Preparation, properties and applications of polypyrroles

Lin-Xia Wang\textsuperscript{a}, Xin-Gui Li\textsuperscript{a,}\textsuperscript{*}, Yu-Liang Yang\textsuperscript{b}

\textsuperscript{a}Department of Polymer Materials Science Engineering, College of Materials Science and Engineering, Tongji University, 1239 Sipin Road, Shanghai 200092, People’s Republic of China

\textsuperscript{b}Department of Macromolecular Science, Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, People’s Republic of China

Received 21 August 2000; received in revised form 30 November 2000; accepted 10 December 2000

Abstract

Polypyrrole (PPY) is one of the most promising materials for multifunctionalized applications. Preparation, characterization, properties and applications of PPYs are reviewed in this paper. In addition, the PPY composites are described in detail according to the synthetic methods and their applications. At the same time, effects of various parameters such as doping anions, additives, and oxidant, on the PPY properties are also concerned. The PPY films and membranes used for ion exchange, pervaporation, and gas separation are mentioned. In this review, ion exchange membranes are highlighted. Moreover, the further investigation of PPY composite membranes for oxygen enrichment is predicted. A total of 117 references are cited.

Keywords: Polypyrrole; Oxidatively chemical polymerization; Electrochemical polymerization; Conductive polymer; Gas separation membrane; Oxygen enriching membrane

1. Introduction

In recent years, intrinsic conducting polymers with conjugated double bonds have been attracted much attention as advanced materials. Among those conducting polymers, polypyrrole (PPY) is especially promising for commercial applications because of its good environmental stability, facile synthesis, and higher conductivity than many other conducting polymers. PPY can often be used as biosensors [1,2], gas sensors [3,4], wires [5], microactuators [6], antielectrostatic coatings [7], solid electrolytic capacitor [8,9], electrochromic windows and displays, and packaging, polymeric batteries, electronic devices and functional membranes, etc. [10–12]. PPY coatings have an excellent thermal stability and are good candidate for use in carbon composites [13]. Furthermore, the electrochemical process parameters affecting the properties of the PPY coatings are also investigated [14]. PPY can be easily prepared by either an oxidatively chemical or electrochemical polymerization of pyrrole. However synthetically conductive PPY is insoluble and infusible, which restricts its processing and applications in other fields. The problem has been extensively investigated and new application fields have also been explored in the past several years. For
example, PPY-based polymers can be used to load and release drugs and biomolecules [15]. PPY-based polymer blends can protect the corrosion of metals [16]. Because of the strong adhesion of PPY to iron or steel treated with nitric acid, PPY polymers can be used as good adhesives [17]. In a recent report [18], PPY-modified tips for functional group recognition are applied in scanning tunneling microscopy. However, there are no systematical publications on PPY as far as we know. The aim of this review not only introduces what have been done, but also prospects the new development of PPYs.

2. Syntheses, properties and applications of polypyrrole

In the past decade, many reports about PPY have been published [14]. As a conducting polymer, the conductivity and other electrical properties were attracted most interests. At the same time, the relationships between the properties and the polymerization conditions (i.e. protein-binding capacity, pH value [19]) were also studied. Additionally, thermal stability and mechanical properties of PPY have been given much concern. In 1994, Biswas and Roy [20] studied the thermal, stable, morphological, and conductive characteristics of the PPY prepared in aqueous medium. The results showed that the PPY exhibits a spongy texture, the initial decomposition temperature at 180–237°C, glass-transition temperature at 160–170°C, and conductivity below 3 S cm⁻¹. Furthermore, all results depended on the FeCl₃/pyrrole feed composition. In a recent report, PPY films with a thickness of 3–4 μm have been obtained by chemical oxidation of pyrrole at the interface of chloroform and water with an oxidant (NH₄)₂S₂O₈ [21]. The films prepared were compact and could be removed with a solid plate. The quality and compositions of these films varied with the molar ratios of the monomer to oxidant of the reaction systems. Structural studies of PPYs through an ab-initio evaluation of bonding [22] and a Monte Carlo growth approach to the branch formation have been reported [23]. The energy differences of different types of structures suggest that a great deal of branching is probable. The approximate probability function generated in this manner is used in a statistical mechanical approach to estimate the extent of bonding involving β carbons as well as branching in PPYs [22]. The statistical analysis of the growth process shows that the branching occurs even at very short chains. The extent of the branching does not depend on the chain length but it is a slowly varying function of the temperature [23]. The surface morphology of PPY film has also been studied through atomic force microscopy (AFM) [24,25]. The surface morphology of electrogenerated PPY films of various thicknesses and with different dopant anions such as chloride, sulfate, perchlorate and dodecylsulfate was discussed, as well as films both as-prepared and after potential dynamic cycling in various supporting electrolytes. The AFM data show that the characterization of surface roughness with one common parameter (RMS, roughness factor or $R_s$) is not justified. In general, two types of surface globules with different heights are present on the film surface, independent of film thickness and dopant nature [24]. Interaction energy anisotropy of the pyrrole dimer has been discussed using ab-initio theoretical method [26]. The influence of selected geometry variations on the interaction energy components was investigated. The results show that any structure variation connected with the external attraction energy is more than compensated for by the repulsion energy.

In the series of conducting polymers, considerable attention has been drawn to the polypyrrole family prepared by electrochemical oxidation such as PPY, poly (N-methyl pyrrole) and their copolymers for their application in solid state devices. Several investigations [27,28] have been performed to observe the effect of various parameters such as solvent, electrolyte
choice of monomer, polymerizing temperature, annealing temperature, etc., on the mechanical strength, stability, and conductivity of the films prepared. Surface morphology studies suggest 3D-type growth and it is found that there is no change in conductivity and good handling strength after a certain annealing time [28]. A one-step synthesis of adherent PPY films on zinc electrodes is achieved by electrooxidation of pyrrole in aqueous oxalate solution [29].

In chemical polymerization, the oxidants used generally are as follows: \((\text{NH}_4)_2\text{S}_2\text{O}_8, \text{H}_2\text{O}_2\) and many kinds of salts containing transition metal ions, for example, \(\text{Fe}^{3+}, \text{Cu}^{2+}, \text{Cr}^{6+}, \text{Ce}^{4+}, \text{Ru}^{3+}\) and \(\text{Mn}^{2+}\). When only \((\text{NH}_4)_2\text{S}_2\text{O}_8\) is used as the oxidant [30], the addition of anionic surfactants caused moderate increases in the yields and great decreases in the conductivities (see Table 1). In addition, it took a very long time to filter the resultant polymers for the formation of fine colloidal particles. These phenomena were caused by interaction between \((\text{NH}_4)_2\text{S}_2\text{O}_8\) and the surfactant PPY doped with sulfonate, since the dissociation of the anionic surfactant is prevented due to the presence of the highly concentrated and strongly electrolytic oxidant, the undissociated molecules of the surfactant appear to be thickly absorbed on the PPY surface in the polymerization process so that it may act as the steric stabilizer. The presence of the steric stabilizer led to the increase in yield, and the decrease in particle size and conductivity of PPY, as Aldissi et al. mentioned [31]. The relationship between time and yield was also discussed as well as the effect of the temperature [30]. The results showed that the addition of the surfactant accelerated the polymerization reaction and PPY also showed a small dependence of room-temperature conductivity on the polymerization temperature.

Table 1

<table>
<thead>
<tr>
<th>Oxidant Additive</th>
<th>Conductivity (S cm(^{-1}))</th>
<th>Yield (g)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{NH}_4)_2\text{S}_2\text{O}_8) (0.1)</td>
<td>NaDBS (0.0225)</td>
<td>4.42</td>
<td>1.36</td>
</tr>
<tr>
<td>((\text{NH}_4)_2\text{S}_2\text{O}_8) (0.1)</td>
<td>NaANS (0.024)</td>
<td>0.57</td>
<td>2.01</td>
</tr>
<tr>
<td>(\text{Fe}_2(\text{SO}_4)_3) (0.1)</td>
<td>NaDBS (0.0225)</td>
<td>0.221</td>
<td>1.91</td>
</tr>
<tr>
<td>(\text{Fe}_2(\text{SO}_4)_3) (0.1)</td>
<td>NaANS (0.024)</td>
<td>26.1</td>
<td>2.44</td>
</tr>
<tr>
<td>(\text{Fe}_2(\text{SO}_4)_3) (0.1)</td>
<td>NaAS (0.022)</td>
<td>15.7</td>
<td>2.65</td>
</tr>
<tr>
<td>(\text{Fe}_2(\text{SO}_4)_3) (0.1)</td>
<td>NaANS (0.04)</td>
<td>40.7</td>
<td>2.24</td>
</tr>
<tr>
<td>(\text{Fe}_2(\text{SO}_4)_3) (0.1)</td>
<td>(p)-Nitrophenol (0.0375)</td>
<td>25.6</td>
<td>2.79</td>
</tr>
<tr>
<td>(\text{Fe}_2(\text{SO}_4)_3) (0.1)</td>
<td>NaANS (0.04)</td>
<td>(m)-Nitrophenol (0.0375)</td>
<td>23.9</td>
</tr>
<tr>
<td>(\text{Fe}_2(\text{SO}_4)_3) (0.1)</td>
<td>NaANS (0.04)</td>
<td>(p)-Cyano phenol (0.0375)</td>
<td>22.2</td>
</tr>
</tbody>
</table>

*Polymerization time 60 min, temperature 25°C, pyrrole monomer concentration 0.375 mol dm\(^{-3}\), solvent 200 dm\(^3\) of deionized water.

*NaDBS, sodium dodecylbenzene sulfonate; NaANS, sodium alkylnaphthalene sulfonate; NaAS, sodium alkylsulfonate.
for as follows: (1) in order for each divalent sulfate to be incorporated into PPY as the dopant, two close cation sites have to be prepared in the intrachains or interchains of the PPY backbone. (2) the incorporation of divalent and the small-sized sulfate probably produce a distorted PPY backbone. The latter can also explain why PPY doped with sulfate shows low conductivity. Kudoh et al. [32] studied the properties of chemically prepared PPY with an aqueous solution containing Fe$_3$(SO$_4$)$_3$ and a phenol derivative. PPY obtained under the coexistence of a sulfonic surfactant and a phenol derivative with an electron-withdraw group has high conductivity (see Table 1) and superior environmental stability. These favorable properties seemed to be caused by the surfactant anion being selectivity incorporated into the PPY backbone as the dopant and the electron-withdrawing substituent of the phenol derivative interacting with pyrrole monomer so as to improve the regularity of the PPY backbone. The oxidative matrix polymerization of pyrrole by Fe(III), Cu(II) etc. in the presence of polyacrylic acid (PAA) was also studied [33].

Poor processibility of PPY due to its insolvency and infusibility has retarded further investigation on the structure and structure-physical properties. To improve the processibility, many researchers have been engaged in the development of soluble or swollen PPY and dispersible fine-powdered PPY. At the same time, the electric properties and/or stability of chemically prepared PPY have also been investigated at many laboratories because the stability of conducting polymers seems to be the main limiting factor in their practical applications. A review has been reported the long and fruitful history on processibility of conducting polymers [34]. Several methods for PPY were introduced in that review. For example, several kinds of soluble PPY have been synthesized, such as poly (3-alkylpyrrole) with an alkyl group equal to or greater than a butyl group [35]. Poly (3-alkylpyrrole) is easily soluble in common solvents or soluble in water when the substituents bear hydrophilic groups, such as $-\text{SO}_2\text{H}$, giving conducting ranging from $10^{-2}$ to $10^1$ S cm$^{-1}$ depending on the bulkiness of the alkyl group. However, the main problem of this method is the complicated synthesis of 3-substituted pyrrole monomer. And poly (N-substituted pyrroles) have much lower conductivity due to greatly suppressed conjugation along the polymer chains by the substituents on nitrogen [36,37]. At the same time, they are only partly soluble in some organic solvents even with long alkyl groups on the nitrogen of pyrrole rings. Although recently, a facile synthesis of 1,2,3-trisubstituted pyrrole from the reaction of chlorocarbons with 1-azabuta-1,3-dienes is reported [38]. The structure is shown as follows:

Where Ar = phenyl, 4-toluyl, 4-Cl-phenyl, R$^1$ = methyl and benzyl, R$^2$ = phenyl and methyl.

Development of classical and modern methods of synthesis of arypyrroles is summarized by Korostova et al. [39]. An emphasis is made on a new simple and effective procedure for preparation of arylpyrroles by the Trofimov reaction from alkyl aryl ketone oximes and acetylene.

Compared to the substitution method to prepare soluble poly (3-substituted pyrrole) and poly (N-substituted pyrrole), doping is simple for PPY which may give comparable conductivity to poly (3-substituted pyrrole), but much higher than poly (N-substituted pyrrole). For instance, PPY doped by p-dodecylbenzene sulfonic acid (DBSA) with a high conductivity of 2 S cm$^{-1}$ dissolves in m-cresol or chloroform in the presence of an extra amount of DBSA [40]. The later research [41,42] by Lee et al. has been found that there is a critical concentration range of the oxidant at a given polymerization temperature to obtain soluble PPY. When O/M<
0.2 (oxidant/monomer) and D/M < 1.0 (dopant/monomer), PPY obtained was partially soluble in m-cresol or NMP. Its solubility decreases as the increase of O/M. When O/M was greater than 0.2, the polymer obtained was totally insoluble in any solvent [42]. Shen and Wang studied the solubility in m-cresol, room-temperature conductivity, morphology and thermal stability of PPY synthesized by in situ doping polymerization in the present of sulfonic acid [43]. It was noted that good solvating ability of sulfonic acid, such as DBSA and BNSA (5-butylnaphthalene), renders PPY soluble, while sulfonic acids only having large molecular size, such as CSA (camphor sulfonic acid) and MBSA (p-methylbenzenesulfonic acid or p-toluene sulfonic acid), fail to make PPY soluble. The nature of sulfonic acid also has an influence on morphology of the resulting PPY. The images of PPY doped with CSA, DBSA and MBSA have typical granular morphology but PPY doped with NSA (β-naphthalene) is fibrillar. And it was also observed that PPY doped with NSA and BNSA are thermostable based on the measurement of weight loss. But it has been found that doping PPY with mixed acid containing CSA and DBSA could get soluble conductive PPY with room temperature conductivity (2–18 S cm⁻¹) [44] (Table 2). Pressure effects on the electrical conductivity of doped PPY have been studied [45]. The pressure dependence has characteristics of a phase transition and is interpreted as a conformational wít-rod transition. The pressure effect should be considered in experiments with PPY gas sensors. The pressure and temperature dependences of the electric condition of thin films composed of doped PPY microtubules are also measured [46]. In addition, it was found that the conductivity of PPY electrochemically polymerized in acrylamide solution is lower than that of PPY prepared in the absence of acrylamide [47]. The difference is attributed to the insulating effect of acrylamide. Besides above, synthesis of nanostructures composed of PPY can enhance in electronic conductivity compared to analogue polymer bulk conductivity [48].

The long-term stability of the electrical conductivity of PPYs is a crucial property from an application point of view. It has been shown that the conductivity and the aging behavior of PPYs can be altered by treatment with acid or base [49]. Properties of PPYs obtained by electrochemical polymerization were studied [50]. With NaOH, conductivities smaller than that of the initial sample can be obtained whereas an H₂SO₄ treatment leaves the conductivity nearly unchanged. Both procedures result in an increase in the long-term stability of the conductivity at least at 80°C and 140°C. Using elemental analysis and energy dispersive X-ray spectroscopy it was shown that the chemical treatment has an effect on ion exchange properties of the polypyrrole salt film

<table>
<thead>
<tr>
<th>Sulfonic acid</th>
<th>Conductivity (S cm⁻¹)</th>
<th>Solubility in m-cresol</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Methylbenzene sulfonic acid (MBSA)</td>
<td>16.0</td>
<td>IS⁺</td>
</tr>
<tr>
<td>p-Hydroxybenzene sulfonic acid (HBSA)</td>
<td>11.0</td>
<td>SS⁺</td>
</tr>
<tr>
<td>p-Dodecylbenzene sulfonic acid (DBSA)</td>
<td>2.0</td>
<td>S⁺</td>
</tr>
<tr>
<td>β-Naphthalene sulfonic acid (NSA)</td>
<td>18.0</td>
<td>S</td>
</tr>
<tr>
<td>5-n-Butylnaphthalene sulfonic acid (BNSA)</td>
<td>0.5</td>
<td>S</td>
</tr>
<tr>
<td>5-Sulfo-isophthalic sulfonic acid (SIA)</td>
<td>3.0</td>
<td>SS</td>
</tr>
<tr>
<td>8-Hydroxy-7-iodo-5-quinoline sulfonic acid (QSA)</td>
<td>3.0</td>
<td>SS</td>
</tr>
<tr>
<td>Alizarin red acid (ARA)</td>
<td>8.0</td>
<td>SS</td>
</tr>
<tr>
<td>Camphor sulfonic acid (GSA)</td>
<td>18.0</td>
<td>IS</td>
</tr>
</tbody>
</table>

⁺IS, insoluble; SS, slightly soluble; S, soluble.
such as conductivity, weight, thickness, and oxygen permeability closely related to the count-

erions. It was found that exposure of the film to 0.1% NaOH, which reduced the conductivity

only slightly, improved the stability quite significantly. The electrical properties of PPY can

be also drastically modified by a strong base or acid, as well as upon treatment with various

anions. Zhang et al. [51] studied the surface of pristine and surface-modified PPY films (modi-

fied with acrylic acid or sodium salt of 4-styrenesulfonic acid). The results showed that the
density of surface grafting decreased with ozone pretreatment. Surface grafting of the two poly-
meric acids also gives rise to a self-protonated surface structure. A substantial proportion

of the grafted protonic acid groups at the surface remains free for further surface func-
tionalization. Kudoh et al. have reported that electropolymerized PPY doped with a large-
sized anion [52], for example, alkynaphthalene sulfonate, has excellent thermal and moisture

stabilities. Recently, Ghosh et al. [53] have studied the electrochemical oxidative degra-
dation of PPY, known as overoxidation, in aqueous media by using Raman and FT-IR spec-
troscopies. It was noted that PPY degrades at potentials as low as 10.5 V versus the satu-
rated calomel electrode, in the presence of chloride ions. The rate of overoxidation of PPY is
higher potential and at higher pH. Furthermore, PPY prepared with surfactants in chemical polymeri-
ization also showed high thermal and moisture stabilities in air at 125°C, and at 85°C and 85%
RH (relative humidity) [30]. The study of Shen and Wan indicated that PPY doped by CSA or
DBSA showed similar thermal stability [44]. Both samples begin to lose weight at about
217°C, but PPY–CSA decomposes more rapidly. PPY doped with NSA or BNSA is more
thermostable. Weight loss of these PPY samples begins at 317°C [44]. Thin films of a sub-
stituted PPY synthesized via the chemical oxidation of a chloroform solution of 5-acetamido-4,5,6,7-
tetrahydro-2H-benzol pyrrole have established

their long-term stability as floating monolayer [54].

In practical applications, the mechanical properties of PPY are also important. As a result, a lot of interest has put on the studies on the mechanical properties of PPY. In general, PPY showed a much larger Young’s modulus but lower tensile strength in the doped state compared with the undoped material.

Fukuyama et al. [55] have studied the effect of monosubstituted phenol additives on some mechanical properties of PPY. Both properties, tensile strength and elongation, were higher than those in undoped PPY films. Zinger et al. [56] reported that PPY prepared electrochemically in aqueous solutions containing perchlorate salt as an electrolyte exhibits a high conductivity and superior mechanical properties. For example, when concentration of phthalate was 0.05 M, the elongation of the film was 3.6%, maximal strength was 50.4 MPa, modulus of elasticity was 0.075 GPa, and the conductivity was as high as 33.4 S cm⁻¹ (before stretching) and 45.0 S cm⁻¹ (after stretching) (Fig. 1). Murray et al. have studied the in situ mechanical properties of PPY doped with pTS (tosylate) in a range of electrolytes and at different applied potentials [57]. A brittle-ductile transition was observed when the polymer was reduced at low

![Fig. 1. Variation of tensile properties of PPY films with phthalate concentration.](image)
potentials. The brittleness in the oxidized state was found to be due to the ionic crosslinking between charged polymer chains and the counterion species present in the polymer structure (Fig. 2). Compared to the two systems, it can be found that the mechanical properties of PPY/phthalate films, such as tensile strength, are better than the properties for PPY/pTS films prepared in organic solutions (Figs. 1 and 2). Polypyrrole films and fibers are proved to have highly sensitive electromechanical effects so that they are useful as artificial valves, chemical valves, actuators and chemomechanical materials [58].

The research by Kaynak et al. [59] proved that the electrical conductivity of the doped films has a significant effect on transmission, reflection, and absorption of microwaves. Heavily doped, conducting films were highly reflective, whereas lightly doped, semiconducting films had very high transmission. Intermediate conductivity PPY samples were highly absorptive. Shielding effectiveness of PPY films was also discussed.

Electron spin resonance (ESR) was carried out at atmosphere as well as low pressures to find any relation between paramagnetic species and the charge carriers in pyrrole-based electric conducting polymers [60]. ESR spectrum suggests that there is no link between the paramagnetic centers and bipolarons which serve as the major charge carriers in these materials. ESR measurements at low temperatures for pyrrole-based polymers show that most of the polymers obey Curie–Weiss law in terms of increase in spin populations.

3. Preparation, properties and applications of PPY-based composites

The formation of polymer blends, alloys or composites can prepare new polymeric materials with interesting combinations of physical properties. When a comparison is made among the three conducting polymers (polyaniline(PAN), polythiophene(PTP) and PPY), PPY can form blends easily with the insulating polymers, whereas PAN-based absorbents had the ability to be deposited onto reinforcing textiles and polyalkylthiophene had excellent solubility and melting properties that were more difficult with other conducting polymers. As for PPY, it has high conductivity and good environmental stability, but poor mechanical properties. This has been overcome to some extent by use of composite structures, for example, combination of the PPY film with the good mechanical properties of insulating polymers such as poly-N-vinyl-carbazole [61,62], poly(styrene) (PS) [63], poly(N-vinylimidazole) (PVI) [64], polyvinylphosphate (PVP) [65], polyvinyl alcohol (PVA) [66–68], poly(vinyl-methyl ketone) (PVMK) [69] and so on. The conducting composite films are prepared either by electrochemical polymerization of pyrrole on an electrode substrate whose surface is coated with an ordinary insulating polymer film [70], or by exposing a polymer film containing an oxidizing agent such as ferric or cupric chloride to pyrrole vapor [71,72]. In every case conducting composite films are obtained whose mechanical properties are considerably improved compared to the brittle PPY. The effect of low temperature...
conditions on the electrochemical polymerization of PPY-hexafluorophosphate (PPY-PF₆) films has been researched [73]. An electrochemism of the composite film of ethylene-vinyl alcohol copolymer and PPY has been reported [74], too.

Tieke and Gabriel studied pyrrole–polyimide (PPY–PI) composite films [75]. It reported that the composite films had high electrical conductivity with thermal stability. The composite films were prepared either by electrochemical polymerization of pyrrole on a PI coated electrode (type I) or by exposing PI films containing ferric chloride as an oxidizing agent to pyrrole vapor (type II). Type I films consist of a sequence of three layers with the PI sandwiched between two layers of PPY. The maximum conductivity is about 10 S cm⁻¹. Type II films consist of PI containing finely dispersed PPY particles of 10 to 500 nm in diameter. The composite films are thermally stable up to 350°C. The choice of the matrix PI is crucial for the preparation of the composite films. Conventional PIs are insoluble after amidization and therefore do not swell enough in organic solvents in order to allow the pyrrole monomer to penetrate the film and to become polymerized with the film or at its electrode side. Conductive pyrrole–polystyrene sulfonate (PPY–PSS) was chemically prepared using FeCl₃ as an oxidant [76]. The chemical formula proposed for conductive PPY–PSS is \([\{(C₆H₅N)₃C₆H₄SO₃ \cdot y(H₂O)\}_x\), where \(x\) denotes the degree of oxidation, and \(y\) takes into account some hydration of ionic species. The method is based on the different precipitation rates of the two PPY-based polymers: PPY–PSS and PPY–Cl. In general, chemical synthesis of PPY yields a conducting polymer that incorporates the anion of the oxidant salt as counterion. But by choosing a short reaction time (a few minutes), pure PPY–PSS, free of conductive PPY–Cl, can be obtained after filtration. The presence of meta-hydroxy benzoic acid in the reaction medium allows shorter reaction times to be used, and higher yield values of conductive material to be obtained. Rueda et al. [77] also reported on the chemical polymerization of PPY on the sulfonated surface of polyethylene films (PPY–PES) using FeCl₃. Another conducting composite of PPY and poly(tetramethylbisphenol A carbonate) (TMPC) had been prepared electrochemically [78]. The method is that monomers of conducting element diffuse into the insulating polymer coated on an electrode and start polymerization in the interface between the electrode surface and the host polymer film. This kind of conducting polymer synthesis not only improves the poor mechanical and physical properties of heterocyclic polymers but also retains the conductivity to a desirable value. Intrinsically conducting hot melt adhesives (ICHMAs) have been developed, based on PPY blends, for use in electronic and telecommunication applications requiring shielding against electromagnetic interference (EMI) [79]. These advanced materials have been formulated to exhibit significant EMI shielding effectiveness (SE) while retaining the superior properties of conventional hot melt adhesives. The fabrication of a PPY-Heparin composite film modified electrode in pyrrole with coexistence of heparin was investigated [80]. The PPY-Heparin modified electrode was easy to make and very stable, which can be used for the detection of calcium in children’s hair and the results of detection was satisfactory.

A recent work indicated that PPY could be also blend or composite with other conducting polymers. Sacak et al. prepared PPY/PAN (polyaniline) (or inverse order) films on platinum foil electrodes by sequential electrode sides of the films [62]. It was found that depending upon conditions, either the second polymer was incorporated into the initially coated layer or a double-layer film was formed with a well-defined interface. Electrolysis of pyrrole and aniline monomer mixtures having molar ratios of pyrrole over aniline greater than 0.12 gave films rich in pyrrole. Because of the layered structure with each layer having distinctly different electronic, optical and other physico-
chemical properties, these block copolymers could be used to fabricate electronic devices, selective membranes and biosensors. Kojima et al. studied PPY–PTP double layers prepared by electrochemical polymerization of pyrrole in presence of thiophene [81]. At a constant current, only pyrrole is electrochemically polymerized in the electrolytic solution containing pyrrole and thiophene in the present experiments. The resulting double layers showed good rectification characters dependent on thickness. Zarbin et al. have successfully obtained two glass I conducting polymer by in situ oxidative polymerization of pyrrole and aniline inside the pores of Porous Vycor Glass (PVG) [82].

Biswa and Roy studied variable properties of PPY after chemical modification [83,84]. PPY can be prepared in ether and in aqueous medium as modified by polycondensation with phthalic anhydride (PA) and pyromellitic dianhydride (PMDA) in presence of Friedel-Crafts catalysts such as anhydrous zinc chloride and anhydrous ferric chloride at high temperature. Previous work by Biswas and Roy [20,61] indicated that PPY prepared in aqueous medium possesses appreciably higher conductivity than the same obtained in ethereal medium. Furthermore, PPY produced by aqueous polymerization of pyrrole in FeCl₃ exhibits fairly well-defined crystalline peaks in contrast to PPY produced in ether (FeCl₃, catalytic mount) which is totally amorphous. Structural characterization was studied by IR, X-ray diffraction and SEM. The SEM for PPY–PA reveals, in general, the formation of larger particles of spherical shapes and lesser agglomeration tendency. The base polymer (PPY) appeared to be rendered crosslinked through intrachain as well as interchain incorporation of the anhydride moieties [83]. Polymers modified PA and PMDA showed interesting improvements in thermal stability and dielectric behavior, but the conductivity is somewhat deteriorated relative to the unmodified PPY [84]. The overall thermal stability is in the order PPY < PPY–PA < PPY–PMDA, which may be rationalized in terms of intra- and intermolecular cross-linked structures of the polycondensates. Both PPY–PA and PPY–PMDA exhibit high dielectric constants (200 and 125) at low frequency (10³ Hz), which fall monotonically with increasing frequency, suggesting the possibility of interfacial polarization. These modified polymers exhibit frequency-dependent dielectric behavior, which is a feather that is totally absent in the unmodified PPY. The conductivity values of PPY–PA and PPY–PMDA are in the range 10⁻⁴–10⁻³ S cm⁻¹, which are obviously lower than that for unmodified PPY (2.5). This is due to the adverse effect of increasing temperature on the PPY chain stability, whereby structural conjugation and eventually conductivity will be affected.

Classical conducting polymers are usually insoluble and infusible materials. Beside the methods mentioned above, another attempt to improve their processability is the synthesis of block and graft copolymers containing conventional and conducting sequences, where conventional sequences increase the solubility of the resultant block and graft copolymer. Nazzal et al. [85] were successful in electrochemical grafting of pyrrole onto a polystyrene backbone while Hallensleben et al. [86] described the preparation of poly[(methyl methacrylate)-co-(2-N-pyrrole/ethyl methacrylate)] which contains pyrrole moieties in the side chains. Further study described the chemical synthesis of graft copolymers from poly(methyl methacrylate) containing pyrrole moieties in the side chains via several routes [86–88]. Recently, the synthesis of conducting H-type polysiloxane-poly-pyrrole block copolymers was reported [89]. A conducting interpenetrating polymer network (IPN) was prepared by sequential crosslinking of tetra-ethyl orthosilicate (TEOS) with acrylic acid grafted styrene-isoprene-styrene triblock copolymer (SIS) and PPY doped with DBSA [90]. The resulting IPN has good condition and exhibits far superior thermal stability. Poly(aniline-co-pyrrole) has also been successfully synthesized by Wei et al. [91]. The polymerization process is neither the classical step nor the
classical chain polymerizations but something in-between, which can be called tentatively ‘the non-classical chain polymerization’ or ‘the re-activated chain polymerization’, because before every growth step the chain ends would have to be oxidized (i.e. ‘reactivated’) to give the electrophilic species that will attack incoming monomers. A typical process is illustrated in Scheme 1 for the preparation of a bilayered block poly(aniline-co-pyrrole). The copolymers having the properties of both homopolymer blocks were obtained.

4. Formation and liquid separation of PPY membranes

PPY can not only be used as conductive films, but also be used as functional membranes. Conducting electroactive polymer membranes such as PPY membranes have attracted much interest over the past decade because of their dynamic chemical/electrochemical properties. Electrochemically controlled transport of ionic species across conducting electroactive polymer membranes has been reported [92–94]. The transport of ionic species across the membrane can be switched on and off by mean of application of an appropriate electrical potential. In addition, the rate of transport and the selectivity of the membrane can be dynamically controlled in situ by application of different electrical potential waveforms. Furthermore, membranes synthesized using different counterions show a remarkable influence not just on the electrical conductivity, mechanical property and electroactivity of the membrane, but also on the transport and dynamic control transport properties. Zhao et al. [95] produced asymmetric membranes based on conducting polymers. A free-standing conducting polypyrrole membrane can be electrochemically synthesized according to the following reaction:

where, $C^-$ is the counterion. Two layers of different PPY films (PPY-$p$-toluene sulphonate and PPY-dodecyl sulfate) were electrodeposited onto an electrode to form a sandwich or layer structure. The results showed that the films had sufficiently good mechanical properties to be used as free-standing membranes in simple experiments. In mixtures of simple salts such as KCl and NaCl, it was possible to derive some reasonable selectivity between cations with selectivity of $K^+:Na^+$ in ratios up to 4.5:1. Comparative studies have been reported on diffusion behavior of electrochemically prepared polythiophene and PPY, especially the effect of ionic size of dopant [96].

Various methods have been used to induce transport of ionic species across CP membranes.
Partridge [97] reported that continuous monodirectional transport of cations through PPY membranes could be achieved by applying a potential gradient across the membrane. This gradient was implemented by using 3-electrode systems in both the feed and permeate compartments, with the PPY membranes as the common working electrode separating the two. Ehrenbeck and Juttner [98] reported a method, which combines potential gradient induced transport, using a 4-electrode system, with a more conventional 3-electrode system to control the oxidation state of the membrane. The combined effect was to switch the membrane between a cation and anion exchange material depending on the oxidation potential applied to the membrane. In essence, the membrane acted as an ion ‘gate’, which could be either opened, closed or reversed depending on the magnitude and sign of the applied potential. More recently, Partridge et al. [99] also described the effect on cation fluxes across a CP membrane of varying the physical parameters used during the transport experiment. The parameters included the concentration of the feed solution, the membrane orientation, the magnitude of the potential gradient and the dopant type employed during fabrication of the membrane. The results indicated that the PPY membranes doped with a combination of polystyrenesulphonate (PSS) and 1% dodecylbenzene sulfonate (DBS) (PSS/DBS 1%) displayed the best physical characteristics, in terms of conductivity, strength and cation fluxes. Partridge et al. [100] studied the effects of the various parameters employed in the synthesis of the membranes, on the physical characteristic and cation transport properties of the resulting membranes, including temperature, current density, dopant concentration, applied potential gradient and growth time on flux. The results indicated that the optimal membrane growth was achieved when using a growth temperature at or below 20°C, a current density between 1 and 3 mA/cm², and a dopant concentration of 0.1 M.

Electronically conducting polymers (ECPs) for membrane-based separations, including gas separation and pervaporation were also reported [101]. Martin et al. used interfacial polymerization to synthesize thin films of the desired electronically conductive polymer (e.g. PPY). The interfacial polymerization yields thin film composite membranes in which the microporous support provides the requisite mechanical strength and the conductive polymer provides the chemical selectivity. ECPs provide a wealth of opportunities for fundamental investigation of the effects of molecular and supermolecular structure on gas and vapor-transport in polymers. Polymers with a large variety of chemical structures and substituents can be easily synthesized and the counterion in the doped form can be charged at will. Pervaporation data were listed in Table 3 for the uncoated hollow fiber and for hollow fibers coated with PMPY and PPY films. Because the interfacially polymerized PPY films are porous, it is not surprising that the selectivity data for the PPY-coated fiber is only slightly different from that for the fiber itself PMPY shows good selectivity for methanol vs. MIBE (methyl-t-butyl ether) transport, because PMPY is polycations and PMPY (interfacially polymerized) film is defect-free.

In recent years, composite membranes based PPY were also studied [102,103]. Morita [102] has reported the effects of applied potentials on permselectivity of ions through PPY/porous-polypropylene composite membrane. The results showed that the composite membrane worked effectively as a functional separation membrane to control the ionic permeability by potential application. Using porogen-leaching techniques, a series of porous membranes consisting of

<table>
<thead>
<tr>
<th>Polymer membrane</th>
<th>Selectivity coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated hollow fiber</td>
<td>1.06</td>
</tr>
<tr>
<td>PPY</td>
<td>1.40</td>
</tr>
<tr>
<td>PMPY</td>
<td>3.90</td>
</tr>
</tbody>
</table>
polymethyl methacrylate (PMMA) and PPY were prepared [103]. The potential advantage of the composite polymer membrane approach (as opposed to a coated membrane) is that the PPY can be dispersed throughout the entire pore structure and yet the mechanical properties of the host polymer can be used to advantage. This can allow the membrane potential to be exerted over the filtration medium through the entire length of the pore (or the thickness of the membrane) instead of being restricted to the surface. The use of polypropylene glycol and sodium chloride as porogens in developing porous PMMA–PPY composite membranes was investigated. Porosity was introduced via the use of a polymeric liquid porogen (PPG) or sodium chloride powder. PPY–PMMA composite films have been prepared previously by chemical polymerization followed by heating [104] or by dipping PMMA film containing pyrrole monomer into FeCl₃ [105]. However, none of these methods obtained controlled porosity films. The membranes could be made to be permeable to small amino acid (tryptophan) or large proteins (BSA, bovine serum albumin). The membranes demonstrated conductivities up to 19.8 S cm⁻¹ and with further development may have applications in bioseparations and other areas that require controlled porosity conducting polymer composites.

5. Prospect of PPY membranes for gas separation

In recent years, the use of conjugated polymer membrane for gas separations has been reported a lot. Why the ECPs can be used in gas-transport lies in: (1) it was found that polymers, which contain high concentrations of fixed ionic sites can show exceptional gas-transport selectivity; the doped forms of ECPs are exactly such polymers [106]. (2) It is easy to synthesize thin films of ECPs; this is important because flux of permeate is inversely proportional to film thickness in nearly all membrane-based chemical separation. (3) ECPs can be reversible ‘switched’ between polyionic and neutral forms [107]. This raises the interesting prospect of reversibly switching the gas-permeability of a film between two well-defined values. In 1986, Münstedt et al. have studied the permeability for oxygen through PPY films differently treated with acid and base. The main properties of the film are shown in Table 4 [50]. The rate and selectivity of gas transport in the conductive, heterocyclic polymer, poly(N-methyl pyrrole) (PMPY) have been studied [108]. It showed that PMPY has interesting and potentially useful gas-transport properties. These two investigations of very different members of the ECP family suggest that ECPs warrant further investigations for potential applications in gas membrane-based separation. It was also found that the thin films were essentially defect-free and the permeability coefficient (P) values for all gases in the polycationic form of PMPY are lower than the permeability for the neutral form of this polymer. It is well known that introduction of ionic groups into a polymer lowers the available void volume [109]. This decrease in void volume is undoubtedly responsible for the diminution in the permeability values for PMPY–NO₃. The results showed that PMPY–NO₃ has extraordinary gas-transport characteristics. The oxygen over nitrogen selectivity coefficient (α₂/₃) of PMPY–NO₃ approached 7.9, and PS₂ was

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Oxygen permeability (10⁻¹⁰ mol/m s Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A⁺</td>
</tr>
<tr>
<td>23</td>
<td>1.34</td>
</tr>
<tr>
<td>40</td>
<td>4.02</td>
</tr>
<tr>
<td>60</td>
<td>20.2</td>
</tr>
<tr>
<td>80</td>
<td>88.07</td>
</tr>
</tbody>
</table>

* A, an initial sample; B, treated with 10% H₂SO₄ for 240 min; C, treated with 10% NaOH for 240 min.
Table 5

<table>
<thead>
<tr>
<th>Membranes</th>
<th>$P_{O_2}$</th>
<th>$P_{N_2}$</th>
<th>$\alpha_{O_2/N_2}$</th>
<th>$P_{CO_2}$</th>
<th>$P_{CH_4}$</th>
<th>$\alpha_{CO_2/CH_4}$</th>
<th>$P_{N_2}$</th>
<th>$\alpha_{N_2/N_2}$</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMPY–NO₃</td>
<td>1.26</td>
<td>0.16</td>
<td>7.9</td>
<td>2.82</td>
<td>0.17</td>
<td>16.2</td>
<td>–</td>
<td>–</td>
<td>[101]</td>
</tr>
<tr>
<td>PMPY</td>
<td>2.04</td>
<td>0.33</td>
<td>6.2</td>
<td>6.90</td>
<td>0.22</td>
<td>31.9</td>
<td>–</td>
<td>–</td>
<td>[101]</td>
</tr>
<tr>
<td>PAN–NO₃</td>
<td>0.129</td>
<td>0.0087</td>
<td>14.8</td>
<td>0.401</td>
<td>0.0073</td>
<td>54.9</td>
<td>–</td>
<td>–</td>
<td>[114]</td>
</tr>
<tr>
<td>PAN–Cl</td>
<td>0.142</td>
<td>0.0096</td>
<td>14.7</td>
<td>0.462</td>
<td>0.0089</td>
<td>51.9</td>
<td>–</td>
<td>–</td>
<td>[114]</td>
</tr>
<tr>
<td>PAN</td>
<td>0.141</td>
<td>0.015</td>
<td>9.4</td>
<td>0.421</td>
<td>0.032</td>
<td>18.3</td>
<td>3.308</td>
<td>205.3</td>
<td>[113]</td>
</tr>
<tr>
<td>PAN d/ud</td>
<td>0.546</td>
<td>0.063</td>
<td>8.7</td>
<td>2.60</td>
<td>0.017</td>
<td>152.9</td>
<td>17.6</td>
<td>279.4</td>
<td>[113]</td>
</tr>
<tr>
<td>PAN as-cast</td>
<td>0.280</td>
<td>0.0382</td>
<td>7.3</td>
<td>1.44</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>[112]</td>
</tr>
<tr>
<td>PAN d/ud</td>
<td>0.172</td>
<td>0.00323</td>
<td>53</td>
<td>1.59</td>
<td>0.608</td>
<td>2.6</td>
<td>10.6</td>
<td>3281</td>
<td>[112]</td>
</tr>
<tr>
<td>PAN rd</td>
<td>0.110</td>
<td>0.00253</td>
<td>43.5</td>
<td>0.732</td>
<td>&lt;0.005</td>
<td>146</td>
<td>–</td>
<td>–</td>
<td>[112]</td>
</tr>
</tbody>
</table>

* d = doped.
* ud = undoped.
* rd = redoped.

1.26 × 10⁻¹⁰ cm³ (STP) cm/cm² s cmHg (or 5.63 × 10⁻¹⁶ mol/m s Pa). PMPY–NO₃ provides both high selectivity and high flux. But generally, enhanced selectivity in a polymer film can only be achieved at the expense of flux.

Musselman et al. studied the separation properties of poly(3-dodecythiophene) (PDDT) membrane and found the results unsatisfactory ($\alpha_{O_2/N_2}=2.2–3.0$ [110]). But it was reported that PAN films show significantly larger selectivity coefficients than that for PMPY–NO₃ and also found that the rate and selectivity of gas transport depend on doping level [111]. The selectivity of the polyaniline emeraldine base was reported by Kaner et al. [112,113], Kawabata and Martin [114] and Pellegrino et al. [115] to be quite high ($\alpha_{O_2/N_2}=7.3$ [112], $\alpha_{O_2/N_2}=9.4$ [113,114], $\alpha_{O_2/N_2}=7.2$ [115]). Furthermore, the selectivity was observed to increase with chemically induced doping ($\alpha_{O_2/N_2}=15$ [111]). As for PPY membrane, the same result was obtained. Martin et al. demonstrated that as cast ($\alpha_{O_2/N_2}=6.2$) and doped with NO₃ ($\alpha_{O_2/N_2}=7.9$) for poly(N-methylpyrrole) as mentioned before [101]. Table 5 showed permeability and selectivity coefficient of different gases. It can be found that PAN films show higher selectivity coefficient, but lower permeability. However, PPY films display relatively high permeability. It suggests that a copolymer of pyrrole and aniline should be a suitable material for gas separation, especially for oxygen enrichment.

6. Conclusions

Polypyrrrole and its derived polymers have been discussed in detail. Polypyrrroles can be synthesized by many different and facile methods including electrochemical and oxidatively chemical polymerization. Different methods to improve the processability of PPYs were discussed. From the discussion, it is obvious that PPY has excellent properties, including electrical, thermal, and mechanical properties. Owing to these properties, PPYs have been widely studied and exhibit a wide potential application, especially, in the studies of the PPY-based membrane for the potential application in gas separation [101]. Compared with three conducting polymers (PPY, PAN, PTP), in order to get functionalized membranes with excellent permeability, selectivity, stability, as well as enhanced conductivity, the copolymers of pyrroles and aniline derivatives have been investigated in our laboratory [116,117].

Acknowledgements

This research was supported by (1) the National Natural Science Foundation of China...
(Grant No. 29804008); (2) the Foundation of University Key Teacher by the Chinese Ministry of Education; (3) the Phosphor Plan of Science Technology for Young Scientists of Shanghai, China (Grant No. 98QE 14027); and (4) the Key Laboratory of Molecular Engineering of Polymers of the Chinese Ministry of Education.

References
