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Use of High Energy Radiation for Synthesis and Kinetic Study of Conjugated Polymers

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4.1 Recent Advancements Toward Facile Preparation of Processable CPs

Intrinsically conducting polymers (CPs) are extraordinary class of material that combines the electrical properties of metals and semiconductors with a polymer's ability to flex and/or stretch [1]. Generally, the synthesis of CPs is feasible and easy. However, CPs have some limitations that restrict their applications due to the poor processability that is attributed to the rigidity and interchain interactions of the polymer chains [2]. Moreover, these polymers are highly branched and crosslinked due to polaron/bipolaron charge interactions. CPs are therefore poorly soluble in common industrial solvents. Thus, the key hurdle to uptake these polymers in commercial products is lack of existing facile synthetic methods of producing useful quantities as well as simple approaches for processing bulk polymer into useful forms [1].

Nowadays, the scientific community is tremendously endeavoring to develop and upgrade new synthesis methodologies for CPs [3, 4]. The common methods to synthesize CPs are chemical oxidation or electrochemical polymerization [5–7]. Based on these conventional methods, numerous studies were carried out to optimize the properties of CPs, to control structure and to functionalize CPs [8]. Research reports showed that nanostructured conducting polymers in the form of nanofibers and nanosponges are characterized by significantly improved capacitance values as compared with their non-nanostructured counterparts [9]. For this purpose, reverse microemulsion polymerization [10, 11] and CPs composite with carbon nanotubes (CNTs) [12, 13] have been employed to fabricate polymers nanotubes [14], wires [15], nano-rods [16], fibers [17], etc. Furthermore, polymer-metal oxide nanocomposites were used to enhance their thermal, mechanical, and chemical properties [18]. Even though these previously mentioned methods are well understood and controlled, still remain many obstacles to overcome such as chemical contamination, purification steps, and processability. In literature, there are several

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approaches that have been adopted towards production of processable forms of CPs as follows [1, 19]:

- i) Removal of interchain charge interactions by reducing CPs to their non-conducting state making them soluble in some solvents such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO)
- ii) Resorting to use of substitute polymers by flexible and long alkyl chains rendering them soluble in common solvent (chloroform, toluene, etc.)
- iii) Preparation of water-soluble CPs using a template-guided enzymatic approach
- iv) Preparation of aqueous colloidal dispersions of CPs in the presence of a water-soluble polyelectrolyte such as polystyrene sulfonic acid
- v) Vapor phase polymerization method to produce thin films of both soluble and insoluble CPs, and nanocomposites thereof
- vi) Self-doping approach for increasing the solubility of CPs in aqueous solutions by using ionizable functional groups.

For the sake of simplifying the preparation of nanostructured CPs with the view to obtain processable polymers, finding an alternative synthesis and processing approaches would be immensely helpful. In this respect, radiolysis synthesis is already known as an interesting method for the synthesis of non-conducting polymers [20]. However, radiation induced polymerization via the interaction of high energetic rays with the matter is narrowly used to prepare CPs [21]. The preparation of CPs using gamma irradiation was predominantly accompanied by the addition of chemical oxidants. As reported in the literature, ionizing radiation affects polymer morphology and leads to tailoring their nanostructure. Indeed, Karim et al. synthesized polypyrrole (PPy) using γ -radiation induced oxidative polymerization with ammonium peroxydisulfate (APS) as chemical oxidant [22]. Moreover, they also prepared buckyball shaped conducting polythiophene by gamma induced polymerization method in presence of FeCl_3 as an oxidizing agent [23]. However, in order to produce CPs, radiation induced polymerization was used alone for the first time, in the absence of any external oxidizing species, only few years ago. This radiation methodology based on either γ -rays or accelerated electrons and dedicated to the synthesis of nanostructured CPs was recently developed by Remita's team [21]. Hence, we concisely preview in this chapter all the potential approaches to proceed with CPs nanostructures production by radiolytic methodology.

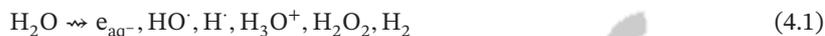
4.2 Preface to Radiation Induced Oxidative Polymerization of CPs Nanostructures in Aqueous Solutions

It is well known that γ -rays and X-rays radiolysis are very often used at ambient temperature and pressure in order to initiate, in the absence of external chemical initiators, oxidation, or reduction reactions through the control of the initiator radicals, which depend on the nature of the irradiated medium (atmosphere, solvent, potential solute) [24–27]. The principle is that upon irradiation the deoxygenated

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aqueous solutions at neutral pH generate the following various radiolytic species [28–30]:



The radiolytic products of water radiolysis are varied between oxidizing species and reducing ones. In the presence of air, $\text{H}\cdot$ atoms and solvated electrons e_{aq}^- are scavenged by molecular oxygen O_2 to produce respectively perhydroxyl radicals ($\text{HO}_2\cdot$) and superoxide radicals ($\text{O}_2^{\cdot-}$), which are the two acido-basic forms of the couple $\text{HO}_2\cdot/\text{O}_2^{\cdot-}$ ($\text{p}K_{\text{a}}(\text{HO}_2\cdot/\text{O}_2^{\cdot-}) = 4.8$ at 298 K) [29, 31]. As a consequence, when irradiating aerated aqueous solutions at neutral pH, only two short-lived transient species are formed, namely, hydroxyl radicals ($\text{HO}\cdot$) and $\text{O}_2^{\cdot-}$ with radiolytic yields of 2.8×10^{-7} mol/J and 3.4×10^{-7} mol/J, respectively [32]. The standard redox potential of $\text{HO}\cdot$ (at pH = 7) is quite high and amounts to $E^\circ(\text{HO}\cdot/\text{H}_2\text{O}) = 2.2 V_{\text{SHE}}$ [29]. On the contrary, $\text{O}_2^{\cdot-}$ is almost a poor oxidizing species with relatively low redox potential that amounts to $E^\circ(\text{HO}_2\cdot/\text{H}_2\text{O}_2) = 0.9 V_{\text{SHE}}$ [29]. Hence, $\text{HO}\cdot$ radicals are strong oxidizing species and should evidently enable oxidation induced polymerization of some interesting organic monomers, such as 3,4-ethylenedioxythiophene (EDOT), which has oxidation potential that amounts to 1.4 V vs. Ag/AgCl [33].

Now, if aqueous solutions are degassed with nitrous oxide (N_2O), e_{aq}^- are quantitatively and immediately converted into $\text{HO}\cdot$. As a consequence, when irradiating N_2O -saturated aqueous solutions at neutral pH, only two short-lived transient species are formed: $\text{HO}\cdot$ and $\text{H}\cdot$ (hydrogen atoms). In these conditions, due to the poor reactivity and to the low yield of formation of hydrogen atoms, $\text{HO}\cdot$ radicals can be considered as the only oxidizing species, and their radiolytic yield of formation ($G(\text{HO}\cdot) = 5.6 \times 10^{-7}$ mol/J) is higher than that obtained under aerated conditions ($G_{\text{HO}\cdot} = 2.8 \times 10^{-7}$ mol/J).

EDOT molecules are soluble in water and present some specific chemical properties, which make them interesting building blocks for the synthesis of functional π -conjugated systems such as PEDOT [21, 34]. In fact, due to their strong electron donor effect, the ether groups at the β and β' positions of thiophene rings, which confer a high reactivity to the free α and α' positions, prevent the formation of parasite α - β' linkages during polymerization. These interesting properties of EDOT enabled Remita and co-workers [21] to successfully synthesize PEDOT polymers by using γ -irradiation. Starting from an aqueous solution of EDOT monomers, it was possible to synthesize polymers under soft conditions: at air and at room temperature without introduction of any external chemical initiators [21]. In addition, the synthesis was feasible under various conditions (O_2 or N_2O saturated aqueous solutions) [21, 35]. In comparison with the usual electrochemical methods, this new γ -rays-based radiolytic way presents some advantages concerning the easy preparation of the samples, where no supporting electrolyte is needed, and the ability to work under atmospheric conditions without purging solutions with an inert gas. In contrast to the electrochemical approach, which leads to the direct deposition of CPs onto conducting substrates, the described radiolysis method leads to the formation of CPs dispersed in water enabling their further deposition over conducting or even non-conducting surfaces [21].

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Radiation induced polymerization of CPs is a promising method towards producing processable CPs nanostructures and noticeably exhibits several advantages over other conventional methods. As it appears, radiation-based method does not require special equipment, can be performed under various conditions, and is free from metal contaminations. Moreover, this method could lead to formation of suspended nanostructured CPs in aqueous solutions as well as directly onto substrates. Using radiolysis should also lead to chemical processes, which can be switched on and off upon exposure or removal of ionizing radiation instead of using initiator or stopper molecules.

4.2.1 Studying Kinetic Mechanism of HO \cdot -Induced EDOT Polymerization in Aqueous Solution

Understanding the mechanism of oxidative polymerization of conducting polymers and studying the reaction mechanism between the generated radicals from radiolysis process and the studied monomers is a pivotal point to advance the development of this original synthetic method. For this purpose, time resolved absorption spectroscopy coupled with pulsed radiolysis was used in order, first, to study EDOT oxidation mechanism and, second, to definitely identify the nature of PEDOT growth process. In this context, the reaction between hydroxyl radicals and EDOT monomers was mainly followed with the aim to identify the different transient species involved in the first steps of HO \cdot -induced PEDOT polymerization. Spectrokinetic analysis of experimental data and molecular simulations of absorption spectra was used to confirm the rate constants values and to identify the transient and stable species involved in the mechanism. The experimental setup (available at LCP, Orsay, Paris-Sud University) includes a picosecond laser-triggered electron accelerator ELYSE [36, 37] coupled with a time-resolved absorption spectroscopic detection system. A mixed simulation method was used, using the Monte-Carlo (MC) sampling of the molecular geometries, the density functional theory (DFT) calculation of the electron structures, and the polarized continuum modeling (PCM) of the solvent (Figure 4.1). An N $_2$ O-purged stock EDOT aqueous solution of 200 ml was used, which circulated in the 10 \times 10 mm fused silica irradiation cell at a flow rate of 100 ml/min by means of a peristaltic pump. Since the electron pulses were applied at a frequency of 5 Hz, the solution was renewed between each pulse and it was possible to apply up to 400 pulses for each kinetic measurement [31, 38].

In acidic and neutral aqueous solutions under N $_2$ O, HO \cdot -induced oxidation of EDOT was found to imply the oxidation of EDOT into a transient species, EDOT \cdot^+ radical cation and possibly into (EDOT-HO) \cdot adduct, which dimerizes and deprotonates leading to a stable product, namely, EDOT $_2$ dimer. In alkaline medium, this mechanism is mostly different since HO \cdot deprotonates into its alkaline form, O $^{\cdot-}$, the oxide radical, which adds onto EDOT monomer. This addition leads to the formation of an open cycle, which prevents any dimerization of EDOT and consequently any polymerization of PEDOT. Hence, in acidic and neutral aqueous solutions, after one pulse irradiation (40 Gy), no other products than EDOT $_2$ dimers were observed,

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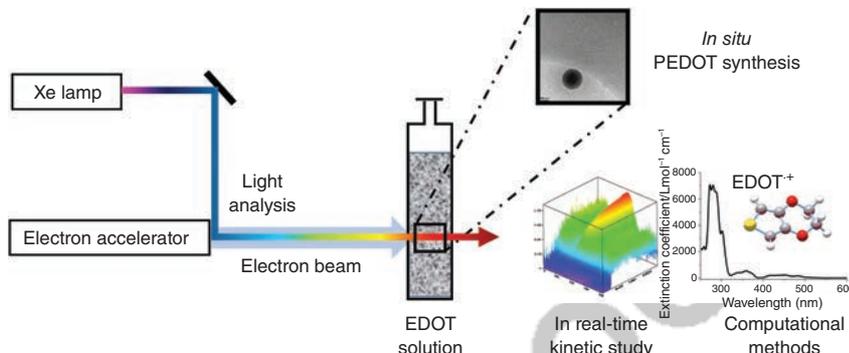


Figure 4.1 The picosecond laser-triggered electron accelerator ELYSE at University Paris-Sud (Orsay) coupled with a time-resolved absorption spectroscopic detection system. The figure shows the involvement in the work of the in real-time kinetic study of the growth mechanism, of the molecular simulations of the absorption spectra of the transient species involved in the growth mechanism as well as the experimental characterizations of the obtained PEDOT polymers as observed on the Cryo-TEM image [31]. Source: Adapted with permission from Copyright 2015, American Chemical Society.

demonstrating that no polymerization takes place in these experimental conditions. The interesting results obtained by pulse radiolysis proved without any ambiguity that PEDOT polymerization is not a chain reaction. On the contrary, it has been demonstrated to proceed through a step-by-step mechanism made up of the following recurrent steps: (i) oxidation/activation, (ii) growth/chain length increase, and (iii) deprotonation [31].

In fact, the amount of hydroxyl radicals generated by one pulse during the pulsed radiolysis study was not enough to ensure polymerization. It only enabled the incomplete transformation of EDOT monomers into dimers. According to a step-by-step mechanism, the quantitative polymerization of EDOT into PEDOT requires a very much higher concentration in hydroxyl radicals, which should reach at least twice that of EDOT. Nevertheless, in pulse radiolysis experiments, the dose per pulse could not be significantly increased. Then, in order to check whether EDOT polymerization effectively proceeds through a step-by-step oxidation process and with the aim to synthesize conducting PEDOT polymers by using an electron beam, aqueous solutions containing 10 mM in EDOT were irradiated in a closed cell under N_2O atmosphere with a series of consecutive electron pulses of 40 Gy (delivered at a frequency of 10 Hz).

Taking into account a step-by-step polymerization process, 10 mM in hydroxyl radicals are needed for the quantitative dimerization of 10 mM in EDOT into 5 mM in $EDOT_2$, then an additional amount of 5 mM in $HO\cdot$ is needed for the quantitative transformation of $EDOT_2$ into 2.5 mM in $EDOT_4$ and so on. This means that at least 20 mM in hydroxyl radicals are necessary to ensure the quantitative polymerization of EDOT monomers into PEDOT polymers. The use of two $HO\cdot$ radicals for one EDOT molecule is understandable since each EDOT monomer is bound to two EDOT neighbors inside the same polymer chain, which means that it must be twice oxidized. Thus, the theoretical irradiation dose (D_{max}), which should lead to the total

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oxidation of EDOT into PEDOT by HO· radicals, can be determined as follows:

$$D_{\max} (\text{Gy}) = \frac{2[\text{EDOT}]_0 (\text{mol/l})}{G_{\text{ox}} (\text{mol/J}) d (\text{kg/l})} \quad (4.2)$$

where D_{\max} is the irradiation dose (in Grays, 1 Gy corresponding to 1 J/kg), where $[\text{EDOT}]_0$ is the initial concentration of EDOT monomers, G_{ox} is the yield of EDOT oxidation which is equal to the radiolytic yield of HO· production (5.6×10^{-7} mol/J under N_2O atmosphere), and d is the solution density ($d \sim 1$ kg/l for diluted aqueous solutions).

According to Eq. (4.2), 36 kGy were necessary for the total polymerization of 10 mM in EDOT. Knowing that each pulse corresponded to a dose of 40 Gy, complete polymerization was requiring more than about 1000 successive pulses. In order to quantitatively polymerize EDOT, the colorless and limpid aqueous solution of 10 mM in EDOT was irradiated at a dose of 180 kGy, which corresponds to the accumulation of 4500 pulses of 40 Gy/pulse. After this irradiation, the solution became turbid. Its UV-Vis absorption spectrum is displayed in Figure 4.2a [31]. No noticeable absorption band was present in the spectrum. Nevertheless, a continuous scattering appeared due to the presence of a brown-yellow suspension in the bulk of the irradiated solution (inset of Figure 4.2a). This spectrum and the turbidity of the solution were in good agreement with results previously obtained by steady-state radiolysis suggesting that polymerization effectively took place [21].

The ATR-FTIR spectrum of the polymer powder is presented in the upper part of Figure 4.2b in the wave number region $1600\text{--}600\text{ cm}^{-1}$ together with the spectrum of pure non irradiated EDOT (bottom of Figure 4.2b) [31]. The two spectra were found in good agreement with those reported for PEDOT and EDOT when polymerized by γ -rays. The IR spectrum of the polymer powder displays vibrations at 1485, 1441, and 1365 cm^{-1} which are attributed to C=C and C-C stretching modes in the thiophene ring. The vibrations observed at 1288, 1240, 1171, and 1059 cm^{-1} are assigned to the stretching modes of the ethylenedioxy groups (C-C and C-O-R-O-C). The vibration modes of C-S bond, which are present in the thiophene ring, can be observed at 941 and 901 cm^{-1} . Note that the intense C-H stretching band at 754 cm^{-1} , observed in the spectrum of EDOT, is clearly absent in the ATR-FTIR spectrum of polymers. This definitely demonstrates, without any ambiguity, that EDOT polymerization has quantitatively taken place thanks to α,α' -coupling reactions and that the resulting solid powder obtained after lyophilization is effectively composed of PEDOT polymers. This demonstrates that such as γ -irradiation, electron beam irradiation enables the radiosynthesis of PEDOT polymers. [33] While one electron pulse lead to the formation of EDOT₂ dimers as stable products, the use of a series of successive pulses is necessary to generate enough hydroxyl radicals to form PEDOT polymers. Here it is evidenced that electron irradiation can successfully be used as an alternative way for the synthesis of PEDOT polymers and also that PEDOT growth effectively proceeds through a step by step oxidation process as expected.

Aqueous solutions containing 10 mM in EDOT and irradiated by the electron beam at 180 kGy were observed by Cryo-transmission electron microscopy just

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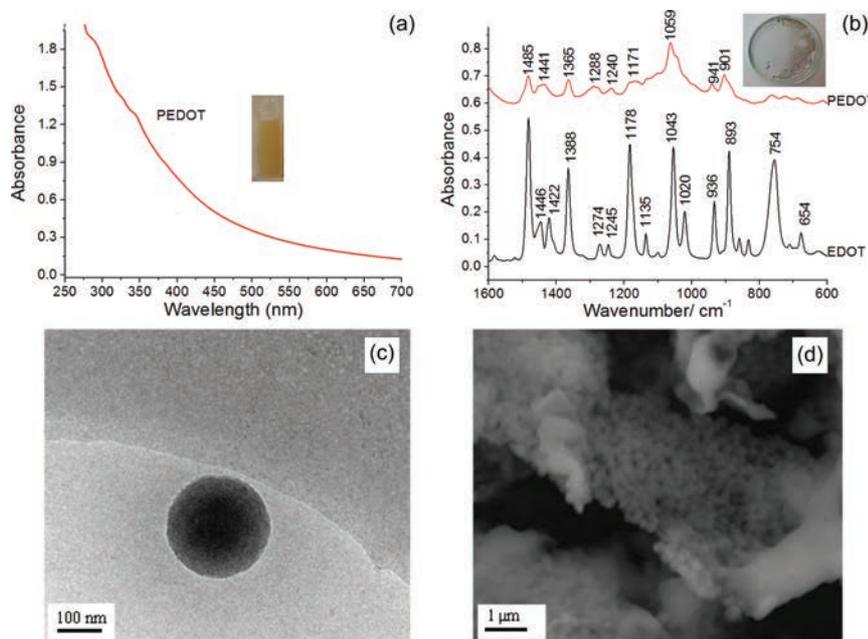


Figure 4.2 (a) Absorption spectrum of a N_2O -saturated aqueous solution of EDOT (10 mM) irradiated by an electron beam at a dose of 180 kGy (4500 pulses, 40 Gy/pulse). The reference was water, and path length was 1 mm; (inset) photograph of a cell containing PEDOT aqueous suspension radiosynthesized by an electron beam. (b) ATR-FTIR spectra of pure EDOT (bottom spectrum) and PEDOT polymers radiosynthesized at 180 kGy (top spectrum); (inset) photo of a cup containing the lyophilized radiosynthesized PEDOT powder. (c) Cryo-TEM image of radiosynthesized PEDOT in aqueous solution. A PEDOT nanoparticle of around 250 nm is observed. (d) SEM image of lyophilized radiosynthesized PEDOT powder. Aggregates of spherical PEDOT nanoparticles are observed [31]. Source: Adapted with permission from Copyright 2015, American Chemical Society.

after irradiation in order to investigate the structure and morphology of PEDOT polymers in aqueous solution. Representative images show the presence of low density globular structures forming spherical nanoparticles with a diameter ranging between 200 and 250 nm (Figure 4.2c) [31]. This result was in agreement with polymer size and shape found after γ -rays induced PEDOT synthesis. Since no other low-density objects were observed during Cryo-TEM experiments, these spherical nanoparticles were supposed to be made up of PEDOT polymer nanostructures. Each observed nanoparticle should be composed of interdigitated polymer chains. Since no α - β' linkages could occur during polymerization, radiosynthesized PEDOT nanostructures should be composed of linear chain polymers, which are not branched nor networked. Thus, the globular structure observed on Figure 4.2c should correspond to a self-assembly of independent amorphous PEDOT chain polymers. The presence of ethylenedioxy groups (H-bond acceptors) should explain not only the hydrosolubility of PEDOT polymers but also the as-observed packing and nanostructuring of the spherical supramolecular PEDOT self-assemblies.

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In order to characterize the morphology of the polymers after a deposition procedure, the 180 kGy-irradiated sample was lyophilized and the black powder obtained was deposited then characterized by scanning Electron Microscopy (SEM) microscopy. The images indicated the presence of very close packed polymeric particles (Figure 4.2d) [31]. Once more PEDOT polymers appear as spherical nanoparticles. These structures should come from the globular nanostructures already observed in aqueous solution by Cryo-TEM. The particles observed by SEM were almost monodisperse in size with a mean diameter of 220 nm, which is close to that observed by Cryo-TEM in aqueous solution. This proves that neither phase transition nor deposition procedure affects the size and shape of radiosynthesized PEDOT nanoparticles. This would imply the existence of very strong hydrogen-bond interactions into each polymer nanoparticle. Therefore, the synthesis of nanostructured PEDOT polymers is successful, thanks to the electrons beam irradiation of EDOT aqueous solution. The radiosynthesized PEDOT polymers form monodisperse nanoparticles the morphology of which is kept after deposition onto substrate.

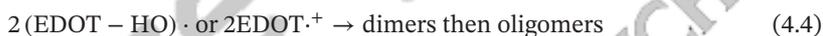
Further investigation based on pulsed electron beam irradiation was proceeded to oxidize EDOT monomers and to induce polymers growth by using sulfate radicals, $\text{SO}_4^{\cdot-}$, instead of hydroxyl radicals, HO^{\cdot} [38]. The purpose of this study was to check the influence of the nature of the oxidizing species and of the presence of an inorganic compound (namely, $\text{K}_2\text{S}_2\text{O}_8$) onto the morphology of radiosynthesized polymers. The results demonstrated the versatility of the radiolytic methodology based on pulse electron beam irradiation, and highlighted, without any ambiguity, the efficiency of alternative oxidizing radicals, such as sulfate radicals for the preparation of nanostructured conducting polymers. The success of PEDOT polymers synthesis by using accumulated electron pulses definitely demonstrates that conducting polymers growth proceeds through a step-by-step oxidation mechanism and not according to a chain reaction.

4.2.2 Gamma-Radiation Induced Oxidative Polymerization of EDOT in Aerated Aqueous Solutions at Neutral pH

The incipient form of this method was initially instituted by γ -radiolysis of aerated aqueous solutions of 3,4-ethylenedioxythiophene (EDOT) [21]. The concept is that the radiolysis of aerated aqueous solutions provides the medium with several oxidizing species namely HO^{\cdot} and $\text{O}_2^{\cdot-}$. These generated oxidizing species could insure the oxidation of EDOT monomers. Accordingly, the irradiation conditions were studied in details to get the product in optimal form. Within this framework, to approach the synthesis of PEDOT by γ -radiolysis, the yield of oxidation was needed to be determined. As elucidated in related studies [21, 31], by knowing the extinction coefficients of EDOT in aqueous solution that were calculated from UV-Vis absorption spectra, one can deduce the initial radiolytic yield of EDOT consumption from the variation of EDOT concentration as a function of the irradiation dose. The extrapolated value of the radiolytic yield of EDOT consumption under air was found equal to the radiolytic yield of production of HO^{\cdot} that amounts

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to $G_{\text{-EDOT}0} = G_{\text{HO}\cdot} = 2.8 \times 10^{-7}$ mol/J [21]. Note that this value was found almost constant whatever the initial concentration of EDOT. This finding demonstrates that EDOT amount was sufficient to scavenge all the hydroxyl radicals produced by gamma-radiolysis and highlights the fact that only hydroxyl radicals react with EDOT. As mentioned earlier, $\text{HO}\cdot$ is a strong oxidizing species since its apparent standard redox potential at pH = 7 amounts to $E^{\circ}_{\text{SHE}}(\text{HO}\cdot/\text{H}_2\text{O}) = 2.2 V_{\text{SHE}}$ [29] enabling oxidation of EDOT. Contrariwise, the formed $\text{O}_2\cdot^-$ radicals possess very low redox potential [$E^{\circ}_{\text{SHE}}(\text{O}_2\cdot^-/\text{H}_2\text{O}_2) = 0.9 V_{\text{SHE}}$] [29], making them being considered as poor oxidizing species. As a consequence, the relatively low apparent redox potential of $\text{O}_2\cdot^-$ does not allow the reaction with EDOT the oxidation potential of which amounts to 1.4 V Ag/AgNO₃ [33]. Whatever EDOT concentration ranging from 1 to 10 mM, the results showed that EDOT disappearance parallels the formation of species that absorb at both 290 and 350 nm. These absorption maxima could be attributed to dimers and oligomers of EDOT, which could be formed according to the step by step oxidation process highlighted by pulse radiolysis:



These absorption bands are in good agreement with the absorption spectra of dimers experimentally and theoretically found by the previously described pulsed radiolysis studies. [31] Auxochromic substitution (by the ethylenedioxy group) in EDOT dimers can explain the shift in their absorption maxima as compared with those of bithiophene molecules, which are known to absorb at 246 and 301 nm [39].

The yield of EDOT oxidation, $G_{\text{-EDOT}0}$, was found decreasing with the dose and became much lower than $G_{\text{HO}\cdot}$ at high doses. This is because of the competitive reactions of hydroxyl radicals with EDOT dimers and oligomers, which take place in the medium and which become more and more preponderant as the amount of EDOT decreases. Indeed, the oxidation potential of the dimers and the oligomers is lower than that of the monomers enabling their oxidation by hydroxyl radicals. So the process of oxidative coupling of the units continues as the polymer grows [40].

On the other hand, the yield of EDOT consumption was found independent of the initial EDOT concentration. This definitely demonstrates that the process attributed to PEDOT radio-induced synthesis does not proceed through a chain reaction. In particular, $\text{EDOT}\cdot^+$ radical cation does not react with EDOT monomer. This is consistent with the pulsed radiolysis results previously described: PEDOT radio-induced synthesis could only proceed through a recurrent $\text{HO}\cdot$ oxidation process: $\text{HO}\cdot$ reacts with EDOT monomers, then with dimers, and then with oligomers. The quantitative synthesis of PEDOT polymers throughout such a step-by-step mechanism necessarily implies the use of two $\text{HO}\cdot$ radicals for the oxidation of one EDOT molecule (in α and α' positions). Thus, the theoretical irradiation dose (D_{max}) that should lead to the total oxidation of EDOT into PEDOT can be calculated from Eq. (4.2). For instance, 7.2 and 72 kGy are necessary for the total polymerization of respectively 1 and 10 mM in EDOT dissolved in aerated aqueous solution.

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In the respect of PEDOT characterizations, the ATR-FTIR observations evidenced their successful formation [21]. Moreover, the obtained spectra were in very good agreement with those previously reported for PEDOT in literature [41–43] and for PEDOT synthesized by accelerated electrons as highlighted before [31]. The PEDOT nature of the radiosynthesized polymers, which compose the solid phase, was also proved thanks to the determination of its melting point. Indeed, a temperature of 145 °C was measured, which is very close to the reported PEDOT melting point value (146 °C) [44]. This result also proves the absence of impurities in the radiosynthesized products. The morphological features were also observed directly in the aqueous solution by Cryo-TEM and after deposition onto substrate by AFM [21]. The microscopic observations revealed formation of globular self-assembled structures made up of PEDOT polymeric chains. The mean diameter of the observed nanoparticles was 200 nm. The dimensions of the nano-objects observed by Cryo-TEM closely match those of AFM. As at will be demonstrated in the next paragraph, the presence of substituted hydroxyl groups along the polymer chains explains the packing and the nanostructuring of the observed spherical supramolecular PEDOT self-assemblies besides their hydrosolubility and the solvation of PEDOT polymers.

In order to enhance the yield of oxidation and in order to check whether other oxidizing species can enable the oxidative polymerization in aqueous solutions, the radiolysis methodology took further advances by varying the experimental conditions (atmosphere and additive). For this purpose, the radiolytic methodology was extended to the synthesis of PEDOT polymers in N₂O-saturated aqueous solutions in the presence and in the absence of sodium azide. The oxidative polymerization was induced through two different oxidizing species: HO· (hydroxyl) and N₃· (azide) radicals, as will be discussed in the following text.

4.2.3 Effect of Oxidizing Species on Gamma-Radiation-Induced Synthesis of PEDOT

The original radiolytic methodology based on γ -rays was extended to the synthesis of PEDOT polymers in N₂O-saturated aqueous solutions of EDOT at neutral pH. In these conditions and depending on the presence of sodium azide salt, two different oxidizing species are formed, namely, hydroxyl radicals (HO·) and azide radicals (N₃·) [35]. Since the redox potentials of these two oxidative radicals (which are higher than that of EDOT monomers) and their well-known oxidation mechanisms are quite different, one can expect the formation of two kinds of PEDOT polymers with tuned characteristics. Under N₂O in the absence of NaN₃ as already explained, e_{aq}⁻ are quantitatively and immediately converted into HO· which can be considered as the only oxidizing species with a radiolytic yield of formation [G(HO·) = 5.6 × 10⁻⁷ mol/J]. Under these conditions H· atoms are present in the medium with a radiolytic yield G_{H·} = 0.6 × 10⁻⁷ mol/J. Nevertheless, due to their relatively small amount and unknown reactivity, the presence of H· atoms is often neglected [45]. Now, in aqueous solutions containing sodium azide (NaN₃ at 10 mM for 1 mM in EDOT or 100 mM for 10 mM in EDOT, dissociated into Na⁺ and N₃⁻ ions) and saturated by nitrous oxide, HO· radicals are very quickly scavenged by

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N_3^- ions leading to the quantitative formation of $N_3\cdot$. In the presence of NaN_3 , the concentration of EDOT monomers being always ten times lower than that of N_3^- ions, the direct oxidation of EDOT by $HO\cdot$ can be neglected. Thus, when irradiating N_2O -saturated aqueous solutions at neutral pH in the presence of NaN_3 , the radiolytic yield of formation of $N_3\cdot$ amounts to 5.6×10^{-7} mol/J.

Once again, according to a step by step mechanism, in the absence of NaN_3 , the total irradiation dose (D_{max}) that should enable the quantitative synthesis of PEDOT in N_2O -saturated aqueous solutions is twice the dose necessary for the total oxidation of EDOT monomers and can be calculated as previously explained according to Eq. (4.2), but by using $G(HO\cdot)$ instead of $G_{HO\cdot}$. In a N_2O -saturated aqueous solution containing 10 mM in EDOT, the dose that is necessary for the total oxidation of EDOT amounts to 18 kGy, and the dose D_{max} that is necessary for the complete synthesis of PEDOT amounts to 36 kGy.

In the absence of sodium azide salt, N_2O -saturated aqueous solutions containing 10 mM in EDOT were irradiated at increasing doses up to 70 kGy. This latter dose was high enough to ensure the total polymerization of EDOT. Figure 4.3a displays the evolution of the UV-Vis absorption spectrum of this solution as a function of the dose. The spectra show at low irradiation doses, up to about 20 kGy (the dose that produces 10 mM hydroxyl radicals), two absorption bands that appear at 290 and 350 nm (Figure 4.3a), which demonstrates the formation of dimers as highlighted by pulse radiolysis study [31]. Above 20 kGy, no absorption band is observed around 250 nm. This clearly indicates that EDOT has completely disappeared. If the dose is higher than the total irradiation dose, as observed in the case of 70 kGy irradiation dose in Figure 4.3a, the absorption bands of the dimers disappear and an intense absorption band appears at around 370 nm together with a continuous scattering, the intensity of which increases with the irradiation dose. This has been ascribed to the lengthening of EDOT oligomers. In fact, at doses higher than 36 kGy, the appearance of a continuous scattering component, in the extinction spectrum of the irradiated solutions, was explained to result from the formation of a brown-yellow suspension in the bulk solution. This suspension became denser and the solution appeared more turbid as the irradiation dose was increasing.

After the deposition of this suspension onto ITO substrate, the resulting film displayed an intense absorption band at 550 nm. According to the performed ATR-FTIR analysis, this indicates that the suspension was made up of polymers, denoted PEDOT-OH, formed at high doses, thanks to the recurrent step-by-step $HO\cdot$ oxidation process. After irradiation at high doses (from 36 to 70 kGy), very slow precipitation of the suspension was observed. This precipitation corresponds to a sedimentation process of the PEDOT-OH polymers of relatively high molecular weights. Note that this precipitation cannot be assigned to the hydrophobia of the radiosynthesized polymers. Indeed, after adding either cyclohexane or dichloromethane to the aqueous suspensions (v/v) and after stirring and decantation, the polymer particles always remain in the aqueous phase, whereas the organic phase systematically appears colorless, as illustrated in the case of dichloromethane (Figure 4.3a, insert). This result definitely proves the hydrophilic properties of PEDOT-OH polymers.

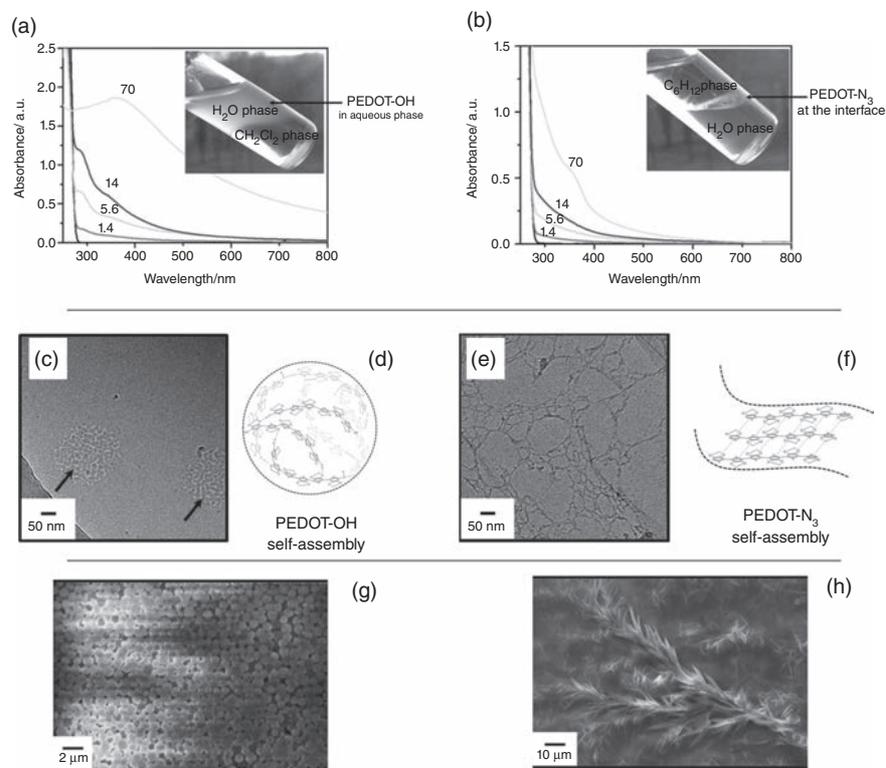


Figure 4.3 Absorption spectra of a N_2O -saturated aqueous solution containing 10 mM EDOT irradiated in the absence of NaN_3 (a) and in presence of NaN_3 (b) with increasing doses: 0, 1.4, 5.6, 14, and 70 kGy. The optical path length was 0.1 cm. The reference was water. Inset (a) Image of an aqueous solution irradiated at 70 kGy after the addition of dichloromethane as a denser organic phase (v/v): PEDOT-OH suspension remains in the upper aqueous phase. Inset (b) Image of an aqueous solution irradiated at 70 kGy after the addition of cyclohexane as a less dense organic phase (v/v): PEDOT- N_3 polymers remains at the interface between the two liquid phases. Cryo-TEM images of aqueous samples containing 10 mM in EDOT irradiated at 36 kGy under N_2O atmosphere: (c) in the absence of NaN_3 (PEDOT-OH) and (e) in the presence of NaN_3 (PEDOT- N_3). (d) A schematic representation of a single spherical polymer nanoparticle that highlights H-bond interactions between the chains. (f) A schematic representation of a single nanostructure highlighting π -stacking interactions between the chains. SEM images of PEDOT polymers after deposition onto gold substrates. Polymers were obtained after irradiation at 70 kGy: (g) in the absence of NaN_3 (PEDOT-OH) and (h) in the presence of NaN_3 (PEDOT- N_3). Source: Lattach et al. [35].

When considering γ -radiolysis under N_2O this time in the presence of NaN_3 , $\text{HO}\cdot$ radicals are scavenged by N_3^- leading to $\text{N}_3\cdot$ radicals, which can then be considered as the only oxidizing species able to react with EDOT. However, $\text{N}_3\cdot$ radicals are known as an alternative oxidizing system more selective than $\text{HO}\cdot$: it is a soft one-electron oxidant $E^\circ(\text{N}_3\cdot/\text{N}_3^-) = 1.33 \text{ V}_{\text{SHE}}$ at pH = 7. All in all, by analogy with the case of hydroxyl radicals, in the presence of NaN_3 , the total irradiation dose (D_{max}), which should enable the quantitative synthesis of PEDOT in N_2O -saturated

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aqueous solutions, is twice the dose necessary for the total oxidation of EDOT monomers and can be calculated according to Eq. (4.2), but by using $G(N_3\cdot)$ instead of $G(HO\cdot)$ or $G_{HO\cdot}$. In an N_2O -saturated aqueous solution containing 10 mM in EDOT in the presence of azide salt, the dose that enables the total oxidation of EDOT amounts to 18 kGy and the dose D_{max} , which is necessary for the complete production of PEDOT is then about 36 kGy.

Accordingly, in the presence of sodium azide salt, N_2O -saturated aqueous solutions containing EDOT (10 mM) were irradiated at increasing doses up to 70 kGy. The evolution of the UV-Vis absorption spectrum of this solution as a function of the dose is displayed (Figure 4.3b). At low irradiation doses, up to about 20 kGy (the dose that produces 10 mM in azide radicals), two shoulders appear and grow up at 290 and 350 nm demonstrating once again the formation of dimers. When the dose becomes higher than the total irradiation dose, as observed in the case of 70 kGy-irradiation on Figure 4.3b, the absorption bands of dimers disappear and a more intense absorption band grows up around 370 nm. Again, this should result from the lengthening of EDOT oligomers. Moreover, a brown-colored suspension was observable within the bulk, which quickly deposits at the bottom of the solution. Note that the fast precipitation process, observed in this case, explains the absence of any scattering component in the extinction spectra of Figure 4.3b.

After the deposition of this suspension onto ITO substrate, the resulting film displayed a broad absorption between 500 and 600 nm, indicating that the suspension was made of polymers, noted PEDOT- N_3 , formed at high doses, thanks to the $N_3\cdot$ -induced oxidation process. After irradiations at high doses (from 36 to 70 kGy), a precipitate was systematically observed. This precipitation is not only due to a sedimentation process of the PEDOT- N_3 polymers of relatively high molecular weight. It also results from the poor hydrophilic properties of these systems. Indeed, after adding either cyclohexane or dichloromethane solvents to the aqueous suspensions (v/v) and after stirring and decantation, the polymer particles always remain at the organic solvent-water interface as illustrated in the case of cyclohexane (insert of Figure 4.3b). This result proves the amphiphilic properties of PEDOT- N_3 polymers. Note that at the interface, these polymers appear as clustered fibers.

One can note that, for the same initial concentration in EDOT (10 mM), the spectral evolution in the presence of NaN_3 (Figure 4.3b) is similar to that observed in the absence of this salt (Figure 4.3a). However, when comparing both evolutions, one can note that for a given irradiation dose, the maximal absorption is always lower in the presence of NaN_3 . Even if hydroxyl radicals and azide radicals oxidize EDOT and induce polymerization through the formation of EDOT dimers, it seems that the two implied mechanisms are somewhat different. Maybe the kinetic growth of dimers, oligomers, and polymers is slower in the case of $N_3\cdot$. This would induce a lower polymerization yield and lower values of the maximal absorbance. However, such an interpretation is not in agreement with the observed dose effect. On another hand, the products of EDOT oxidation could be chemically and structurally different depending on $N_3\cdot$ or $HO\cdot$ nature of the oxidizing radicals. This could explain the different spectral properties of the products obtained either in the presence or in the absence of azide salt. In addition, the poor hydrophilic properties of the products

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formed in the presence of NaN_3 lead to their deposition at the bottom of the solution and their adsorption onto the walls of the samples.

The assertion of the successful formation of PEDOT-OH and PEDOT- N_3 was realized by ATR-FTIR and melting point measurements. The obtained results were in good agreement with those previously reported about PEDOT in literature. The melting point of both PEDOT-OH and PEDOT- N_3 was found at a temperature of 145°C , which is very close to the PEDOT melting point value (146°C) already reported. This result demonstrates once again the high purity of the radiosynthesized products and thus the efficiency of the radiolytic procedure. Also, the recorded ATR-FTIR spectra demonstrate without any ambiguity that $\text{N}_3\cdot$ and $\text{HO}\cdot$ -induced EDOT polymerizations both take place thanks to α - α' coupling reactions and that the resulting solid powders obtained after centrifugation are effectively composed of PEDOT polymers. The wavenumber region $2000\text{--}700\text{ cm}^{-1}$ of the spectra of PEDOT-OH and PEDOT- N_3 shows remarkably comparable spectral features. However, significant differences were observed above 2000 cm^{-1} . Indeed, the spectrum of PEDOT-OH was found to exhibit a very large band between 3200 and 3600 cm^{-1} which was attributed to the presence of hydroxyl groups all along the polymers. The spectrum of PEDOT- N_3 was in turn characterized by an absorption in two different infrared regions: between 2110 and 2065 cm^{-1} and between 3565 and 3525 cm^{-1} . These characteristic peaks were attributed to the presence of azide anions in the solid phase. The noticeable differences between these two kinds of polymers were explained by the difference that exists between the well-known oxidizing behaviors of $\text{HO}\cdot$ and $\text{N}_3\cdot$. The $\text{HO}\cdot$ radical either adds onto aromatic molecules to afford radical adducts or abstract electrons leading to radical cations, whereas $\text{N}_3\cdot$ azide radicals only form radical cations through electron abstraction. The presence of hydroxyl groups in PEDOT-OH (coming from $\text{HO}\cdot$ -adducts) explains the existence of strong intermolecular interactions between the functionalized polymers through hydrogen bonds. It also confers to PEDOT-OH polymers hydrophilic properties, which explain their poor solubility into organic solvents as previously discussed. Contrarily to PEDOT-OH, PEDOT- N_3 polymers, which result from $\text{N}_3\cdot$ -induced EDOT oxidation, should not contain alcohol functionalities. This was proven by the absence of a large O-H band in the ATR-FTIR spectrum of PEDOT- N_3 . The absence of such a polar group in the PEDOT- N_3 polymer impacts its solubility in water and explains its poor hydrophilic properties.

From what was observed in the spectral findings (UV-Vis and ART-FTIR), no doubt that the difference between oxidizing behaviors of $\text{HO}\cdot$ and $\text{N}_3\cdot$ influences the nanostructures morphology of PEDOT-OH and PEDOT- N_3 . The captured Cryo-TEM images clearly show these differences in nanostructures (Figure 4.3c and Figure 4.3e) [35]. $\text{HO}\cdot$ induces the polymerization of EDOT leading to spherical nanoparticles with a diameter comprised between 100 and 300 nm . These observations are consistent with previous results concerning hydroxyl-induced radiosynthesis of PEDOT under air atmosphere. PEDOT-OH globular nanostructures should correspond to self-assemblies of independent amorphous PEDOT-OH chain polymers as schematically represented (Figure 4.3d). The presence of hydroxyl groups, which has previously been demonstrated, should explain not only

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the hydrosolubility of PEDOT-OH polymers but also the as-observed packing and nanostructuring of the spherical supramolecular PEDOT-OH self-assemblies. Note that ethylenedioxy groups (H-bond acceptors) present all along the polymer chains could also be involved in hydrogen bonds with the hydroxyl groups.

Differently, $N_3\cdot$ induces the polymerization of EDOT leading to different PEDOT nanostructures quite different from those obtained in the case of PEDOT-OH. Instead of a compact spheroidal morphology, which was found in the case of PEDOT-OH (Figure 4.3c), the obtained Cryo-TEM images clearly display nano-objects forming fibrillar or lamellar (plate-like) nanostructures, more or less folded, with a maximal fiber thickness of 10 nm and a length that can reach several microns (Figure 4.3e) [35]. Due to the thickness of the fibers, each of them should correspond to a self-assembly of linear PEDOT- N_3 polymer chains as schematically represented in Figure 4.3f. Since hydroxyl groups are not present in PEDOT- N_3 polymers, the packing of these polymers cannot result from H-bonds. This self-assembling should come from π -stacking interactions between conjugated polymers, which maintain the polymer chains parallel to each other and which can maybe confer to the polymers a lamellar structure. On another hand, this self-assembling could explain the macroscopic observation of PEDOT- N_3 polymers as clustered fibers at the interface between water and organic solvent. Also, the fact that PEDOT- N_3 polymers can either interact by van der Waals interactions (π -stacking interactions) or by hydrogen bonds, thanks to the presence of ethylenedioxy groups, could explain the amphiphilic properties of these polymers.

The observed nanostructures of PEDOT-OH and PEDOT- N_3 by SEM after a deposition procedure, as might be expected, were found consistent with what had been observed by cryo-TEM in aqueous solutions. SEM images of PEDOT-OH indicate the presence of very close-packed spheroidal polymeric particles (Figure 4.3g). The particles observed by SEM after deposition are polydisperse in size with a diameter comprised between 200 nm and 1 μ m. Differently, the SEM images of PEDOT- N_3 highlighted the presence of close-packed lamellar (plate-like) structures characterized by a maximal thickness of about 1 μ m (Figure 4.3h).

As demonstrated earlier, changing oxidizing species ($HO\cdot$ or $N_3\cdot$) leads to different UV-Vis absorption properties of radiosynthesized CPs, different hydrophilicities and different morphologies. This has been confirmed thanks to the use of an alternative strong oxidizing species, namely, $SO_4^{\cdot-}$, which was used to oxidize and polymerize EDOT monomers dissolved in aqueous solutions in the presence of an inorganic salt, the potassium persulfate ($K_2S_2O_8$). [38] This study once again showed the versatility of the radiolytic methodology based on gamma-rays and pulsed electron beam irradiation, and highlighted, without any ambiguity, the efficiency of alternative oxidizing radicals for the preparation of nanostructured conducting polymers.

4.2.4 Extension of the Radiolytic Procedure to the Synthesis of Polypyrrole (PPy) Nanostructures

To demonstrate the versatility of the radiolytic method in water under N_2O , the radiolytic procedure based on $HO\cdot$ -induced polymerization was extended to the

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successful synthesis of another representative CP, namely, PPy starting from Py monomers [46]. Similar properties, in terms of nanostructuring and hydrophilicity, were obtained in case of PPy when comparing to PEDOT-OH. In solution and after deposition, PPy nanostructures show as highlighted by Cryo-TEM, SEM, and AFM chaplet like spherical nanoparticles with diameters comprised between 80 and 200 nm. The merit of the work is that radiosynthesized PPy nanostructures are characterized by a very good thermal stability and an electrical conductivity that is five times higher than that of chemically synthesized PPy.

As previously described, the versatility of radiation-based methodology for the synthesis of CPs nanostructures was largely demonstrated in neutral aqueous media. Differently, in alkaline medium, in particular under N_2O , $HO\cdot$ radical deprotonates into its alkaline form, which adds onto EDOT monomer, leading to an open cycle and preventing any dimerization of EDOT and consequently any polymerization of PEDOT as demonstrated by pulsed radiolysis [31]. In order to check the effect of pH on radiation induced CPs growth, works were conducted in acidic aqueous media.

4.2.5 Effect of pH on the Polymerization of EDOT Monomers

It has been shown in literature that low pHs prevent conducting polymers from overoxidation [47] and improve their electrical conductivity by doping effect [48] and structural optimization [49]. Gamma-irradiation was then used to radiolytically prepare conducting organic materials in acidic aqueous media and then to study their properties. In this framework, the endeavor was to polymerize EDOT monomers in very acidic aqueous solutions under N_2O (at $pH = 0$ in presence of $HClO_4$ or HCl), by exploiting the oxidizing species produced by γ -radiolysis in these acidic conditions ($HO\cdot$ or $Cl_2\cdot^-$, respectively) [50].

In case of using $HClO_4$ to adjust the pH of the aqueous solution under N_2O , knowing that perchlorate ions (ClO_4^-) remain unreactive upon radiolysis, two reactive species should be considered: $HO\cdot$ and $H\cdot$ with the following radiolytic yield $G(HO\cdot) = 2.8 \times 10^{-7}$ mol/J and $G(H\cdot) = 3.4 \times 10^{-7}$ mol/J. $HO\cdot$ is known as a very oxidizing species that enables in particular oxidation-induced polymerization of EDOT monomers in neutral aqueous solutions. Differently, $H\cdot$ is generally known as less reactive and its reactions are often neglected in neutral media due to its low G value at $pH = 7$ [31]. Nevertheless, $H\cdot$ becomes predominant at $pH = 0$ and thus its reactivity onto EDOT monomers cannot be omitted as demonstrated in some cases in literature [39]. Interestingly, when hydrochloride acid (HCl) is used (instead of $HClO_4$) in order to adjust the pH, $HO\cdot$ radicals are quantitatively transformed into dichloride radical anions, $Cl_2\cdot^-$ [51]. Therefore, the main species produced by γ -radiolysis of very acidic aqueous solutions containing HCl under N_2O are $Cl_2\cdot^-$ (instead of $HO\cdot$) and $H\cdot$ [45]. While the total radiolytic yield of production of H -atoms remains the same as that found in the case of $HClO_4$, the radiolytic yield of $Cl_2\cdot^-$ amounts to $G(Cl_2\cdot^-) = 2.8 \times 10^{-7}$ mol/J. Such as $HO\cdot$, $Cl_2\cdot^-$ is a strong oxidizing species with a very high standard redox potential: $E^\circ(Cl_2\cdot^-/Cl^-) = 2.1 V_{SHE}$ [52]. As in the case of hydroxyl radicals, the oxidation of EDOT monomers and their polymerization into PEDOT should then be possible thanks to $Cl_2\cdot^-$ [50].

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Thus, under N_2O at pH 0, in presence of $HClO_4$ or with HCl , $HO\cdot$, or Cl_2^- should quantitatively oxidize EDOT. Effectively, in both cases, the effective yield of oxidation of EDOT monomers was found equal to 2.8×10^{-7} mol/J, proving by the same way that hydrogen atoms are not involved in EDOT polymerization. With such an oxidation yield, the dose needed for quantitative polymerization of 10 mM in EDOT amounts to 72 kGy at pH = 0 according to Eq. (4.2).

Acidic aqueous solution containing 10 mM in EDOT and 1 M in $HClO_4$ and acidic aqueous solution containing 10 mM in EDOT and 1 M in HCl were then both irradiated at 72 kGy under N_2O atmosphere. Also, for comparison purpose a neutral aqueous solution containing 10 mM in EDOT in the absence of acids was irradiated under N_2O at the same dose. The photographs of the three solutions obtained after irradiation (insert of Figure 4.4) as well as their UV-Vis absorption spectra are displayed on Figure 4.4. After a 72 kGy-irradiation, the solution prepared in neutral medium appears yellow (photography c in insert of Figure 4.4) and its absorption spectrum (spectrum c of Figure 4.4) displays an intense absorption band at around 350 nm in total agreement with the previous works conducted in neutral aqueous media [21, 35, 53]. This band was shown to be characteristic of PEDOT oligomers produced in the neutral medium by water radiolysis. Differently, after irradiation at 72 kGy, the solutions prepared at pH 0 in the presence of HCl (photography a in insert of Figure 4.4) or in the presence of $HClO_4$ (photography b) both appear as dark blue suspensions, which is the typical color of PEDOT polymers when obtained in their oxidized state [54, 55]. Remarkably, when considering the absorption spectra of the two acidic solutions irradiated at 72 kGy in presence of HCl (spectrum a of Figure 4.4) or $HClO_4$ (spectrum b), two shoulders are observed in both cases at 350 and 450 nm, which can be attributed to the presence, in very acidic medium, of PEDOT polymers prepared upon irradiation. As a matter of fact, PEDOT polymers are known to usually display, in solution, characteristic peaks in this wavelength region, which are assigned to $\pi-\pi^*$ transitions in the polymer backbones. In addition to these shoulders, a large absorption band was observed in both cases at around 700 nm in the case of HCl (spectrum a) and in the case of $HClO_4$ (spectrum b). This large band can be considered as polaron or bipolaron bands, which are both characteristic of PEDOT polymers when obtained in their oxidized state (p-type doping) [56].

The *in situ* doping process of PEDOT polymers radiosynthesized in very acidic aqueous solutions was definitely confirmed by both ATR-FTIR spectroscopy and Energy-Dispersive X-ray (EDX) analysis: first EDX enabled the detection of an additional chemical element, namely, chlorine atom, not present in the organic monomers but found homogeneously dispersed in the deposited solid sample; second, ATR-FTIR spectrum of PEDOT polymers radiosynthesized in very acidic aqueous solutions highlighted the presence of a less common infrared band located at 1640 cm^{-1} [12, 57]. This band had already been observed in earlier works in the case of PEDOT polymers synthesized by conventional methods and doped with chloride ions. This peak originates from the quinoidal structure of thiophene ring. The presence of this band together with the results obtained by EDX highlights the doping of PEDOT synthesized in very acidic media either by Cl^- or ClO_4^- anions coming from HCl or $HClO_4$ dissociation. This point is in full agreement with the

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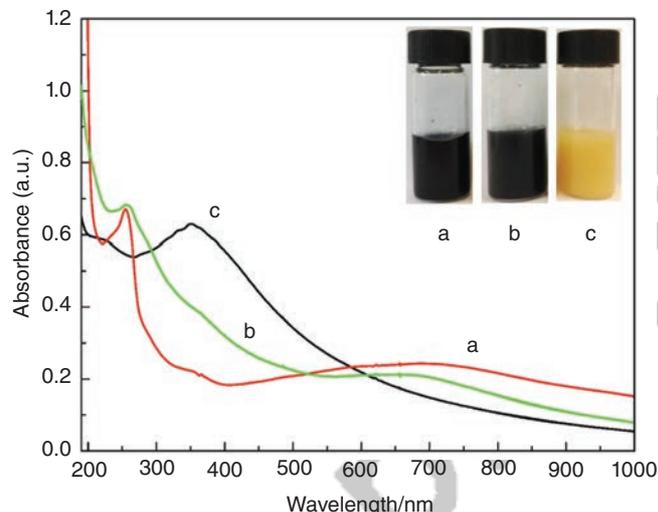


Figure 4.4 UV-Vis absorption spectra of PEDOT polymers synthesized after 72 kGy irradiation of aqueous solutions containing 10 mM in EDOT under N_2O atmosphere (a) in presence of HCl (1 M) at $pH = 0$, (b) in presence of $HClO_4$ (1 M) at $pH = 0$, and (c) in the absence of acids at neutral pH. All the spectra were recorded after 10 times dilution. The optical path length was 0.2 cm. The reference was water. Insert: photographs of the corresponding aqueous solutions. Source: Cui et al. [50].

results obtained by UV-Vis absorption spectroscopy (absorption band at 700 nm) and with the colors of the irradiated solutions.

Contrarily to PEDOT oligomers produced in neutral aqueous media, PEDOT polymers synthesized under the same atmosphere (N_2O) at $pH = 0$ were found doped. The doping of radiosynthesized PEDOT polymers should result from the presence in the medium of considerable amounts (1 M) of hydrochloric acid or perchloric acid. PEDOT polymers produced in presence of either HCl or $HClO_4$ seem to be in the same oxidized state since the doping bands are located at approximately the same wavelength. In terms of morphology, the observations made by SEM and AFM microscopies showed that PEDOT polymers self-assemble into polydisperse globular nanoparticles (size comprised between 200 and 500 nm) [50]. Since PEDOT morphology in very acidic medium is comparable with that of PEDOT nanostructures obtained in pure neutral aqueous media (in the absence of any additive such as NaN_3 or $K_2S_2O_8$), one can conclude that neither the acidity of the medium (presence of HCl or $HClO_4$ at 1 M) nor the reactivity of $Cl_2^{\cdot-}$ radicals affect the final morphology of PEDOT radiosynthesized polymers.

4.3 Radiation-Induced Synthesis of CPs Nanostructures by Reduction-Polymerization Route

Usually CPs are synthesized by oxidation of monomers as previously shown. Nevertheless, there are some works in literature concerning the synthesis of CPs by

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4.3 Radiation-Induced Synthesis of CPs Nanostructures by Reduction-Polymerization Route | 135

reduction of monomers by the way of conventional methods [58]. Radiation-based methodology was moreover used in order to radiolytically produce PEDOT nanostructures, thanks to a reduction-polymerization route. In particular, γ -rays were used to produce solvated electrons (e_{aq}^-) in an aqueous solution containing EDOT monomers under N_2 atmosphere. Contrarily to the common approach based on the use of oxidizing radicals, such as hydroxyl radicals ($HO\cdot$), azide radicals ($N_3\cdot$), sulfate radicals ($SO_4^{\cdot-}$), or dichloride radical anions, $Cl_2^{\cdot-}$, hydrated electrons produced by water radiolysis are known as very reducing species and were used to reduce EDOT and then to initiate the reduction-polymerization of PEDOT polymers through coupling reactions.

Evidently in order to quantitatively reduce EDOT and then to synthesize PEDOT, hydroxyl radicals produced under N_2 atmosphere must be scavenged. This is possible, under N_2 atmosphere, in the presence of isopropanol, $(CH_3)_2CHOH$ (at a relatively high concentration, 0.2 mol/l, for example). In these conditions $HO\cdot$ (as well as H- atoms) are quantitatively converted into $(CH_3)_2C\cdot OH$ isopropanol radicals [59, 60], which are not able to oxidize EDOT. In fact, they are almost reducing species, the redox potential of which amounts to $-1.8 V_{SHE}$ at $pH = 7$. As a consequence, when irradiating N_2 -saturated aqueous solutions in the presence of isopropanol, in addition to hydrated electrons ($Ge_{aq^-} = 2.8 \times 10^{-7} \text{ mol/J}$), only an additional reducing short-lived transient species is quantitatively formed, namely, isopropanol radicals, the radiolytic yield of which being $G((CH_3)_2C\cdot OH) = G_{HO\cdot} = 3.4 \times 10^{-7} \text{ mol/J}$.

The radiolytic study demonstrated that, under N_2 in presence of isopropanol, the yield of EDOT reduction is equal to Ge_{aq^-} . [61] This means that isopropanol radicals don't reduce EDOT and that only hydrated electrons react onto EDOT molecules. Consequently, the dose that is necessary for the total reduction of 10 mM in EDOT amounts to 36 kGy, while, assuming once again a step-by-step growth mechanism, the dose D_{max} that is necessary for the complete synthesis of PEDOT amounts to 72 kGy according to Eq. (4.2). Indeed, from a kinetic point of view, the dose effect study showed that similarly to hydroxyl radicals that lead to PEDOT by the way of oxidation of monomers ($PEDOT_{ox}$), the process initiated by hydrated electrons that leads to $PEDOT_{red}$ does not proceed through a chain reaction. In fact, the quantitative synthesis of $PEDOT_{red}$ polymers throughout a reduction-polymerization route proceeds through a step-by-step mechanism and therefore the use of two hydrated electrons per EDOT molecule is needed.

In terms of optical properties, the recorded UV-Vis absorption spectrum of the aqueous solution irradiated at 72 kGy under N_2 in the presence of isopropanol and containing $PEDOT_{red}$ did not show any change or shift when comparing with the spectrum previously obtained for $PEDOT_{ox}$ synthesized at the same irradiation dose in water under N_2O . When it comes to ATR-FTIR, the spectra of $PEDOT_{red}$ and $PEDOT_{ox}$ appeared relatively slightly displaced. Nevertheless, the findings proved, without any ambiguity, that PEDOT polymers were obtained by radiolysis either by reduction-polymerization or by oxidation polymerization [61].

Figure 4.5 displays the resulted morphological structures of $PEDOT_{red}$ synthesized, thanks to e_{aq}^- in aqueous solution under N_2 atmosphere, as obtained

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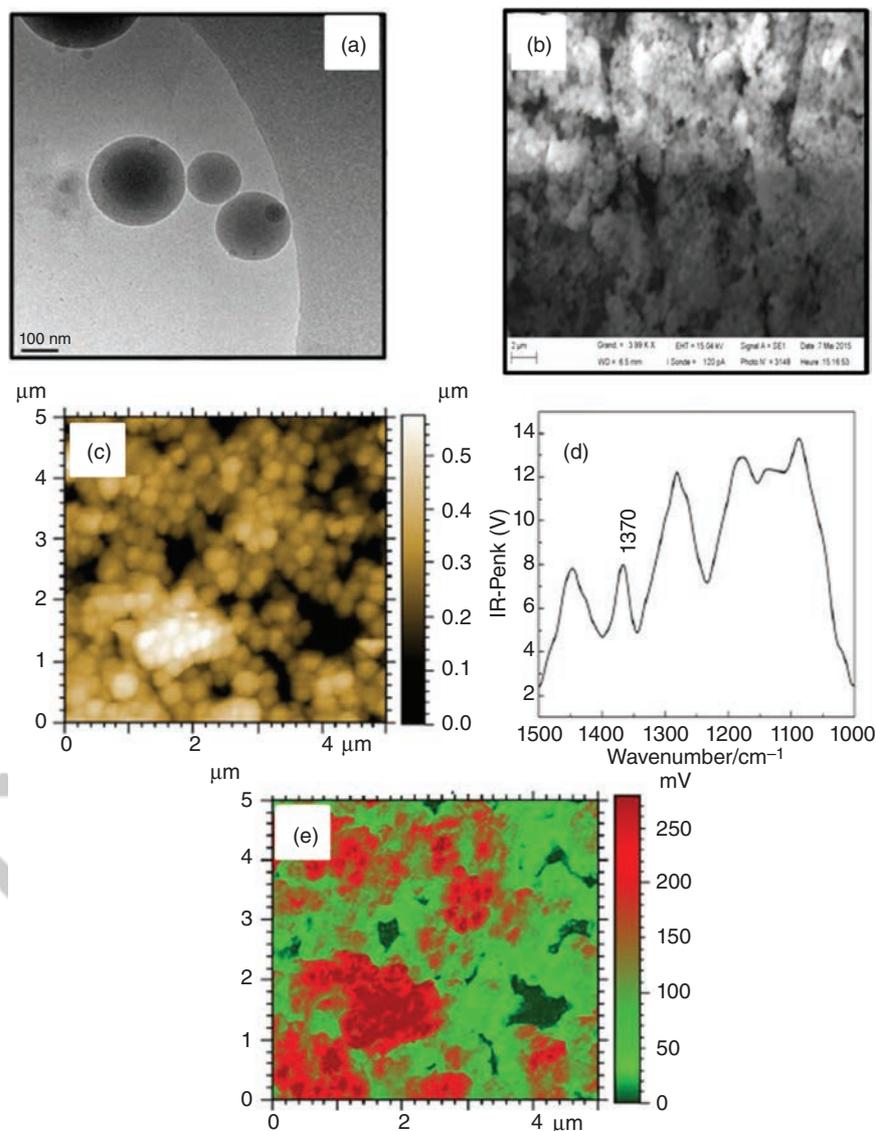


Figure 4.5 Microscopic and AFM-IR characterizations of aqueous samples containing 10 mM in EDOT irradiated at 72 kGy under N₂ in the presence of isopropanol. (a) Cryo-TEM image of PEDOT_{red} polymers exhibiting spherical nano-objects with diameters comprised between 100 and 500 nm, (b) SEM image of PEDOT_{red} polymers after lyophilization and deposition onto carbon tape adhered to aluminum mounts, (c) AFM topographic image of PEDOT_{red} polymers in contact mode after lyophilization and deposition onto ZnSe prism, (d) AFM-IR spectrum of PEDOT_{red} polymers, and (e) AFM-IR chemical mapping of PEDOT_{red} polymers with the IR source tuned to the C–C band at 1370 cm⁻¹. Source: Cui et al. [61].

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by cryo-TEM, SEM, and AFM-IR. Representative cryo-TEM image shows the presence of low-density globular nanostructures forming polydisperse spherical nanoparticles with a diameter comprised between 100 and 500 nm as observed on Figure 4.5a. The displayed SEM image in Figure 4.5b depicts very close-packed spheroidal polymeric nanoparticles. These SEM observations agree well with the morphology of PEDOT_{red} particles observed in aqueous solution by cryo-TEM (Figure 4.5a) without any significant change in the mean size and in the shape. Then, the packing of the particles and their flattening onto the substrate when deposited and dried do not seem to affect the nanostructuring of PEDOT_{red} polymers. All these observations are consistent with the reported characterizations of PEDOT_{ox} polymers synthesized under N₂O by oxidation-polymerization route induced either by γ -rays or by accelerated electrons.

In order to further prove that the spherical nanoparticles observed by cryo-TEM and SEM were effectively made up of PEDOT polymer chains, PEDOT_{red} polymers were imaged and characterized by AFM-IR (Figure 4.5c–e). According to the topological image of PEDOT_{red} recorded in contact mode (Figure 4.5c), the bottom dark areas having no thickness correspond to the substrate. The topography of PEDOT_{red} displayed as the bright areas corresponds to the thicker regions made up of close-packed spherical nanoparticles (100–300 nm in diameter). This AFM observation agrees well with the morphology of PEDOT_{red} globular nanoparticles observed by Cryo-TEM and SEM (Figure 4.5a,b). In order to confirm that these nanostructures are made up of PEDOT polymers, the sample was observed by AFM-IR in the range of 1000–1500 cm⁻¹ (Figure 4.5d). The obtained spectrum displays a peak at 1370 cm⁻¹, which corresponds to the C–C stretching band of PEDOT as observed in typical ATR-FTIR spectra. This definitely demonstrates that the nanoparticles observed in Figure 4.5a–c contain close-packed PEDOT polymer chains. Since the AFM-IR technique also enables the chemical mapping of the sample, this wavenumber 1370 cm⁻¹ was chosen for AFM-IR chemical mapping of the sample. The chemical map was scanned and the absorption strength was recorded (Figure 4.5e). In this figure, the red areas indicate a stronger absorption at the characteristic wavenumber, which is caused by a thicker layer of PEDOT_{red} (~300 nm). When comparing the topography (Figure 4.5c) and the chemical mapping (Figure 4.5e), one can observe that the stronger absorbing areas fit very well with the thicker regions, which implies that the spherical nanoparticles are mainly composed by PEDOT polymer chains. In conclusion, radiation chemistry in reducing conditions leads to the reduction of EDOT monomers and to the growth of PEDOT polymers, which self-assemble into spherical nanostructures (nanoparticles of few hundred nanometers in diameter), those observed by cryo-TEM, SEM, and AFM (Figure 4.5).

4.4 Radiation-Induced Synthesis of CPs/Metal Nanocomposites

As described in previous chapters, CPs were successfully synthesized through either radiation-induced reduction or oxidation polymerization routes. In the same way,

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synthesis of nanocomposites made of CPs and metal nanoparticles was attempted by the way of radiation chemistry. In literature, PEDOT/Ag nanocomposites had already been successfully synthesized by means of both chemical and electrochemical methods [62–64] and had also been shown to possess various potential applications [34, 65, 66]. According to these conventional synthetic methodologies, two-step method or one-pot method is usually applied to synthesize CPs nanocomposites [67, 68]. These latter usually show core–shell structures, the composition of which fundamentally depends on the preparation procedure [69, 70].

In fact the use of radiation-induced synthesis of shape controlled silver nanoparticles in aqueous solution was already conducted by Remita and coworkers [71, 72] on one hand, and the radiolytic preparation of nanostructured conducting PEDOT polymers was also realized as previously highlighted on the other hand [21, 35]. Thus, these two approaches represented good omens for the successful synthesis of PEDOT/Ag composites by radiolysis. Starting from an aqueous solution containing metal ions and EDOT monomers, the use of radiation chemistry for the *in situ* production of hydrated electrons as reducing species or hydroxyl radicals as oxidizing radicals was then conducted in order to synthesize CPs/metal nanocomposites [53].

It was shown that based on γ -radiolysis, PEDOT/Ag nanocomposites can simply be prepared by both two-step and one pot method. According to the two-step method, PEDOT polymers were first synthesized by either oxidation (PEDOT_{ox}) or reduction (PEDOT_{red}) of EDOT monomers and then, PEDOT/Ag nanocomposites were prepared by the further reduction of silver ions into metal nanoparticles. Differently, according to the one pot method, EDOT polymerization and metal ions reduction were achieved in parallel, in one step. As lastly previewed in reduction-polymerization route, γ -induced synthesis of PEDOT_{red} proceeds in N₂-saturated aqueous solutions and in the presence of isopropanol. Under these conditions, two short-lived reactive transient species are formed, namely, e_{aq}⁻ and (CH₃)₂C·OH radicals, with corresponding radiolytic yields (G-values), which amount to 2.8 × 10⁻⁷ mol/J and 3.4 × 10⁻⁷ mol/J. [73] Note that isopropanol radical is a reducing species with a redox potential of -1.8 V_{SHE} at pH = 7, which can quantitatively act as a reducing species towards Ag⁺ but which cannot reduce EDOT monomers. [74] Consequently, EDOT is reduced with a radiolytic yield G_{red}(EDOT) = 2.8 × 10⁻⁷ mol/J, while Ag⁺ ions are reduced by both e_{aq}⁻ and (CH₃)₂C·OH, with a radiolytic yield: G((CH₃)₂C·OH) + G_{aq}⁻ = G_{red}(Ag⁺) = 6.2 × 10⁻⁷ mol/J. [75]

The ratio between EDOT (10 mM) and Ag was changed in case of one pot method, from 10:1 to 10:20, by varying the amount of AgClO₄ salt (from 1 to 20 mM). Whatever the ratio of EDOT to Ag, the aqueous solutions were always added with isopropanol (0.2 M), degassed with N₂ and irradiated at 72 kGy, which enables in all cases the total reduction of both EDOT and Ag⁺ and production of (PEDOT/Ag)_{red}. Regarding two steps method, PEDOT polymers were first synthesized either by reduction (10 mM in EDOT in N₂-saturated aqueous solutions and in the presence of isopropanol, 0.2 M) or by oxidation of EDOT molecules (10 mM in EDOT in N₂O-saturated aqueous solutions) as highlighted before [35], and then silver nanoparticles were obtained by reduction of silver ions (10 mM in AgClO₄

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in N_2 -saturated aqueous solutions and in the presence of isopropanol, 0.2M). The formed CPs nanocomposites from these two step methods were so-called $PEDOT_{red}/Ag_{red}$ and $PEDOT_{ox}/Ag_{red}$. At each step, a dose of 36 kGy was delivered to enable the quantitative synthesis of PEDOT/Ag nanocomposites [53].

UV-Vis absorption spectrophotometry, ATR-FTIR spectroscopy (spectra not shown), and EDX spectroscopy (Figure 4.6) [53] showed that no matter what was the opted procedure, all the prepared nanocomposites were made of PEDOT polymer nanostructures and silver nanoparticles. More interestingly, they all were found to be doped with perchlorate anions [73]. Nevertheless, the morphologies of PEDOT/Ag nanocomposites were almost different and depend on the preparation procedure. As can be seen from the presented cryo-TEM images in Figure 4.6a,b, the observations made on $(PEDOT_{ox}/Ag_{red})$ and $(PEDOT_{red}/Ag_{red})$ in aqueous solution appear similar. In both cases, representative images show the presence of low-density globular structures forming polydisperse spherical nanoparticles with a diameter comprised between 100 and 500 nm. This result was in very good agreement with the observations already made in the case of PEDOT synthesized alone (in the absence of silver) by radiolysis, either by EDOT oxidation or by EDOT reduction. Thus, these low-density globular objects were identified as self-assembled PEDOT polymers. As can be seen in Figure 4.6a,b, smaller nanoparticles (from few nm to 50 nm), which appear very more contrasted (darker), are systematically found adsorbed onto the bigger globular PEDOT nanoparticles. The relatively high

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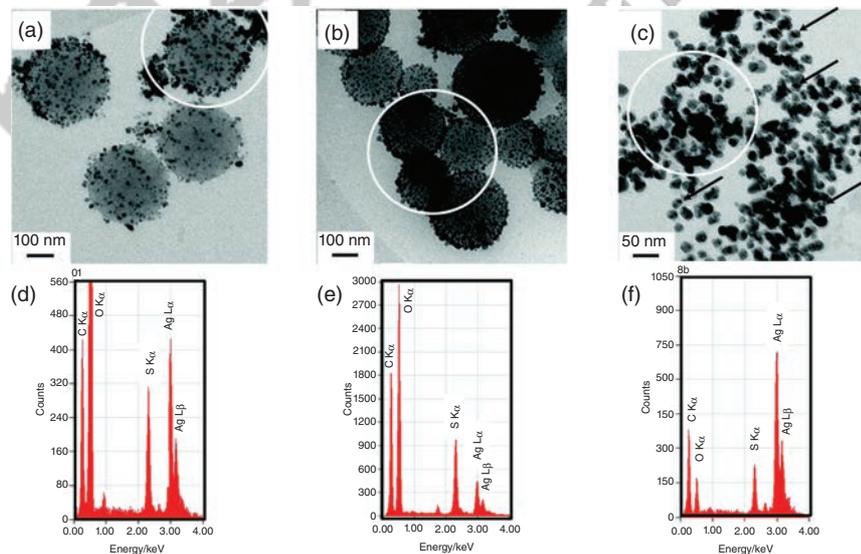


Figure 4.6 Cryo-TEM images of (a) sample containing $(PEDOT_{ox}/Ag_{red})$ synthesized according to two step method, (b) sample containing $(PEDOT_{red}/Ag_{red})$ also synthesized according to two step method and (c) sample containing $(PEDOT/Ag)_{red}$ prepared according to the one-pot method. Energy-dispersive X-ray (EDX) spectra (d), (e), and (f) corresponding to the elemental analysis of the circled areas of the cryo-TEM images [53]. [53] Source: Reproduced by permission of The Royal Society of Chemistry (RSC) on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC.

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contrast of these small particles suggests their metal nature. Since no other objects were observed during Cryo-TEM experiments, these small spherical nanoparticles were attributed to silver nanoparticles.

When it comes to $(\text{PEDOT}/\text{Ag})_{\text{red}}$ formed by one pot method, the structure and morphology shown in Figure 4.6c appear as granular mixtures. This observation was totally different from those made in case of $(\text{PEDOT}_{\text{ox}}/\text{Ag}_{\text{red}})$ and $(\text{PEDOT}_{\text{red}}/\text{Ag}_{\text{red}})$. Indeed, Figure 4.6c shows the presence of low-density globular nanostructures forming polydisperse spheroidal nanoparticles with a diameter between 10 and 50 nm. These organic particles, made of PEDOT polymers and obtained via the one-pot method, are ten times smaller than the PEDOT nanoparticles obtained via the two-step method. On the other hand, as can also be observed in Figure 4.6c, smaller nanoparticles, which appear much more contrasted (darker), are found to be embedded into the core of the bigger globular PEDOT nanoparticles. Some of these dark nanoparticles are indicated in the figure by arrows. The relatively high contrast of these smaller particles suggests once again that they are made of silver.

During Cryo-TEM observations, *in situ* EDX spectroscopy was used to check the chemical composition of radiosynthesized materials in order to prove the presence of sulfur atoms (which are only present in PEDOT polymers, one sulfur atom per EDOT molecule) and of silver atoms (which would be the signature of silver nanoparticles). The aim was also to check the molar ratio between both atoms in radiosynthesized PEDOT/Ag composites. EDX spectra (Figure 4.6, spectra d–f), which correspond respectively to the elemental analysis of the surrounded areas of cryo-TEM images (**a**, **b**, and **c**) of Figure 4.6, highlight the presence, in all samples, of S ($K\alpha$ 2.31 keV) and Ag ($L\alpha$ 2.98 keV and $L\beta$ 3.15 keV). The detection of both sulfur and silver elements definitely demonstrated the concomitant presence, in all the analyzed areas of images **a**, **b**, and **c** of Figure 4.6, of both PEDOT polymers and silver nanoparticles. Also, a quantitative analysis performed in the surrounded areas of Figure 4.6 proved as scheduled the stoichiometric ratio (50% S and 50% Ag) between sulfur and silver in the radiosynthesized composites.

As demonstrated by cryo-TEM microscopy and EDX spectroscopy, composites prepared by two-step method are made of large spherical PEDOT nanoparticles at the surface of which smaller silver nanoparticles adsorb. Due to the two-step method used to produce $(\text{PEDOT}_{\text{ox}}/\text{Ag}_{\text{red}})$ and $(\text{PEDOT}_{\text{red}}/\text{Ag}_{\text{red}})$, PEDOT polymers are first synthesized, in the absence of inorganic ions, and self-assemble, thanks to Van der Waals interactions into globular organic nanoparticles. Silver nanoparticles are formed only during the second step. This explains their presence outside PEDOT nanoparticles. By contrast, in the one-pot method, silver ion reduction takes place in parallel with EDOT reduction. Then, since silver reduction is faster than that of EDOT [53], metal nanoparticles can form prior to the existence of PEDOT nanoparticles. Thus, as shown in Figure 4.6, image **c**, all silver nanoparticles are found surrounded by an organic shell. This could mean that EDOT reduction and polymerization occur in the vicinity of silver nanoparticles. Such a growth mechanism could be explained by the strong interaction, which exists between silver ions (or even atoms) and sulfur atoms of the EDOT monomers. Or maybe, PEDOT polymers are formed far from the silver nanoparticles, in the bulk of the

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4.5 Toward Radiation-Induced Synthesis of CPs Nanostructures in Organic Solvents | 141

aqueous solution, and then diffuse and adsorb at their surface, due to weak van der Waals interactions, enabling the thermodynamic stabilization of silver particles and avoiding their aggregation and sedimentation. This effect of polymers on silver nanoparticles had already been reported in the literature [76].

SEM was also used as a corroboratory tool to check the morphology of PEDOT/Ag nanocomposites [53]. In case of (PEDOT_{ox}/Ag_{red}) and (PEDOT_{red}/Ag_{red}), the composite nanoparticles observed using SEM after deposition were found poly-disperse in size with a diameter comprised between 100 and 500 nm. These SEM observations agree well with the size and the shape of the (PEDOT_{ox}/Ag_{red}) and (PEDOT_{red}/Ag_{red}) particles previously observed in aqueous solution using cryo-TEM observations (Figure 4.6, images a and b). In contrast to these observations, no spherical nanoparticles were observed in case of (PEDOT/Ag)_{red}, which may be due to the fact that their relatively small size avoids their observation during SEM microscopy. In fact, SEM characterization showed that (PEDOT/Ag)_{red} composites had become a compact hybrid after deposition. Also, when varying the EDOT/Ag ratio, from 10:5 to 10:20, as the proportion of silver increases, the (PEDOT/Ag)_{red} composites become denser and form more compact blocks.

4.5 Toward Radiation-Induced Synthesis of CPs Nanostructures in Organic Solvents

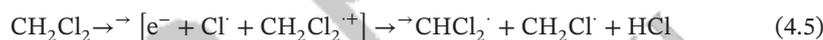
All previous radiolytic studies were conducted in aqueous solutions with the aim to produce CPs nanostructures or CPs composites. Different strategies were adopted: oxidation and reduction routes, changing the atmosphere, varying the oxidizing species, and adjusting the pH. Nevertheless, the following question remains: what about changing the solvent? This is important for instance in order to enhance the processability and to synthesize CPs starting from hydrophobic monomers such as 3-hexylthiophene (3HT). The extension of original radiolytic methodology to the use of organic solvents is indeed a need since radiation-induced polymerization in aqueous solution cannot always be used. In fact, there are several obstructions that have been faced with γ -radiolysis of aqueous solutions, such as the poor processability, low solubility, and even sometimes the insolubility of some of concerned monomers, namely, 3-alkylthiophenes.

Indeed, the use of organic solvent to synthesize CPs was investigated by Koizumi and coworkers. [77] who studied the mechanism of oxidative polymerization of conducting polymers in several organic solvents by γ -irradiation. The study was performed on 3-octylthiophene (3OT) and the oxidative polymerization was initiated by γ -radiolysis of chloroform, hexane, and neat monomer solution. The polymerization was successfully induced in chloroform. The study showed that the products contain large amounts of small oligomers, and the yield of polymers with high molecular weight was found low. Furthermore, high irradiation dose and removal of the oligomers was shown to be necessary to obtain usable polymers for any potential applications.

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A similar radiolytic approach was conducted in dichloromethane (DCM). Indeed, DCM is a very good solvent for many organic compounds and its gamma radiolysis is relatively well known under different conditions [78]. Moreover, DCM was already used to carry out electrochemical or radiolytical one-electron oxidation of solutes [78, 79], and it has been proved that irradiated DCM is a good oxidizing system [80]. Indeed, γ -irradiation of DCM solvent yields several oxidizing species that could enable first the oxidation of dissolved organic monomers and then their polymerization into CPs. With these in mind, strategy based on radiation chemistry was extended to the preparation of conducting polymers into organic solvents. In particular, starting from EDOT monomers dissolved in DCM solvent, the synthesis by γ -rays of PEDOT polymers was elaborated and optimized [81].

It is well established that γ -irradiation of deoxygenated solutions of DCM (under N_2 for instance) leads, within short nanosecond time scale, to the formation of solvated electrons in addition to neutral radicals and solvent radical cations which quickly lead to dichloromethyl ($CHCl_2^\cdot$) and chloromethyl (CH_2Cl^\cdot) radicals [79, 82]:



All the generated radicals are well known as strong oxidizing agents toward organic materials. Some investigations highlighted the possibility of oxidation of aromatic hydrocarbons by neutral dichloromethyl and chloromethyl ($CHCl_2^\cdot$ and CH_2Cl^\cdot) radicals in spite of their relatively low redox potentials [80, 83], suggesting the idea that all these radicals should enable the oxidation of EDOT monomers and then their polymerization into PEDOT polymers, the yield of EDOT oxidation being equivalent to the yield of production of the oxidizing species coming from DCM radiolysis (G_{ox}). Once again, taking into account the step by step mechanism involved during CPs growth, the theoretical irradiation dose (D_{max}) that should lead to the total oxidation of EDOT into PEDOT can be expressed as a function of G_{ox} through Eq. (4.2) [31, 35], in which this time the density, d , is that of DCM solvent ($d = 1.35 \text{ kg/l}$).

In this context, in order to check the dose effect and to evaluate the required irradiation dose for quantitative PEDOT preparation and then to determine the effective yield of EDOT oxidation, DCM solutions containing 10 mM in EDOT under N_2 atmosphere were irradiated at increasing doses up to 70 kGy. The UV-Vis absorption spectrum of the solution before irradiation is shown in insert of Figure 4.7. As observed, EDOT exhibits two absorption maxima at 242 nm and 259 nm, which are features of the π - π^* electronic transitions in the thiophene rings within the DCM solvent. As demonstrated in previous works [31, 35], the study of the variation in EDOT concentration as a function of the irradiation dose should enable the determination of the radiolytic yield of EDOT oxidation (G_{ox}). However, stable and transient products (dimers of 1,1-dichloroethane, 1,2-dichloroethane, 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane) [84] were detected in irradiated solution of DCM and were found to absorb in the same wavelength region avoiding any direct calculation of G_{ox} . Nevertheless, as it will be shown, following the evolution of the intensity of PEDOT UV-Vis absorption spectrum as a function of the absorbed dose allowed first

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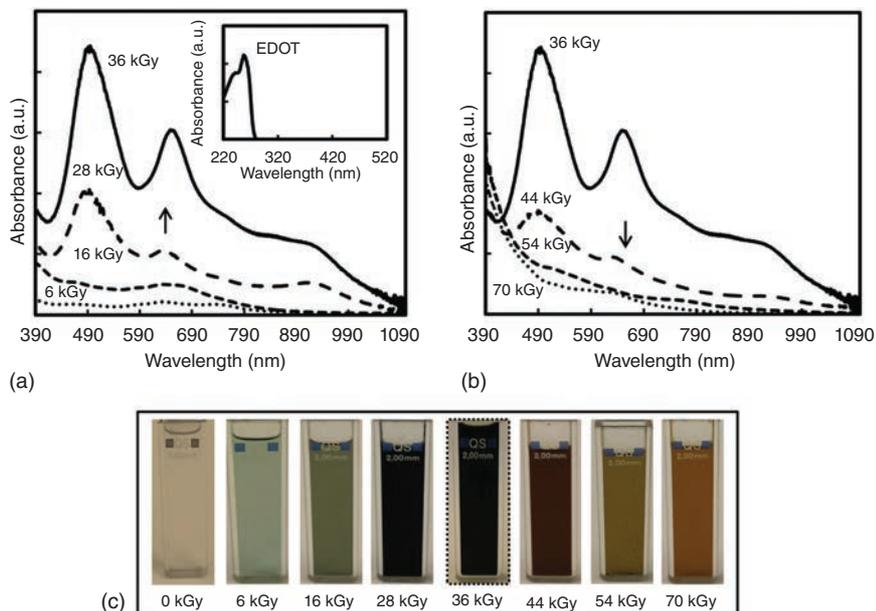


Figure 4.7 UV-Vis absorption spectra of DCM solution containing 10 mM in EDOT and irradiated under N_2 atmosphere at increasing doses from: (a) 0 to 36 kGy and (b) from 36 to 70 kGy. The reference was DCM. Insert of (a) UV-Vis absorption spectrum of the solution before irradiation (c) Photographs of DCM solution before and after irradiation at increasing doses [81]. [81] Source: Reproduced by permission of The Royal Society of Chemistry (RSC) on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC.

the estimation of the radiation dose needed to achieve quantitative polymerization of EDOT monomers (D_{max}) and second the calculation of G_{ox} according to Eq. (4.2).

In order to follow the progressive formation of PEDOT polymers, the DCM solution containing 10 mM in EDOT was irradiated under N_2 at increasing doses up to 70 kGy (Figure 4.7) and its absorption spectrum was recorded as a function of the irradiation dose. Up to irradiation dose of 36 kGy, progressively and remarkably, two peaks were being protruded at 490 and 650 nm (Figure 4.7a). These peaks were attributed to formation of PEDOT polymers and ascribed to the $\pi-\pi^*$ transitions along the polymer chains. [85, 86] Whereas the observed peaks at approximately 800–1000 nm were attributed to polaron and/or bipolaron bands, which are characteristic of oxidized state of PEDOT [57, 87]: the considerable amount of hydrochloride acid produced from γ -radiolysis of DCM yields to different doping states of PEDOT polymers. As a consequence, the doped PEDOTs with chloride ions show an absorption peak at approximately 900 nm corresponding to the charge carrier band of the charged polymers [57]. In agreement, the corresponding ATR-FTIR spectra also showed the presence, whatever the irradiation dose, of a less common infrared band located at 1640 cm^{-1} . This band had already been observed in earlier studies in the case of PEDOT polymers doped with chloride ions [12, 57].

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Proceeding, the solutions with irradiation doses higher than 36 kGy leads to gradual decrease in the absorption of PEDOT polymers at both 490 and 650 nm (Figure 4.7b). DCM solution containing 10 mM in EDOT appears colorless before irradiation (Figure 4.7c). Distinctly, the irradiated solutions that are shown in Figure 4.7c got colored with sky blue right after gamma irradiation. This color parallel darkens after with proceeding the irradiation with higher doses up to 36 kGy. Dark blue and black precipitants were observed in irradiated solutions at doses of 28–36 kGy. However, when exceeding the dose of 36 kGy and continuing the irradiation up to 70 kGy, the solution gradated towards brown, then yellow, and finally orange, while the black precipitant appeared to be glue. These color fluctuations above 36 kGy and the spectral variations upon using overdose were ascribed to the overoxidation of PEDOT polymers, which evidently leads to degradation and breaking down of the polymer chains.

This overoxidation and degradation of PEDOT polymers irradiated above 36 kGy in DCM under N_2 atmosphere was demonstrated by ATR-FTIR spectroscopy and SEC chromatography. Indeed, the IR spectra showed the presence, in the case of an irradiation dose above 36 kGy, of a broadband from 1650 to 1730 cm^{-1} , which is the sign of an overoxidation state [88]. In particular, this band could be attributed to

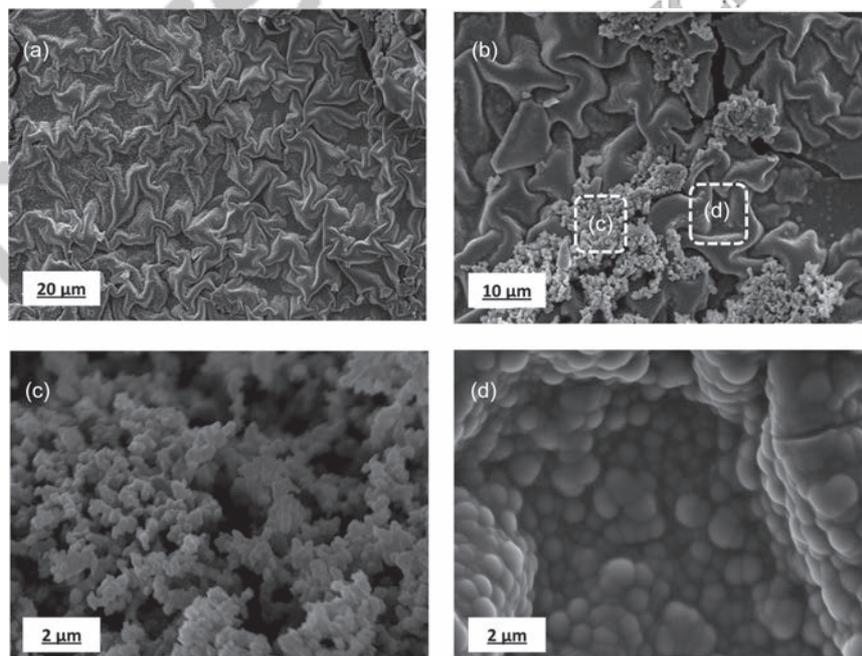


Figure 4.8 SEM images of dried PEDOT polymers powder after deposition onto carbon tape adhered to aluminum mounts and gold coating: (a) and (b). Images (c) and (d) are close view of SEM image (b). The powder was obtained after solvent evaporation. PEDOT polymers were synthesized by γ -radiolysis at 36 kGy of a DCM solution containing 10 mM in EDOT under N_2 atmosphere [81]. [81] Source: Reproduced by permission of The Royal Society of Chemistry (RSC) on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC.

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the formation of a carbonyl group. While, SEC analysis showed that more and more oligomers of lower molecular weight are formed at doses above 36 kGy, indicating the occurrence of damage and breaking down of the polymer chains. Subsequently, these findings suggest that the radiation dose needed for quantitative polymerization of 10 mM in EDOT monomers (D_{\max}) in DCM solvent under N_2 atmosphere amounts to 36 kGy and that, according to Eq. (4.2), the yield of EDOT oxidation (G_{ox}) amounts to 4.12×10^{-7} mol/J in these experimental conditions.

Morphology of PEDOT polymers synthesized under N_2 atmosphere in a DCM solution was checked by SEM microscopy after solvent evaporation. SEM images recorded after deposition of dried PEDOT polymers powder onto carbon tape adhered to aluminum mounts and gold coating are displayed on Figure 4.8. As can be seen in Figure 4.8a, SEM image displays a comprehensive view of creased film of PEDOT. Figure 4.8b shows closer view of this film in which globular clusters are observed. These globular particles can be clearly seen in Figure 4.8c. In a close view of the film creases in Figure 4.8d, it is possible to see that PEDOT film is composed of aggregated globules and packed spheroid particles with average size of 0.5 to 2 μm . These results are in good agreement with previous observations reported in the literature in the case of PEDOT polymers doped with chloride ions as prepared by electrochemical method [12]. To further confirm that PEDOT polymers radiosynthesized in DCM solvent are doped with chloride ions, *in situ* energy dispersive X-ray (EDX) analysis was performed on the PEDOT sample synthesized at 36 kGy during SEM experiments (but without gold coating). These experiments undoubtedly confirmed the presence of chlorine atoms within the sample.

4.6 The Electrical and Physical Properties of Radiosynthesized CPs

The importance of radiation induced polymerization is to achieve effective and simple synthesis of processable and usable forms of conducting polymers either in solution or after deposition. The radiation-based methodology is certainly one of the most appropriate techniques for promising production of CPs. As previewed, the methodology is versatile and reliable. In addition, as it will be presented, the properties of radiosynthesized CPs were in most cases evaluated and found comparable with those of conducting materials that were obtained by conventional methods in terms of physical and electrical properties.

One of the most important properties that characterize the polymers is generally their molecular weight. Indeed, the presence of long polymer chains, or more precisely having high π - π^* conjugation, gives CPs their remarkable electrical properties. Thus, size exclusion chromatography (SEC) analysis was used in order to characterize the molecular weight and the chain length of the radiosynthesized conducting polymers. Another important property of CPs is their electrochemical behavior. This behavior was highlighted in case of different CPs synthesized by radiation methodology by using cyclic voltammetry analysis and optical band gap

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($E_{\text{gap.op}}$) calculations. The CV analysis enabled the determination of oxidation and reduction potentials of radiosynthesized polymers and thus the estimation of the energy level of the highest occupied molecular orbital (HOMO) from the ionization potential, the energy level of the lowest unoccupied molecular orbital (LUMO) from the electronic affinity, as well as the electronic band gap ($E_{\text{gap.el}}$). In addition, the electrical conductivity of the radiosynthesized CPs and CPs nanocomposites, as measured by four-point probe technique, was also checked and compared with the electrical conductivities reported in literature for CPs synthesized by conventional methods. Besides, the physical properties of the radiosynthesized CPs and CPs nanocomposites were evaluated by using thermogravimetric analysis (TGA).

4.6.1 CPs Chain Lengths

The weight average molecular weight (M_w) and the molar mass at the maximum peak (M_p) of some processable radiosynthesized CPs were estimated from SEC with a polystyrene calibration. The SEC data obtained for these radiosynthesized conducting polymers (dissolved in THF at a concentration of 3 mg/ml) are displayed in Table 4.1. M_w and M_p were found to be 2630 and 1297 g/mol (around 18 and 9 monomer units, respectively) for PEDOT nanostructures synthesized in water under N_2O atmosphere, thanks to hydroxyl radicals oxidation (PEDOT-OH or PEDOT_{ox}), 4145 and 2484 g/mol (around 29 and 17 monomer units respectively) for PEDOT synthesized in water under N_2 atmosphere, thanks to solvated electrons reduction (PEDOT_{red}), 1423 and 1128 g/mol (around 10 and 8 monomer units) for PEDOT synthesized in very acidic aqueous medium (PEDOT_{pH0}) [50] and finally 1308 and 1015 g/mol (around 9 and 7 units) for PEDOT synthesized in DCM solvent (PEDOT_{DCM}) [81].

Table 4.1 Summary of some optical and electronic band gaps reported in case of radiosynthesized CPs together with their molecular weights as deduced from SEC chromatography.

Radiosynthesized conducting polymers	Optical band gap $E_{\text{gap.op}}$ (eV)	Electronic band gap $E_{\text{gap.el}}$ (eV)	SEC data	
			Molar mass M_p (g/mol)	Molecular weight M_w (g/mol)
PPy [46]	1.90	—	—	—
PEDOT-OH (PEDOT _{ox}) [35]	2.00	—	1297 (~9 units)	2630 (~18 units)
PEDOT-N ₃ [35]	2.30	—	—	—
PEDOT _{red} [61]	1.90	—	2484 (~17 units)	4145 (~29 units)
PEDOT _{pH0} [50]	1.14	1.04	1128 (~8 units)	1423 (~10 units)
PEDOT _{DCM} [81]	1.65	1.61	1015 (7 units)	1308 (~9 units)

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SEC data showed that all the detected polymers have reasonable molecular weights. Between all radiosynthesized CPs, PEDOT_{red} polymers are clearly characterized by the longer polymer chains (up to 29 monomer units). Nevertheless, the solubility of all radiosynthesized CPs was found poor in THF solvent. This clearly means that in all cases the longer radiosynthesized polymers were not detected by SEC and that the molar masses reported in Table 4.1 don't correspond to the maximal ones.

4.6.2 Optical and Electronic Band Gaps of CPs

The electronic ($E_{\text{gap,el}}$) and optical ($E_{\text{gap,op}}$) band gaps reported in case of radiosynthesized PEDOT polymers (PEDOT-OH, PEDOT-N₃ synthesized, thanks to azide radical oxidation, PEDOT_{red}, PEDOT_{pH0}, and PEDOT_{DCM}) and radiation induced PPy polymers are shown in Table 4.1. Note that cyclic voltammetry measurements were carried out only in case of PEDOT_{pH0} and PEDOT_{DCM} thanks to their better processability. These electrochemical experiments enabled to calculate the electronic energy band gaps ($E_{\text{gap,el}}$) of PEDOT_{pH0} and PEDOT_{DCM} that amount, respectively, to 1.04 eV [50] and 1.61 eV [81]. Besides, the UV-Vis absorption spectra of PEDOT_{pH0} and PEDOT_{DCM} (see Figure 4.4 spectrum a and Figure 4.7 spectrum a) enabled the determination of the optical energy band gaps ($E_{\text{gap,op}}$) of these two CPs which amount to 1.14 eV [50] and 1.65 eV [81], respectively. In case of the other radiosynthesized CPs, the optical energy band gaps were calculated from the UV-Vis absorption spectra obtained in previous works [35, 46, 61] and amount to 1.90 eV for PPy, 2.00 eV for PEDOT-OH, 2.30 eV for PEDOT-N₃, and 1.90 eV for PEDOT_{red}.

As seen from Table 4.1, PEDOT polymers obtained by reduction-polymerization route (PEDOT_{red}) present lower optical band gap than those of PEDOT polymers obtained by oxidation polymerization route (PPy, PEDOT-OH, and PEDOT-N₃). This difference is evidently originated from the fact the PEDOT_{red} polymers are characterized by a higher molecular weight (see Table 4.1). Interestingly, despite their relatively low molecular weight, the polymers radiosynthesized in very acidic medium (PEDOT_{pH0}) are characterized by the lowest optical and electrical band gaps in comparison with the other radiosynthesized CPs. This could be explained by the important *in situ* doping of PEDOT_{pH0} polymers by Cl⁻ ions [50]. In the same manner, the doping of PEDOT_{DCM} polymers that are characterized by a low molecular weight should explain the small optical and electronic band gaps values obtained. A more likely reason of these findings is also the poor solubility of the prepared polymers, which prevents the detection by SEC of polymers with higher molecular weight.

4.6.3 Electrical Conductivities of CPs

The electrical conductivities reported in case of radiosynthesized CPs (PEDOT-OH, PEDOT synthesized by accelerated electrons, PEDOT_{red}, PEDOT_{pH0}, PEDOT_{DCM}, PPy polymers, and PEDOT composites (PEDOT_{ox}/Ag_{red}, PEDOT_{red}/Ag_{red}, and (PEDOT/Ag)_{red}) are shown in Table 4.2. The electrical conductivities measured

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Table 4.2 Electrical conductivities of radiosynthesized CPs nanostructures and CPs nanocomposites as measured by using the four-point probe technique.

Radiosynthesized conducting polymers	Electrical conductivity (S/cm)
Radiosynthesized PPy	57×10^{-3} [46]
PEDOT-OH (PEDOT _{ox})	9.8×10^{-3} [61]
PEDOT by accelerated electrons	0.9×10^{-3} [31]
PEDOT _{red}	3.4×10^{-3} [61]
PEDOT _{pH0}	3.3×10^{-3} [50]
PEDOT _{DCM}	2.6×10^{-3} [81]
PEDOT _{ox} /Ag _{red}	3.2×10^{-3} [53]
PEDOT _{red} /Ag _{red}	5.6×10^{-3} [53]
(PEDOT/Ag) _{red}	3.6×10^{-3} [53]

using the four-point probe technique after doping process were found interestingly remarkable for all radiosynthesized materials. For instance, the electrical conductivity of PPy polymers radiosynthesized in N₂O-saturated aqueous solutions was found equal to 57×10^{-3} S/cm. This value is nearly five times higher than that of chemically synthesized PPy (12×10^{-3} S/cm) [46]. The measured electrical conductivities of PEDOT_{ox} and PEDOT_{red} were $9.8 \times 10^{-3} \frac{S}{cm}$ and 3.4×10^{-3} S/cm respectively [61]. The value found in the case of PEDOT_{red} is somewhat lower than that of PEDOT_{ox}. Note that PEDOT polymers synthesized through accelerated electrons also possess a remarkable electrical conductivity (0.9×10^{-3} S/cm). Furthermore, the electrical conductivity of PEDOT/Ag nanocomposites, which were radiolytically prepared according to two-step method or one-pot method, are all in the same order of magnitude (about 10^{-3} S/cm) and remain not far from the values found for PEDOT_{ox} and PEDOT_{red} [53]. The conductivity of PEDOT polymers synthesized in very acidic aqueous medium (PEDOT_{pH0}) was found to be 3.3×10^{-3} S/cm, and that of PEDOT polymers prepared in organic solvent (PEDOT_{DCM}) was found equal to 2.6×10^{-3} S/cm. These latter values have the same order of magnitude as the conductivities of PEDOT synthesized by radiolysis in neutral aqueous solutions and remain close to the conductivities reported in literature for PEDOT polymers produced by conventional methods [56, 89, 90]. The obtained electrical conductivity findings prove that the radiosynthesized materials are certainly semiconductors and no doubt about their implementation in practical applications.

4.6.4 Thermal Properties of CPs

The thermal properties of radiosynthesized CPs nanostructures and CPs nanocomposites were analyzed by TGA. TGA analysis of PEDOT_{red} and PEDOT_{ox} polymers

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4.7 Comparative Studies Between Radiolytic Methodology and Conventional Methods | 149

and their degradation processes were found quite similar. In case of PEDOT/Ag composites, TGA revealed that all composites were characterized by the same thermal stability, which remains higher, over a wide range of temperatures, than that of pure PEDOT polymers synthesized in aqueous solutions by both radiolytic routes (oxidation and reduction). Also, the TGA analysis showed that the thermal stability can be enhanced by increasing the amount of silver into the composites. Besides, TGA analysis revealed that PEDOT polymers radiosynthesized in DCM solvent under N_2 atmosphere were characterized by the same good thermal stability as that of PEDOT polymers synthesized by γ -radiolysis in aqueous media. In case of PPy, a comparative study was carried out between chemically synthesized PPy by using $K_2S_2O_8$ as oxidant and radiosynthesized conducting PPy in aqueous solutions under N_2O . TGA analysis showed that both PPy polymers possess comparable good thermal stability [46]. Moreover, the TGA analysis was found in very good agreement with TGA data already reported in the literature concerning PPy polymers [91].

4.7 Comparative Studies Between Radiolytic Methodology and Conventional Methods

Different kinds of CPs were successfully synthesized by radiolysis under different experimental conditions either in aqueous solution or in organic solvent. While in most of related studies, the physicochemical properties of radiosynthesized CPs were found intrinsically good, in some studies these properties were also compared with those of CPs synthesized by conventional chemical or electrochemical methods.

Optical and electrical properties of PEDOT polymers synthesized by radiolysis in aerated aqueous solutions (containing 100 mM $LiClO_4$) were compared after deposition onto ITO substrate with those of PEDOT polymers electrosynthesized onto ITO electrode in the same environmental conditions [21]. Both polymers, doped with perchlorate ions, showed comparable UV-visible spectral features and capacitive current behavior as highlighted by cyclic voltammetry analysis [21]. Note that the UV-visible absorption spectrum of the PEDOT film obtained after deposition of radiosynthesized CPs displayed, in agreement with electrosynthesized PEDOT layers, an intense absorption band at 550 nm in addition to a shoulder at around 750 nm. This result was in agreement with the fact that polymer films, which are characterized by longer conjugation lengths in the solid state absorb at higher wavelengths than polymers in solution [92]. This result was also in agreement with absorption spectra of solid films of doped polythiophenes, which are characterized by absorption maxima in the region 480–520 nm [92]. The similarity in the absorption spectra and cyclic voltammograms of both radiosynthesized and electrosynthesized PEDOT polymers definitely highlight the successful synthesis of doped PEDOT polymers by the way of radiation chemistry [21].

Optical properties of PEDOT polymers synthesized in aqueous solution at very low temperature by the way of electron beam irradiation (by using sulfate radicals, $SO_4^{\cdot-}$,

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as oxidizing species) were also found very close to those of PEDOT polymers chemically synthesized in water at different temperatures (by using $K_2S_2O_8$ as oxidizing agent) [38].

Structural, optical, electrical, and thermal properties of PPy polymers synthesized by gamma-radiolysis in aqueous solutions under N_2O atmosphere were finally compared with those of PPy polymers chemically synthesized in the bulk by using $K_2S_2O_8$ as oxidant [46]. As highlighted in this study, both PPy polymers were characterized by comparable optical and thermal properties. Nevertheless, as previously mentioned, radiosynthesized PPy polymers were characterized by an electrical conductivity, which was found five times higher than that of chemically synthesized PPy [46].

4.8 Summary

Monomers oxidation induced polymerization, by using oxidizing species, is the conventional way to obtain conducting polymers. The most common approaches that are used to synthesize CPs are either chemical polymerization through adding oxidizing reagents or electro-polymerization by applying a potential across a solution containing the monomers. Even though these two methods are well understood and their mechanism is relatively well known, there still remain some problems such as chemical contamination, purification steps, and sometimes need to use a catalyst. On the other hand, conducting polymers have some limitations that restrict their applications due to difficult processability, low solubility in common solvents, and poor thermal stability.

Current research aims to develop new synthesis strategies and new conducting polymers with tuned morphologies and optimized properties. Apart from traditional methods of polymers synthesis, ionizing radiation induced polymerization by γ -rays or accelerated electrons has recently been developed. This new alternative methodology based on radiation chemistry was developed in order to polymerize different kinds of conducting polymers in aqueous solutions, in the absence of any external chemical initiators, thanks to the oxidation (and alternatively the reduction) of dissolved organic monomers by oxidizing (or reducing) radicals *in situ* produced in the medium during water radiolysis. Interestingly, by the use of pulse radiolysis, the growth of CPs was shown to proceed through a recurrent step-by-step oxidation process.

With radiolytic method, nanostructured PEDOT materials were obtained in water by EDOT oxidation using hydroxyl radicals ($HO\cdot$), azide radicals ($N_3\cdot$), sulfate radicals ($SO_4\cdot^-$), dichloride radical anions ($Cl_2\cdot^-$), and even by EDOT reduction, thanks to the use of hydrated electron (e_{aq}^-) generated by water radiolysis. Interestingly, chemical, morphological, optical, electrical, and thermal properties of PEDOT polymers were found dependent on the nature of the initiating radiolytic species. The versatility of the radiolytic method was demonstrated since PEDOT polymers were successfully produced in water under different atmospheres (air, O_2 , N_2O , N_2), in presence of solutes which potentially act as doping agents, in very acidic aqueous

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medium and also in an organic solvent, such as DCM. Interestingly, CPs synthesized by radiolysis in acidic aqueous medium or in DCM are *in situ* produced in a doped state. The radiolytic procedure was also extended to the synthesis of other kinds of conducting materials since PPy polymer nanostructures as well as PEDOT/Ag nanocomposites were successfully prepared.

All the radiosynthesized CPs nanostructures were characterized by remarkable optical and electrical properties. Interestingly their performance was found comparable with other conducting polymers synthesized by chemical or electrochemical methods. From now on, radiolytic methodology fully appears as a promising alternative method for the preparation, not only in water but also in organic solvents, of conducting polymers with enhanced properties. The considerable electrical conductivity of some radiosynthesized polymers and, above all, their *in situ* doping and their low band gap foreshadow further advances in the field of conducting polymers synthesis and applications.

Finally, radiation induced synthesis of conducting polymers could interestingly be considered in soft or hard templates and even in complex matrices since high energy radiations are characterized by a strong penetrating power and are known to lead to very homogeneous processes. This evidently gives a glimpse of future promising applications

References

- 1 Freund, M.S. and Deore, B.A. (2007). *Self-Doped Conducting Polymers*. Wiley.
- 2 Ruiz, J., Gonzalo, B., Dios, J.R. et al. (2013). Improving the processability of conductive polymers: the case of polyaniline. *Adv. Polym. Tech.* 32 (S1): 180–188.
- 3 Heeger, A.J. (2001). Semiconducting and metallic polymers: the fourth generation of polymeric materials. *J. Phys. Chem. B* 105 (36): 8475–8491.
- 4 MacDiarmid, A.G. (2001). “Synthetic Metals”: a novel role for organic polymers (Nobel Lecture). *Angew. Chem.* 40 (14): 2581–2590.
- 5 Gospodinova, N. and Terlemezyan, L. (1998). Conducting polymers prepared by oxidative polymerization: polyaniline. *Prog. Polym. Sci.* 23 (8): 1443–1484.
- 6 Paradee, N. and Sirivat, A. (2014). Synthesis of poly(3,4-ethylenedioxythiophene) nanoparticles via chemical oxidation polymerization. *Polym. Int.* 63 (1): 106–113.
- 7 Zhang, X. and Manohar, S.K. (2004). Bulk synthesis of polypyrrole nanofibers by a seeding approach. *J. Am. Chem. Soc.* 126 (40): 12714–12715.
- 8 Roncali, J. (1992). Conjugated poly(thiophenes) – synthesis, functionalization, and applications. *Chem. Rev.* 92 (4): 711–738.
- 9 Tebyetekerwa, M., Yang, S., Peng, S. et al. (2017). Unveiling polyindole: free-standing As-electrospun polyindole nanofibers and polyindole/carbon nanotubes composites as enhanced electrodes for flexible all-solid-state supercapacitors. *Electrochim. Acta* 247: 400–409.
- 10 Zhang, X.T., Zhang, J., Song, W.H., and Liu, Z.F. (2006). Controllable synthesis of conducting polypyrrole nanostructures. *J. Phys. Chem. B* 110 (3): 1158–1165.

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- 11 Siju, C.R., Narasimha Rao, K., Ganesan, R. et al. (2011). Synthesis of poly(3,4-ethylenedioxythiophene) nano structure using reverse microemulsion polymerization. *Phys. Status Solidi* 8 (9): 2739–2741.
- 12 Zhou, H., Han, G., Chang, Y. et al. (2015). Highly stable multi-wall carbon nanotubes@poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) core-shell composites with three-dimensional porous nano-network for electrochemical capacitors. *J. Power Sources* 274: 229–236.
- 13 Gupta, B., Mehta, M., Melvin, A. et al. (2014). Poly (3,4-ethylenedioxythiophene) (PEDOT) and poly (3,4-ethylenedioxythiophene)-few walled carbon nanotube (PEDOT-FWCNT) nanocomposite based thin films for Schottky diode application. *Mater. Chem. Phys.* 147 (3): 867–877.
- 14 Zhang, X., Lee, J.-S., Lee, G.S. et al. (2006). Chemical synthesis of PEDOT nanotubes. *Macromolecules* 39 (2): 470–472.
- 15 Choi, W., An, T., and Lim, G. (2009). Fabrication of conducting polymer nanowire sensor array. In: *2009 IEEE Sensors*, 1153–1151. IEEE.
- 16 Jang, J. and Yoon, H. (2005). Formation mechanism of conducting polypyrrole nanotubes in reverse Micelle systems. *Langmuir* 21 (24): 11484–11489.
- 17 Huang, J. (2006). Syntheses and applications of conducting polymer polyaniline nanofibers. *Pure Appl. Chem.* 78 (1): 15.
- 18 Aydın, M., Durmus, Z., Kavas, H. et al. (2011). Synthesis and characterization of poly(3-thiophene acetic acid)/Fe₃O₄ nanocomposite. *Polyhedron* 30 (6): 1120–1126.
- 19 Brooke, R., Cottis, P., Talemi, P. et al. (2017). Recent advances in the synthesis of conducting polymers from the vapour phase. *Prog. Mater. Sci.* 86: 127–146.
- 20 Chapiro, A. (1979). Radiation induced polymerization. *Radiat. Phys. Chem.* 14 (1): 101–116.
- 21 Lattach, Y., Deniset-Besseau, A., Guigner, J.-M., and Remita, S. (2013). Radiation chemistry as an alternative way for the synthesis of PEDOT conducting polymers under “soft” conditions. *Radiat. Phys. Chem.* 82: 44–53.
- 22 Karim, M.R., Lee, C.J., and Lee, M.S. (2007). Synthesis of conducting polypyrrole by radiolysis polymerization method. *Polym. Adv. Technol.* 18 (11): 916–920.
- 23 Karim, M., Jae Lee, C., Jin Kim, H. et al. (2007). Preparation of buckyball-shaped conducting polythiophene by the gamma radiation-induced polymerization method. *Macromol. Symp.* 249–250: 234–240.
- 24 Remita, S. (2001). Radiation induced lipid peroxidation: factors which determine the oxidizability of lipids. *Can. J. Physiol. Pharmacol.* 79: 144–153.
- 25 Remita, S., Fontaine, P., Lacaze, E. et al. (2007). X-ray radiolysis induced formation of silver nano-particles: A SAXS and UV-visible absorption spectroscopy study. *Nucl. Instrum. Methods Phys. Res.* 263 (2): 436–440.
- 26 Varmenot, N., Remita, S., Abedinzadeh, Z. et al. (2001). Oxidation processes of N,S-diacetyl-L-cysteine ethyl ester: influence of S-acetylation. *J. Phys. Chem. A* 105 (28): 6867–6875.
- 27 Attia, J., Remita, S., Jonic, S. et al. (2007). Radiation-induced synthesis and cryo-TEM characterization of silver nanoshells on linoleate spherical micelles. *Langmuir* 23 (19): 9523–9526.

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Without corrections/ ohne Korrekturen	<input type="checkbox"/>
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- 28 Spinks, J.W.T.W. and Woods, R.J. (1990). *An Introduction to Radiation Chemistry*, vol. 3. John-Wiley and Sons, Inc.
- 29 Ferradini, C. and Jay-Gerin, J.-P. (1999). La radiolyse de l'eau et des solutions aqueuses: historique et actualité. *Can. J. Chem.* 77 (9): 1542–1575.
- 30 Ferradini, C. and Jay-Gerin, J.-P. (2000). The effect of pH on water radiolysis: a still open question – a minireview. *Res. Chem. Intermed.* 26 (6): 549–565.
- 31 Coletta, C., Cui, Z., Archirel, P. et al. (2015). Electron-induced growth mechanism of conducting polymers: a coupled experimental and computational investigation. *J. Phys. Chem. B* 119 (16): 5282–5298.
- 32 Buxton, G.V., Greenstock, C.L., Helman, W.P., and Ross, A.B. (1988). Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot\text{OH}/\cdot\text{O}^-$ in aqueous solution). *J. Phys. Chem. Ref. Data* 17 (2): 513–886.
- 33 Lattach, Y., Garnier, F., and Remita, S. (2012). Influence of chemical and structural properties of functionalized polythiophene-based layers on electrochemical sensing of atrazine. *ChemPhysChem* 13 (1): 281–290.
- 34 Roncali, J., Blanchard, P., and Frère, P. (2005). 3,4-Ethylenedioxythiophene (EDOT) as a versatile building block for advanced functional π -conjugated systems. *J. Mater. Chem.* 15 (16): 1589–1610.
- 35 Lattach, Y., Coletta, C., Ghosh, S., and Remita, S. (2014). Radiation-induced synthesis of nanostructured conjugated polymers in aqueous solution: fundamental effect of oxidizing species. *ChemPhysChem* 15 (1): 208–218.
- 36 Belloni, J., Monard, H., Gobert, F. et al. (2005). ELYSE – a picosecond electron accelerator for pulse radiolysis research. *Nucl. Instrum. Methods Phys. Res., Sect. A* 539 (3): 527–539.
- 37 Marignier, J.L., de Waele, V., Monard, H. et al. (2006). Time-resolved spectroscopy at the picosecond laser-triggered electron accelerator ELYSE. *Radiat. Phys. Chem.* 75 (9): 1024–1033.
- 38 Coletta, C., Cui, Z., Dazzi, A. et al. (2016). A pulsed electron beam synthesis of PEDOT conducting polymers by using sulfate radicals as oxidizing species. *Radiat. Phys. Chem.* 126: 21–31.
- 39 Saunders, B.B., Kaufman, P.C., and Matheson, M.S. (1978). Reactions of thiophene with radiolytically produced radicals. 1. The hydroxyl radical. *J. Phys. Chem.* 82 (2): 142–150.
- 40 Bhattacharya, A., Amitabha, D., and Mandal, P.C. (1998). Carbonate radical induced polymerisation of pyrrole: a steady state and flash photolysis study. *J. Radioanal. Nucl. Chem.* 230 (1): 91–95.
- 41 Randriamahazaka, H., Noël, V., and Chevrot, C. (1999). Nucleation and growth of poly(3,4-ethylenedioxythiophene) in acetonitrile on platinum under potentiostatic conditions. *J. Electroanal. Chem.* 472 (2): 103–111.
- 42 Kvarnström, C., Neugebauer, H., Blomquist, S. et al. (1999). In situ spectroelectrochemical characterization of poly(3,4-ethylenedioxythiophene). *Electrochim. Acta* 44 (16): 2739–2750.

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Signature/Zeichen:	

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- 43 Bazzaoui, E.A., Aeiyaeh, S., and Lacaze, P.C. (1996). Electropolymerization of bithiophene on Pt and Fe electrodes in an aqueous sodium dodecylsulfate (SDS) micellar medium. *Synth. Met.* 83 (2): 159–165.
- 44 Irwin, M.D., Roberson, D.A., Olivas, R.I. et al. (2011). Conductive polymer-coated threads as electrical interconnects in e-textiles. *Fibers Polym.* 12 (7): 904.
- 45 Elliot, A.J., Geertsen, S., and Buxton, G.V. (1988). Oxidation of thiocyanate and iodide ions by hydrogen atoms in acid solutions. *J. Chem. Soc., Faraday Trans. 1 F* 84 (4): 1101–1112.
- 46 Cui, Z., Coletta, C., Dazzi, A. et al. (2014). Radiolytic method as a novel approach for the synthesis of nanostructured conducting polypyrrole. *Langmuir* 30 (46): 14086–14094.
- 47 Tehrani, P., Kancierzewska, A., Crispin, X. et al. (2007). The effect of pH on the electrochemical over-oxidation in PEDOT:PSS films. *Solid State Ionics* 177 (39): 3521–3527.
- 48 Ouyang, J. (2013). Solution-processed PEDOT:PSS films with conductivities as indium tin oxide through a treatment with mild and weak organic acids. *ACS Appl. Mater. Interfaces* 5 (24): 13082–13088.
- 49 Yun, D.J., Jeong, Y.J., Ra, H. et al. (2016). Effective way to enhance the electrode performance of multiwall carbon nanotube and poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) composite using HCl-methanol treatment. *J. Phys. Chem. C* 120 (20): 10919–10926.
- 50 Cui, Z., Bahry, T., Dazzi, A. et al. (2019). Conducting polymers synthesized by γ -radiolysis in very acidic aqueous medium. *Radiat. Phys. Chem.* 159: 47–56.
- 51 Jayson, G.G., Parsons, B.J., and Swallow, A.J. (1973). Some simple, highly reactive, inorganic chlorine derivatives in aqueous solution. Their formation using pulses of radiation and their role in the mechanism of the Fricke dosimeter. *J. Chem. Soc., Faraday Trans. 1 F* 69: 1597–1607.
- 52 Schwarz, H.A. and Dodson, R.W. (1984). Equilibrium between hydroxyl radicals and thallium(I I) and the oxidation potential of OH (aq). *J. Phys. Chem.* 88 (16): 3643–3647.
- 53 Cui, Z., Coletta, C., Bahry, T. et al. (2017). A novel radiation chemistry-based methodology for the synthesis of PEDOT/Ag nanocomposites. *Mater. Chem. Front.* 1 (5): 879–892.
- 54 Heuer, H.W., Wehrmann, R., and Kirchmeyer, S. (2002). Electrochromic window based on conducting poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate). *Adv. Funct. Mater.* 12 (2): 89–94.
- 55 Pei, Q.B., Zuccarello, G., Ahlskogt, M., and Ingan, O. (1994). Electrochromic and highly stable poly(3,4-ethylenedioxythiophene) switches between opaque blue-black and transparent sky blue. *Polymer* 35 (7): 1347–1351.
- 56 Rumbau, V., Pomposo, J.A., Eleta, A. et al. (2007). First enzymatic synthesis of water-soluble conducting poly(3,4-ethylenedioxythiophene). *Biomacromolecules* 8 (2): 315–317.

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Signature/Zeichen:	

- 57 Jang, J., Chang, M., and Yoon, H. (2005). Chemical sensors based on highly conductive poly(3,4-ethylenedioxythiophene) nanorods. *J. Adv. Mater.* 17 (13): 1616–1620.
- 58 Kitada, K. and Ozaki, S. (1995). Reductive polymerization of halothiophene. *Polym. J.* 27 (12): 1161–1166.
- 59 Song, L., Wang, M., Cong, Y. et al. (2007). The mechanism of ^{60}Co γ -ray radiation induced interfacial redox reaction in inverse emulsion and its application in the synthesis of polymer microcapsules. *Polymer* 48 (1): 150–157.
- 60 Belloni, J., Mostafavi, M., Remita, H. et al. (1998). Radiation-induced synthesis of mono- and multi-metallic clusters and nanocolloids. *New J. Chem.* 22 (11): 1239–1255.
- 61 Cui, Z., Coletta, C., Rebois, R. et al. (2016). Radiation-induced reduction–polymerization route for the synthesis of PEDOT conducting polymers. *Radiat. Phys. Chem.* 119: 157–166.
- 62 Gangopadhyay, R. and De, A. (2000). Conducting polymer nanocomposites: a brief overview. *Chem. Mater.* 12 (3): 608–622.
- 63 Xu, P., Han, X., Zhang, B. et al. (2014). Multifunctional polymer–metal nanocomposites via direct chemical reduction by conjugated polymers. *Chem. Soc. Rev.* 43 (5): 1349–1360.
- 64 Armel, V., Winther-Jensen, O., Kerr, R. et al. (2012). Designed electrodeposition of nanoparticles inside conducting polymers. *J. Mater. Chem.* 22 (37): 19767–19773.
- 65 Groenendaal, L., Jonas, F., Freitag, D. et al. (2000). Poly(3,4-ethylenedioxythiophene) and its derivatives: past, present, and future. *Adv. Mater.* 12 (7): 481–494.
- 66 Jung, H.-R. and Lee, W.-J. (2011). Ag/poly(3,4-ethylenedioxythiophene) nanocomposites as anode materials for lithium ion battery. *Solid State Ionics* 187 (1): 50–57.
- 67 Mo, Z., Zuo, D., Chen, H. et al. (2007). Synthesis of graphite nanosheets/AgCl/polypyrrole composites via two-step inverse microemulsion method. *Eur. Polym. J.* 43 (2): 300–306.
- 68 Pillalamarri, S.K., Blum, F.D., Tokuhiko, A.T., and Bertino, M.F. (2005). One-pot synthesis of polyaniline–metal nanocomposites. *Chem. Mater.* 17 (24): 5941–5944.
- 69 Fujii, S., Aichi, A., Akamatsu, K. et al. (2007). One-step synthesis of polypyrrole-coated silver nanocomposite particles and their application as a coloured particulate emulsifier. *J. Mater. Chem.* 17 (36): 3777–3779.
- 70 Feng, X., Huang, H., Ye, Q. et al. (2007). Ag/polypyrrole core–shell nanostructures: interface polymerization, characterization, and modification by gold nanoparticles. *J. Phys. Chem. C* 111 (24): 8463–8468.
- 71 Remita, S., Mostafavi, M., and Delcourt, M.O. (1994). Stabilization, growth and reactivity of silver aggregates produced by radiolysis in the presence of edta. *New J. Chem.* 18: 581–588.

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- 72 Mostafavi, M., Remita, S., Delcourt, M., and Belloni, J. (1996). Ligand effects on solvated metal cluster properties. *J. Chim. Phys. Phys.- Chim. Biol.* 93 (10): 1828–1842.
- 73 Remita, S. (1995). Effect of ligands on thermodynamics, kinetics and spectral properties of metallic aggregates synthesized by radiolysis. Doctoral thesis. University of Paris-Sud.
- 74 Mostafavi, M., Dey, G.R., François, L., and Belloni, J. (2002). Transient and stable silver clusters induced by radiolysis in methanol. *J. Phys. Chem. A* 106 (43): 10184–10194.
- 75 Remita, S., Fontaine, P., Rochas, C. et al. (2005). Radiation induced synthesis of silver nanoshells formed onto organic micelles. *Eur. Phys. J. D* 34 (1–3): 231–233.
- 76 Remita, S., Orts, J.M., Feliu, J.M. et al. (1994). STM identification of silver oligomer clusters prepared by radiolysis in aqueous-solution. *Chem. Phys. Lett.* 218 (1–2): 115–121.
- 77 Ishigaki, A. and Koizumi, H. (2012). Radiation-induced polymerization of 3-octylthiophene. *Radiat. Phys. Chem.* 81 (7): 803–806.
- 78 Emmi, S.S., Poggi, G., D’Angelantonio, M. et al. (2003). The solvatochromic effect on some oligothiophene radical cations: a pulse radiolysis and semiempirical investigation. *Radiat. Phys. Chem.* 67 (3): 251–256.
- 79 Alfassi, Z.B., Mosseri, S., and Neta, P. (1989). Reactivities of chlorine atoms and peroxy radicals formed in the radiolysis of dichloromethane. *J. Phys. Chem.* 93 (4): 1380–1385.
- 80 Emmi, S.S., Beggiato, G., and Casalbore-Miceli, G. (1989). Transient species in the pulse radiolysis of methylene chloride and the self-reaction of chloromethyl radicals. *Int. J. Radiat. Appl. Instrum. Part C* 33 (1): 29–37.
- 81 Bahry, T., Cui, Z., Deniset-Besseau, A. et al. (2018). An alternative radiolytic route for synthesizing conducting polymers in an organic solvent. *New J. Chem.* 42 (11): 8704–8716.
- 82 Emmi, S.S., D’Angelantonio, M., Beggiato, G. et al. (1999). The generation and spectral characterization of oligothiophenes radical cations. A pulse radiolysis investigation. This paper was presented at the 10th International Meeting on Radiation Processing, 11–16 May 1997, Anaheim, California, U.S.A. *Radiat. Phys. Chem.* 54 (3): 263–270.
- 83 Ushida, K., Yoshida, Y., Kozawa, T. et al. (1999). Evidence of oxidation of aromatic hydrocarbons by chloromethyl radicals: reinvestigation of intersolute hole transfer using pulse radiolysis. *J. Phys. Chem. A* 103 (24): 4680–4689.
- 84 Truskowski, S. and Szymański, W. (1994). Stable products and radicals in the radiolysis of dichloromethane and 1,1-dichloroethane gamma-irradiated in an oxygen-free atmosphere. *J. Radioanal. Nucl. Chem.* 177 (2): 415–423.
- 85 Nie, T., Zhang, K., Xu, J. et al. (2014). A facile one-pot strategy for the electrochemical synthesis of poly(3,4-ethylenedioxythiophene)/Zirconia nanocomposite as an effective sensing platform for vitamins B2, B6 and C. *J. Electroanal. Chem.* 717–718: 1–9.

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- 86 Hohnholz, D., MacDiarmid, A.G., Sarno, D.M., and Jones, J.W.E. (2001). Uniform thin films of poly-3,4-ethylenedioxythiophene (PEDOT) prepared by in-situ deposition. *ChemComm*. 23: 2444–2445.
- 87 Kim, T., Kim, J., Kim, Y. et al. (2009). Preparation and characterization of poly(3,4-ethylenedioxythiophene) (PEDOT) using partially sulfonated poly(styrene-butadiene-styrene) triblock copolymer as a polyelectrolyte. *Curr. Appl Phys*. 9 (1): 120–125.
- 88 Hui, Y., Bian, C., Wang, J. et al. (2017). Comparison of two types of overoxidized PEDOT films and their application in sensor fabrication. *Sensors* 17 (3): 628.
- 89 Van de Ruit, K., Cohen, R.I., Bollen, D. et al. (2013). Quasi-one dimensional in-plane conductivity in filamentary films of PEDOT:PSS. *Adv. Funct. Mater*. 23 (46): 5778–5786.
- 90 Jones, B.H., Cheng, K.-Y., Holmes, R.J., and Lodge, T.P. (2012). Nanoporous poly(3,4-ethylenedioxythiophene) derived from polymeric bicontinuous microemulsion templates. *Macromolecules* 45 (1): 599–601.
- 91 Hazarika, J. and Kumar, A. (2013). Controllable synthesis and characterization of polypyrrole nanoparticles in sodium dodecylsulphate (SDS) micellar solutions. *Synth. Met*. 175: 155–162.
- 92 Tour, J.M. and Wu, R. (1992). Synthesis and UV-visible properties of soluble α -thiophene oligomers. Monomer to octamer. *Macromolecules* 25 (7): 1901–1907.

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Abstract

This chapter describes the original and successful use of high energy radiations in the field of conducting polymers (CPs) synthesis. Indeed, these conjugated polymers can be easily and directly produced by means of radiation-induced (by gamma rays or accelerated electrons) polymerization of various organic monomers dissolved either in aqueous solutions or in organic solvents, in the absence of any external oxidizing agent. As described, the polymerization is intrinsically initiated by oxidizing or reducing radicals *in situ* generated in the irradiated media during solvents radiolysis. This chapter also highlights the successful use of pulse radiolysis for understanding the growth mechanism of CPs, which is shown to proceed through a recurrent step-by-step oxidation or reduction process. The versatility of the described radiolytic methodology is clearly demonstrated since nanostructured PEDOT and PPy conjugated polymers as well as PEDOT/Ag nanocomposites can be produced in various experimental conditions (different atmospheres and solvents, at various pHs, in the presence of solutes...). This chapter finally describes the properties (chemical, morphological, optical, electrical, and thermal) of the different radiosynthesized CPs, which are found dependent on the chemical nature of the initiating radiolytic species. These physicochemical properties are gathered to evaluate the performance of radiosynthesized CPs in practical application and to compare the pros and cons of radiolytic methodology with those of conventional methods.

Keywords

gamma-radiolysis; pulse-radiolysis; conducting polymers; PEDOT; PPy

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