Chapter 4
Chemical and Electrochemical Syntheses of Conducting Polymers

Polymers can be prepared using chemical and/or electrochemical methods of polymerization (see Chap. 2), although most redox polymers have been synthesized by chemical polymerization. Electrochemically active groups are either incorporated into the polymer structure inside the chain or included as a pendant group (prefunctionalized polymers), added to the polymer phase during polymerization, or fixed into the polymer network in an additional step after the coating procedure (post-coating functionalization) in the case of polymer film electrodes. The latter approach is typical of ion-exchange polymers. Several other synthetic approaches exist; in fact, virtually the whole arsenal of synthetic polymer chemistry methods has been exploited. Polyacetylene—now commonly known as the prototype conducting polymer—was prepared from acetylene using a Ziegler–Natta catalyst [1–7]. Despite its historical role and theoretical importance, polyacetylene has not been commercialized because it is easily oxidized by the oxygen in air and is also sensitive to humidity. From the point of view of applications, the electrochemical polymerization of cheap, simple aromatic (mostly amines) benzoid (e.g., aniline, o-phenylenediamine) or nonbenzoid (e.g., 1,8-diaminonaphthalene, 1-aminoanthracene, 1-pyreneamine) and heterocyclic compounds (e.g., pyrroles, thiophenes, indoles, azines) is of the utmost interest. The reaction is usually an oxidative polymerization, although reductive polymerization is also possible [8, 9]. Chemical oxidation can also be applied (e.g., the oxidation of pyrrole or aniline by $Fe(ClO_4)_3$ or peroxydisulfate in acid media leads to the respective conducting polymers), but electrochemical polymerization is preferable, especially if the polymeric product is intended for use as a polymer film electrode, thin-layer sensor, in microtechnology, etc., because potential control is a prerequisite for the production of good-quality material and the formation of the polymer film at the desired spot in order to serve as an anode during synthesis. A chemical route is recommended if large amounts of polymer are needed. The polymers are obtained in an oxidized, high conductivity state containing counterions incorporated from the solution used in the preparation procedure. However, it is easy to change the oxidation state of the polymer electrochemically, e.g., by potential cycling between the oxidized, conducting state and the

neutral, insulating state, or by using suitable redox compounds. The structure and conductivity can be altered through further chemical reactions [10].

The mechanism and the kinetics of the electropolymerization—especially in the cases of polyaniline [11–49] (see Fig. 4.1) and polypyrrole [11, 13, 50–88]—have been investigated by many researchers since the first reports were published [89–92]. Two points have been addressed: the chemical reaction mechanism and kinetics of the growth on a conducting surface. Owing to the chemical diversity of the compounds studied, a general scheme cannot be provided. However, it has been shown that the first step is the formation of cation radicals. The subsequent fate of this highly reactive species depends on the experimental conditions (composition of the solution, temperature, potential or the rate of the potential change, galvanostatic current density, material of the electrode, state of the electrode surface, etc.). In favorable cases, the next step is a dimerization reaction and then stepwise chain growth proceeds via the association of radical ions (RR route) or the association of a cation radical with a neutral monomer (RS route) [6, 93–95]. There may even be parallel dimerization reactions leading to different products or to a polymer with a disordered structure.

The inactive ions present in the solution may play a pivotal role in the stabilization of the radical ions. Potential cycling is usually more efficient than the potentiostatic method, i.e., at least a partial reduction of the oligomer helps the polymerization reaction. This might be the case if the RS route is preferred and the monomer carries a charge, e.g., a protonated aniline molecule. (PANI can only be prepared in acidic media; at higher pH values other compounds such as *p*-aminophenol, azobenzene, and 4-aminodiphenylamine are formed.) A relatively high concentration of cation radicals should be maintained in the vicinity of the electrode. The radical cation and the dimers can diffuse away from the electrode. Intensive stirring of the solution usually decreases the yield of the polymer produced. The radical cations can react with the electrode or take part in side reactions with the nucleophilic reactants (e.g., solvent molecules) present in the solution. Usually the oxidation of the monomer is an irreversible process and takes place at higher positive potentials than that of the reversible redox reaction of the polymer. However, in the case of azines (e.g., 1-hydroxy-phenazine [96–98], methylene blue [99, 100], neutral red [101, 102]), reversible redox reactions of the monomers occur at less positive potentials and this redox activity can be retained in the polymer, i.e., the polymerization reaction that takes place at higher potentials does not substantially alter the redox behavior of the monomer. For instance, the catalytic activity of methylene blue towards the oxidation of biological molecules (e.g., hemoglobin) is preserved in the polymer [103].

A knowledge of the kinetics of the electrodeposition process is also of the utmost importance. It depends on the same factors mentioned above, although the role of the material and the actual properties of the electrode surface are evidently more pronounced. For example, the oxidation of aniline at Pt is an autocatalytic process. The specific interactions and the wetting may determine the nucleation and the dimensionality of the growth process. Two or more stages of the polymerization process can be distinguished. In the case of PANI it has been found
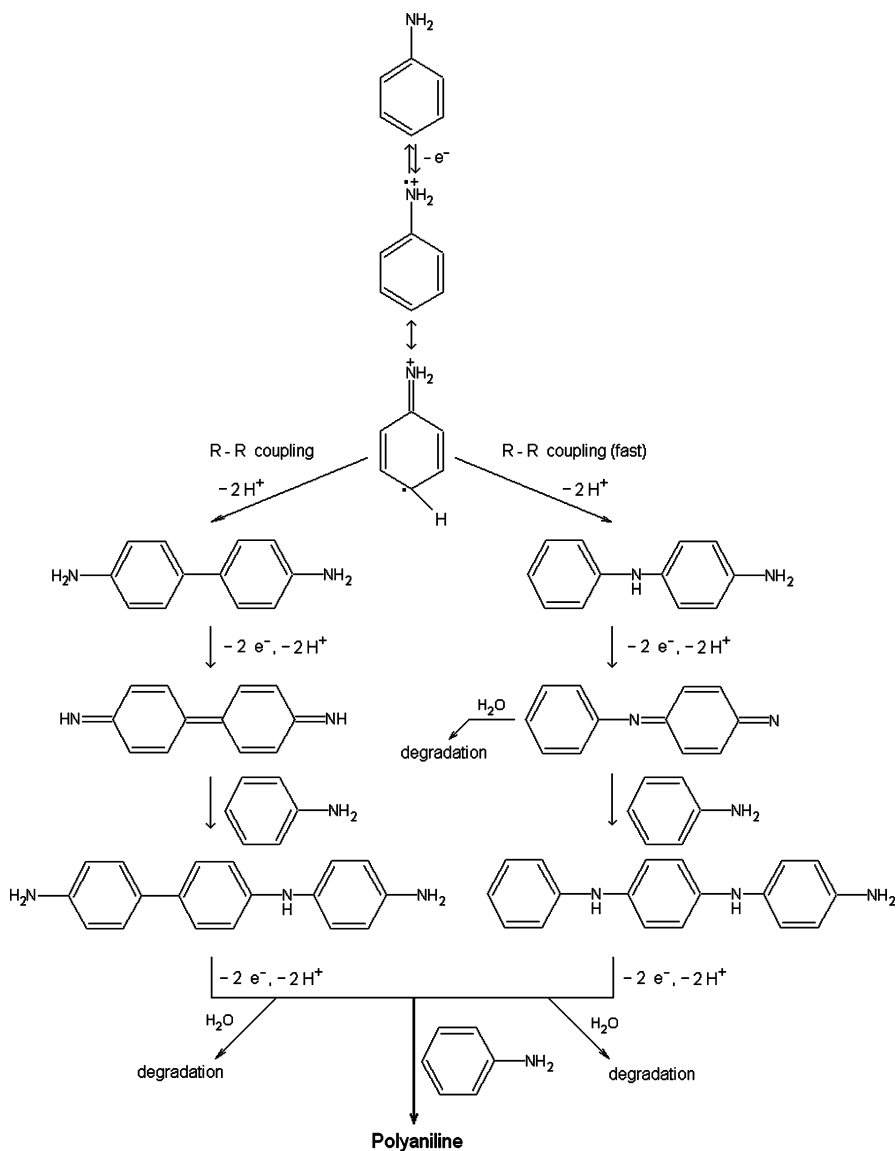
Fig. 4.1 The reaction scheme for the electropolymerization of aniline. (Reproduced from [49] with the permission of Elsevier Ltd.)

that initially a compact layer ($L \sim 200$ nm) is formed on the electrode surface via potential-independent nucleation and the two-dimensional (2-D, lateral) growth of PANI islands. At the advanced stage, 1-D growth of the polymer chains takes place with continuous branching, leading to an open structure [17, 21]. It is established that—in accordance with theory [104]—the density of the polymer layer decreases

with film thickness, i.e., from the metal surface to the polymer|solution interface. The very first stages of the electropolymerization were investigated using in situ FTIR, attenuated total reflection (ATR) and IR reflection absorption spectroscopy (IRRAS), which revealed that the mechanism of PANI formation is influenced by the deposition of oligomers, and the highest growth rate in cyclic electropolymerization occurs during the cathodic potential scan [44]. The film morphology (compactness, swelling) is strongly dependent on the composition of the solution, notably on the type of counterions present in the solution, and the plasticizing ability of the solvent molecules [31, 34, 38, 40, 45]. The effect of the counterions is illustrated in Fig. 4.2. The order of the growth rate depends on the nature of the anions (at the same positive potential limit and acidity) as follows: 4-toluenesulfonic acid (HTSA) > 5-sulfosalicylic acid (HSSA) > $HClO_4$. This may be assigned to the stabilizing effect of the larger anions, i.e., lesser cationic oligomers formed at the surface diffuse into the solutions due to the lower solubility of the salts (ion pairs). It has been established that BF_4^-, ClO_4^- and CF_3COO^- ions promote the formation of a more compact structure, while the use of Cl^-, HSO_4^-, NO_3^-, TSA^- and SSA^- results in a more open structure during electropolymerization [31, 38, 40, 45]. Another finding is that certain anions (Cl^-, HSO_4^-, ClO_4^-) also affect the apparent dissociation constant of PANI in its reduced form [105–107].

The formation of the polymer involves about 2 mol electrons, associated with 1 mol of aniline [27, 50–52, 108, 109]. The growth rate is proportional—except for during the early induction period—to the square root of the film volume, and it is first-order with respect to aniline concentration [41]. Due to the autocatalytic nature of the electropolymerization, the positive potential limit of cycling can be decreased after 2–10 cycles, which is a common practice used to avoid the degradation of the polymer due to the hydrolysis of the oxidized PANI (pernigraniline form) [28, 33, 110] (see Fig. 4.2). Although it is still debated, the appearance of the "middle peak" most likely reflects the occurrence of oxidative hydrolysis and degradation, and it can be assigned to the redox reaction of benzoquinone [49]. As well as the head-to-tail coupling that results in the formation of *p*-aminodiphenylamine, tail-to-tail dimerization (benzidine) also occurs; however, the latter is considered to be a minor dimer intermediate because the rate constant of dimerization for RR coupling that produces the former product (k is ca. 10^8 dm^3 mol^{-1} s^{-1}) is about 2.5 times higher than that for the tail-to-tail dimer [49]. The degradation process should be considered for other polymer films, but it can also be controlled electrochemically [84]. If the conditions are not carefully optimized, a mixed material containing electrochemically active and conducting as well as inactive and insulating parts is generally deposited on the surface [84]. It has been demonstrated that the current density is a crucial parameter in the synthesis of polypyrrole (PP) [72,85,87]. The structure of PP is dominated by one-dimensional chains at low current densities, while two-dimensional microscopic structures of the polymer are formed at high current densities [72, 85]. The structure substantially affects the conductivity of the polymer phase, the conductivity of the 2-D form is higher, and its temperature dependence is lower, which is of importance when this polymer is used for practical purposes. Detailed studies have shown that the more conductive 2-D islands are in-
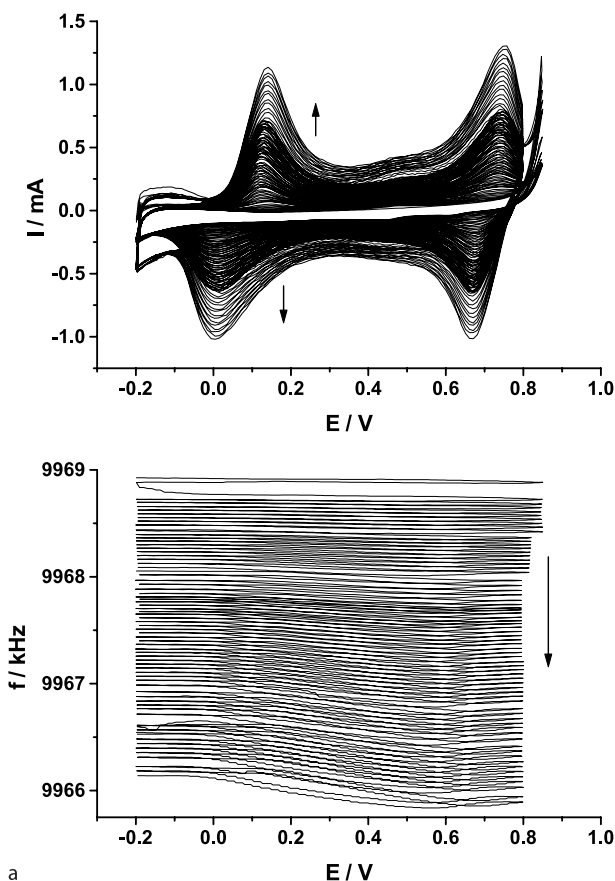
Fig. 4.2a–c The cyclic voltammograms and the simultaneously detected EQCM frequency changes during the electropolymerization of aniline at a platinum electrode. Sweep rate: $100 \, \text{mV s}^{-1}$. Solution composition: $0.2 \, \text{mol dm}^{-3}$ aniline in $1 \, \text{mol dm}^{-3}$ (From [40], reproduced with the permission of Elsevier Ltd.) **a** $HClO_4$

terconnected by short 1-D chain segments which act as tunneling barriers [85]. As described in Sect. 3.2.6.2, during the electropolymerization of polythionine films structural changes occur during film thickening [111].

It has also been demonstrated by scanning microscopies that film growth at sub-μm- or μm-structured substrates is not restricted to conductive substrate domains. Instead, after the film thickness has risen to the level of the surrounding insulator, lateral outward growth on the nonconductive part also occurs [98]. This is a phenomenon that should be taken into account in microtechnical applications.

Although the region close to the electrode surface exhibits a more or less well-defined structure, in general the polymer layer can be considered to be an amorphous material [17,21,22,86]. However, there are rare reports of crystalline structures too.
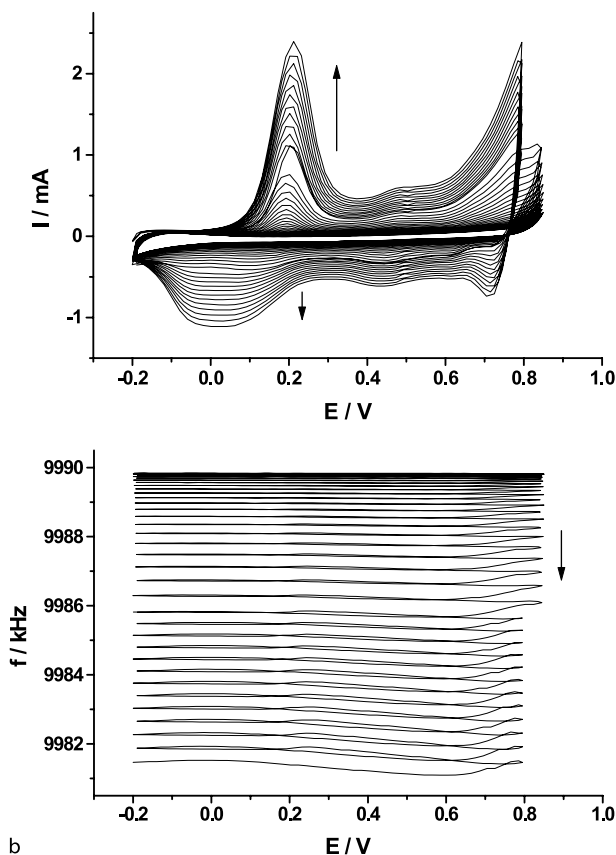
Fig. 4.2 (continued) **b** 4-toluenesulfonic acid

For instance, poly(*p*-phenylene) films obtained by the electrooxidation of benzene in concentrated H_2SO_4 emulsion show a highly crystalline structure [112, 113].

The conditions for polymerization were also found to be crucial in relation to polythiophene and polybithiophene films [58, 80, 84, 114–121]. The relatively high potential required for the oxidation prevents the use of many metallic substrates. The electrochemical oxidation of substituted thiophenes and thiophene oligomers yields conducting polymers, and these compounds can be electropolymerized at less positive potentials, so it is a good strategy to use these derivatives instead of thiophene (see Sect. 2.2.6). Another approach is the deposition of a thin polypyrrole layer that ensures the deposition of polythiophene on these substrates (e.g., Ti, Au) [115]. Interestingly, other polymers as well as copolymers and composites (see Chap. 2) can also be synthesized.

Although deaerated solutions are usually used during electropolymerization, it has been proven that the presence of oxygen increases the amount of poly(neutral red) deposited on the electrode [122].
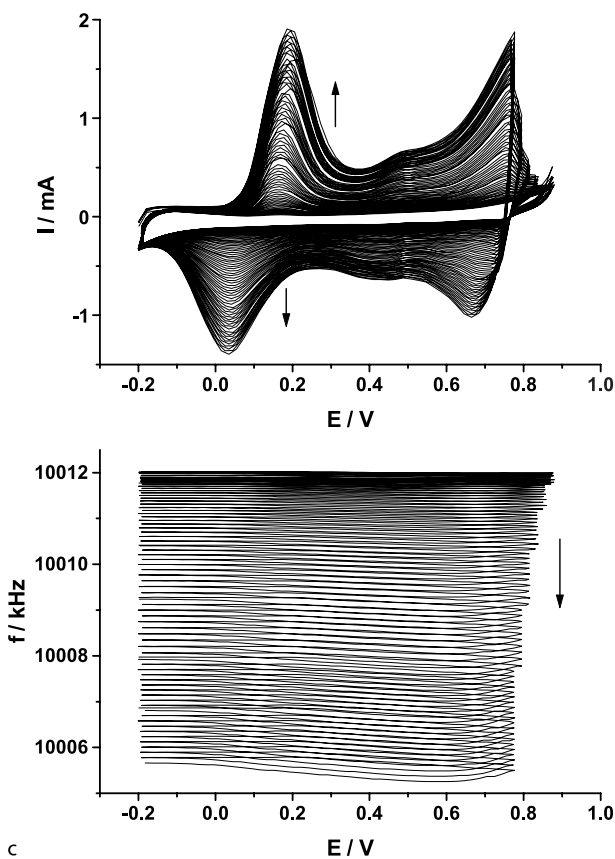
Fig. 4.2 (continued) **c** 5-sulfosalicylic acid

The choice of the supporting electrolyte is important not only in relation to the morphology and properties of the polymer; in several cases the formation and deposition of the polymer can only be achieved using special electrolytes.

For instance, poly(9-fluorenone) can be electropolymerized in boron trifluoride diethyl etherate (BFEE) media, while the polymerization takes place in $CH_2Cl_2|Bu_4NBF_4$, albeit with a much smaller rate, and polymer formation cannot be observed in acetonitrile$|Bu_4NBF_4$, as seen in Fig. 4.3 [123].

This effect has been explained by the interactions between the BFEE, which is a mid-strength Lewis acid, and the aromatic monomers. The interactions lower the oxidation potential of the monomers, and the catalytic effect of BFEE facilitates the formation of high-quality polymer films.

As well as the nature and concentration of the supporting electrolytes (monomer concentration, temperature etc.), organic additives also influence the morphology of the polymer film. Figure 4.4 shows SEM pictures of PANI prepared by the electropolymerization of aniline in the absence and presence of methanol, respectively.
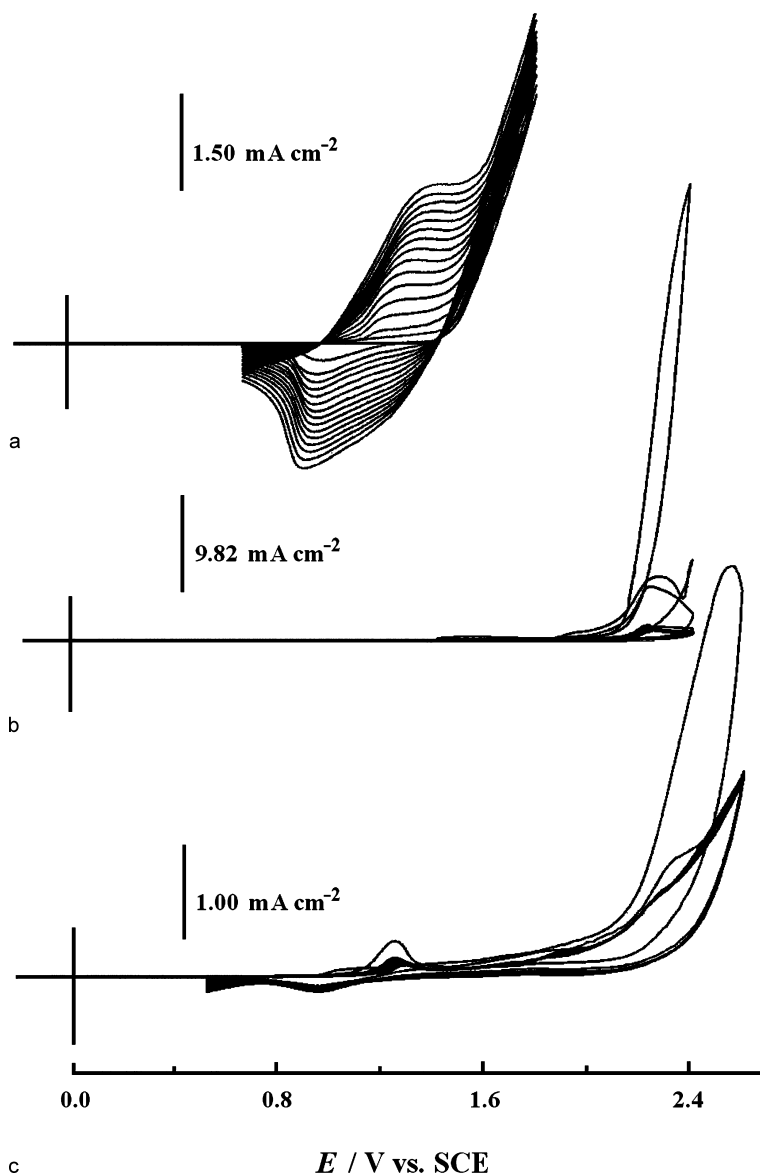
Fig. 4.3a–c Cyclic voltammograms of 3×10^{-2} mol dm^{-3} 9-fluorenone in **a** BFEE, **b** acetonitrile $+0.1$ mol dm^{-3} Bu$_4$NBF$_4$, and **c** CH$_2$Cl$_2 + 0.1$ mol dm^{-3} Bu$_4$NBF$_4$, respectively. Scan rate: 50 mV s^{-1}. (Reproduced from [123] with the permission of Elsevier Ltd.)

When alcohols were added to the electrolyte used in the electropolymerization, PANI nanofibers were formed with diameters of approximately 150 nm, which agglomerate into interconnected networks. This effect has been explained in terms of
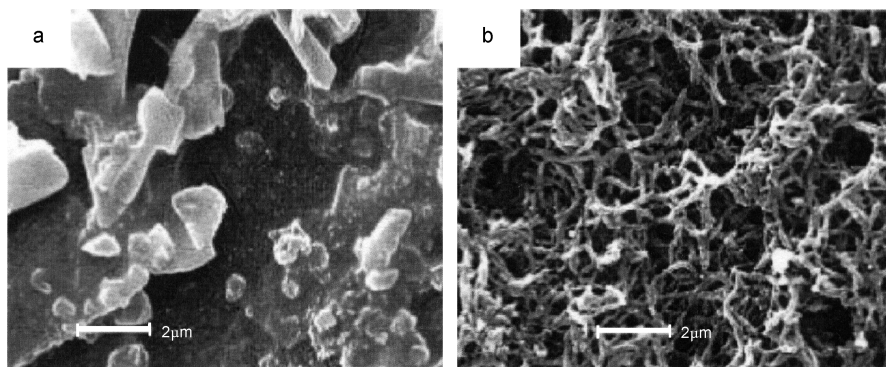
Fig. 4.4a,b Scanning electron microscopic pictures showing the effect of alcohols on the morphology of PANI films. The films were synthesized under potentiostatic conditions at 0.8 V vs. SCE from solutions containing $1\,mol\,dm^{-3}$ HCl and $0.2\,mol\,dm^{-3}$ aniline without (**a**) and with (**b**) $0.5\,mol\,dm^{-3}$ methanol. (Reproduced from [48] with the permission of Elsevier Ltd.)

interactions between the methanol molecules and the polyaniline chains; i.e., the PANI chains are wrapped by alcohol molecules due to intermolecular H-bonding, which is advantageous to the one-dimensional growth of the polymer [48].
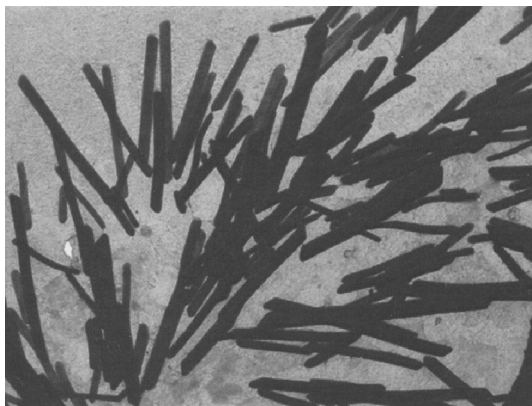
Rotation of the electrode during electrochemical polymerization has been shown to have a strong influence on the rate of formation of electrochemically polymerized films, and it affects the morphology and conductivity of the polymer. For instance, it has been demonstrated that $\Delta 4,4'$-di-cyclopenta [2.1-b; $3',4'$-b$'$]-dithiophene grows faster at higher rotation rates, and the morphology changes from fibrillar to globular structures. Both the electronic and ionic conductivities of the polymer increased by two orders of magnitude [124]. It is thought that the main effect of electrode rotation, when high monomer concentrations are used, is the removal of oligomers from the vicinity of the electrode, minimizing their precipitation. Consequently only the polymerization of the species grafted on the electrode surface takes place, which results in a better-quality polymer film. It should be mentioned that in other cases a drop in the deposition rate has been reported [125].

Ultrathin functional films can be prepared with finely adjusted film thickness and properties by a layer-by-layer (LbL) method. Such multilayers are fabricated by the alternated adsorption of anionic and cationic polyelectrolytes. These polyelectrolyte multilayers are self-compensated in terms of the charge; however, the introduction of redox ions such as $Fe(CN)_6^{4-}$ or $Os(bpy)_3^{3+}$ is also possible [126].

Higher electronic conductivity has been achieved by template synthesis using polycarbonate membranes [127], and this method has also been exploited to obtain nanostructures [83, 128].

Figure 4.5 shows a transmission electron micrograph of PANI nanotubes obtained by chemical oxidative polymerization and separated from a polycarbonate membrane. The polycarbonate template was removed by dissolving the samples in chloroform, and then by filtering the green precipitate. The rest of the polycarbon-

ate was removed by extraction using H_2SO_4 when the PANI nanotubes precipitate at the chloroform–acid interface [128].

Spectacular fractal patterns can be obtained by utilizing a needle-to-circle electrode configuration [79].

It is also possible to modify the deposited conducting polymer in order to change its electrical, optical and other properties. For instance, polyaniline film was modified by subsequent electrodeposition of diaminomethylbenzoate (Fig. 4.6) [10, 129]. As a comparison of the spectrum of PANI—where the absorbance related to the delocalized electrons at $\lambda > 600$ nm is clearly apparent—with the spectrum of the modified PANI shown in Fig. 4.7 reveals, the electronically conductive parent polymer can be transformed into a redox polymer. However, the electrochemical behavior, the color [10] and the conductivity [129] of the polymer during the modification procedure can easily be regulated, and so the required properties can be finely turned [10, 129].

Electropolymerization can be executed using droplets and particles immobilized on the surfaces of inert electrodes [130]. Water-insoluble monomers can be used for this purpose, and the electropolymerization is carried out in aqueous electrolytes. Microcrystals can be attached to platinum, gold or paraffin-impregnated graphite (PIGE) by wiping the electrode with a cotton swab or filter paper containing the material. Alternatively the electrodes can be covered with the monomer using an evaporation technique; i.e., the microcrystals are dissolved in appropriate solvents (e.g., tetrahydrofuran), and some drops of the solution are placed onto the electrode surface. After the evaporation of the solvent, a stable monomer layer remains on the surface. The attachment of microdroplets requires more skill. A $1-2\,\mu$l drop of monomer is placed on the electrode surface using a micropipette or syringe. If this electrode is carefully immersed into the aqueous solution, the droplet remains on the electrode. The surface tension of water, which is much higher than that of most organic liquids, plays an important role, but the difference in densities can also be controlled by varying the concentration of the electrolyte. A small "spoon" made from Pt plate can also be fabricated, which can be used to place the
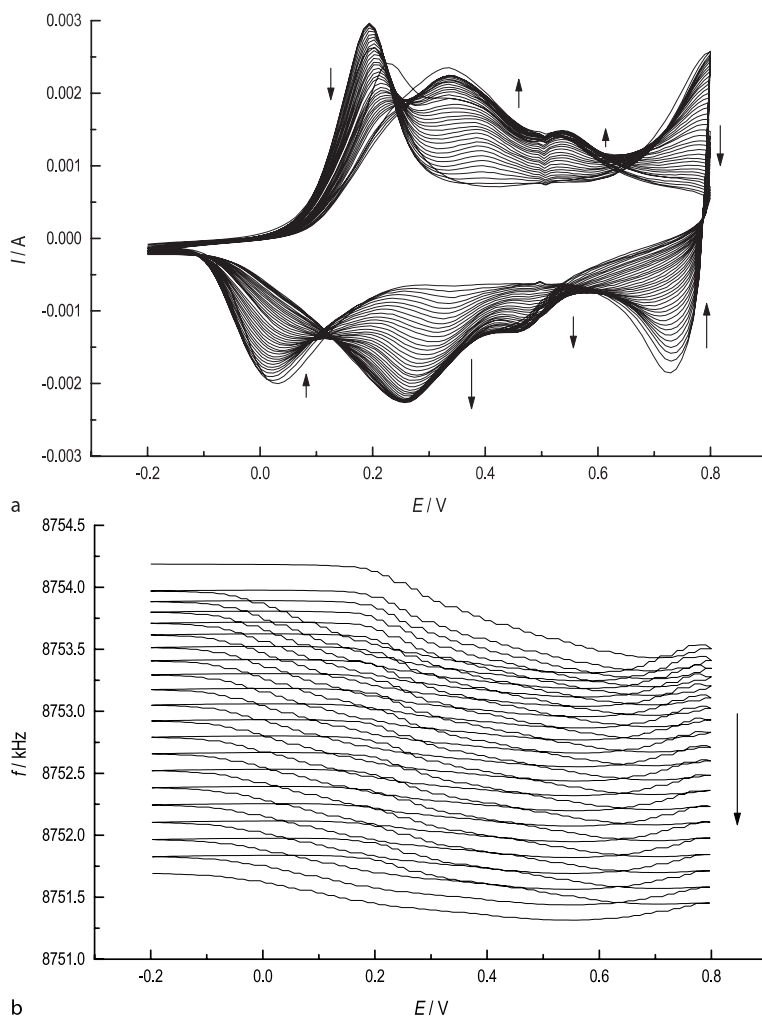
Fig. 4.6a,b Cyclic voltammograms (**a**) and the simultaneously obtained EQCM frequency changes (**b**) during the deposition of 3,5-diaminomethylbenzoate onto PANI film on Au. Solution composition: $0.13 \, mol \, dm^{-3}$ diaminomethylbenzoate and $2 \, mol \, dm^{-3}$ H_2SO_4. Scan rate: $100 \, mV \, s^{-1}$. (Reproduced from [10] with the permission of Elsevier Ltd.)

organic droplet in this small vessel. Figure 4.8 shows the electropolymerization of 3-methylthiophene droplets attached to a PIGE in the presence of an aqueous solution containing $0.5 \, mol \, dm^{-3}$ $LiClO_4$ [131].

The cyclic voltammograms and the changes that occur to them during repetitive cycling are similar to those of 3-methylthiophene oxidation in acetonitrile. When a platinum electrode is used, the color change (red–blue) due to the redox transformation of poly(3-methylthiophene) is easily visible. A visual inspection also reveals that the electropolymerization reaction starts at the three-phase junction, as theoret-
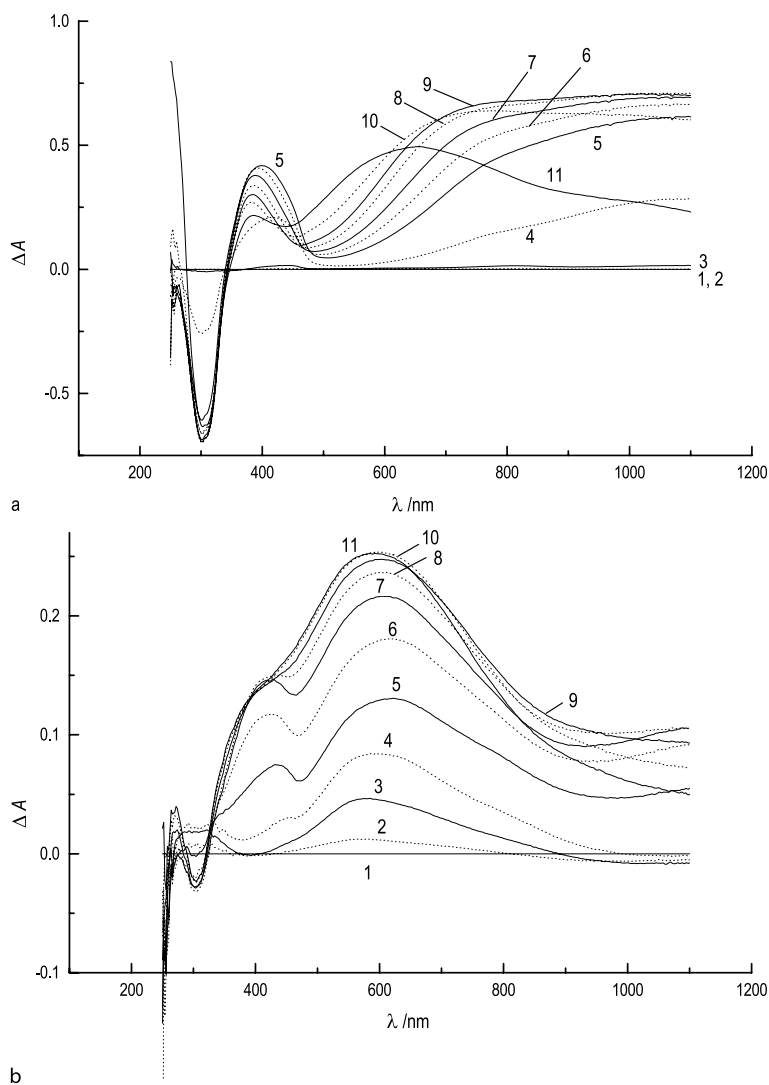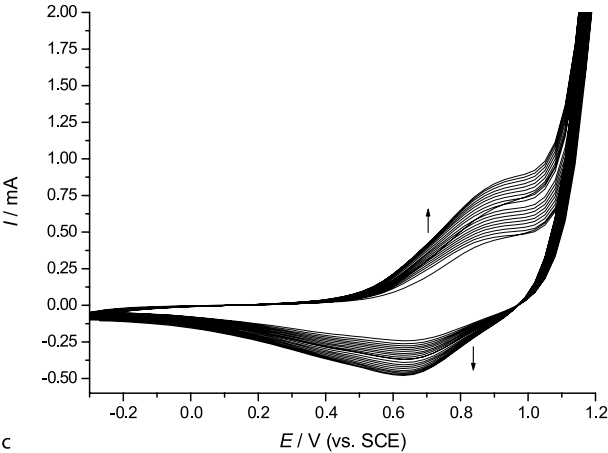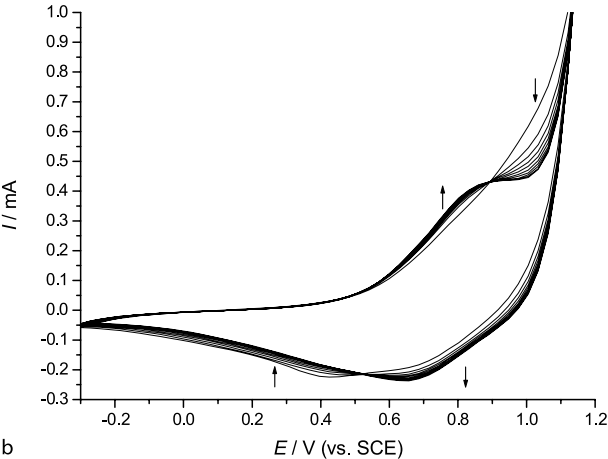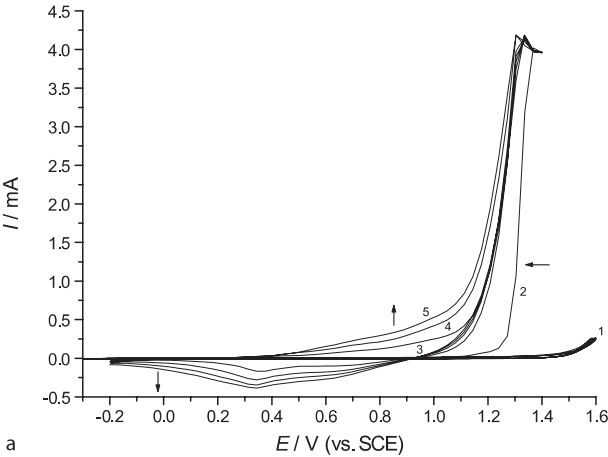
a

b

Fig. 4.7a,b The subtracted UV–Vis–NIR spectra of PANI (**a**) and modified PANI (**b**), respectively, obtained in situ at different potentials: (*1*) -0.35 V; (*2*) -0.25; (*3*) -0.15; (*4*) -0.05; (*5*) 0.05; (*6*) 0.15; (*7*) 0.25; (*8*) 0.35; (*9*) 0.45; (*10*) 0.55; and (*11*) 0.65 V. Solution: 1 mol dm^{-3} H$_2$SO$_4$. $\Delta A = \text{Abs}(E) - \text{Abs}(E = -0.35$ V). (Reproduced from [10] with the permission of Elsevier Ltd.)

Fig. 4.8a–c Consecutive cyclic voltammetric curves obtained for 3-methylthiophene droplets attached to a paraffin-impregnated graphite electrode in the presence of an aqueous solution containing 0.5 mol dm^{-3} LiClO$_4$. Cycles: **a** 1 to 4 (*curves 2–5*); **b** 5–14; **c** 15–24 and 25–34. *Curve 1* shows the background current of the uncoated PIGE. Scan rate: 100 mVs^{-1}. (Reproduced from [131] with the permission of Elsevier Ltd.)

a

b

c