Conducting polymer coatings in electrochemical technology

Part 1 – Synthesis and fundamental aspects

S. A. Campbell¹, Y. Li¹, S. Breakspear², F. C. Walsh³ and J. R. Smith^{*1}

Conducting polymers are materials which combine the electronic characteristics of metals with the engineering properties of polymers. Poly(pyrrole) (PPy), poly(thiophene) (PTh) and poly(aniline) (PAn) are common examples of conducting polymers and can be produced either chemically or electrochemically from their respective heterocycles. This review describes the properties and synthesis of such materials.

Keywords: Inherently conducting polymers, Electroactive polymers, Synthesis, Properties, Coatings, Review

Introduction

Letherby reported the first occurrence of conducting (or 'electroactive') polymers in 1862,¹ although their synthesis and initial characterisation were only reported in the 1960s.^{2–4} A few years later, it was discovered that certain polymers, namely, poly(sulphur nitride) and poly(acetylene), could be converted from insulating or semiconducting films into highly conducting materials in the presence of certain additives, a process referred to as 'doping'.^{5–12}

Poly(acetylene) (PA) is the most widely studied conducting polymer¹³ due to its simple structure and high conductivity (10^4 – 10^6 S cm⁻¹), approaching that of metals.¹⁴ More recently, poly(pyrrole) (PPy), and other polyaromatic compounds, have been electrodeposited from organic or aqueous electrolytes to produce conducting films, albeit of conductivity (~ 100 S cm⁻¹) less than PA (Fig. 1).¹⁵ Such materials are finding applications in the fields of battery materials,¹⁶ electrochromic displays,¹⁷ electromagnetic shielding,¹⁸ sensor technology,¹⁹ non-linear optics,²⁰ molecular electronics^{21,22} and as coatings for corrosion protection.^{23–30} This review considers the background and properties of these interesting materials. In Part 2, the numerous applications of conducting polymers will be discussed.

Poly(acetylene)

The current interest in conductive polymers began in the 1970s when it was found that the electrical conductivity of PA, a semiconductor when pristine, could be increased by over 15 orders of magnitude by treatment

with oxidising agents such as iodine. The most research on PA has been performed on the 'Shirakawa' type, which is synthesised via the Ziegler–Natta polymerisation of acetylene (equation (1))^{31–33}

Poly(acetylene) (PA) is formed as two isomers, (E) and (Z), of which the (E) form is the more conducting and thermodynamically stable. The relative proportions of the two isomers depend upon the reaction temperature, solvent and the nature of the catalyst. By varying the catalyst concentration in the solvent, it is possible to obtain PA as a gel, powder or thin film.³⁴ PA produced by this method, however, has two main disadvantages: the electrical conductivity decreases rapidly upon exposure to air and the polymer is entirely intractable. Exposure to air results in the formation of carbonyl, hydroxyl and epoxide groups, which lead to the destruction of the conjugated structure. The Naarmann process, a modified version of the Shirakawa process, results in a vast improvement in environmental stability.^{35,36} In addition, this process yields materials with extremely high electrical conductivity per unit weight ($\sim 16\,000$ S cm⁻¹) upon doping with iodine.³⁶ Aging the Ti(OC₄H₉)₄/Al(C₂H₅)₃ catalyst in silicone oil that had been mixed with n-butyllithium before exposure to acetylene produced highly regular, crystalline PA films that could be stretched by up to 400% giving films with a conductivity greater than $100\,000$ S cm⁻¹ per unit weight after doping.³⁶ Stretching PA allows alignment of the polymer backbone thereby facilitating charge transfer between the chains, improving direct current (DC) conductivity.

A number of approaches have been developed to resolve the intractability problem inherent with the Shirakawa method of synthesis of PA. One approach has been the use of copolymerisation, with monomers such as isoprene, styrene and butadiene, which

¹Applied Electrochemistry Group, School of Pharmacy and Biomedical Sciences, University of Portsmouth, St Michael's Building, White Swan Road, Portsmouth PO1 2DT, UK

²Global R&D, Kao Corporation, 2-1-3 Bunka Sumida-ku, Tokyo 131 8501, Japan

³Electrochemical Engineering Laboratory, Energy Technology Research Group, School of Engineering Sciences, University of Southampton, Highfield, Southampton SO17 1BJ, UK

*Corresponding author, email james.smith@port.ac.uk

1 Conductivities of conducting polymers in comparison with other organic compounds and typical inorganic materials¹⁵

offer the potential to combine the high conductivity of PA with the processability normally associated with conventional polymers.^{37,38} In practice, however, the properties of these copolymers tend to be significantly different from those of the constituent polymers and while some of the intractability problems are overcome, this is at the expense of high conductivity.

To obtain materials of a more controllable morphology, soluble precursor systems have been developed which, upon elimination of some small molecule, produce fully conjugated PA.^{39,40} One of the most successful of these processes is that which was developed at the University of Durham, UK (equation (2))⁴¹

where 'ROMP' is ring opening metathesis polymerisation, using $(\text{CH}_3)_4\text{Sn}$ and WCl_6 .

When chemically doped using a variety of oxidising agents, such as bromine, iodine or arsenic pentafluoride, the resultant material exhibited electrical conductivities similar to that obtained by Shirakawa. However, the main advantage of 'Durham polyacetylene' is the ability to apply a stress to the precursor during heat treatment to produce highly oriented films, which allow detailed studies of the anisotropic conduction of this material.

In addition to chemical doping, PA can also be doped electrochemically, with electro-oxidation resulting in the incorporation of negative species (p doping) and reduction leading to n doping.⁴² This is discussed further in the section on 'Electrochemical synthesis'.

Polyheterocycles as conducting polymers

The synthesis of PA in the highly conducting doped form was a starting point for a considerable number of studies. Electrodeposition of free standing films of other conjugated systems, such as PPy from organic and aqueous media,⁴³⁻⁴⁵ opened the way to intensive research into polyheterocyclic and polyaromatic conducting polymers.^{46,47} The use of aqueous media has obvious environmental advantages and, therefore, water solubility of the monomer, typically through the use of

2 a and b two degenerate (E) structures of PA, and c soliton defect at phase boundary between two degenerate (E) phases of PA, where bond alternation is reversed

sulphonate groups on the parent heterocycle, is a requirement.^{48,49}

The electrochemical oxidation of these resonance stabilised aromatic molecules has become one of the principal methods of preparing conjugated, electronically conducting polymers. Since the first reports of the oxidation of pyrrole, many other aromatic systems have been found to undergo electropolymerisation to produce conducting polymers (Table 1). These include thiophene,⁵⁰⁻⁵³ furan,⁵⁰ aniline,⁵⁴⁻⁵⁷ azulene,^{58,59} indole,⁵⁰ paraphenylene,^{60,61} as well as many substituted, multi-ring and polynuclear aromatic hydrocarbon systems. All the resulting polymers have a conjugated backbone which is required for electroactivity.

Mechanisms of conduction

The mechanisms of electronic conductivity and the nature of charge carriers in conjugated polymers are still a subject of debate. A brief summary of the various theoretical models for the electronic conductivity of conjugated polymers, using PA and PPy as examples, is given below.

The degeneracy of the ground state of (E)-poly(acetylene) (Fig. 2a and b) produces structural defects in polymer chains, causing a change in bond alternation (Fig. 2c). At the defect site, a single unpaired electron exists, although the overall charge remains zero, creating a new energy level at midgap (a non-bonding orbital). This neutral defect state, known as a 'soliton', is singly occupied, possessing a spin of 1/2, and is delocalised over ~15 carbon atoms.⁶² The soliton energy level can accommodate zero, one or two electrons and thus the soliton may also be positively or negatively charged, giving the unusual property of separating spin and charge, with neutral solitons possessing spin, but no charge, and charged solitons having no spin. In a doped polymer, charge is located in the midgap states, since these provide the highest occupied molecular orbital for charge removal and the lowest unoccupied molecular orbital for charge injection. Since a defect can occur anywhere along the chain, there is translational symmetry in the system, providing mobility of the soliton along the chain, offering a mechanism for electronic conductivity.

Two neutral solitons usually recombine eliminating structural defects, although single solitons can arise on chains with imperfections.^{63,64} In contrast, charged solitons repel each other and lead to isolated charged defects.⁶² A neutral soliton and a charged one can however achieve a minimum energy configuration by pairing,⁶⁵ producing a 'polaron',⁶⁶ which is essentially a radical cation, and gives rise to two states in the band gap, a bonding and an antibonding orbital, with symmetry placed about the midgap energy.

(E)-poly(acetylene) is the only conjugated polymer to possess a degenerate ground state. All other conjugated polymers possess non-degenerate ground states, and this affects the nature of charges which they can support.⁶⁷ In such polymers, where two non-degenerate regions are separated by a topological defect, the formation of single solitons is energetically unfavourable,⁶² and paired sites are formed.⁶⁵ This is the case for PPy, which can be drawn with either aromatic (Fig. 3a) or quinoid (Fig. 3b) structures, the latter possessing a higher energy configuration. Two neutral radicals on a single chain will recombine to eliminate the structural defect,⁶² although, if one is charged, a polaron is formed which is delocalised over about four rings (Fig. 3c). In contrast to PA, where both defects are charged, they are predicted to pair up to form a 'bipolaron',⁶² consisting of a doubly charged defect with no spin (Fig. 3d) and extending over a similar number of rings to the polaron. At higher doping levels, bipolarons may also combine to form 'bipolaron bands' within the gap.⁶⁸

Although these charge carriers are responsible for electrical conductivity in conjugated polymers, many structural imperfections are present in all polymers and

3 Possible structures of poly(pyrrole) (PPy) showing non-degenerate *a* aromatic and *b* quinoid configurations, and *c* polaron defect and *d* bipolaron defect

thus when mechanisms of bulk conductivity are discussed, these defects need to be considered. Conductivity is not only a result of charge transfer along the chain, but is also due to electron hopping between chains and between different conjugated segments of the same chain. In addition to these effects, which act at a

Table 1 Examples of more common conducting polymers

Polymer	Structure	Polymer	Structure
Poly(acetylene) (PA)		Poly(indole) (Pln)	
Poly(pyrrole) (PPy)		Poly(aniline) (PAn)	
Poly(thiophene) (PTh)		Poly(o-anisidine) (POA)	
Poly(furan) (PF)		Poly(2-methoxyaniline-5-sulphonic acid) (PMAS)	
Poly(thienylene vinylene) (PTV)		Poly(azulene)	
Poly(isothianaphthene) (PITN)		Poly(3,4-ethylenedioxy thiophene) (PEDOT)	
Poly(p-phenylene) (PP)		Poly(p-phenylene vinylene) (PPV)	

molecular level, bulk conductivity values are also dominated by electron transfer between grain boundaries and variations in morphology.^{69,70} Thus, the bulk conductivity of a conjugated polymer may be described by equation (3)⁷¹

$$\sigma = \sum \frac{n_i Z_i q_e v_i}{\delta E / \delta x} \quad (3)$$

where σ is the conductivity (S cm^{-1}), n_i is the number of charges carried by each species i , Z_i is the carrier type, q_e is the electronic charge ($1.60 \times 10^{-19} \text{ C}$), v_i is the drift velocity of electron (cm s^{-1}) and $\delta E / \delta x$ is the electrical field gradient over the polymer of film thickness x (V cm^{-1}).

Equation (3) takes into account different types of charge carrier which contribute to the overall observed electrical conductivity in the bulk polymer.

Synthesis of conducting polymers

Conducting polymers can be synthesised via chemical or electrochemical routes, although the former route has now been largely superseded by electrochemical methods. Many polymers, most notably PA, are still only accessible by chemical synthesis. The following sections describe these two synthetic routes.

Chemical synthesis

A large number of conducting polymers can be synthesised via catalytic oxidation.^{72,73} Iron(III) chloride is a common reagent used to produce PPy and poly(thiophene) (PTh) in their oxidised (doped) forms. For monomers of high oxidation potential, such as poly(3,4-ethylenedioxythiophene) (Table 1), cerium(IV) sulphate has been used as an oxidant.⁷⁴ With chemical polymerisations, however, control over polymer morphology is extremely limited, purification can be problematic and processing is virtually impossible. To alleviate these problems, a number of alternative synthetic routes have been developed which involve soluble precursor polymeric species. For example, poly(2,5-thienylene vinylene) is usually produced via a soluble methoxy precursor method.⁷⁵

Electrochemical synthesis

Electrochemical synthesis of conducting polymers offers many advantages over chemical synthesis, including the *in situ* deposition of the polymer at the electrode surface, and hence, eliminating processability problems and the control of the thickness, morphology and degree of polymer doping by control of the quantity of charge passed (Fig. 4).

Electropolymerisation is achieved by the electro-oxidation of the heterocycle either in an inert organic solvent, such as acetonitrile, containing supporting electrolyte, e.g. tetrabutylammonium tetrafluoroborate (TBABF_4), or in an aqueous electrolyte, typically Na_2SO_4 .⁷⁶ Conducting polymers have been deposited on a range of electrode materials, such as platinum, gold, indium–tin oxide glass, mild and stainless steel, nickel, aluminium and others. Electrodeposition is usually performed using cyclic voltammetry⁷⁷ or potential step methods. Figure 5a shows a typical cyclic voltammogram (CV) of pyrrole (0.01 mol dm^{-3}) in anhydrous acetonitrile containing TBABF_4 at a platinum disc electrode.⁴⁴ The two oxidation peaks are

4 Typical electropolymerisation process: anodic polymerisation of insoluble polymer is shown

shifted to more positive potentials when the scan rate is increased. A CV of pyrrole (0.1 mol dm^{-3}) on platinum in aqueous Na_2SO_4 (0.1 mol dm^{-3}) is shown in Fig. 5b. With continued potential cycling, at the same sweep rate, the current density of the polymer oxidation and reduction peaks increases as PPy continues to be formed. In both cases, a thick black film is produced on the first scan as the potential passes the onset of pyrrole oxidation.

The schematic of the generally accepted mechanism for electropolymerisation of five membered heterocycles⁷⁸ is shown in Fig. 6. The initial electrochemical step (E) is a one electron oxidation of the monomer to form its radical cation. A high concentration of these species is maintained at the anode surface because the rate of electron transfer greatly exceeds the monomer diffusion rate to the electrode surface. The second step, a chemical reaction (C), involves the spin pairing of two radical cations to form a dihydro dimer dication, which subsequently undergoes the loss of two protons and rearomatisation to form the dimer. Aromatisation is the driving force of the chemical step (C). Coupling occurs primarily through the α -carbon atoms of the heterocyclic ring (2- and 5-positions) since these are the positions of the highest unpaired electron π spin density and hence reactivity.⁷⁹ At the applied potential, the dimer, which is more easily oxidised than the monomer, exists in a radical cation form and undergoes further coupling reactions with other radical cations. This electropolymerisation mechanism, according to the general scheme $\text{E}(\text{CE})_n$, continues until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the anode surface.⁸⁰ This mechanism for electropolymerisation is greatly simplified, with the nature of the rate limiting step and the exact role of oligomers in the initial deposition step, remaining unresolved.⁶⁷

Non- α,α' -linkages (e.g. α,β' - and β,β' -couplings) can occur to variable extents, causing breaks in conjugation and reduction in film conductivity. Such linkages are more common in the later stages of electropolymerisation where the unpaired electron π spin density of the β -carbon atom of the oligomer approaches that of the α -carbon atom.⁸¹

5 Cyclic voltammograms (CVs) of pyrrole on platinum disc electrodes: *a* pyrrole (0.01 mol dm^{-3}) in anhydrous acetonitrile containing TBABF_4 : potential sweep rate: (a) 0.025 , (b) 0.05 , (c) 0.1 , (d) 0.2 , (e) 0.4 and (f) 0.8 V s^{-1} ; $T=295 \text{ K}$, and *b* pyrrole (0.1 mol dm^{-3}) in aqueous Na_2SO_4 (0.1 mol dm^{-3}): $\text{pH}=7.00$, scan rate= 0.03 V s^{-1} , $T=295 \text{ K}$; current density increases with cycling (shown by arrows)⁴⁴

Since conjugated oligomers are oxidised at less positive potentials than their corresponding monomer, polymer oxidation occurs concurrently with electrodeposition. Typically, one electron is removed from the polymeric backbone for every three or four monomer units to form polar structures, responsible for inherent conductivity (Fig. 7). Anions, termed 'dopants', are thus incorporated into the film to maintain electroneutrality. The doping terminology of conducting polymers should be distinguished from its conventional use in

semiconductor physics, since considerably higher concentrations of dopant are employed in the former, typically up to 33%.⁸² Conductive polymers can be cycled between the oxidised conducting state and the neutral insulating state,⁵¹ this process partly being controlled by the transport of counter ions into and out of the film.⁷⁸ For some polymers, it is also possible to reduce the neutral form to produce an *n* doped conducting material (Fig. 7). The negative charge on the polymer backbone is balanced by cations from solution.

6 Idealised mechanism for electrochemical polymerisation of aromatic five membered heterocycles: $X=\text{NH}$, S or O⁷⁸

7 Schematic showing redox behaviour of conducting polymer: neutral (undoped) form can be oxidised to p doped form or reduced to n doped form, both of which are conducting; former process is most common and hence neutral form is often referred to as reduced form; X=NH, S or O

Electrochemical methods have the advantage of controlling the extent of doping from the charged passed, using Faraday's laws of electrolysis.

The type of counterion used can greatly affect the conductivity of the film.⁸³ For example, for equal degrees of tetrafluoroborate doping, PPy typically has conductivities in the range of 30–100 S cm⁻¹, whereas with perchlorate anions, enhanced conductivities of 60–200 S cm⁻¹ can be achieved.⁸⁴

It is generally assumed that polymer growth occurs via a nucleation process similar to that of metal deposition. However, ellipsometric measurements of PPy formation⁸⁵ suggest that polymerisation does not occur via localised nucleation but that the product grows homogeneously on the surface. Potential step experiments have shown instantaneous nucleation on the bare metal surface followed by rapid formation of a polymer monolayer.⁸⁶ Spectroscopic measurements⁸⁶ have confirmed that initially short oligomers are produced with longer chains appearing subsequently and that the electrical properties of the bulk material only become evident when the growth centres have overlapped to form a continuous film.

Derivatised conducting polymers

Derivatisation provides one of the best methods of achieving a molecular level control of the structure and electronic and electrochemical properties of conductive

8 Variation of monomer oxidation potential with Hammett constant for β substituted thiophene monomers: β =Me, H, Br and COOH from left to right, respectively⁵¹

polymers.^{51,87–90} This was originally achieved through the use of dimers,^{70,91} trimers^{70,92} and tetramers⁹³ of thiophene and pyrrole which were found to undergo electropolymerisation to produce electroactive films with modified properties to those of the parent monomer. For example, poly(bithiophene) and poly(terthiophene) are usually obtained as powdery deposits rather than homogeneous films, showing lower conductivities [about 0.02–3 S cm⁻¹, in the case of poly(bithiophene)] than typically observed for PTh.^{70,80} This is reflected in the electronic absorption spectra, which show a hypsochromic shift in the absorption maximum, suggesting a decrease in the mean free conjugation length of the polymer. Thus, electropolymerisation of monomers and oligomers does not always produce the same polymer.

Pyrroles and thiophenes substituted at the 3-(β)-position (and also the N position for pyrrole) can often undergo electropolymerisation to produce conducting polymers, since the 2- and 5-(α -) positions remain available for monomer coupling.⁶⁷ The electrochemical behaviour of a wide range of β substituted pyrroles and thiophenes has been investigated, although β substituted thiophenes are generally more suitable than their pyrrole analogues due to their high stability and ease of preparation.⁸⁴ The products formed from electro-oxidation are highly dependent on the substituent, with some reactions producing conducting polymers and others, insulating layers or soluble species. This has been attributed to electronic and steric factors.⁸⁴

For a series of β substituted thiophenes, a linear correlation has been found between the ability of the substituent to donate or accept electrons (the Hammett constant) and the monomer oxidation potential (Fig. 8), suggesting that electronic effects dramatically affect the electronic density and hence reactivity, of the thiophene ring.⁵¹ Highly electron withdrawing substituents, such as nitro and nitrile groups, coupled directly to thiophenes at the β position, cause the monomer oxidation process to shift to much higher anodic potentials than thiophene itself (e.g. 2000 mV compared to 1400 mV) and as a result, electropolymerisation does not occur. Similarly, highly electron donating species, such as amino groups, increase the electron density at the thiophene ring, thus allowing monomer oxidation to occur at less anodic potentials relative to that of thiophene itself. Such a stabilisation of the radical cation results in diffusion of

9 Water soluble, self-doped poly(aniline): poly(aniline-co-N-propanesulphonic acid-aniline (PAPSAH))⁴⁸

the species away from the electrode interface into the bulk electrolyte before eventually being attacked by the electrolyte or other nucleophilic species in solution. In cases where conducting polymers are produced, electronic effects also have an effect on redox behaviour, where polymer oxidation potentials are also found to vary linearly with the Hammett constant.⁵¹ In principle, a substituent may be chosen to produce the desired electrochemical properties. In addition to electronic effects, steric factors also influence the electropolymerisation reaction and properties of conducting polymers, where they are formed.⁸⁰

Steric effects do not significantly hinder the formation of the radical cation but appear to become important in the subsequent coupling reaction.⁸⁰ For example, 3-methylthiophene undergoes electropolymerisation at a potential of 200 mV less anodic than that of thiophene, as might be expected from Hammett constant considerations. However, a polymer of higher conductivity than PTh (σ : 450–510 S cm⁻¹ compared to 270 S cm⁻¹) is produced⁸⁹ and this can be explained by blockage of one of the β positions of the thiophene ring by a methyl substituent which reduces the incidence of defect α,β' - and β,β' -linkages. It might, therefore, be expected that 3,4-dimethylthiophene would produce a polymer of even higher conductivity than poly(3-methylthiophene). However, a polymer of significantly reduced conductivity (σ : 0.5 S cm⁻¹) is produced and this may be explained by steric interactions between methyl substituents grafted on consecutive thiophene rings which distort the planarity (dihedral angle) of the rings and hence decrease the degree of conjugation.

Self-doped conducting polymers may be formed if the dopant anion is covalently attached to the polymeric backbone.^{48,80,94,95} In these systems, charge compensation upon doping involves the expulsion of cationic species rather than the insertion of anions and since the β substituent is often a sulphonate group, these polymers exhibit water solubility.⁸⁰ These films need to be electropolymerised from methyl ester derivatives, followed by conversion to the polyelectrolytic form by methyl iodide in acetone, since thiophenes bearing sulphonic acids or sodium salt substituents do not undergo polymerisation. Water soluble self-doped poly(anilines), such as poly(aniline-co-N-propanesulphonic acid-aniline (Fig. 9) and poly(2-methoxyaniline 5-sulphonic acid (Table 1), have also been synthesised.^{48,49}

Redox centres, such as ferrocene, have been covalently attached to PPy to act as cofactors for immobilised glucose oxidase in the construction of amperometric glucose sensors.⁹⁶ However, only a few examples of derivation of PTh by redox active groups, such as ferrocene⁹⁷ and bipyridyl,⁹⁸ have been described, owing to degradation of the attached redox centre under the much higher oxidation potentials required for thiophene electropolymerisation. Fluoroalkyl

derivatives have been shown to produce elastomeric materials with higher electroactivity than poly(alkylthiophenes).⁹⁹ Alkyl spacer linkages are necessary between the fluoroalkyl group and the thiophene ring to neutralise the strong electron withdrawing effect of the substituent. Electroactive polymers containing optically active substituents show potential technological applications as materials for enantioselective modified electrodes.¹⁰⁰

In some cases, polymers produced from electrochemical methods are poorly conducting ($\sim 10^{-6}$ S cm⁻¹) and redox inactive. For example, some (E)-styrylthiophenes and (Z)- α,β -2-diarylacrylonitriles were found to produce insulating films upon electropolymerisation.^{79,101–103}

Conclusion

This review has described the nature, synthesis and properties of conducting polymers. These materials, which combine high conductivity with the processability of polymers, can be conveniently electrodeposited on a variety of surfaces. Films can be tailor-made by controlling the monomer type and concentration, dopant/electrolyte, use of additives and electrochemical conditions, although the precise control of these parameters on film properties remains a challenge. The applications of these materials continues to grow and will be described in Part 2.

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