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Conducting polymers synthesized by γ -radiolysis in very acidic aqueous medium

Zhenpeng Cui ^a, Teseer Bahry ^a, Alexandre Dazzi ^a, Thanh-Tuân Bui ^b,
Fabrice Goubard ^b and Samy Remita ^{a,c *}

^a *Laboratoire de Chimie Physique, LCP, UMR 8000, CNRS, Université Paris-Sud, Campus d'Orsay, 15 avenue Jean Perrin, 91405 Orsay Cedex, France.*

^b *Laboratoire de Physicochimie des Polymères et Interfaces, LPPI, EA 2528, Université de Cergy-Pontoise, 5 mail Gay Lussac, Neuville sur Oise, 95031 Cergy-Pontoise Cedex, France.*

^c *Department of Health, Life and Chemical Sciences, EPN 7, Conservatoire National des Arts et Métiers, CNAM, 292 rue Saint-Martin, 75141 Paris Cedex 03, France.*

* Corresponding author. E-mail: samy.remita@u-psud.fr. Tel.: +33 (0)1 69 15 44 41

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Abstract

In this work, conducting polymers were synthesized for the first time in acidic aqueous solutions by means of γ -irradiation. Poly(3,4-ethylenedioxythiophene) (PEDOT) polymers were prepared under N₂O atmosphere in the presence of highly concentrated hydrochloric acid (HCl) at pH $\sim$ 0, thanks to the oxidation of 3,4-ethylenedioxythiophene (EDOT) monomers by Cl₂^{•-} oxidizing radicals produced in the medium by water radiolysis. UV-Vis absorption spectroscopy was used to estimate the radiolytic yield of EDOT oxidation as well as the required dose for quantitative PEDOT preparation. After a 72-kGy irradiation, PEDOT polymers, which form dark blue suspensions, were characterized by a large absorption band at around 700 nm. Size exclusion chromatography demonstrated that these radiosynthesized PEDOT polymers contain up to 20 EDOT units. After deposition, ATR-FTIR spectroscopy and Energy-Dispersive X-ray (EDX) analysis highlighted the doping of PEDOT polymers prepared in the presence of HCl. The morphology of radiosynthesized PEDOT polymers was characterized by SEM microscopy and by high-resolution AFM-IR microscopy coupled with infrared nanospectroscopy. Aggregated spheroidal PEDOT particles with diameters comprised between 200 and

500 nm were detected. In addition, cyclic voltammetry (CV) and four-point probe measurements demonstrated that PEDOT polymers radiosynthesized in very acidic medium are characterized by prominent electronic properties (small band gap and considerable electrical conductivity). Promisingly, the present radiolytic study should offer a new synthetic approach for the preparation in acidic aqueous media of conducting polymers with enhanced properties.

1. Introduction

Conducting polymers (CPs) possess intrinsic electrical conductivity due to the unique π -conjugated systems along the polymer chains (Li et al., 2009; Shirakawa, 2001). As the fourth generation of polymeric materials (Heeger, 2001a, b), CPs are also called “synthetic metals” and have attracted great research interest for their potential applications (MacDiarmid, 2001), such as organic conductors (Cho et al., 2014), biomaterials (Balint et al., 2014), electrochromic windows (Heuer et al., 2002) and solar cells (Na et al., 2008). To date, various electrical conducting polymers have been developed (Heeger, 2001b), among which poly(3,4-ethylenedioxythiophene) (PEDOT, Scheme 1) has been widely investigated for its easy synthesis, good stability and high conductivity (Roncali et al., 2005; Groenendaal et al., 2000).

In general, polymerization of 3,4-ethylenedioxythiophene (EDOT, Scheme 1) monomers can be achieved by both traditional chemical (Zhang et al., 2005; Bashir et al., 2014) and electrochemical methods (Xiao et al., 2007; Akoudad and Roncali, 1998). In addition to the traditional synthetic routes, alternative approaches such as microwave-assisted (Dong et al., 2013) and enzyme-catalyzed polymerizations have also been reported (Rumbau et al., 2007). In our previous work, gamma-irradiation induced polymerization of EDOT monomers was successfully carried out enabling the development of an easy and clean alternative methodology for the preparation of PEDOT polymers (Lattach et al., 2013; Cui et al., 2017).

With radiolytic method, nanostructured PEDOT materials were obtained by EDOT oxidation using either hydroxyl radical ($\text{HO}^\bullet$) (Lattach et al., 2013; Lattach et al., 2014) or azide radical ($\text{N}_3^\bullet$) (Lattach et al., 2014) and even by EDOT reduction thanks to the use of hydrated electron (e_{aq}^-) generated by water radiolysis (Cui et al., 2016). Interestingly, morphology of PEDOT polymers was found dependent on the

nature of the initiating radiolytic species: while $\text{HO}^\bullet$ and e_{aq}^- lead to spherical nanoparticles, $\text{N}_3^\bullet$ leads to fibrillar structures (Lattach et al., 2014).

It is worth noting that all the above works were conducted by our team in neutral aqueous solutions and never in acidic aqueous media even though low pHs were shown in literature to prevent conducting polymers overoxidation (Tehrani et al., 2007) and to improve their electrical conductivity by doping effect (Ouyang, 2013) and structural optimization (Yun et al., 2016). We therefore wanted to use γ -irradiation in order to radiolytically prepare for the first time conducting organic materials in acidic aqueous media and then to study their properties.

In this work, we extend our methodology based on radiation chemistry in order to polymerize, under N_2O , EDOT monomers in very acidic aqueous solutions (in presence of HClO_4 or HCl at $\text{pH} \sim 0$), by exploiting the oxidizing species produced by γ -radiolysis ($\text{HO}^\bullet$ or $\text{Cl}_2^\bullet$). The as-prepared PEDOT polymers are then characterized in solution and after deposition by complementary techniques and are compared with those usually synthesized in neutral aqueous media under the same atmosphere (N_2O). The specific influence of the acidity of the medium on morphological, optical and electrical properties of radiosynthesized PEDOT polymers is then discussed.

2. Materials and methods

2.1 Chemical products

3,4-ethylenedioxythiophene (EDOT) ($\geq 98\%$, Sigma-Aldrich) was used as the monomer at a final concentration of 1 or 10 mM while ultra-pure water (Millipore system, $18.2 \text{ M}\Omega \text{ cm}$) was used as the solvent. Hydrochloric acid (HCl) (37%, ACS reagent) or perchloric acid (HClO_4) were used at a concentration of 1 M in order to get a pH value of the aqueous solution close to 0. Nitrous oxide gas (N_2O) (Air Liquid Co.) was used for degassing. Nitrosyl tetrafluoroborate (NOBF_4) ($\geq 95\%$, Sigma-Aldrich) was dissolved in acetonitrile ($\geq 99.9\%$, Sigma-Aldrich) and used as dopant for *p*-doping of PEDOT polymers during four-point probe measurements. All experiments were conducted at ambient temperature.

2.2 Radiolysis of acidic aqueous solutions under N₂O

It is well known that water radiolysis at neutral pH under nitrogen (N₂) atmosphere produces various species (Spinks and Woods, 1990; Ferradini and Jay-Gerin, 1999; Ferradini and Jay-Gerin, 2000) according to:

In these deaerated conditions and at a neutral pH, the radiolytic yields, G values, of the most reactive radical species (e_{aq}^- , $\text{HO}^\bullet$ and $\text{H}^\bullet$) are:

$$G_{e_{\text{aq}}^-} = 2.8 \times 10^{-7} \text{ mol J}^{-1} \quad (2)$$

$$G_{\text{HO}^\bullet} = 2.8 \times 10^{-7} \text{ mol J}^{-1} \quad (3)$$

$$G_{\text{H}^\bullet} = 0.6 \times 10^{-7} \text{ mol J}^{-1} \quad (4)$$

Among these radicals, solvated electron (e_{aq}^-) and hydroxyl radical ($\text{HO}^\bullet$) are the most abundant and reactive species (Ferradini and Jay-Gerin, 2000). Indeed, e_{aq}^- is a very reducing species with a redox potential of $-2.8 \text{ V}_{\text{SHE}}$ (Spinks and Woods, 1990; Schwarz, 1981) while $\text{HO}^\bullet$ is a strong oxidizing species with an apparent standard redox potential which amounts to $E^\circ(\text{HO}^\bullet/\text{H}_2\text{O}) = 2.2 \text{ V}_{\text{SHE}}$ at pH = 7 (Buxton et al., 1988).

When, at neutral pH, irradiated aqueous solutions are saturated with nitrous oxide, e_{aq}^- is quantitatively converted into $\text{HO}^\bullet$ radical according to the following reaction (Hart, 1969):

As a consequence, radiolytic yields of production of both e_{aq}^- and $\text{HO}^\bullet$ species are modified in presence of N₂O.

The G values of radiolytic species depend not only on the atmosphere (N₂O or N₂), but also on the pH value of the aqueous solution. Indeed, when water radiolysis happens in acidic medium, e_{aq}^- is quickly transformed into its acidic form, namely hydrogen atom ($\text{H}^\bullet$), by reacting with hydrogen ion (H^+) (Spinks and Woods, 1990):

Now, if we consider radiolysis of water under N₂O atmosphere and at very low pH (pH ~ 0, in presence of 1 M in perchloric acid, HClO₄, for instance), which corresponds to the experimental conditions used in the present paper, hydrated electrons are quickly scavenged according to the two competitive reactions (5) and (6). Let us then consider these two competitive reactions of e_{aq}⁻ onto N₂O (leading to additional HO• radicals) and onto H⁺ (leading to additional H• atoms) which induce the total consumption of hydrated electrons. The branching ratio (R) between these two competitive reactions, which corresponds to the ratio between the additional amount of HO• and that of H• produced by reactions (5) and (6) respectively, can be expressed as:

$$R = \frac{G'_{HO^\bullet}}{G'_{H^\bullet}} = \frac{k_{N_2O} [N_2O]}{k_{H^+} [H^+]} \quad (7)$$

where [N₂O] and [H⁺] are the concentrations in N₂O and H⁺, where k_{N₂O} and k_{H⁺} are the rate constants of reactions (5) and (6) respectively and where G'_{HO•} and G'_{H•} are the radiolytic yields of production of the additional amounts in HO• and H• according to reactions (5) and (6). Note that:

$$G'_{HO^\bullet} + G'_{H^\bullet} = G_{e_{aq}^-} = 2.8 \times 10^{-7} \text{ mol J}^{-1} \quad (8)$$

Taking into consideration the effective values of the concentrations ([N₂O] = 0.0265 mol L⁻¹ and [H⁺] = 10^{-pH} = 1 mol L⁻¹) as well as the rate constants values (k_{N₂O} = 9 × 10⁹ L mol⁻¹ s⁻¹ and k_{H⁺} = 2.3 × 10¹⁰ L mol⁻¹ s⁻¹) (Buxton et al., 1988; Hart, 1969), one can calculate the branching ratio, R, at pH ~ 0: R = 0.01. This calculation indicates without any ambiguity that only one hundred percent of hydrated electrons are converted, under N₂O at pH ~ 0, into HO• (G'_{HO•} ~ 0). In fact, nearly all e_{aq}⁻ are converted into H• atoms (G'_{H•} ~ G_{e_{aq}⁻} = 2.8 × 10⁻⁷ mol J⁻¹). It is then possible to evaluate, under N₂O at pH ~ 0, the total radiolytic yields of production of HO• radicals and of H• atoms according to:

$$G(\text{HO}^\bullet) = G_{\text{HO}^\bullet} + G'_{\text{HO}^\bullet} = 2.8 \times 10^{-7} \text{ mol J}^{-1} \quad (9)$$

$$G(\text{H}^\bullet) = G_{\text{H}^\bullet} + G'_{\text{H}^\bullet} = 0.6 \times 10^{-7} + 2.8 \times 10^{-7} = 3.4 \times 10^{-7} \text{ mol J}^{-1} \quad (10)$$

In very acidic medium and under N_2O , two reactive species should then be considered: $\text{HO}^\bullet$ and $\text{H}^\bullet$. This is the case when perchloric acid (HClO_4) is used to adjust the pH of the aqueous solution. Indeed, perchlorate ions (ClO_4^-) remain unreactive upon radiolysis. While $\text{HO}^\bullet$ is known as a very oxidizing species which enables in particular oxidation-induced polymerization of EDOT monomers in neutral aqueous solutions, $\text{H}^\bullet$ is less reactive and its reactions are often neglected in neutral media due to its low G value at $\text{pH} = 7$ (Coletta et al., 2015). Nevertheless, as highlighted thanks to equations (9) and (10), $\text{H}^\bullet$ becomes predominant at $\text{pH} \sim 0$ and thus its reactivity onto EDOT monomers cannot be omitted as demonstrated in some cases in literature (Saunders, 1978).

Interestingly, when hydrochloride acid (HCl) is used (instead of HClO_4) in order to adjust the pH, $\text{HO}^\bullet$ radicals are quantitatively transformed into dichloride radical anions, $\text{Cl}_2^{\bullet-}$, according to the following reactions (Jayson et al., 1973):

Therefore, the main species produced by γ -radiolysis of very acidic aqueous solutions containing HCl under N_2O are $\text{Cl}_2^{\bullet-}$ (instead of $\text{HO}^\bullet$) and $\text{H}^\bullet$ (Elliot et al., 1988). Under N_2O and at $\text{pH} \sim 0$, while the total radiolytic yield of production of $\text{H}^\bullet$ atoms remains the same as that found in the case of HClO_4 (equation (10)), that of $\text{Cl}_2^{\bullet-}$ can be easily deduced from equation (9):

$$G(\text{Cl}_2^{\bullet-}) = 2.8 \times 10^{-7} \text{ mol J}^{-1} \quad (14)$$

Such as $\text{HO}^\bullet$, $\text{Cl}_2^{\bullet-}$ is a strong oxidizing species with a very high standard redox potential: $E^\circ(\text{Cl}_2^{\bullet-}/\text{Cl}^-) = 2.1 \text{ V}_{\text{SHE}}$ (Schwarz and Dodson, 1984). This should enable, as in the case of hydroxyl radicals, the oxidation of EDOT monomers by $\text{Cl}_2^{\bullet-}$ and their polymerization into PEDOT.

2.3 Radiation induced synthesis of PEDOT polymers in acidic aqueous medium

As demonstrated in our previous study (Coletta et al., 2015), conducting polymers growth proceeds through a step-by-step mechanism. In this context, radiation induced polymerization of EDOT implies recurrent oxidation reactions induced by oxidizing radicals: oxidation of monomers followed by that of dimers, tetramers, oligomers... According to this growth mechanism, the amount of oxidative radicals which is needed for quantitative formation of PEDOT polymers is twice that of EDOT monomers. As a consequence, the absorbed dose, D (expressed in Grays, 1 Gy corresponding to 1 J kg^{-1}) (Mlekodaj, 1995), which should lead to the quantitative production of PEDOT polymers is the double of the one required for the total oxidation of EDOT monomers (Coletta et al., 2015):

$$D \text{ (Gy)} = \frac{2[\text{EDOT}]_0 \text{ (mol L}^{-1}\text{)}}{G_{\text{ox}} \text{ (mol J}^{-1}\text{)} d \text{ (kg L}^{-1}\text{)}} \quad (15)$$

where $[\text{EDOT}]_0$ is the initial concentration of EDOT, where G_{ox} is the effective yield of EDOT oxidation and where d is the density ($d = 1 \text{ kg L}^{-1}$ in case of water).

If we suppose that, under N_2O at $\text{pH} \sim 0$, in presence of HClO_4 or HCl , $\text{HO}^\bullet$ or $\text{Cl}_2^{\bullet-}$ quantitatively oxidize EDOT and if we assume that $\text{H}^\bullet$ remains unreactive, then the effective yield of EDOT oxidation, G_{ox} , corresponds to the total radiolytic yield of production of $\text{HO}^\bullet$, $G(\text{HO}^\bullet)$, or to that of $\text{Cl}_2^{\bullet-}$, $G(\text{Cl}_2^{\bullet-})$ (see equations (9) and (14)):

$$G_{\text{ox}} = 2.8 \times 10^{-7} \text{ mol J}^{-1} \quad (16)$$

This will be confirmed later in the manuscript in results and discussion section. Then, if we consider the value of the oxidation yield given by equation (16), the dose required for quantitative polymerization of EDOT amounts to 72 kGy in the case of a N_2O -saturated aqueous solution containing 10 mM in EDOT at $\text{pH} \sim 0$ (in presence of HCl or HClO_4).

Aqueous solutions of different concentrations of EDOT ranging between 1 and 10 mM were first prepared at room temperature in presence of HClO_4 or HCl at a

concentration of 1 M in order to adjust the pH at 0. The pH value of each solution was measured by using a pH-meter (CyberScan pH 500). The solutions were then degassed and saturated with N₂O for 20 min and finally irradiated, using a ⁶⁰Co panoramic γ -ray source at LCP laboratory, with increasing doses up to 72 kGy in order to quantitatively synthesize PEDOT polymers. In all experiments, the dose rate was 5 kGy h⁻¹.

2.4 Characterization of PEDOT polymers

Ultraviolet-visible (UV-Vis) absorption spectrophotometry was used to study the optical properties of EDOT monomers and of PEDOT polymers prepared in acidic aqueous solutions (at pH $\sim$ 0 in presence of HCl or HClO₄) as a function of the dose. Absorption spectra were recorded on a HP 8453 UV-Vis spectrophotometer using quartz cells with optical path lengths of 0.2 cm. The reference was always pure water.

After irradiation, in order to extract PEDOT polymers, irradiated solutions were dried under reduced pressure. The obtained powders were washed with ethanol and water in order to eliminate residual EDOT monomers, then dried in the oven at 50 °C for 24 h. The washed PEDOT powders were finally used for further characterizations.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was used for chemical characterization of PEDOT powders obtained after a 72-kGy irradiation in presence of HCl at pH $\sim$ 0. The spectra were recorded on a Bruker Vertex 70 FTIR spectrometer with a diamond ATR attachment (PIKEMIRACLE crystal plate diamond/ZnSe) and MCT detector equipped with a liquid nitrogen cooling system. The washed solid samples were placed on the diamond substrate of the apparatus and scanned from 4000 to 600 cm⁻¹ with a resolution of 4 cm⁻¹ for 100 times.

Size exclusion chromatography (SEC) was used to estimate the average molecular weight of PEDOT polymers synthesized in acidic aqueous medium (in presence of HCl) at 72 kGy. After solvent evaporation and washing, powder made of radiosynthesized PEDOT polymers was dissolved in tetrahydrofuran (THF) solvent by stirring for 24 h and then 100 μ L of the obtained solution was injected into SEC apparatus. SEC was performed at 40 °C on a Malvern Viscotek TDA device equipped with two columns, Malvern T3000 and T6000, with a Malvern refractive index

detector at an elution rate of 1 mL min⁻¹. Polystyrene polymers were used as standards and THF as eluent

Scanning electron microscopy (SEM) was used to check the morphology of PEDOT polymers synthesized in acidic aqueous solution (in presence of HCl) after a 72-kGy irradiation. The dried polymers powders were first sprinkled onto carbon tape adhered to aluminum mounts and then coated with gold and finally imaged by an EVO MA 10 Zeiss microscope. The applied voltage was 15 kV and the scale bar was 1 μ m. During SEM observations, *in situ* energy dispersive X-Ray spectroscopy (EDX) was carried out (without gold coating) to check the chemical composition and to perform the elemental analysis of the solid powders within a selected area of the samples. The EDX spectra were recorded with a beam energy of 15 keV.

Atomic force microscopy coupled with infrared nanospectroscopy (AFM-IR) was performed to further study the morphology and composition of the radiosynthesized PEDOT polymers synthesized at 72 kGy in acidic aqueous solution (in presence of HCl). After irradiation and water evaporation, the blue dark powder made of PEDOT polymers was solubilized in ethanol and then few drops of the sky-blue ethanolic solution were deposited onto the upper surface of ZnSe prism of AFM-IR apparatus and dried at air. The system used in this work was a nanoIR (@Anasys Instruments) which combines an AFM microscope with an infrared pulse source. The microscope was used in contact mode while the pulsed infrared laser setup was covering the IR range from 3600 to 1000 cm⁻¹. During all the measurements, the tip of the AFM microscope remained in contact with the surface of the sample. As described in our previous works, absorption by the sample of IR laser pulse causes AFM cantilever oscillation. The fact that the amplitude of cantilever oscillation is proportional to the intensity of the absorption originally enables the recording of the local infrared spectrum at a fixed position of the tip (by changing the wavenumber of the IR laser source) and the acquisition of a chemical map of the sample (by scanning the surface at a characteristic wavenumber).

Cyclic voltammetry (CV) was used in order to investigate the electrochemical properties and to determine the electrochemical band gap of PEDOT polymers radiosynthesized at 72 kGy in acidic aqueous solution at pH $\sim$ 0 (in presence of HCl). The electrochemical setup was a three-electrodes cell made of Pt disc as working electrode, an Au wire as counter-electrode and an Ag/AgCl wire as pseudo-reference electrode. Calibration of pseudo-reference electrode was ensured by probing

ferrocenium/ferrocene (Fc^+/Fc) redox potential measured at the end of each experiment, as recommended by IUPAC. PEDOT powder (1 mg) obtained after irradiation and after solvent evaporation was dissolved in 5 mL of acetonitrile solution containing 0.1 M in tetrabutylammonium hexafluorophosphate, TBAPF₆, used as electrolyte. The cyclic voltammograms were all recorded between - 2.5 V and + 2.5 V at a scan rate of 20 mV s⁻¹.

Four-point probe technique was finally used in order to evaluate the electrical conductivity properties of PEDOT polymers synthesized at 72 kGy in the presence of HCl. Few drops of PEDOT suspension obtained after irradiation were deposited by spin coating onto a glass substrate at a speed of 1000 rpm for 60 s. The spin-coated film was doped with an acetonitrile solution containing 10 mM in NOBF₄. Then, in order to dry the film and to quantitatively evaporate the solvent, the substrate was heated up for 30 min in a hot plat at 130°C. The thickness of the dried PEDOT film was measured by using a 3 Veeco Dektak 150 surface profiler, while the resistance of the film was evaluated by the means of a Kelvin four-point probe technique. The conductivity, ρ (S cm⁻¹), was calculated based on the following equation:

$$\rho = \left(\frac{\pi}{\ln 2} \times \frac{V}{I} \times t \right)^{-1} \quad (17)$$

where V is the voltage (V), I the applied current (A) and t the film thickness (cm).

3. Results and discussion

3.1 Mechanistic study of EDOT oxidation in aqueous solution at pH ~ 0

With the aim to check the influence of the acidity of the medium on the oxidation and polymerization of EDOT, aqueous solutions containing 1 mM in EDOT were prepared in the presence of either HClO₄ or HCl at a concentration of 1 M. The pH values of both solutions were measured with a pH-meter and found close to 0. Before irradiation, the acidic solutions were both transparent and their spectra are identical and similar to that of neutral aqueous solution containing 1 mM in EDOT (Lattach et al., 2013). As in the case of neutral aqueous medium, EDOT is characterized by two absorption maxima at 235 and 255 nm which are features of π -

π^* electronic transitions in the thiophene rings as shown in Figure 1. Also, at these two wavelengths, the molar extinction coefficients have the same values as in neutral medium (Lattach et al., 2013).

Aqueous solutions containing 1 mM in EDOT and 1 M in either HCl or HClO₄ (at pH $\sim$ 0) were degassed with N₂O and irradiated at increasing doses up to 8 kGy. Interestingly, the evolution with the dose of the absorption spectra of the two acidic solutions (that with HCl and that with HClO₄) is strictly similar. Thus, only one series of spectra, which traduces both evolutions, is displayed on Figure 1. As observed, the intensity of the UV-visible absorption spectrum of EDOT decreases with increasing dose. This indicates the progressive consumption of EDOT monomers upon γ -irradiation in presence of HCl or HClO₄. This decrease of EDOT absorption at 235 and 255 nm parallels an increase in the absorbancy at higher wavelengths. Note that an isosbestic point already observed and explained in our previous works (Lattach et al., 2013) is present at around 270 nm. From the values of the extinction coefficients at 235 and 255 nm (Lattach et al., 2013) and starting from 1 mM in EDOT, one can deduce the variation in EDOT concentration as a function of the dose (Insert of Figure 1). The initial yield of EDOT oxidation at pH $\sim$ 0 in presence of either HCl or HClO₄, G_{ox} , can then be experimentally estimated since it corresponds to the value of the initial slope of the curve displayed in insert of Fig. 1. In particular, it can be deduced from an exponential fit:

$$G_{ox} = 2.5 \pm 0.5 \times 10^{-7} \text{ mol J}^{-1} \quad (18)$$

In the case of HClO₄, this yield of EDOT oxidation is close to the value of $G(\text{HO}^\bullet)$ at pH $\sim$ 0 ($2.8 \times 10^{-7} \text{ mol J}^{-1}$, equation (9)) and much lower than that of $G(\text{HO}^\bullet) + G(\text{H}^\bullet)$ at the same pH ($6.2 \times 10^{-7} \text{ mol J}^{-1}$). This result demonstrates that in the case of HClO₄, $\text{HO}^\bullet$ radicals quantitatively oxidize EDOT monomers (as already demonstrated in neutral aqueous media), while $\text{H}^\bullet$ atoms remain totally unreactive towards EDOT oxidation.

Similarly, in the case of HCl, the oxidation yield, G_{ox} , is close to the value of $G(\text{Cl}_2^{\bullet-})$ at pH $\sim$ 0 ($2.8 \times 10^{-7} \text{ mol J}^{-1}$, equation (14)) and remains much lower than that of $G(\text{Cl}_2^{\bullet-}) + G(\text{H}^\bullet)$ at the same pH ($6.2 \times 10^{-7} \text{ mol J}^{-1}$). This highlights once again the fact that $\text{H}^\bullet$ radicals are unreactive towards EDOT monomers. This proves moreover

than $\text{Cl}_2^{\bullet-}$ radicals, such as hydroxyl radicals, quantitatively oxidize EDOT monomers thanks to their high redox potential.

3.2 Radio-induced synthesis of PEDOT polymers at pH ~ 0

As demonstrated, under N_2O at pH ~ 0 , in presence of HClO_4 or with HCl , $\text{HO}^{\bullet}$ or $\text{Cl}_2^{\bullet-}$ quantitatively oxidize EDOT. If we assume, in both cases, effective oxidation yields of $2.8 \times 10^{-7} \text{ mol J}^{-1}$, the dose needed for quantitative polymerization of 10 mM in EDOT amounts to 72 kGy at pH ~ 0 according to equation (15).

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 pictures of the three solutions after irradiation (in insert) as well as their UV-Vis absorption spectra are displayed on Figure 2.

After a 72 kGy-irradiation, the solution prepared in neutral medium appears yellow (photography c in insert of Figure 2) and its absorption spectrum (spectrum c of Figure 2) displays an intense absorption band at around 350 nm in total agreement with our previous works (Lattach et al., 2013; Cui et al., 2017; Lattach et al., 2014). 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 2) 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 (Heuer et al., 2002; Pei et al., 1994). Remarkably, when considering the absorption spectra of the two acidic solutions irradiated at 72 kGy in presence of HCl (spectrum a of Figure 2) 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 π - π^* 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) (Rumbau et al., 2007; Kudrjasova et al., 2014). This will be further demonstrated in the paper. This interesting result, which is in total agreement with the colors of the irradiated solutions, demonstrates that contrarily to PEDOT oligomers produced in neutral medium, polymers synthesized under the same atmosphere (N_2O) at $pH \sim 0$ are 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 approximatively the same wavelength.

3.3 Chemical and structural characterizations of PEDOT polymers synthesized in presence of HCl at $pH \sim 0$

Since the results obtained in very acidic aqueous medium are quite similar (after a 72 kGy-irradiation) whatever the nature of the acid, we can conclude that the reactivity of $Cl_2^{\bullet-}$ onto EDOT monomers is comparable to that of $HO^{\bullet}$, leading to PEDOT polymers with similar absorption properties. Since we already studied, in previous works, the reactivity of hydroxyl radicals onto EDOT monomers in neutral medium and characterized the polymers produced in these experimental conditions, we decided to focus our work on the reactivity of an alternative oxidizing species, namely $Cl_2^{\bullet-}$, but this time in very acidic medium, and chose to characterize in more detail PEDOT polymers produced by radiolysis at 72 kGy in the presence of HCl.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to confirm the successful radiation induced synthesis of PEDOT polymers under N_2O after a 72 kGy-irradiation of a very acidic aqueous solution containing 10 mM in EDOT in the presence of 1 M in HCl. After irradiation, in order to remove water and EDOT monomer residues, irradiated solution was washed and dried. The dried dark blue powder was then characterized by ATR-FTIR spectroscopy and its spectrum was compared with the spectrum of pure EDOT monomers within wavenumber region from 4000 to 600 cm^{-1} (Figure 3). It is quite important to note that the difference between the intensity and the resolution of PEDOT polymers

spectrum and those of EDOT monomers spectrum originates from the way of deposition on the ATR-FTIR crystal: liquid phase deposition in case of EDOT against solid phase deposition in case of PEDOT.

As observed on Figure 3, ATR-FTIR spectra of pure EDOT and of radiosynthesized PEDOT are in good agreement with literature. All the characteristic bands of PEDOT polymers can be identified without any ambiguity, which confirms the effective polymerization of EDOT monomers. The vibration modes of the C–S bond can be located at 835, 902 and 981 cm^{-1} (Kvarnström et al., 1999; Ghosh et al., 2014). The vibration bands at 1054 and 1182 cm^{-1} are attributed to stretching of the C–O–C bond in the ethylenedioxy group (Kvarnström et al., 1999; Dams et al., 2006). The stretching vibrations of C=C in thiophene ring are observed at 1390 and 1471 cm^{-1} , while the bands at 1226 and 1349 cm^{-1} originate from C–C bonds (Lattach et al., 2014; Kvarnström et al., 1999; Ghosh et al., 2014). Remarkably, the ATR-FTIR spectrum of EDOT displays typical bands at 755 cm^{-1} , attributed to the =C–H in-plane and out-of-plane deformation vibrations, which are not detected in the infrared spectrum of PEDOT (Hagiwara et al., 1989). The disappearance of these bands upon irradiation highlights the involvement of α,α' -coupling reactions during PEDOT growth (Lattach et al., 2013; Lattach et al., 2014; Akimoto et al., 1986) (see Scheme 1), confirming that the dose of 72 kGy used during irradiation leads, as expected, to quantitative polymerization of EDOT.

The ATR-FTIR spectrum recorded after a 72 kGy-irradiation displays the typical bands of PEDOT polymers. However, at close up view of PEDOT spectrum, it is possible to detect at 1640 cm^{-1} the presence of an additional less common band, which nevertheless has already been notified in literature specifically in the case of PEDOT polymers doped with chloride ions (Bahry et al., 2018). It is worth noting that this peak which results from polymers doping has never been observed in our previous works concerning radiation induced synthesis of PEDOT in neutral aqueous media. The presence of this band in acidic medium at $\text{pH} \sim 0$ demonstrates the doping of PEDOT by chloride anions in full agreement with the results obtained by UV-vis absorption spectroscopy, since a large absorption band at 700 nm was observed (Figure 2). Note that chloride ions should come from the quantitative dissociation in aqueous solution of hydrochloric acid (a strong acid) which is present at very high concentration. These chloride anions are thus found to remain in PEDOT powder even after washing procedure. It is worth noting that PEDOT polymers which were

prepared in the presence of HClO_4 instead of HCl , should be doped by perchlorate ions (ClO_4^- coming from perchloric acid dissociation) instead of chloride ions, which explains the doping band also observed in this case at around 700 nm (Figure 2).

Size exclusion chromatography (SEC) was used to estimate the number average molecular weight (M_n), the weight average molecular weight (M_w) and the peak molecular weight (M_p , at the maximum of the highest peak of the chromatogram) of PEDOT polymers radiosynthesized, in the presence of 1 M in hydrochloric acid, at an absorbed dose of 72 kGy (Figure 4). We chose to use and to measure the molar masses, M_p , at the maxima of the peaks since the calculation of the average molecular weight, M_n , can be skewed by the overlapping of the peaks of the chromatogram. The more intense peak observed on Figure 4, peak (a), corresponds to the molar mass (M_p) of 1128 g mol^{-1} (obtained with a polystyrene calibration). This indicates the presence of approximatively 8 EDOT units per PEDOT chain. This is consistent with our recent results concerning PEDOT polymers prepared by radiolysis in dichloromethane solvent (Bahry et al., 2018). Note that PEDOT polymers with higher molecular weights ($M_w > 3000$) were also detected indicating that longer polymer chains were formed (up to 20 EDOT units). Interestingly, SEC experiments highlighted the low polydispersity of radiosynthesized PEDOT polymers since the polydispersity index, M_w/M_n , was found equal to 1.27, which is consistent with a relatively well controlled step-by-step polymerization reaction (Aldabbagh et al., 2008; Kwak and Matyjaszewski, 2010).

3.4 Morphological characterization of PEDOT polymers synthesized in presence of HCl at pH ~ 0

The study by UV-Vis absorption spectrophotometry and by ATR-FTIR spectroscopy demonstrates the successful preparation by the way of radiation chemistry of PEDOT polymers in very acidic aqueous solution under N_2O atmosphere. Also, the polymers were found doped with chloride anions which come from HCl acid used to adjust the pH of the medium.

In order to check the morphology of PEDOT polymers obtained by γ -radiolysis in very acidic aqueous medium, SEM microscopy was used. We considered in particular PEDOT powders obtained after the 72 kGy-irradiation of an acidic aqueous

solution containing EDOT monomers (10 mM in EDOT and 1 M in HCl) and after water evaporation. A typical SEM image, recorded after deposition of the dried dark blue PEDOT polymers powder and after its coating with gold, is displayed on Figure 5. In the absence of gold coating, *in situ* Energy-Dispersive X-ray spectroscopy (EDX) highlighted the presence in the whole sample of sulfur, carbon and oxygen elements (results not shown) underlining the presence of PEDOT in the materials observed in Figure 5. Besides, 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. This finding, in good agreement with our UV-vis and ATR-FTIR spectroscopies results, definitely proves the doping by chloride ions of PEDOT polymers radiosynthesized in acidic medium.

Figure 5 highlights the presence in the deposit of compact spheroidal particles. As explained in our previous works, these globular structures result from the self-assembly of interdigitated PEDOT polymer chains which are neither branched nor networked but nevertheless in weak interactions. These aggregated PEDOT spheroidal particles appear heterogeneous in size with diameters comprised between 200 and 500 nm.

With the aim to definitely demonstrate that the particles observed by SEM are made of PEDOT polymers, AFM microscopy coupled with IR nanospectroscopy was used. Few drops of the dark blue suspension obtained after irradiation (at 72 kGy) of EDOT acidic aqueous solution (presence of HCl) were deposited onto the ZnSe prism of AFM-IR apparatus leading, after drying, to a thin film which was scanned and imaged by AFM-IR as shown in Figure 6. The topography of the deposited materials as obtained by AFM in contact mode is displayed in Figure 6a. The brighter areas observed in this image correspond to the thicker regions made up of aggregated spheroidal particles with diameters of about few hundreds nm, in agreement with reported results (Wang et al., 2016; Poverenov et al., 2010). Interestingly, these particles have the same size and shape as those previously observed by SEM.

AFM-IR experiments were extended by recording the local infrared absorption spectra of the particles observed in Figure 6a in the range of 1020-1600 cm^{-1} (Figure 6b). It is worth noting that all the probed particles were found characterized by the same infrared spectrum, highlighting their single chemical structure. This infrared spectrum fits well with the ATR-FTIR spectrum of PEDOT displayed in Figure 3.

This demonstrates that the particles observed at present by AFM and earlier by SEM contain without any ambiguity PEDOT polymers.

In order to record the chemical map of the film and in order to check its absorption at a given wavenumber, we scanned its surface by AFM-IR. In particular, in the spectrum of Figure 6b, we considered the peak at 1478 cm^{-1} which corresponds to C=C stretching band in PEDOT polymers (Kvarnström et al., 1999; Jang et al., 2005). Besides, this band is also observed at 1471 cm^{-1} in the ATR-FTIR spectrum of PEDOT (Figure 3). We selected the corresponding wavenumber (1478 cm^{-1}) to map the sample and recorded the absorption strength as a function of the tip position onto the surface (Figure 6c). In this figure, the red areas indicate a stronger absorption at the chosen wavenumber which should correspond to a thicker layer of PEDOT deposited onto the prism. When comparing the AFM topographic image (Figure 6a) and the AFM-IR chemical mapping (Figure 6c), one can note that the stronger absorbing areas of Figure 6c and the thicker regions of Figure 6a are perfectly stackable. This definitely proves that the observed spheroidal particles are mainly composed by PEDOT polymers as expected.

SEM and AFM observations together with EDX spectroscopy and AFM-IR nanospectroscopy characterizations enable us to conclude with certainty that radiolysis under N_2O of very acidic aqueous solutions (containing EDOT monomers in presence of 1 M in HCl) leads to the oxidation of monomers and to the synthesis of PEDOT polymers. The latter are doped with chloride ions and self-assemble into polydisperse globular nanoparticles, the diameters of which remain comprised between 200 and 500 nm as observed by SEM and AFM.

3.5 Electrical and electrochemical properties of PEDOT polymers synthesized in presence of HCl at pH ~ 0

The morphology of PEDOT polymers radiosynthesized in acidic aqueous solution through EDOT oxidation by $\text{Cl}_2^{\bullet-}$ radicals appears similar to that of PEDOT polymers reported in literature (Wang et al., 2016; Patterson et al., 2017; Kim et al., 2014; Zhou et al., 2015; Mumtaz et al., 2008; Van de Ruit et al., 2013; Louet et al., 2015) and to that of PEDOT polymers we already synthesized by radiolysis either in dichloromethane solvent (Bahry et al., 2018) or in neutral aqueous medium through EDOT oxidation by $\text{HO}^{\bullet}$ radicals (Lattach et al., 2014; Cui et al., 2016). We can then

conclude that neither the acidity of the medium nor the reactivity of $\text{Cl}_2^{\bullet-}$ radicals influence the final morphology of PEDOT polymers. Nevertheless, as previously mentioned, the presence of HCl during the growth process leads to the presence of Cl^- anions into the polymer matrices which induces the doping of PEDOT polymers (Jang et al., 2005) when synthesized in very acidic medium.

In order to investigate electrochemical and electronic properties of PEDOT polymers synthesized by water radiolysis in the presence of HCl at $\text{pH} \sim 0$ and in order to check whether *in situ* doping of the polymers (by Cl^- anions) affects their band gap, cyclic voltammetry (CV) experiments were undertaken. The purpose was to determine first the oxidation and reduction potentials of radiosynthesized PEDOT polymers, then the energy levels of both their highest occupied molecular orbital (HOMO, from the ionization potential) and their lowest unoccupied molecular orbital (LUMO, from the electronic affinity) and finally their characteristic electronic band gap.

Cyclic voltammetry (CV) was used to check the electrochemical behavior of PEDOT polymers synthesized by radiolysis at 72 kGy in an aqueous solution containing 10 mM in EDOT and 1 M in HCl under N_2O atmosphere. In this context, PEDOT powder obtained after irradiation and water evaporation was dissolved in acetonitrile solution containing tetrabutylammonium hexafluorophosphate (TBAPF_6 , used as electrolyte) and then electrochemically studied. The resulting cyclic voltammogram is displayed in Figure 7 together with the characteristic oxidation and reduction peaks of PEDOT polymers.

As observed in cyclic voltammogram of Figure 7, PEDOT oxidation (p-doping process) starts at onset potential, $E_{\text{ox}}^{\text{onset}}$, of + 1.01 V, whereas PEDOT reduction (n-doping process) occurs at onset potential, $E_{\text{red}}^{\text{onset}}$, of -0.03 V. Starting from these two onset potential values, one can calculate, from the equations given in legend of Figure 7, the HOMO and LUMO energy levels of PEDOT radiosynthesized in very acidic medium: $E_{\text{HOMO}} = -5.44$ eV and $E_{\text{LUMO}} = -4.40$ eV. Consequently, the corresponding electrochemical band gap, E_g^{el} , amounts to 1.04 eV. This band gap value is found smaller than those (around 1.60 eV) already reported in literature for PEDOT polymers (Groenendaal et al., 2000; Bahry et al., 2018; Sotzing and Reynolds, 1991). The narrow bandgap found in the present case indicates that polymers radiosynthesized in very acidic medium may possess good electrical conductivity.

Four-point probe technique was then used to evaluate the electrical conductivity of PEDOT polymers synthesized by radiolysis at 72 kGy in presence of 10 mM in EDOT and 1 M in HCl under N₂O atmosphere. PEDOT dark blue suspension obtained after irradiation was deposited by spin coating onto a glass substrate and then doped with NOBF₄. The thickness of the film was then measured by a surface profiler and the conductivity was finally determined by four-point probe technique. The conductivity of PEDOT polymers synthesized in this work in very acidic aqueous medium was found to be $3.3 \times 10^{-3} \text{ S cm}^{-1}$, which is of the same order of magnitude as the conductivities of PEDOT we already synthesized by radiolysis in neutral aqueous solutions or in organic solvents and remains close to the conductivities reported in literature for PEDOT polymers produced by conventional methods (Rumbau et al., 2007; Cui et al., 2016; Bahry et al., 2018; Van de Ruit et al., 2013).

Cyclic voltammetry characterizations together with four-point probe experiments allow us to deduce and to note down the interesting electronic properties (band gap and conductivity) of PEDOT polymers synthesized in this work in very acidic aqueous medium by the way of our alternative radiolytic method. It is worth noting that the π -conjugated systems present all along the polymer chains and the oxidized states induced by polymers doping should both contribute to the good electrical conductivity of organic conducting materials (Jang et al., 2005; Stöcker et al., 2012). Nevertheless, it seems that *in situ* doping of PEDOT polymers by Cl⁻ anions (when prepared by radiolysis in very acidic medium in the presence of HCl) does not drastically enhance their conductivity. Although the relatively good electrical conductivity of PEDOT polymers synthesized, at pH $\sim$ 0, in presence of HCl is in good agreement with the small band gap deduced from CV experiments, its value still needs to be enhanced for instance by increasing the conjugation length into the polymers and also by controlling the stacking and the organization of the polymer chains into the sample (Saunders, 1978; Hawkins and Ratcliffe, 2000).

4. Conclusion

In the present paper, we undertook the use of γ -irradiation in order to radiolytically prepare, for the first time, conducting polymers in very acidic aqueous media and then to study their morphological, optical and electrical properties. We

extended our strategy based on radiation chemistry to the oxidation and then polymerization, under N_2O and at $\text{pH} \sim 0$, of EDOT monomers, in presence of either HClO_4 or HCl as strong inorganic acids, by exploiting the strong oxidizing power of $\text{HO}^\bullet$ (in case of HClO_4) or $\text{Cl}_2^{\bullet-}$ (in case of HCl) radicals produced by γ -radiolysis. We demonstrated that both $\text{HO}^\bullet$ and $\text{Cl}_2^{\bullet-}$ radicals quantitatively oxidize EDOT monomers, while $\text{H}^\bullet$ atoms remain totally unreactive towards EDOT oxidation. The determination of the yield of EDOT oxidation by $\text{HO}^\bullet$ and $\text{Cl}_2^{\bullet-}$ enabled us to evaluate the dose needed for quantitative polymerization of EDOT polymers at $\text{pH} \sim 0$, in the presence of either HClO_4 or HCl . Evidently, we also highlighted the PEDOT nature of the products by the use of complementary characterization techniques.

The as-prepared PEDOT polymers, which form dark blue suspensions just after irradiation, are characterized, in the presence of HClO_4 or HCl , by a large absorption band at around 700 nm. As highlighted by ATR-FTIR spectroscopy and Energy-Dispersive X-ray (EDX) analysis, this band results from the *in situ* doping of PEDOT polymers radiosynthesized in very acidic aqueous solutions. Besides, SEC chromatography highlighted the low polydispersity of PEDOT polymers synthesized at $\text{pH} \sim 0$ and demonstrated that their polymer chains contain up to 20 EDOT units. It is worth noting that, differently, in neutral aqueous solution, radiation induced EDOT oxidation leads to a yellow suspension which contains, instead of doped polymers, PEDOT oligomers (with shorter chain lengths) in the neutral state (not doped).

After deposition from the aqueous phase, the observations and characterizations made by SEM and AFM microscopies, EDX spectroscopy and AFM-IR nanospectroscopy showed that water radiolysis in the presence of HCl leads to the production of PEDOT polymers (doped with Cl^- anions) which self-assemble into polydisperse globular particles (size comprised between 200 and 500 nm). Since PEDOT morphology in very acidic medium is comparable to that of PEDOT polymers obtained in neutral aqueous medium, one can conclude that neither the acidity of the medium (presence of HCl at 1 M) nor the reactivity of $\text{Cl}_2^{\bullet-}$ radicals affect the final morphology of PEDOT polymers.

Electronic properties of PEDOT polymers synthesized in very acidic medium, in the presence of HCl , were finally evaluated thanks to CV experiments and four-point probe measurements. The conductivity of the polymers synthesized in this work, in very acidic aqueous medium, was found relatively high, but remains of the same

order of magnitude as the conductivities of PEDOT polymers we previously synthesized by radiolysis in neutral aqueous media. Interestingly, the band gap value corresponding to the polymers prepared by radiolysis at pH $\sim$ 0 was found smaller than those already reported in literature for PEDOT. Although the relatively good electrical conductivity of PEDOT polymers synthesized at pH $\sim$ 0 is in good agreement with the small bandgap, its value needs to be enhanced by increasing the conjugation length into the polymer chains and by controlling their nanostructuration.

From now on, our radiolytic methodology fully appears as a promising alternative method for the preparation, not only in neutral solutions but also in acidic aqueous media, of conducting polymers with enhanced properties. The considerable electrical conductivity of the polymers radiosynthesized in very acidic aqueous solutions and, above all, their *in situ* doping and their low band gap foreshadow further advances in the field of conducting polymers synthesis and applications.

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Scheme 1

Scheme 1. Chemical structures of 3,4-ethylenedioxythiophene (EDOT) monomer and poly(3,4-ethylenedioxythiophene) (PEDOT) polymer. EDOT structure shows free α, α' positions where coupling reactions occur.

Figure 1

Figure 1- Evolution of UV-vis absorption spectrum of EDOT aqueous solutions (1 mM) added with HCl or HClO₄ (1 M, pH = 0) under N₂O atmosphere as a function of the dose (from 0 to 8 kGy). The optical path length was 0.2 cm. The reference was water. **Insert:** variation of EDOT concentration as a function of the dose. The radiolytic yield of EDOT oxidation corresponds to the initial slope of the curve.

Figure 2

Figure 2- 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.

Figure 3

Figure 3- ATR-FTIR spectra of pure EDOT monomers and of PEDOT polymers radiosynthesized through a 72 kGy-irradiation of an aqueous solution containing 10 mM in EDOT under N₂O atmosphere in presence of HCl (1 M) at pH 0.

Figure 4

Figure 4- SEC chromatogram of PEDOT polymers radiosynthesized through a 72 kGy-irradiation of an aqueous solution containing 10 mM in EDOT and 1 M in HCl (pH = 0) under N_2O atmosphere.

Figure 5

Figure 5- SEM image of dried PEDOT polymers powder. The powder was obtained after solvent evaporation. PEDOT polymers were synthesized by gamma-radiolysis at 72 kGy of an aqueous solution containing 10 mM in EDOT and 1 M in HCl (pH = 0) under N₂O atmosphere.

Figure 6

Figure 6- AFM-IR images of PEDOT polymers after deposition onto the upper surface of ZnSe prism. PEDOT polymers were synthesized by gamma-radiolysis at 72 kGy of an aqueous solution containing 10 mM in EDOT and 1 M in HCl (pH = 0) under N₂O atmosphere. **(a)** AFM topographic image of PEDOT polymers in contact mode. **(b)** AFM-IR spectrum of PEDOT. **(c)** AFM-IR chemical mapping of PEDOT with the IR source tuned to the C-C band at 1478 cm⁻¹.

Figure 7

Figure 7- Cyclic voltammogram of PEDOT polymers recorded in acetonitrile containing 0.1 M of TBAPF₆ at a scan rate of 20 mV s⁻¹. PEDOT polymers were synthesized by gamma-radiolysis at 72 kGy of an aqueous solution containing 10 mM in EDOT and 1 M in HCl (pH = 0) under N₂O atmosphere. Redox potential of ferrocenium/ferrocene (Fc⁺/Fc) was measured to calibrate the pseudo reference electrode (0.37 V vs. Ag/AgCl in the present study). The HOMO/LUMO energetic levels of PEDOT are determined as follows: E_{HOMO} (eV) from ionization potential = $-4.8 - e (E_{\text{ox}}^{\text{onset}} - 0.37)$ and E_{LUMO} (eV) from electronic affinity = $-4.8 - e (E_{\text{red}}^{\text{onset}} - 0.37)$ where e is the elementary charge. The electrochemical band gap can then be deduced: $E_{\text{g}}^{\text{el}} = E_{\text{LUMO}} - E_{\text{HOMO}}$ (eV).

Table of Content Graphic

**PEDOT polymers
prepared by radiolysis
in very acidic aqueous medium**