in this book.

## 2.8 Synthesis of Conducting Polymers

Conducting polymers can be prepared by chemical or electrochemical oxidation polymerization or by chemical catalytic synthesis.

### 2.8.1 *Electrochemical Oxidation Polymerization of Conducting Polymers*

The electrochemical preparation of conducting polymers is usually carried out through oxidative polymerization of their corresponding monomers by constant current, constant potential, or cyclic voltammetry in a potential range. The electropolymerization is performed in an electrolyte solution which contains solvent, electrolyte salt, and the monomer. There are many factors influencing the electropolymerization processes, such as solvents, supporting electrolyte salts, concentration of the monomers, and pH value of the electrolyte solutions, as well as polymerization potential, current, temperature, etc. Among these factors, the polymerization potential of the monomers is the most important. Table 2.2 lists the oxidation polymerization potentials of the most important monomers pyrrole, aniline, and thiophene. The lower oxidation polymerization potentials of pyrrole and aniline make the electropolymerization of polypyrrole and polyaniline easier, and it can be performed in aqueous solutions.

#### 2.8.1.1 Electrochemical Preparation of Conducting Polypyrrole

Polypyrrole (PPy) is one of the most stable and environmentally-friendly conducting polymers. In 1979, Diaz et al. [23] first reported the preparation of a PPy film with conductivity ( $\sigma$ ) of ca. 100 S/cm by electrochemical polymerization on Pt electrode in acetonitrile solution. Pyrrole can be electropolymerized both in organic and in aqueous solutions benefitting from its lower polymerization potential. Of course, aqueous solutions are the first selection for the preparation of conducting PPy.

The anions of the salts in the aqueous solutions influence conductivity of the as-prepared PPy films by electrochemical polymerization [24]. Flexible PPy films with

**Table 2.2** Oxidative polymerization potential of monomers and conductivity of the as-prepared conducting polymers [39]

Monomer	Polymerization potential (V vs. SCE)	Conductivity of the as-prepared polymers (S/cm)
Pyrrole	0.7	30–100
Aniline	0.8	1–20
Thiophene	1.6	10–100

$\sigma$  higher than 100 S/cm can be produced with the surfactant anions such as tosylate, benzene sulfonate, etc. Warrant et al. found that the acidity of the anions plays an important role in the conductivity of PPy films, the stronger the conjugated acids of the anions the higher the conductivity of the PPy films prepared from the anion-containing solution [25]. The concentration of the electrolyte anions also plays an important role. The concentration of the anions should be no lower than 0.1 M; too low an anion concentration leads to poor PPy films. The concentration of pyrrole monomer is usually 0.1 M.

The effect of solvent on the electropolymerization depends on the donor number (DN) of the solvent [26]. The low DN solvents, such as acidic water, propylene carbonate (PC), and  $\text{CH}_3\text{NO}_2$ , are very important for getting high conductivity of the as-prepared PPy films. The solvent effect can be explained from the cation radical coupling mechanism of the electropolymerization. High DN value of the solvent means high nucleophilicity or strong basicity. The solvent molecules with high DN value attack the cation radical formed by oxidation of pyrrole, which hampers the electropolymerization [26]. Water is a special solvent with changeable acidity by changing pH values. The optimum pH value of the aqueous solutions for pyrrole electropolymerization is between pH 2 and pH 5.5 [27].

The quality of the conducting PPy films can be improved by using a small amount of additive in the electrolyte solutions for the electropolymerization. By adding surfactant additives in the electrolyte solution, the smoothness, mechanical property, and conductivity of the as-prepared PPy films improves significantly [28, 29]. By using nonionic surfactant nonylphenol polyethyleneoxy (10) as an additive in the TsONa aqueous solution, the tensile strength of the PPy film produced from the solution reached 127 MPa, which is five times higher than that of the PPy film prepared without the surfactant additive [28].

As mentioned above, the electropolymerization can be performed with a potential-controlled method (constant potential or cyclic voltammetry) or a current-controlled method (constant current). In the potential-controlled method, the potential should be controlled no higher than 0.75 V versus SCE (usually at 0.65–0.70 V vs. SCE) for the electropolymerization of PPy. For the electropolymerization with constant current, Maddison et al. [30] studied the effect of current and found that the PPy film with highest conductivity was obtained at 2.8 mA/cm<sup>2</sup>. Good PPy films can usually be obtained at the current density of 1–2 mA/cm<sup>2</sup>.

Temperature is another factor that influences electropolymerization. High quality PPy films can usually be obtained at lower temperatures (lower than 20 °C). At higher temperature, defect structures of PPy are easily formed, which results in lower conductivity.

For the mechanism of the electrochemical oxidation polymerization of PPy, Genies et al. [31] proposed a cation-radical polymerization in 1983. According to this mechanism, after applying the oxidation polymerization potential, pyrrole monomers are first oxidized into cation radicals on the anode, then two cation-radicals couple together to form a dimer with losing two protons. The dimer is oxidized into its cation radical more easily than monomer because of its lower oxidation potential. The cation radical of the dimer couples with other cation

radicals to make a trimer or longer chain of polymer, and so on. The PPy films produced by electropolymerization should be in its p-doping (oxidized) state, because the p-doping potential of the polymer is much lower than the oxidation potential of the monomers. The cation radical mechanism can successfully explain the effect of solvent and solution anions on the electropolymerization. However, it fails to explain the effect of pH values of the electrolyte solutions. Qian et al. [32] modified the cation radical mechanism and proposed a pre-protonation cation-radical polymerization mechanism to elucidate the pH value effect on the electropolymerization. They think pyrrole monomer is first protonated on its  $\beta$ -carbon, which benefits the formation of the pyrrole cation radical. Then the polymerization follows the cation-radical mechanism.

The cation-radical mechanism and the modified mechanism with pre-protonation doesn't consider the effect of solution anions on the electropolymerization. Actually, the concentration and nature of the solution anions influence the oxidative polymerization rate and the quality of the as-prepared PPy films significantly. Therefore, the solution anions should take part in the electropolymerization processes. In addition, the coupling process of two cation-radicals in the cation-radical mechanism is unreasonable because the two cation radicals with positive charge should expel each other when one approaches to another for coupling. Based on this consideration, Li proposed an anion-participated cation-radical polymerization mechanism [33]. This mechanism proposes that pyrrole monomers and solution anions competitively adsorb on the anode under the oxidation polymerization potentials, and the cation-radicals formed on the anode should combine with solution anions to form neutral cation-anion pairs. Then the cation radical-anion pairs couple together to form a dimer with losing two anions and two protons. The experimental results of competition doping of two kinds of anions into PPy during pyrrole polymerization support the anion-participated mechanism [34].

### 2.8.1.2 Electrochemical Preparation of Polyaniline

Polyaniline (PAn) can be prepared electrochemically in a strongly acidic aqueous solution at ca. 0.8 V versus SCE. However, the PAn product prepared by electrochemical polymerization is powder attached to the electrode, which cannot form flexible films as do electropolymerized PPy and polythiophene (PTh). Therefore, the electrochemical preparation of PAn is mainly for deposition of a PAn modified electrode for electrochemical studies and for some applications in electrocatalysis, sensors, and electrode materials in lithium batteries.

Common electrolyte solution for the electrochemical preparation of PAn is 0.1 M aniline in 1 M  $\text{H}_2\text{SO}_4$ , HCl,  $\text{HClO}_4$ , or  $\text{HBF}_4$  aqueous solutions. Conductivity of the electropolymerized PAn is usually of the order of  $10^{-1} \sim 10^1$  S/cm. The electropolymerization of aniline in the acidic aqueous solutions at a constant potential (such as 0.8 V vs. SCE) often produces PAn with partial overoxidation [35]. Therefore, cyclic voltammetry in a potential range (such as  $-0.15$  to  $0.78$  V vs. SCE [36]) is usually preferred for the preparation of a high quality PAn product.

### 2.8.1.3 Electrochemical Preparation of Polythiophene

The most important characteristic of thiophene electrochemical polymerization is its high polymerization potential of 1.6 V versus SCE (see Table 2.2), which requires the electrochemical polymerization of thiophene to be performed in organic solution and the conducting polythiophene (PTh) produced is easily overoxidized during the electropolymerization. Therefore, much effort has been devoted to decreasing the polymerization potential with various strategies. Diaz et al. [37] and Garnier et al. [38] studied the effect of substituents of thiophene on the polymerization potential (see Table 2.3). The oxidative polymerization potentials of bithiophene (dimer of thiophene) and the thiophene derivatives with the electron-donating substituents are obviously decreased, which benefits the electropolymerization.

Tourillon and Garnier [39] prepared polythiophene (PTh) electrochemically at 1.6 V versus SCE on a Pt anode in a solution of  $\text{CH}_3\text{CN} + 0.1 \text{ M}$   $(\text{Bu})_4\text{NClO}_4 + 0.01 \text{ M}$  thiophene (containing ca. 0.01 M water) with Ar pretreatment (bubbling) for 15 min. They obtained PTh film with a conductivity of 10–100 S/cm. They found that the pretreatment of the polymerization solution by Ar bubbling is very important. Without the Ar pretreatment to remove oxygen in the electrolyte solution, the conductivity of the as-prepared PTh films is only ca. 0.1 S/cm. The PTh films deposited on the anode are easily overoxidized in the presence of oxygen and water at the high electropolymerization potential. Sato et al. [40] performed the electropolymerization of thiophene in a dry solution (removed water carefully) under an Ar atmosphere, and they obtained the PTh film with the high conductivity of 190 S/cm.

Thiophene derivatives with electron-donating substituents, such as alkyl or alkoxy groups, show lower oxidative polymerization potentials, which is beneficial for the electropolymerization. For example, the oxidative polymerization potential

**Table 2.3** Oxidative polymerization potential of thiophene and its derivatives [38]

Monomers	Oxidative polymerization potential (V vs. SCE)
Thiophene (T)	1.65
2,2'-Bithiophene (2,2'-bT)	1.20
3-Methyl thiophene (3-MeT)	1.35
3-Bromothiophene (3-BrT)	1.85
3,4-Dibromo thiophene (3,4-BrT)	2.00
3,4-Dimethyl thiophene (3,4-MeT)	1.25
3,4-Methyl ethyl thiophene (3,4-MeEtT)	1.26
3,4-Diethyl thiophene (3,4-EtT)	1.23
3-Thiomethyl thiophene (3-SCH <sub>3</sub> T)	1.30

of 3-methyl thiophene (3-MeT) dropped to 1.35 V in comparison with 1.65 V for thiophene (see Table 2.3). The conductivity of poly(3-methylthiophene) [P(3-MeT)] film, prepared in a solution of 0.2 M 3-methylthiophene, 0.03 M Et<sub>4</sub>NPF<sub>6</sub>, PC (removing water carefully) at 5 °C under an Ar atmosphere, reached 450–510 S/cm [40]. 3-Methoxythiophene can be electropolymerized in an aqueous solution thanks to its lower polymerization potential with the substitution of strong electron-donating methoxy group [41].

Poly(3,4-ethylenedioxythiophene) (PEDOT) has drawn much attention recently because of its broad applications in transparent electrode materials, antistatic painting, solid state capacitors, and the electrode buffer layer material on ITO electrodes for PLEDs and PSCs. PEDOT can also be prepared by the electropolymerization of its monomer EDOT. The polymerization potential of EDOT is 1.49 V versus SCE which is lower than that of thiophene. By using dimer of EDOT as the monomer, the potential can be decreased further to 0.84 V versus SCE [42].

The polymerization potential of bithiophene is 1.20 V versus SCE, decreased by 0.45 V in comparison with that of thiophene. The lower polymerization potential makes the bithiophene easy to electropolymerize. Therefore, many researchers prepare PTh by the electropolymerization of bithiophene [43, 44]. The oxidative polymerization potential of terthiophene decreases further [45]. However, the molecular weight and conductivity of the PTh films prepared from bithiophene and terthiophene are lower than that of the PTh films obtained from thiophene, probably because of lower molecular weight of the conducting polythiophene due to the larger size of bithiophene and terthiophene.

In 1995, Shi et al. [46] electropolymerized thiophene in very strongly acidic boron trifluoride/ethylene ether (BFEE) solution, and obtained high quality PTh films with strong mechanical properties. The polymerization potential of thiophene dropped to ca. 1 V versus SCE in the BFEE solution. To improve further the ionic conductivity of the BFEE solution, Li et al. [47] used a mixed solution of BFEE and acetonitrile. By adding 10–20 % acetonitrile to the 0.1 mol/L Bu<sub>4</sub>PF<sub>6</sub> BFEE electrolyte solution, the oxidative polymerization potential is decreased to 1.2–1.3 V versus SCE, and a PTh film with conductivity of ca. 120 S/cm was prepared by such electropolymerization.

The electropolymerization mechanism of thiophene should be very similar to that of the pyrrole electropolymerization [33].

### 2.8.2 Chemical Polymerization of Conducting Polymers

The chemical oxidation preparation of conducting polymers is performed in solution by using oxidants such as FeCl<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, etc., and it is easy to enlarge the production scale with the chemical polymerization. Chemical polymerization is the most important method for the preparation of PAn, and it can also be used to produce conducting PPy.



### 2.8.2.1 Chemical Preparation of PAn

Similar to the electropolymerization of aniline, the chemical polymerization of aniline also has to be performed in a strongly acidic aqueous solution. A typical chemical polymerization method for the preparation of PAn in laboratory was reported by MacDiarmid et al. in 1986 [48]. They performed the chemical polymerization in 1 mol/L HCl solution by using  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as oxidant. The detailed preparation processes are as follows: 2 mL (0.022 mol) aniline was dissolved in 120 mL, 1 mol/L HCl solution, and the solution was cooled to 5 °C in an ice-water bath. At the same time, 0.025 mol  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  was added to 40 mL 1 mol/L HCl solution to prepare the  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  solution. Under vigorous stirring of the aniline HCl solution, the 40 mL  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  HCl solution was dropped into the aniline HCl solution drop by drop, then allowed to react for 8 h with vigorous stirring at 0 °C. The precipitate was collected and dried to obtain the HCl doped conducting polyaniline (PAn-HCl) powder.

The PAn-HCl powder can be further treated by putting it into 0.1 mol/L  $\text{NH}_3$  aqueous solution for 3 h under stirring to get dedoped emeraldine base PAn. The emeraldine base PAn can be dissolved in NMP, then the solution can be used to prepare PAn films. The emeraldine base PAn can also be used to prepare conducting PAn solution by appropriate proton-acid doping [9].

### 2.8.2.2 Chemical Preparation of PPy

PPy can also be prepared by chemical polymerization in aqueous solutions. However, the product is conducting PPy powder, different from the conducting PPy film prepared on electrodes by the electropolymerization mentioned above.

He et al. [49] prepared conducting PPy by the chemical polymerization of pyrrole with  $\text{FeCl}_3$  as oxidant in an aqueous solution. By using 3 % poly(vinyl-alcohol) (PVA) additive in the solution of 0.18 mol/L dodecyl-benzenesulfonic acid (DBSA, used as dopant), 0.18 mol/L pyrrole, and 0.26 mol/L  $\text{FeCl}_3$  (used as oxidant), conducting PPy powder with a conductivity of 43.18 S/cm (for the compressed pellets of the PPy powder) was obtained.

The chemical polymerization method can also be used to prepare conducting PPy nanotubes or nanofibrils by performing the chemical polymerization of pyrrole in polycarbonate template membranes [50].

## 2.9 Summary

Conjugated polymers possess a doped conducting state and a neutral semiconducting state, which lead to different applications. The doped conducting state could be found applications in the fields of electrode materials for batteries, electrochromics and super-capacitors, anti-static and anti-corrosion materials, electrolyte

**Table 2.4** Properties and applications of some representative conjugated polymers

Conjugated polymers	Stable structure	Preparation method	Solubility	Application fields
Polypyrrole (PPy)	p-Doped conducting state	PPy films can be obtained by electrochemical oxidation polymerization from aqueous or organic solution. PPy powder can be prepared by chemical oxidation polymerization	Insoluble	Modified electrode, enzyme electrodes (biosensors), electrochromics, conducting polymer films
Polyaniline (PAn)	p-Doped conducting state (proton-acid doping)	Electrochemical or chemical oxidation polymerization from strong acidic aqueous solution	Insoluble for the PAn doped with common anions, but it can become soluble by counteranions doping induced solubility	Modified electrodes, enzyme electrodes (biosensors), electrochromics, electrode materials for batteries and solid capacitors, anti-corrosion, microwave absorption, electrode buffer layer for optoelectronic devices
Polythiophene (PTh)	Intrinsic semiconducting state	Electrochemical oxidation polymerization from organic solution, or chemical oxidation polymerization in organic solvent	Insoluble	Electrochromics, conducting polymer films
PEDOT:PSS	p-Type doped conducting state	Electrochemical oxidation polymerization from organic solution, chemical oxidation or chemical synthesis in organic solvent	Aqueous solution	Transparent conducting polymer films, anode buffer layer materials in organic/polymer light-emitting diodes and organic/polymer solar cells, anti-static-electricity coating layer materials, electrode materials in solid state capacitors, etc.
Poly(3-hexylthiophene) (P3HT)	Intrinsic semiconducting state	Chemical synthesis in organic solvents	Soluble in THF, chlorobenzene, dichlorobenzene, etc.	Donor material in polymer solar cells, semiconductors in field effect transistors
MEH-PPV and MDMO-PPV	Intrinsic semiconducting state	Chemical synthesis in organic solvents	Soluble in organic solvents	Orange electroluminescent material for polymer light-emitting diodes

capacitors, transparent electrodes, chemical and biosensors, etc. The neutral (intrinsic) semiconducting state makes these materials applicable in PLEDs, PSCs, polymer field effect transistors, etc. Table 2.4 summarizes the properties and applications of some representative conjugated polymers.

In comparison with inorganic semiconductors for optoelectronic applications, conjugated polymers possess the advantages of easy structural design, easy synthesis, good film-forming properties, and flexibility. However, there are some drawbacks to the conjugated polymers, such as poorer stability, lower charge carrier mobility, difficulty in forming ordered structure, etc. How to overcome the drawbacks by structural design and to realize large scale applications is the challenge for researchers in the field of conjugated polymers. At present, the hot research topics are the design and synthesis of highly stable conjugated polymers with high luminescent quantum efficiency, broad absorption, narrow bandgap, high charge carrier mobility, and suitable LUMO and HOMO energy levels for the applications in PSCs and PLEDs etc.

Since the discovery of conducting polyacetylene in 1977, the studies of conducting polymers have achieved great progress and have developed into a multi-discipline science. Conducting polymers including intrinsic semiconducting conjugated polymers are still a hot research fields in polymer science, materials science, and optoelectronic materials and devices. I am sure the studies on conducting polymers will make further great progress in the near future. Optoelectronic materials and devices will reach every corner of our lives.

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