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Electropolymerized Films of π -Conjugated Polymers. A Tool for Surface Functionalization: a Brief Historical Evolution and Recent Trends

G rard Bidan

1.1 Introduction

Electrodeposition of conducting polymer films at the surface of an electrode has opened a field at the convergence between two rich domains: electrochemistry of modified electrode [1–3] and conjugated systems [4]. Consequently, applications of modified electrodes in electrocatalysis, electrochromism, energy storage, electroanalysis, and sensors have been enriched by the specific properties of intrinsically conducting polymers (ICPs), for example, electrochemically tunable doping and dedoping (equivalent to adjustable redox states), polymeric matrix affording electrical wiring, use as immobilized redox mediators, and the capacity to induce new functionalities by the use of specific gratings. Reciprocally, electrochemistry has opened up the route to easy-to-handle polymer films in a manner similar to the way that polyacetylene, $(\text{CH})_x$, prepared as a film by a modification of the Natta reaction [5], resulted in the discovery, in 1977, of the doping effect as presented in the seminal paper of Shirakawa and coworkers [6]. In addition, this cross-fertilization enlarged the panel of new ICP-based materials, such as electrogenerated composites [7], and strengthened or brought in new applications such as energy conversion and storage (Chapter 11); electrotriggered drug delivery [8]; soft actuators (Chapter 11); chemical, bio-, and gas sensors (Chapters 8–10); biocompatible films [9]; and artificial muscles (Chapter 12).

Considering the intense and widespread research activities in these fields, the aim of this historical survey is not to cover the entire field of the various electropolymerization facets detailed in the following chapters, but to give an overview of the successive contributions to and acquisition of knowledge.

The electropolymerization reported here is restricted to oxidative condensation; as a matter of fact, it should be mentioned that as early as in 1983, Fauvarque [10] reported the synthesis of poly(*p*-phenylene) film by electroreduction-assisted catalysis by Ni(0) complex. In the first part, electropolymerization is described in the context of π -conjugated polymers. Four generations have been distinguished in this saga: the “era of physicists,” the “era of electrochemists,” the “era of polymerists,” and the “era of molecular electronics.” This division appears a little artificial, since

the progress in each of these eras resulted from mutual enrichment between these scientific communities; however, this book provides an enlightening presentation of each determining step of the evolution. The “era of electrochemists” starts with the early use of electropolymerization in the 1980s. The second part presents the major milestones reached by the process of electropolymerization in the light of the functionalization of surfaces for the electrodeposition of increasingly sophisticated conjugated architectures endowed with specific functionalities from sensors to active photovoltaic layers. Recent trends in the use of the electropolymerization concerning the elaboration of nanowires or nanotubes of ICPs for sensors or molecular electronics, nanostructured materials (interpenetrated networks with ICPs, carbon nanotubes/ICPs combination, etc.) are not presented here.

It is emphasized that the compilation of bibliographic data has been a very difficult task, since it is pointless to duplicate all the references that are given in the other chapters; so the selection here is a mix of citations of pioneering teams with key contributions made in the 1980s–1990s, easily accessible reviews, and recent representative publications on the new trends in the field.

1.2

Electropolymerization: Epistemological Analysis within the ICP Saga

It is possible to distinguish four generations in the still active saga of ICPs.

The first generation, the “era of physicists,” corresponds to their historical identification as *synthetic* or *organic metals*, and parallel to the development of mixed valence crystals in the family of TTF-TCNQ [11, 12], the domain of electroconductive polymers appeared driven by the interest of physicists in the semiconducting/conducting or even supraconducting conductivity transition. Polysulfur nitride, $(SN)_x$, was investigated in the early 1960s and the metallic properties were studied in the 1970s [13], with a superconducting transition below 0.3 K evidenced in 1975 [14], and the “doping effect” of halogens reported in 1977 [15]. Similarly, $(CH)_x$, the first chemically unsophisticated representative of the π -conjugated structure, that is, with alternative C–C single and double bonds, was extensively investigated after the discovery of halogen doping in 1977 [6]. It must be emphasized at this point that the preparation of $(CH)_x$ as an easy-to-handle film [16, 17] instead of a pressed pellet of powder considerably boosted the field and allowed to carry out electrochemical doping on $(CH)_x$ films as electrodes [18]. The chemical modification of poly(*p*-phenylene) [19] by AsF_5 or alkali metals was reported soon after in 1979.

The second generation of ICPs, the “era of electrochemists,” began with the electropolymerization of aromatic heterocycles and derivatives. In addition to the “easy-to-handle effect” previously illustrated by $(CH)_x$, electropolymerization is based on a new concept of oxidative condensation through the generation of radical cations (Chapter 2). Early work in 1916 [20] and 1937 [21] on chemically prepared “neri di pirrolo” had not been aware of the electronic properties of these powders of poly(oxipyrrole). Chemical oxidation of aniline, reported by Buvet and coworkers

in 1968 [22, 23], and of pyrrole, reported by Hautière Christofini in 1973 [24], was recognized to provide electrically conductive materials. Electropolymerization allowed handling polypyrrole [25, 26], polyaniline [27–29], and poly(*p*-phenylene) [30] films, resulting in completely new polymers films, some of the better known being the polythiophene [31, 32], polyfluorene [33], and polycarbazole [34] classes. Consequently, in early 1980s, the electrochemist community was drawn to use electrochemistry not only as a tool to prepare ICP films [35] but also as a methodology (Chapter 3) to investigate the doping/dedoping process electrochemically tuned with the associated movements of ionic dopants and the concomitant evolution of the electronic structure using electron spin resonance (ESR) spectroscopy [36], UV–vis [37] and surface IR [38] spectrophotometries, ellipsometry [39–41], quartz crystal microbalance (QCM) [42], and mirage effect [43], coupled with voltamperometric methods. In addition to the use of ICPs as substitutes for metals, new ICP applications, traditionally falling into the field of electrochemistry such as electrocatalysis [44, 45], sensors [46–51], biosensors (Chapters 8–10), energy storage (e.g., batteries [52–56] and supercapacitors [57, 58]) (Chapter 11), anticorrosion deposits onto metals [59–61] and semiconductors [62–65], and electrochromism [66–69], were rapidly developed. However, the concept of functionalization was the key breakthrough [45, 70–73]. It is possible to deposit a polymer film including functional moieties into the polymeric backbone in just one step. The tremendous progress in research on sensors and biosensors (Chapters 8–10) originates with the study of sensitive layers based on (bio)functionalized ICP films.

The third generation, the “era of polymerists,” emerged from the inputs of chemists, particularly the macromolecularists, to the ICP domains. The intrinsic advantage of electropolymerization – a straightforward deposition of a redox and an electroconducting film of an electrocontrollable thickness, with tunable interfacial properties for numerous electrochemical applications – is counterbalanced by the complete insolubility of the deposit. Thus, the determination of classical characterization parameters for polymers such as the average chain length, dispersion, crystallinity, and the handling by spin or dip coating for large-scale applications are both impeded. Chemists have played an important role in the development of new routes in chemical synthesis, providing structurally well-defined conducting polymers. In the large family of ICPs, polythiophenes have been by far the more studied, and as early as in 1980, Yamamoto [74] reported the Ni-catalyzed condensation of 2,5-dibromothiophene. Three main properties have been tuned via structural and chemical modifications: the gap, the solubility, and the conductivity. The existence of low-gap thiophene-based ICPs [75, 76] such as poly(isothianathene) was reported in 1984 by Wudl [77], polyfused heterocycles such as poly(thienothiophene) was reported by Taliani in 1986 [78, 79], and poly(dithienylethylene) and related systems by Roncali [80] in 1997. Poly(ethylenedioxiethiophene) (PEDOT), reported by Heinze *et al.* in 1994 [81] and Reynolds *et al.* in 1996 [82] and considered as one of the most stable ICPs, is now commercially available and is used in numerous applications. Soluble poly(3-alkylthiophenes) (P3-ATs) were first reported by Elsenbaumer in 1986 [83]. Regioregularity with the so-called McCullough method

[84] reported in 1993 in the P3-ATs family has been the cornerstone for the development of applications in organic electronics (vide infra). While classical polymerizations by oxidative coupling using $\text{Fe}^{(\text{III})}$ salts provides polymers with 3,4- and 2,5-linkage defects, low molecular weights, and weak conductivities (in the range of $0.1\text{--}1\text{ S cm}^{-1}$), the metal-catalyzed C–C coupling of heterocycles (e.g., Suzuki-, Sonogashira-, and Stille-type reactions) allows to improve their conductivities by more than 2 orders of magnitude [85]. In addition to processable ICP-based materials [86], the above-mentioned chemical methods were also used for the step-by-step synthesis of well-defined length oligothiophene [87]. Considerable progress has been made from the simple sexithiophene reported in 1989 by Garnier *et al.* [88] to the sophisticated oligothiophene-based nanoarchitectures reported in the recent remarkable review by Bäuerle *et al.* [89].

The fourth generation covers the wide domain of organic electronics in its extended acceptance and can be considered as a “renaissance” of the ICP domain of applications by the fruitful cross-fertilization between synthetic chemistry and electronics. It is contemporary to the third generation, and mainly concerns organic light-emitting diodes (OLEDs), ICP-based photovoltaic devices, organic thin film transistors (OTFTs), and molecular electronics. After the first report by Garnier on OTFTs based on sexithiophene [88] in 1989, a significant step in 1990 was the description by Friend and coworkers of the electroluminescent device based on poly(*p*-phenylene vinylene) (PPV), placed between an indium tin oxide (ITO) and an Al electrode [90]. Polymer light-emitting diodes were extended to different classes [91] of conjugated polymers such as poly(carbazole)s, poly(flourene)s, PPVs, and poly(thiophene)s. The reverse phenomenon of photovoltaic cells based on ICPs [92] was soon reported, with the next decisive step resulting in the ultrafast photoinduced electron transfer from ICPs to the C_{60} fullerene, developed independently by Sariciftci *et al.* [93] and Yoshino *et al.* [94] in 1992. These fields are well detailed in the second volume of the third edition of the *Handbook of Conducting Polymers*, edited by Skotheim T A, Reynolds in 2007. Interestingly, we will see in the second part of the following that, in spite of the leading processes of dip or spin coatings to implement ICPs in electronic devices, electropolymerization is still being developed as an alternative method for the fine control of thickness for numerous applications [95–97].

1.3

Electropolymerization: from Pristine Heterocyclic to Sophisticated Functional and Conjugated Architectures

Having, very briefly, traced almost 30 years of scientific venture on ICPs, which have replaced electropolymerization as one of the most important inputs, this section examines more specifically the evolution of this methodology (Figure 1.1) in the context of functionalization of surfaces.

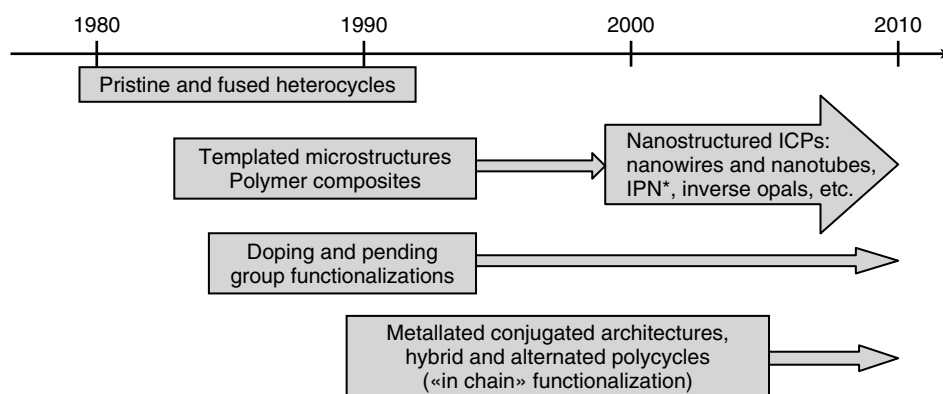


Figure 1.1 Some key milestones in the evolution of electropolymerized heterocycles in the saga of ICPs. These successive main steps are not independent but mutually enriched. *IPN, Interpenetrated network.

1.3.1

Electropolymerization of Pristine Aromatic Heterocycles

The first electropolymerization experiment reported in 1968 by Dall'oxlio [25] on pyrrole in water medium was not the trigger event; as a matter of fact, except for aniline in acidic media, pristine pyrrole, and, as reported later, for thiophene and derivatives in micellar medium [98–100], few heterocycles are soluble and able to electropolymerize in aqueous media. The first determining event was the electropolymerization in an organic medium of pyrrole (0.06 M) in acetonitrile (1% aqueous) containing 0.1 M Et_4NBF_4 , reported in the seminal article of Diaz *et al.* in 1979 [101] from works carried out at IBM San Jose [102]. The route was then opened for the screening of electrochemical synthesis of conducting polymers by anodic oxidative condensation of aromatic heterocycles. Over the next 10 years, electropolymerization of polythiophene [103, 104], poly(*p*-phenylene), polynaphthalene, polyanthracene, polypyrene, polyindole, polyazulene [103], polyfluorene, and polycarbazole [34, 105–107] was reported and reviewed in detail by Simonet and Rault-Berthelot [108]. Many more sophisticated units are still being reported [109]. A special mention must be made of the electropolymerization of thiophene (from among thiophene, azulene, and furan) by Tourillon and Garnier in 1982 [31], since this family, including thiophene-fused cycles [54, 78, 79], has been the most flourishing of the ICP domain. PEDOT, pioneered by Heinze [80] and then by Reynolds [82], still appears as the leading material, including alkyl derivatives [110]. Polyaniline, which was first chemically synthesized and considered as early as in 1968 by Buvet and coworkers [22, 23] as a semiconductor whose redox properties can be tuned by the pH, was electrosynthesized by Diaz *et al.* in 1980 [27], and then “rediscovered” around 1985 in the light of the new concepts of conjugated structures; among leading teams we may cite MacDiarmid [111], Geniés [28, 112], and Bard [29]. After a brilliant start, owing to the attractive potential applications

in energy storage with the pioneering paper by MacDiarmid and coworkers in 1984 [113], polyaniline (Pani) appeared to find greater use in solution-processable applications [114], since as soon as the phenyl cycle is substituted, the electropolymerization is strongly disturbed [115, 116]. A renewing of Pani applications, such as supercapacitors, benefits from the recent use of ionic liquids in addition to the contribution of nanoscience concepts to produce nanostructures.

An important step toward the functionalization of surfaces was the inclusion of a functional dopant during electrodeposition. Applications of these pristine polyheterocycles were limited to the exploitation of their redox properties (batteries and supercapacitors) and related modulations in conductivity (electrochemical transistors), color (electrochromism), and volume changes (actuators).

Functionalization by the inclusion of specific dopants (Figure 1.2) soon appeared as a straightforward route pioneered by Skotheim in 1985 [124] and Shimidzu in 1987 [117], since no specific chemistry on the heterocycle is required – only the choice of a functional anionic (Figure 1.2a) or cationic (Figure 1.2c) (for self-doped ICPs) species. The inclusion of the functional dopant present in the electrolyte during electropolymerization was preferred to the exchange of “classical” nonfunctional dopants (perchlorate, chloride, tetrafluoroborate, etc.) after the electrodeposition just by dipping in a solution containing the functional dopant. In fact, the reverse reaction, that is, the retrodiffusion of the functional dopant in a renewed solution cannot be avoided, even though it had been exploited in a certain

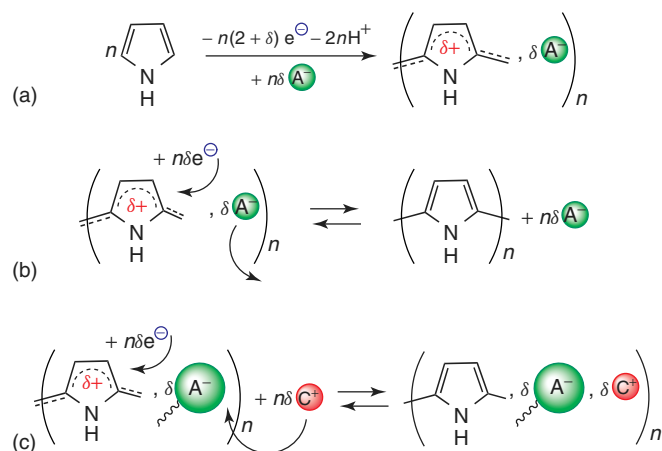


Figure 1.2 Functionalization by doping. (a) The function is introduced during the electrodeposition using a specific dopant A^- entrapped into the polymeric backbone. (b) When the dopant is small, the anionic dopants A^- are mobile and mainly expelled during the dedoping by electroreduction. (c) Provided that the anionic dopants (bulky groups, i.e., $\Phi \geq 10 \text{ \AA}$, entangled ionomeric chains, grafted dopants) are immobilized

(the wavy line symbolizes this immobilization), the dedoping results mainly in the entrance of a cationic “pseudodopant” C^+ and vice versa during doping. The arrows of electronic transfers and ionic movements (from left to right) correspond to the dedoping and must be inverted for the reverse doping reaction. These processes have been exploited for the electrocontrolled delivering of charged drugs.

manner for the electrocontrolled release of species (Figure 1.2b) [118–120]. A fruitful method to increase the ratio of dopants versus monomeric units consisted in the grafting of an additional positive charge on the pyrrole unit via an alkylammonium substituent [121]. This was exploited for the incorporation of enzyme via a solid-state electropolymerization [122]. The inclusion of a specific dopant was demonstrated as an efficient method to incorporate electrochromes [71, 117] and photosensitizers [71, 117]. Sulfonated metalloporphyrins or metallophthalocyanines [123–126], polyoxometallates [127, 128], enzymes [129–131], and single-stranded DNA [132, 133] were inserted in an ICP matrix mainly to induce electrocatalytic and biorecognition properties. On the other hand, use of a bulky dopant (i.e., with a diameter more than 5–6 Å) during electrodeposition allows an almost irreversible trapping in the polymeric matrix due to the entanglement of the polymeric chains around the dopant. The shape of the dopant is also a determining factor and for linear dopants, such as alkylsulfonates, the retention starts from chain length of C₁₀ [134]. In this case, other holding factors such as hydrophobicity of the dopant chain must be considered. When the anionic dopant is immobilized, the dedoping results in the insertion of a cation to insure the electroneutrality [135] (Figure 1.2c). This cationic pseudodoping is also performed when the anionic dopant, usually sulfonate, is directly grafted on the conjugated polymer skeleton (self-doped polymers [136–142]) or is a pending group of an ionomeric polymer such as Nafion[®] [136, 143, 144] or polystyrene sulfonate [145, 146]. Such interpenetrated polymeric networks [70] were investigated for applications in batteries [71, 117], water deionization [71, 117], and electrochemical delivery of drugs [118–120]. This last example was pioneered by Miller for the electrodelivery of dopamine [147]. Bidan and Kaneto introduced doping-specific cavities such as sulfonated cyclodextrines [148] or calixarenes [149] in polypyrrole for the selective trapping of drugs and ions.

1.3.2

Electropolymerization of Substituted Heterocycles

The concept of functionalization by covalent grafting seems to be very familiar by now. In the one-step approach (Figure 1.3a), the monomeric unit is presubstituted by a functional group. Provided some rules are followed, the electropolymerized films exhibit new functionalities while keeping the attributes of ICPs. Instead of prefunctionalization of the starting monomer, more generic methods have been developed based on a two-step approach (Figure 1.3b). Classically, an active group (e.g., amino [150], carboxylic [151], or affinity groups [152, 153]) is grafted by prefunctionalization; then, after electrodeposition via a coupling reaction (e.g., a peptide link), a bond is formed with a specie in solution (e.g., amino–protein). This postfunctionalization of the film mainly affects its surface; this is a limitation in ionic complexation for applications of the modified electrode in electroanalysis and electrocatalysis. On the other hand, this approach is effective and efficient with bulky groups (enzymes, DNA [154, 155]); the active layer acts as a functional interface for biorecognition in biosensors (Chapters 8–10).

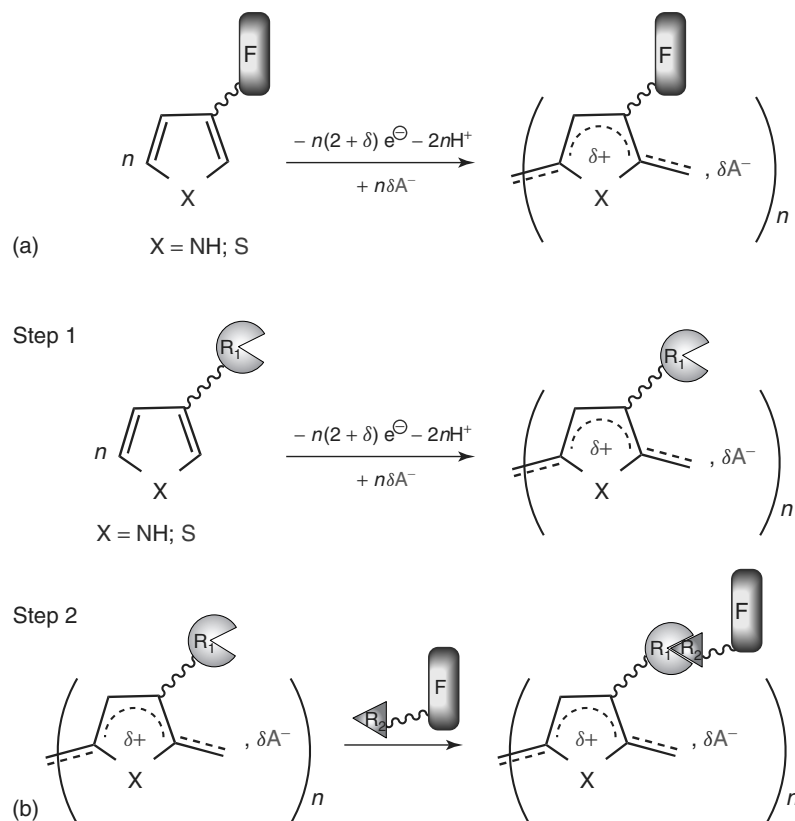


Figure 1.3 Functionalization by covalent grafting via a pending function. (a) One-step functionalization of ICPs by covalent grafting of the function, via a spacing arm, at the 3-position to the precursor monomer, then submitted to electropolymerization. For pyrrole, the N-substitution has also been fully exploited. (b) Two-step functionalization: Step 1, a generic coupling group R_1 is end-grafted as performed

in the one-step strategy (a) and Step 2, after electrodeposition the modified electrode is functionalized by a heterogenic coupling reaction via a reactive group R_2 classically the R_1 – R_2 coupling reaction is a peptide condensation, an affinity recognition (biotine–avidine, single-stranded DNA hybridization, antibody–antigen) or, more recently, click chemistry.

The two-step approach was recently renewed by using click chemistry. Li *et al.* opened the route to a general method for a modified electrode based on “clickable” polypyrrole [156]: two types of N-substituted pyrrole with azide and terminal alkyne were synthesized and functionalized by complementary redox or bioactive elements.

One-step functionalization by grafting of conducting polymers (Figure 1.3a) has been widely reviewed [45, 70–73]. The history of this process is briefly described here: in 1982, Diaz *et al.* reported on poly(*N*-alkylpyrrole) [157] and

on *p*-phenyl-substituted poly(*N*-phenylpyrrole) [158]. Then, in 1985, Skotheim and coworkers reported the first redox-active pending function illustrated by the *N*-(*p*-nitrophenyl) group [159]. An important improvement was made with the grafting of functional molecules using an aliphatic spacing arm. In fact, the use of an alkyl chain spacer arm leads to a more tunable product than that by a phenyl spacer arm. The length of this alkyl arm can be tailored in a manner so as to control the steric hindrance. In the *N*-substituted polypyrrole series, a C₆ spacing arm appears to be a good compromise between a too short C₃ that decreases the electropolymerizability by steric hindrance interaction and a C₁₁ length that moves away the conjugated chains and reduces electronic accessibility [160, 161]. However, the steric hindrance induced by short spacer can be reduced by linking two pyrrole units [160]. In 1984, Bidan and coworkers reported the grafting of the viologen (4,4'-bipyridinium) system [162, 163] and poly(pyridinyl) complexes of ruthenium [164]. This class of polypyrrole–Ru complexes was investigated in detail for their electrocatalytic properties by Deronzier *et al.* [165]. Various substituents, such as the ferrocene group [166], nitroxide functions [167] and anthraquinone groups [168], the camphor chiral unit [169], porphyrin [170], phenothiazine [171], enzyme [172], calixarene [173] and fluorene [174], biotine [152, 153, 175], and single-stranded DNA [176, 177] were soon grafted at the nitrogen – there is no limitation to the substituents that can be used. The basic chemistry to perform *N*-substitution is counterbalanced by a loss in conductivity by 5–7 orders of magnitude. This is not really a limitation in electronic transfer for electrodes modified by a thin film of micrometer thickness; however, for a better transduction of recognition event, grafting in 3-position appeared more attractive in spite of the need to implement a more elaborated chemistry. The 3-substitution was applied on pyrrole by Audebert *et al.* [178] and on thiophene derivatives by Garnier and Lemaire [179] simultaneously in 1989. This, particularly in the thiophene class, opened a route to another field of research. The structural effect of the functionalization in 3-position was rationalized, and a “functionalization space” was defined in terms of three parameters: the length of the spacer, the intrachain distortion, and the interchain distance [180–182]. A wide range of functionalizations of pyrrole and thiophene at the 3-position was developed mainly for sensor applications. Among these functions, the following can also be cited: alkyl chains, fluoroalkyl chains, oligo(oxyethylene) chains [179], chiral and redox groups, and anionic species (self-doped polymers) crown ether [183–185] reviewed by Roncali [186] and by Swager [187]; boronic ester [188]; and peptides [189] (Chapters 8–11). Unlike polypyrrole or polythiophene derivatives, the poor functionalization of Pani has been pointed out. This poor electropolymerizability of aniline derivatives could be got around by an inverse approach; functional molecules bearing a phenyl or naphthalene group were amino-substituted to promote the electrocoupling. In this manner, amino derivatives of porphyrines [190, 191], anthraquinone [192], and naphthol [193] were polymerized. In some cases, substitution by a hydroxyl group also promotes the electropolymerization of aromatic molecules and allows to reach conjugated structures such as those from juglone monomer [194].

1.3.3

Electropolymerization as a Tool to Elaborate Functional Conjugated Architectures

An important step forward was achieved by moving from “simple” functionalization with active pending group to preorganized conjugated architectures.

Electropolymerization of ICPs can be exploited to form or freeze certain molecular shapes. Sauvage, Bidan and coworkers have taken advantage of the relative rigidity of the polymeric matrix to incorporate preformed complexing cavities into polypyrrole by grafting at the *N*- [161] or 3-position [195]. In the first approach, the spacer between the metallic complex and the pyrrole units was still a single alkyl chain. However, the presence of four pyrrolic monomers allowed to maintain the phenanthroline ligands interlocked in a pseudocatenane assembly even after demetallation. More sophisticated molecular units such as rotaxanes were electrodeposited, and it was possible to electrochemically induce gliding motion inside the polypyrrole matrix [196]. Recently, Ikeda *et al.* have prepared polythiophene polyrotaxane by electrochemical polymerization [197], including the Stoddart viologene ring; however, there is no evidence of gliding of the ring during cyclic voltammetry. It should be noted that in these cited works the metal complexes and polypyrrole matrix behave almost independently in terms of electronic interactions.

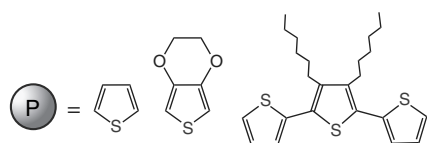
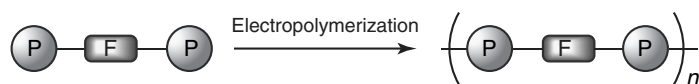
The goal of the direct transduction of a chemical event in an electrical signal for sensing was achieved by grafting or doping a receptor into the ICP matrix.

Provided that the recognition event results in the trapping of a charged or bulky analyte (the guest) such as alkali ions, single-stranded DNA, proteins, and so on, the electrostatic or steric hindrance interaction with the ICP chain conformation modifies the electroactivity of the ICP-electrodeposited film. This ICP-receptor-couple acts as an electrochemical transducer for sensing. This opened a route to a large number of sensor applications (Chapters 10 and 11). As illustrating examples, in the vast literature, the coupling with crown ether, DNA, or enzyme was investigated and reviewed the most; see, for instance, the works of Bryce [198], Swager [199], Bidan [176, 200], Cosnier [201], Wallace [202], Mirsky [203], Bobacka [204], Josowicz [205], and Singh [206].

A step toward chemtronic materials, that is, the direct interaction, via molecular orbital overlap, of a function with the conjugated chain was achieved by moving from the concept of a pending group to the one of an intercalated group.

Now, the concept of end-terminated polymerizing groups (Figure 1.4), based on the use of thiophene [207] and EDOT [208, 209] units as the external heterocyclic rings, is currently used to promote the one-step electrodeposition of molecules unable to electropolymerize alone [210].

Among them, a new class of conjugated materials with novel electronic and electrochemical characteristics was obtained by the hybridization of ICPs with transition metal complexes [211–213]. The cooperative behavior between a large number of photonic and electronic properties of metallic centers and the conjugated matrix can be achieved by forcing the π -conjugation to go through a metallic center or by an electronic coupling via the metal–ligand orbitals. In



F = Vinyl, phenyl, diphenyl, thiophene and derivatives; furans; pyrrole(N-substituted by bulky group); ligands such as pyridine, bipyridine, phenanthroline and their metal complexes; salen types metal complexes; dithiolene metal complexes; fluorenes and carbazoles derivatives; tetrathiafulvalenes; fluorenone; tetrazine; silole; carbene; etc...

Figure 1.4 Functionalization by the strategy of the end-terminated polymerizing groups. The function is inserted between two electropolymerization-promoting heterocycles. In this manner, it is possible to electropolymerize central blocks with specific properties, whereas, on their own, they exhibit poor electropolymerizability. This “in chain” approach is preferred to the pending-group one for applications exploiting the electronic delocalization of the tricyclic units, such as OPVs and molecular electronics.

the first approach, the conjugated chain is interrupted by the metal [214–216] and is not considered here as representative of hybrid compounds. The first hybridization was pioneered by Yamamoto from polypyridine [217] complexed by ruthenium. However, these chemically prepared materials were almost insoluble and the postpolymerization metallation is difficult. A step forward – mutual metal-conjugated chain interaction – was achieved by Wrighton *et al.* in 1994 using electropolymerization of 5,5'-(2-thienyl)-2,2'-bithiazole, followed by metallation of the bithiazolyl units by $\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})$. Oxidation of the conjugated backbone to the conducting state causes a decrease in electron density at the Re metallic center evidenced par IR spectroscopy [218]. Zotti *et al.* [219] tried to compare the efficiency of electron transfer between metal sites by electron hopping or via conjugated linkage using a polythiophene backbone with pending ferrocene unit bound either by an alkyl or by a vinyl spacer. However, their results are ambiguous. To avoid the difficulty of postmetallation of the polymer, the direct electropolymerization of a Ru complex of 5,5'-bis(2''-bithiophene)-2,2'-bipyridine was reported by Swager *et al.*; however, interconnection between the Ru centers and the conjugated poly(bipyridine–bithiophene) chain was not clearly evidenced [220]. A key step had been achieved with the anodic polymerization of metal-directed preassembly of rotaxane unit end terminated by two EDOT or thiophene units reported by Swager *et al.* in 1997 [221] and then by Sauvage *et al.* in 1998 [222]. *In situ* conductivity measurements on interdigitated electrodes coupled with cyclic voltammetry had showed that the redox conductivity of the copper-metallated polymer is strongly amplified compared to the demetallated one [223]. These

metallo-pseudopolyrotaxanes can exhibit remarkably high conductivities when the redox potential matches the oxidation potential of the π -system, such as in copper complexes associated with polythiophene and derivatives. This is well illustrated by the variation in conductivity reported by Swager in the sophisticated structure of the three-strand conducting ladder polymers using a two-step electropolymerization process of metallorotaxanes [224]. During the same period of time, similar approaches to enhance the communication between metal centers and conjugated backbones were developed on other structures of transition-metal-containing conjugated polymers prepared by electropolymerization. Reynolds *et al.* reported the tuning of the electrochromic properties of polythiophene link to salen-type metal complexes [225]. Audebert *et al.* had electropolymerized anil- and salen-type complexes, which exhibit enhanced charge transport when a conjugated backbone is electroassembled [226]. Wolf *et al.* [227] studied polythiophene cross-linked via different Pd complexes and the groups of Pickup *et al.* [228] and Shabara *et al.* [229] presented electropolymerized thiophene derivatives containing dithiolene Ni, Pd, or Au complexes.

1.4

Conclusion

The elaboration of increasingly sophisticated conjugated architectures such as insulated molecular wires reviewed in 2007 by Anderson *et al.* [230] involves an important part of chemical coupling [87, 231] compared to anodic coupling. Nevertheless, it should be noted that the building up of conjugated polymer networks cross-linked by organometallic bridges reviewed in 2005 by Weder [232] accounted for a large panel of electrogenerated structures. Recently, chiral polysalen–thiophene chromium complex was electrosynthesized and used to promote asymmetric reactions [233]; electropolymerization of carbene ended by bithiophene units was reported by Cowley *et al.* [234].

The determining role of conducting polymers as active materials in organic photovoltaics (OPVs) was boosted by the chemical coupling synthesis of new polymers [235] or oligomers [236]. However, here too, the use of electrochemistry for the electrodeposition of active layer in OPV cells is still widely exploited. The benefit of this strategy is the well-controlled thickness at a nanometer scale of the electrodeposited film. Double-cable polymers of poly(thiophenes) containing pendant C₆₀–fullerene groups was electrogenerated [237–240]. Polycarbazole derivatives appear among the more promising polymers for OPVs. Their direct electropolymerization is difficult; however, electrocopolymerization [241] or derivatization-enhanced solubilization [242] allows their electrodeposition. Recently, the application of the end-terminated polymerizing heterocycle strategy has involved the synthesis of a central C₆₀-linked carbazole ended by EDOT units [243].

Although the mechanism of anodic electropolymerization of conducting polymers [244, 245] (Chapter 2) such as polypyrrole [246–248] has been well investigated, there are still gray areas with regard to the relationship between

the morphologies (dense, open structure, fibrillar) and the conditions of electropolymerization, for example, solvent (aqueous, organic) and potential (value, potentiostatic, cyclic potential sweep). The recent use of ionic liquids [249, 250] for the electrosynthesis of ICPs has boosted the renewal of electrochemical applications, which suffered from a lack of stability toward electrochemical cycling such as batteries, supercapacitors [251], artificial muscles [252], or sensors [253, 254]. In addition, the one-step elaboration (without template) of ICP-based nanostructures [255] such as nanowires [256–258] is also exploited in similar applications [259].

Therefore, the electropolymerization of conjugated structures will definitely continue to be an important tool of functionalization and elaboration of nanoobjects as well as an active field of researches for many years.

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