

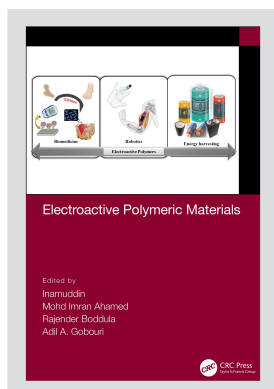
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## Electroactive Polymeric Materials

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### Conductive Electroactive Polymers in Electrocatalysis and Sensing Applications

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# 9 Conductive Electroactive Polymers in Electrocatalysis and Sensing Applications

*Achi Fethi, Benmoussa Fateh, Henni Abdellah,  
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## 9.1 INTRODUCTION

Most polymers are good electrical insulators and any electrical conductivity in a polymer was initially considered to be an undesirable phenomenon. By the 1970s, excellent conductivity properties in certain polymers had been discovered, which allowed the development of a new class of materials called intrinsically electronically conductive polymers (PCEIs) (Heeger, 2001). This class of conductive polymers has become increasingly important, thanks to the awarding of the Nobel Prize for chemistry in 2000 to A. Heeger, A. MacDiarmid, and H. Shirakawa, following the discovery of the first conductive polymer: polyacetylene (PA) in 1977 (Shirakawa *et al.*, 1977). Therefore, many conjugated polymers that combine excellent conductivity and good stability have been developed (Li *et al.*, 2021; Balint, Cassidy, and Cartmell, 2014; Wang, Y. *et al.* 2020). Biosensors based on conducting polymers are miniaturizable and have specific electroactive and mechanical characteristics. The potential benefits of these instruments is their low-cost and detection at trace levels, which potentially leads to improved therapy access (Tandon *et al.*, 2020). Cancer, which has

a high death rate, has become more common worldwide. Early detection, prognosis, and recovery management with robust and non-invasive techniques will potentially be the focus in the future (Wang, L. *et al.* 2017).

Electrochemical biosensors could be a good candidate for cancer theranostics due to their advantage of ultra-sensitivity, high selectivity, low-cost, fast readability and simplicity. In addition, electrochemical biosensors are simpler to miniaturize and mass produce, which makes them more suitable for point-of-care applications (Zhang, W. *et al.*, 2020). The use of polymers as immunosensor materials has been encouraging, especially for cancer biomarkers detection, such as carcinoembryonic antigen (CEA) (Tohill, 2009, Tahalyani, Rahangdale, and Khushbu, 2016). Nanostructured conducting polymers, such as polyaniline (PANI), polythiophene (PTh), and polypyrrole (Ppy) are strongly favored to improve cancer biomarkers immunosensor properties.

This chapter describes the utilization of conducting polymers in sensing applications and highlights their benefits for trace-level monitoring of organic compounds and for monitoring cancer biomarkers. The electrodeposition methods for conductive polymers to obtain thin films for sensing interfaces will be reviewed. In addition, the use of biopolymers and nanocomposites including carbon materials is discussed.

## 9.2 CONDUCTING POLYMERS FOR ELECTROCHEMICAL SENSING APPLICATIONS

The determination of chemical compounds by electrochemical sensing platforms offers real-time monitoring and on-site analysis. The analytical performance of electrochemical sensors strongly depends on the nature of the added nanomaterials (Bensana and Achi, 2020). In addition to their high conductivity, which provides the sensitivity of the electrochemical sensors, conducting polymers offer a rigid, highly stable, and suitable microstructure for immobilizing other biomaterials (Lange, Roznyatovskaya, and Mirsky, 2008) (Janata and Josowicz, 2003).

This section will discuss the effect of this type of nanomaterials on the analytical characteristics of electrochemical sensors for monitoring phenols and cancer biomarkers.

### 9.2.1 CONDUCTING POLYMERS: SYNTHESIS AND APPLICATIONS

#### 9.2.1.1 Polyaniline

PANI is a low-cost conductive polymer, which is easily prepared, has tunable properties, high capacitance values, and enhanced chemical stability (Bhadra *et al.*, 2009). PANI's electric conductivity varies from 10 to 100 S/cm, which makes it a suitable material to construct immunosensors (Epstein, 2007). For instance, a novel conductive and protein-resistant redox PANI-polythionine hydrogel (PANI-PThi gel) that successfully detected tumor markers, such as carcinoma-125 (CA125) with LOD= 0.00125 U/mL (Zhao, L. and Ma, 2018). In addition, electro-polymerized PANI on the surface of a glassy carbon electrode (GCE) forms thin layer modified with functionalized carbon nanotubes (CNTs) for the determination of prostate-specific antigen (PSA) (0.5 pg/mL). This strategy is fast and promotes high electrical conductivity and demonstrates good mechanical properties of thin film-based immunosensing platforms (Assari *et al.*, 2020). Of interest, mixing PANI nanowires with antifouling materials, such as zwitterionic poly(carboxybetaine methacrylate) is stable and displays an ultra-sensitive response for CEA detection in blood serum (LOD=3.05 fg/mL) (Wang, J. and Hui, 2019).

#### 9.2.1.2 Polypyrrole

Ppy is a highly conductive polymer with good stability in oxidized states, its high water solubility and excellent catalytic activity mean that it can be used in constructing chemical sensors using one-step electrodeposition methods. However, compared with PANI, the cost of pyrrole monomers is higher than that of aniline, which means it is less desirable for certain applications (MacDiarmid,

1997). Employing PPy as a conductive polymer significantly improves the electron transfer rate in the recognition process and promotes the integration of high quantities of antibodies. Therefore, Moon *et al.* (2014) developed an immunosensor platform based on direct integration of PSA into PPy electropolymerized three-dimensional nanowire. This method enhanced the molecular interaction with trace-level PSA detection (0.3 fg/mL) and a wide linear range (from 10 fg/mL to 10 ng/mL) (Moon *et al.*, 2014). Similarly, Pei *et al.* (2019) obtained a limit of detection for alpha-fetoprotein (AFP) of 17 fg/mL using PPy nanotubes (PPyNTs) with platinum nano dendrites (PtNDs) functionalized with molybdenum disulfide (MoS<sub>2</sub>) (Pei *et al.*, 2019).

Furthermore, Truong *et al.* (2011) assembled a sensitive immunosensor by screen printing carbon ink based PPy carboxylic acid copolymer to allow HCG antibody immobilization through the COOH groups. The polymer film showed high conductivity and strong biocompatibility with a limit of detection of 2.3 pg/mL (Truong *et al.*, 2011).

A sandwich-type electrochemical immunosensor using functionalized PPy microspheres that could simultaneously monitor two tumor markers (e.g., LOD= 0.40 pg/mL and 0.33 pg/mL) for CEA and AFP, respectively has been developed (Zhao J. *et al.*, 2016a).

### 9.2.1.3 Polythiophene

PTh polymer has abundant carboxyl groups, which improves the electroanalytical performance of immunosensors. For instance, detecting Interleukin 1 $\beta$  in human serum and saliva by ITO modified PTh displays a wide linear range from 0.01–3.00 pg/mL with LOD= 3 fg/mL (Aydın, Aydın, and Sezgintürk, 2018). In addition, PTh derivatives, such as epoxy-substituted-PTh polymer (PThiEpx) has several epoxy groups that facilitate its binding to the NH<sub>2</sub> antibody groups, and therefore, effectively immobilizes Interleukin-1 alpha antibodies (Table 9.1) (Aydın, 2019).

### 9.2.1.4 Poly-amidoamine

This type of conducting polymer has multiple chain ends and is a highly branched dendritic macromolecule. The unique surface properties make it a suitable material for electrochemical sensing interfaces. Therefore, PAMAM can be easily combined with ferric oxide (Fe<sub>3</sub>O<sub>4</sub>) magnetic nanoparticles (Yin *et al.*, 2011), or with CoTe quantum dots (CoTe QDs) composite (LOD=1 nM) in milk (Yin *et al.*, 2010). Similarly, a BPA sensor based on PAMAM dendrimers displays a low detection limit toward BPA detection (LOD=0.5 nM) (Yin *et al.*, 2010).

### 9.2.1.5 Polymerized Ionic Liquids and Other Conducting Polymers

Unlike conductive polymers, where mobility is usually due to the  $\pi$ -conjugated electrons along the polymer chain, this type of polymer has high ionic conductivity without ion doping. Polymerized ionic liquids provide excellent adaptability with various forms of ionicity in polymer chains (Eftekhari and Saito, 2017). Therefore, very high stability of 95% for 2 months for the detection of Bisphenol A was attained using a polymerized ionic liquid (Ma *et al.*, 2014). Moreover, Wang *et al.* (2018) constructed a BSA sensor using a polymerized ionic liquid functionalized with graphene oxide (Go) that displays a high sensitivity of 0.2629  $\mu$ A/ $\mu$ M (Wang, Y. *et al.*, 2018). In addition, a new strategy based on the combination of cetyltrimethylammonium bromide with multi-walled carbon nanotubes (MWCNTs) using an electropolymerization technique onto the surface of pencil graphite electrode. The obtained sensor was highly sensitive toward BPA detection (84.6  $\mu$ A/ $\mu$ M) and provides a lower detection limit (LOD=134 pM) (Bolat, Yaman, and Abaci, 2018).

## 9.2.2 SENSORS BASED ON CONDUCTING POLYMERS FOR THE DETECTION OF PHENOLIC COMPOUNDS

As previously described, PANI is a low-cost and biocompatible polymer with excellent thermal and mechanical properties. The use of PANI as a material modifier with a silver nanowire (AgNWs)

**TABLE 9.1**  
**Electroanalytical performance of conducting polymer-based sensors for cancer detection**

Conductive polymer	Immunosensor composition	Cancer biomarker	Technology	Linear range	LOD	Reference
<b>PANI</b>	GCE/COOH-MWCNTs/PANI/AuNPs/anti-PSA/BSA	PSA	DPV	1.66 ag/mL– 1.3 ng/mL	0.5 pg/mL	(Zhao, J. <i>et al.</i> , 2016b)
	Pt/PANI-Au/N,S-GQDs/anti-CEA	CEA	EIS	0.5–1000 ng/mL	0.01 ng/mL	(Ganganboina and Doong, 2019)
	GCE/rGO/MoS <sub>2</sub> @PANI BSA/anti-CEA	CEA	CV	0.001–80 ng/mL	0.3 pg/L	(Song <i>et al.</i> , 2020)
	anti-CEA/polyCBMA/PANI/GCE	CEA	DPV	1 × 10 <sup>-14</sup> g/mL– 1 × 10 <sup>-10</sup> g/mL	3.05 fg/mL	(Wang J. and Hui, 2019)
<b>PPy</b>	ITO AB/EpxS-PPyr Composite/IL6 receptor/BSA	IL6	EIS	0.01–50 pg/mL	3.2 fg/mL	(Aydm, Aydm, and Sezginürk, 2021)
	BSA/anti-PSA doped Ppy NWs	PSA	DPV	10 fg/mL–10 ng/mL	0.3 fg/mL	(Moon <i>et al.</i> , 2014)
	BSA/Anti AFP/Pt NDs/PDDA/MoS <sub>2</sub> @PPyNTs/GCE	AFP	Amp.	50 fg/mL–50 ng/mL	17 fg/mL	(Pei <i>et al.</i> , 2019)
	CE/PPy–PPa copolymer/anti-HCG	HCG	EIS	0–1000 pg/mL	2.3 pg/mL	(Truong <i>et al.</i> , 2011)
	BSA/anti-PSA/AgPt@PtHNS/PPyNS/GCE	PSA	Amp.	0.0005–50 ng/mL	120.3 fg/mL	(Wang, P. <i>et al.</i> , 2020)
<b>PTh</b>	PPy@signal tags@Au NPs/Ab2/BSA/Ab1/AuNPs/rGO/GCE	AFP CEA	DPV	1 pg ml <sup>-1</sup> - 50 ng ml <sup>-1</sup>	0.33 pg mL <sup>-1</sup> 0.40 pg mL <sup>-1</sup>	(Zhao, J. <i>et al.</i> , 2016a)
	ITO/PThiEpx/anti-IL 1α	IL -1α	EIS	0.01 pg/mL- 5.5 pg/mL	3.4 fg mL <sup>-1</sup>	(Aydm, 2019)
	ITO/Polymer P3-TMA /anti-IL-1β/BSA	IL-1β	EIS	0.01–3 pg/mL	3 fg mL <sup>-1</sup>	(Aydm, Aydm, and Sezginürk, 2018)

composite can detect p-nitrophenol at a nano level scale (LOD=52 nM) (Zhang, C. *et al.*, 2017). PANI can be used to modify the surface of an ITO electrode for the sensing of p-nitrophenol (Roy *et al.*, 2013). Poly(vinyl ferrocenium) perchlorate (PVF<sup>+</sup>) is a conducting polymer that acts as an electron transfer mediator. As shown by Kavanoz and Pekmez (2012), its combination with PANI provided a thin film that promoted wide linear concentration ranges for the detection of hydroquinone from 0.16  $\mu\text{M}$  to 115 mM (Table 9.2).

Wan *et al.* (2016) demonstrated that the sensitivity of a Bisphenol A sensor could be enhanced (1.14  $\mu\text{A}/\mu\text{M}$ ) using electrochemical deposition of Pt nanoclusters on a GCE surface modified with a PTh-MWCNT composite (Wan *et al.*, 2016). Bianchini *et al.* (2014) electrodeposited poly(3,4-ethylenedioxythiophene) on the surface of a Pt electrode using sodium poly(styrene-4-sulfonate) as a surfactant. The method formed a thin film and the sensing interface could determine caffeic acid in wine from 10.00 nM to 6.50 mM (Bianchini *et al.*, 2014). Similarly, the direct electropolymerization of poly(3,4-ethylenedioxythiophene) on the surface of a GCE could detect BPA at a micro level (Mazzotta, Malitesta, and Margapoti, 2013).

### 9.2.3 CONDUCTING POLYMERS AS SENSOR MODIFIERS FOR CANCER DETECTION

The incorporation of PANI decorated gold nanowires via thiol bonding with graphene QDs can anchor anti-CEA and acts as a probe for amplifying the electrochemical current signal. This label-free immunosensor exhibits a wide linear range from 0.5 to 1000.0 ng/mL with a LOD of 0.01 ng/mL (Ganganboina and Doong, 2019). Functionalizing PANI with transition metal dichalcogenides is a method to obtain nanocomposites with a high specific surface area and a good loading ability for antibodies. For instance, an immunosensor for detecting CEA at pico level concentration (0.3 pg/mL) was constructed using PANI functionalized molybdenum disulfide (MoS<sub>2</sub>) mixed with reduced graphene oxide (rGO) (Ganganboina and Doong, 2019). Another electrochemical immunosensor for detecting Interleukin 6 with acetylene black and epoxy-substituted-PPy was constructed (Table 9.2). The nanocomposite deposited on an ITO electrode displayed good biocompatibility and a stable response with a low detection limit (3.2 fg/mL) (Aydın, Aydın, and Sezgintürk, 2021).

### 9.2.4 CONDUCTING POLYMER-BASED CARBON NANOCOMPOSITES

The use of polymer nanocomposites is a suitable approach to improve the performance of polymers, and graphene is possibly the most promising nanofiller. Currently, the chemical synthesis of Go from graphite (GR) is a common method to obtain a layered material with more functional groups (Paredes *et al.*, 2008, Bourlinos *et al.*, 2003, Niyogi *et al.*, 2006). The groups are hydrophilic and good interfacial linkers, which improves polymer incorporation (Madhad and Vasava, 2019).

The use of conducting polymers to construct an efficient sensing platform are essential. Especially, when using molecular imprinting polymers (MIPs) techniques to assemble various graphene materials, such as GR, Go, or rGo (Liang *et al.*, 2017). The use of a graphene nanosheet and poly(4-vinylpyridine) material as electrode modifiers offers sensitive detection of catechol and provides good stability (99% 2 months) with high sensitivity (580  $\mu\text{A}/\mu\text{M}$ ) (Tehrani, Ghadimi, and Ab Ghani, 2013).

To enhance the electron transfer in the electrochemical oxidation of hydroquinone, Kavanoz and Pekmez (2012) synthesized a polydopamine-coated graphene sheets decorated with Ag. The catechol sensor displayed a wide linear range (from 0.5 to 240.0  $\mu\text{M}$ ) and a detection limit of 0.1  $\mu\text{M}$ . Tan *et al.* (2016) prepared graphene quantum dots (GQDs) dropped onto the GCE surface followed by electropolymerization of pyrrole to obtain a PPy film. This method enhanced water solubility and minimized the interface resistance between aqueous solutions and the graphene interface.

**TABLE 9.2**  
**Electrochemical sensors based conductive polymers for the detection of phenolic compounds**

E-Matrix/Electrode	Sensitivity	L.R.	L.O.D.OD	pH	Stability (%)	Reference
NiTPPS/MWCNTs-Nafion/GCE	0.142 $\mu\text{A}/\mu\text{M}$	0.05–50 $\mu\text{M}$	15 nM	7.2	N.R.	(Liu <i>et al.</i> , 2011)
Poly(CTAB)/MWCNTs/PGE	84.6 $\mu\text{A}/\mu\text{M}$	2 nM–0.808 $\mu\text{M}$	0.134 nM	5.0	N.R.	(Bolat, Yaman, and Abaci, 2018)
MIPPy/GQDs/GCE	1,1716 $\mu\text{A}/\mu\text{M}$	0.1–50 $\mu\text{M}$	40 nM	7.0	95% 15 days	(Tan <i>et al.</i> , 2016)
PBPIDS/GCE	0.2008 $\mu\text{A}/\mu\text{M}$	10 nM–10 $\mu\text{M}$	8 nM	8.0	95% 2 months	(Ma <i>et al.</i> , 2014)
Pyrogallol red/CPE	0.623 $\mu\text{A}/\mu\text{M}$	10–120 $\mu\text{M}$	18 nM	7.4	N.R.	(Ganesh <i>et al.</i> , 2018)
Gs-P4VP/GCE	660 $\mu\text{A}/\mu\text{M}$	0.1–10 $\mu\text{M}$	8.1 nM	2.5	99% 2 months	(Tehrani, Ghadimi, and Ab Ghani, 2013)
PVF <sup>-</sup> -PANI/Pt	0.83 $\mu\text{A}/\text{mM}$	0.16 $\mu\text{M}$ –115mM	49,4 nM	4.0	65% 40 days	(Kavanoz and Pekmez, 2012)
GO-poly (NPBimBr)/GCE	0.2629 $\mu\text{A}/\mu\text{M}$	0.2–10 $\mu\text{M}$	17 nM	7.0	N.R.	(Yanying Wang <i>et al.</i> , 2018)
PDNPH/AGCE	1.19 $\mu\text{A}/\mu\text{M}/\text{cm}^2$	20–250 $\mu\text{M}$	0,76 $\mu\text{M}$	7.0	95% 2 weeks	(Lopa <i>et al.</i> , 2017)
MIPs/Go/GCE	1.295 $\mu\text{A}/\mu\text{M}$	4 nM–10 $\mu\text{M}$	0,5 nM	6.0	98,6% 10 days	(Liang <i>et al.</i> , 2017)
AgNWs-PANI/GCE	1.032 $\mu\text{A}/\mu\text{M}$	0.6–32 $\mu\text{M}$	52 nM	7.0	87% 20 days	(Zhang <i>et al.</i> , 2017)
PAMAM/Fe <sub>3</sub> O <sub>4</sub> /GCE	N.R.	0.01–3.07 $\mu\text{M}$	5 nM	7.0	86% 30 days	(Yin <i>et al.</i> , 2011)
PAMAM/CoTeQDs/GCE	59.27 nA/ $\mu\text{M}$	0.013–9.89 $\mu\text{M}$	1 nM	8.0	72% 35 days	(Yin <i>et al.</i> , 2010)
PAMAM-AuNPs-SF/GCE	0.4455 $\mu\text{A}/\mu\text{M}$	1 nM – 1.33 $\mu\text{M}$	0,5 nM	8.0	91,4% 2 weeks	(Yin <i>et al.</i> , 2010)
PANI-PVSA/ITO	1.5 mA/mM	N.R.	1 $\mu\text{M}$	7.0	45 days (shelf-life)	(Roy <i>et al.</i> , 2013)

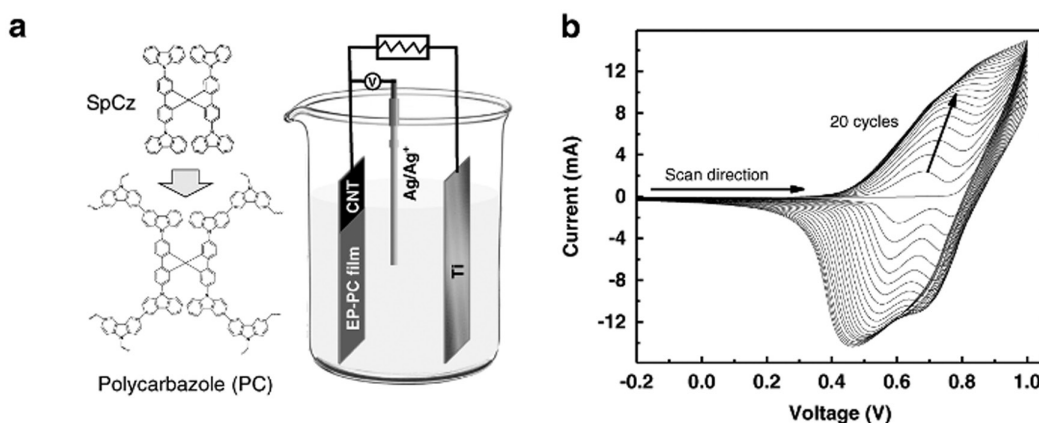
### 9.3 ELECTRODEPOSITION METHODS FOR CONDUCTIVE POLYMERS

Electropolymerization can be defined as an electrochemical process for manufacturing a polymer film on a substrate, which is composed of a working electrode, from a solution that contains the monomer, the solvent, and the supporting electrolyte. These will be incorporated into the polymer during the process as a dopant ion. Electrochemical syntheses are carried out in aqueous or organic solvents, using assemblies with three electrodes: a working electrode that oxidizes the polymer; a reference electrode to control; and a counter electrode that allows the passage of current (Figure 9.1(a)). The electropolymerization process involves the transfer of electrons, in either direction, between the substrate and the monomer in solution (Berkes, Bandarenka, and Inzelt, 2015). It is the charged monomer that then allows the polymerization reaction to take place.

Many electrochemical techniques, such as cyclic voltammetry (Choo *et al.*, 2020, Samukaite-Bubniene *et al.*, 2021), photocurrent spectroscopy (Walsh *et al.*, 2013), electrochemical impedance spectroscopy (Olean-Oliveira, Oliveira Brito, and Teixeira, 2020), or electrochemical quartz–crystal microbalance (Zhao, M. *et al.* 2021) have been applied for the deposition of the polymer onto the surface of the anode. The quality of an electrochemically prepared polymeric film depends on many factors (Mello and Mulato, 2018). The most commonly employed electrochemical methods for forming polymer films from a monomer solution are cyclic voltammetry, chronopotentiometry, or chronoamperometry. As previously described, PTh and its derivatives (Contreras-Herrera *et al.*, 2018; Rajendran *et al.*, 2021), PANI (Korent *et al.*, 2020), and PPy (Rakhrour *et al.*, 2021) are among the most conductive polymers used in electrochemical polymerization.

#### 9.3.1 POTENTIODYNAMIC ELECTROPOLYMERIZATION

These methods allow the very precise control of the morphology of the polymer, and the mass and thickness that is deposited. Cyclic voltammetry is useful for observing the progression of the electrochemical reaction and often displays useful information about the polymerization method and for the development and characterization of polymers (Babaiee, Pakshir, and Hashemi, 2015) (Figure 9.1(a)). It consists of a continuous potential sweep that varies with time. The result is the appearance of the oxidation or reduction reactions of the electroactive species in solution, possibly



**FIGURE 9.1** Showing: (a) setup of a three-electrode electrochemical cell for the electropolymerization process of polycarbazole; (b) CV profiles of the electropolymerization process of polycarbazole recorded for 20 scan cycles.

(From Zhou *et al.* 2020. With permission.)



the adsorption of the species that depends on the potential, and a capacitive current due to the charge of the double layer. In general, polymers are characterized by large waves of oxidation and reduction. During polymerization, oxidation is followed by chemical coupling rather than reduction. Therefore, each oxidation peak is not systematically coupled with a reduction peak.

Polymerization and deposition of polymer films are characterized by the increase in peak currents of oxidation and reduction of the monomer during successive sweeping (Figure 9.1(b)) and the development of redox waves. Polymers have a lower potential than the oxidation of the monomer (Zhou *et al.*, 2020). The PANI film obtained by potential cycling is very adherent to the surface of the electrode (Holze, 2017); this method makes it possible to monitor the redox activity of the deposited polymer because the first redox couple of PANI is constantly monitored during cycling. Therefore, polymerization can be stopped when the voltammetric characteristics of the polymer formed are optimal, the disadvantage of the cycling method is that a large part of the deposition time corresponds to potentials where there is no polymerization; this explains why the yield of this method is lower than that of the other two.

### 9.3.2 POTENTIOSTATIC ELECTROPOLYMERIZATION

Synthesis in the potentiostatic mode can be carried out at a single potential or in successive stages at different potentials and allows a thin and homogeneous film to be obtained (Patois *et al.*, 2011). This method consists of applying a constant potential ( $E$ ) to a working electrode and measuring the variation in the current as a function of time (Ruiz *et al.*, 2004). The applied potential is suitable for the oxidation of the monomer used, which generates oxidized monomer species that can be coupled to the surface of the working electrode. It is generally accepted that the potentiostatic method avoids the effects of overoxidation, because the oxidation potential is strictly controlled; in addition, it is very effective when preparing thick films over a short time. However, the reduction due solely to the binding of the monomer to the PANI chain during potentiostatic deposition is incomplete (Cui, Su, and Lee, 1993). This leads to the buildup of residual oxidized PANI and hydrolysis products in the film.

### 9.3.3 GALVANOSTATIC ELECTROPOLYMERIZATION

The choice of the applied current ( $i$ ) in chronopotentiometry makes it possible to obtain either thin and homogeneous films (i.e., low current densities), or nodular structures (i.e., high current densities). The galvanostatic method consists of applying a fixed current to a working electrode and the potential is recorded as a function of time. The direct relationship between the time of electrosynthesis and the thickness of the polymer that is produced on the electrode surface is an advantage of galvanostatic polymerization (Jiang *et al.*, 2017). The application of a constant current allows a linear increase in the load over time when the current losses in the cell and the phenomena at the interfaces are neglected.

The flexibility of the used potential over time to adapt to variations in solution concentrations or to the passivity of the electrode is considered to be the second advantage of this polymerization method. Therefore, unlike the potentiostatic method, the potential drop at the electrode (i.e., with a large thicknesses of the polymer) is controlled by galvanometry to achieve the required current density. Therefore, galvanostatic polymerization is more suitable than potentiostatic polymerization for the preparation of thick films and especially with materials of low conductivities (Uang and Chou, 2002).

## 9.4 BIOPOLYMER-BASED CONDUCTING NANOCOMPOSITES

Biopolymers are in increasing demands due to their biodegradability, low-cost and versatility, especially due to the increasing harmful effects of non-biodegradable plastics (Touati *et al.*, 2011,

Zembouai *et al.*, 2013). Therefore, the increased use of green polymers (Zembouai *et al.*, 2016), such polylactic acid (PLA) or poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and they are produced at an industrial scale (Zembouai *et al.*, 2018).

#### 9.4.1 POLYLACTIDE

PLA is an aliphatic polyester obtained via the direct polycondensation of lactic acid monomers or via the ring opening polymerization of cyclic lactide dimers using a metal catalyst (Zaidi *et al.*, 2013). There are several different types of PLA, which have slightly different characteristics but are similar in that they are produced from a renewable resource. PLA is transparent with a high gloss (60%–110%) and displays good water and oxygen barrier properties and high oil resistance. The melting temperature ( $T_m$ ) of PLA is generally in the range of 150°C–190°C, depending on PLA grades and their molecular weight (Zaidi *et al.*, 2010).

The mechanical proprieties of PLA are similar to polystyrene (PS) and polyethylene terephthalate (PET). The tensile modulus and tensile strength of PLA are in the range of 3,000–4,000 MPa and 50–60 MPa, respectively. However, PLA is a brittle material with an elongation at break <10% according to ISO 527 conditions (Zembouai *et al.*, 2014).

#### 9.4.2 POLY(3-HYDROXYBUTYRATE-CO-3-HYDROXYVALERATE)

PHBV can be synthesized and accumulated intracellularly by a number of microorganisms (Gerard and Budtova, 2012). The properties of PHBV depend on the structure of the copolymer (Corre *et al.*, 2012). PHBV is semi-crystalline thermoplastic, with a degree of crystallinity from 40% to 60%. PHBV has very high oxygen and water barriers properties.

The melting temperature of PHBV is between 160°C and 180°C. The mechanical and thermal properties of PHBV are similar to those of poly(propylene) (PP) (Bledzki and Jaszkiwicz, 2010) (Hassaini *et al.*, 2017). The density of PHBV is similar to that of PLA (1.25 g/cm<sup>3</sup>). The thermal degradation of PHBV and PLA produces polymeric chains terminated with carboxyl and vinyl groups and carboxyl end groups of polyester catalyze hydrolysis reaction (Figure 9.2).

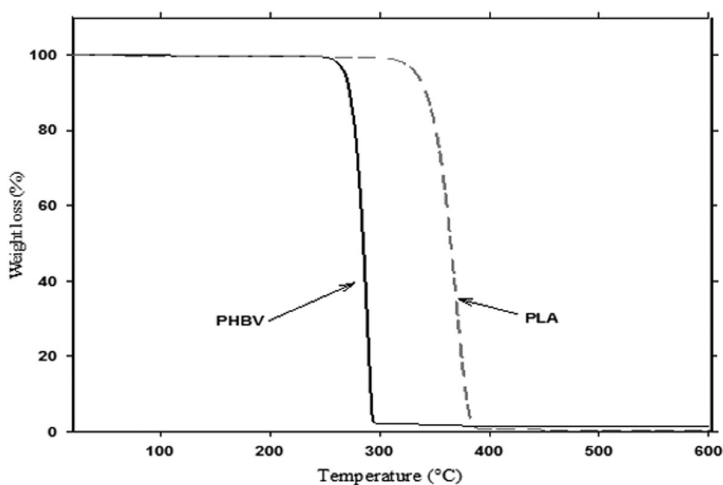


FIGURE 9.2 Thermal degradation of PLA and PHBV.

(From Zembouai *et al.* 2018.)

## 9.5 CONCLUSIONS

This chapter described the effect of conducting polymers on the analytical performance of electrochemical sensing platforms. It described the relationship between the use of conducting polymers and the analytical characteristics of electrochemical sensors, such as stability and sensitivity, linear concentration range, and the limit of detection. This provided advances in the use of conducting polymer functionalized nanocomposites with a focus on the application of electrodeposition methods of conducting polymers for electrochemical sensing applications. These methods are a good route to control the film thickness of conductive polymers. In addition, they are suitable to produce thin films with high conductivity directly rather than using chemical synthesized films. The application of electrodeposition potentiostatic methods minimize and even eliminate the passivation phenomena of electrochemical sensing interfaces. The use of conducting biopolymers is now widespread and offers flexible and stretchable platforms with high conductivity. Innovative experimental strategies applied for the preparation of sensors based conducting polymers will offer various robust and sensitive analytical tools.

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