

Fully undoped and soluble oligo(3,4-ethylenedioxythiophene)s: spectroscopic study and electrochemical characterization

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Fully undoped oligo(3,4-ethylenedioxythiophene)s have been synthesized from polycondensation of the corresponding dibromomonomer in the presence of a catalytic Ni(0)-based complex in *N,N*-dimethylacetamide (DMA). HPLC analysis indicated that the material is constituted of three main oligomers which have also been clearly detected by UV-Visible spectroscopy. Due to its partial solubility in DMA, processability is improved compared to the corresponding insoluble polymer and thin films of oligomers can be deposited by evaporation. Electrochemical and electrochromic properties of undoped film have been carried out. Deep purple in its undoped state, the material becomes sky blue in the oxidized form. The mixture of oligomers was characterized by means of Raman scattering, IR absorption and X-Ray diffraction (XRD), and compared to the poly(3,4-ethylenedioxythiophene) obtained by the oxidative route.

1. Introduction

In the field of polythiophene derivatives, poly(3,4-ethylenedioxythiophene) (PEDOT) has attracted significant attention in recent years. The alkylenedioxy substituents in the 3 and 4 positions prevent the occurrence of α,β coupling, and thus ensure the formation of linear chains. Moreover, the electron-donating oxygen atoms lower the oxidation potential compared to thiophene and stabilize the oxidized polymer. Chemically as well as electrochemically synthesized PEDOT is very stable.¹ The low band gap of PEDOT (1.6 eV)² is also interesting for electro-optical properties. Unlike usual conducting polymers, that become dark after doping, this polymer becomes transparent,² with an absorption maximum around 2 eV (in the middle of the visible region) in its neutral state. These properties are preserved in the presence of substituents introduced to improve solubility and processability. So, not surprisingly, numerous research projects have already been undertaken with the aim of developing various applications such as antistatic coatings,³ electrochromic devices,^{2,4,5} electrochemical capacitors,⁶ biosensors⁷ or chemical sensors.⁸ Usually, two different ways are available to synthesize PEDOT. The chemical route using oxidizing agents (FeCl₃, Fe(Tosylate)₃, Ce(SO₄)₂, (NH₄)₂Ce(NO₃)₆...) leads to the formation of powder of oxidized polymer, the conductivity of which reaches 10–30 S cm⁻¹.¹ The electrochemical oxidative way (applied potential or cyclic voltammetry) leads to the formation of thin films whose thickness is easily controlled by the amount of electricity used for the electrosynthesis. Depending on the electrolyte and the conditions of electropolymerization, the conductivity can reach 200–300 S cm⁻¹.¹⁰

Recently, Yamamoto and Abila have described a new synthesis of PEDOT (and others conducting polymers) based on coupling reactions of dihalogenated aromatic compounds with a zero-valent nickel complex.^{11,12} Organometallic dehalogenation polycondensation of 2,5-dichloro-3,4-ethylenedioxythiophene leads to an undoped neutral and insoluble PEDOT.¹² The present study deals with a similar approach consisting of using a dehalogenative polycondensation which

has been already used by some of us to obtain, notably, polycarbazole, poly-*p*-phenylene and their copolymers.¹³ On the contrary to Yamamoto who synthesized an insoluble polymer, we obtain here a material soluble in some organic solvents due to its low polymerization degree.

Electrochemical, physical and optical properties of this undoped oligomer are here described and compared with those of PEDOT synthesized by oxidative polymerization.

2. Experimental

2.1 Spectral and electrochemical measurements

Raman spectra of PEDOT derivatives obtained with the excitation lines from the visible range (457.9 nm, 514.5 nm and 676.4 nm) were recorded with a multichannel Jobin-Yvon T64000 spectrophotometer connected to a CCD detector. For the near infrared (nir) excitation wavelength (1064 nm) a Fourier Transform (FT) Raman Bruker RFS 100 spectrophotometer was used. The Raman scattering signal was collected in a back scattering configuration with a spectral resolution of about 4 cm⁻¹.

Infrared spectra were recorded on a Nicolet 20 SXC FTIR spectrophotometer with a DTGS detector in the 400–4000 cm⁻¹ frequency range. All spectra were measured at room temperature using pressed KBr pellets in which the powders of PEDOT derivatives were mixed (1 to 2%). A spectral resolution of 4 cm⁻¹ was taken for all experiments and spectra were corrected for substrate absorption.

Absorption spectra were measured with an Otsuka MCPD-1000 multichannel spectrophotometer.

X-Ray powder diffraction diagrams were recorded on a CPS 120 INEL X-ray powder diffractometer equipped with a monochromatized radiation CuK-L₂ and a position-sensitive detector calibrated with Na₂Ca₃Al₂F₁₄ as standard. The powders were introduced in a Lindemann capillary ($\phi = 0.6$ mm).

All electrochemical studies were performed using a PRT20-2X potentiostat (Tacussel). All curves were plotted with an X–

Y recorder (DELFT BV BD94 from Kipp and Zonen). Electrochemical experiments were run under argon atmosphere using CH_2Cl_2 - NBu_4BF_4 0.1 M as electrolyte in a conventional three-electrode cell. Working electrodes were platinum discs (2 mm diameter) and the counter electrode was a Pt wire. Potentials are relative to a saturated calomel electrode (SCE) placed in a separate compartment containing the supporting electrolyte.

2.2 Chemicals

Triphenylphosphine (Merck) was recrystallized from hexane. The catalytic precursor, NiBr_2 -Bipy (Bipy = 2,2'-bipyridine) complex, was prepared as previously described.^{13d} *N,N*-Dimethylacetamide (DMA) was freshly distilled under reduced pressure over calcium hydride prior to use. The activated zinc powder was prepared as follows: under inert atmosphere, 100 ml of glacial acetic acid was added to 5 g of zinc powder (Merck) and stirred for 1 hour. The reaction mixture was then filtered through a fine porosity glass frit and washed with ether. The activated zinc powder was dried under vacuum.

2.3 Synthesis

2,5-Dibromo-3,4-ethylenedioxythiophene. 3 g of 3,4-ethylenedioxythiophene (Bayer) and 8 g of *N*-bromosuccinimide (Aldrich) were dissolved in a solution of 50 ml CHCl_3 and 50 ml glacial acetic acid. The solution was stirred at room temperature for 2.5 hours and poured into 200 ml of distilled water. The organic layer was separated, neutralized with sodium bicarbonate and then filtered. The solvent was then removed under vacuum by rotary evaporation. The crude product was purified by column chromatography using CHCl_3 as an eluent to obtain 4.6 g of white crystals in 73% yield. Mp: 90 °C, ^1H NMR (CDCl_3): (4.5 ppm, s, CH_2). ^{13}C NMR (CDCl_3): 140.1, 85.9, 65.3 ppm.

Oligo(3,4-ethylenedioxythiophene). Activated zinc (0.67 g; 10.3 mmol) then 6.6 ml of DMA were mixed with NiBr_2 bipy (0.063 g; 0.166 mmol), triphenylphosphine (0.52 g; 2 mmol) and 2,5-dibromo-3,4-ethylenedioxythiophene (1 g; 3.3 mmol) under argon atmosphere. The color of the mixture became immediately red and remained unchanged after 2.5 hours under stirring at 95 °C. The reaction was allowed to continue for a further hour, then the mixture was poured into 200 ml of sulfuric acid (5%). A black product precipitated and was filtered, washed with distilled water down to neutral pH, 3 times with 50 ml of ether and 3 times with 50 ml of methanol. After drying under vacuum, a black purple powder was obtained in 72% yield. On the contrary to Yamamoto who obtained no residual halogen atom in the polymer, we determined 1.84% of residual bromine in the material from elemental analyses. This value is quite low and indicates that these chains do not bear systematically one bromine atom per chain end. So, this would have probably little influence on the different properties studied.

3. Results and discussion

Poly(3,4-ethylenedioxythiophene) (PEDOT) is usually obtained by oxidation of 3,4-ethylenedioxythiophene with oxidizing agent leading to a doped material.

By mixing it with ammonia or hydrazine solutions and stirring for several hours, only a partially dedoped material is obtained, due to the good stability of the doped form in air and the low band gap (around 1.6 eV) of this polymer.

Moreover, the main drawback of PEDOT is its poor processability due to its insolubility in classical organic solvents. By using a dehalogenative polycondensation with a zero-valent nickel complex, Yamamoto managed to obtain a

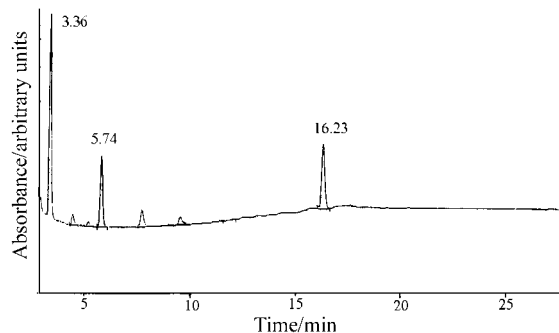


Fig. 1 HPLC analysis of a solution of oligomers in DMA.

fully undoped polymer. Nevertheless, the material was still insoluble and then unprocessable. Dehalogenative polycondensation of a dihalide monomer, by mixing it with activated zinc, triphenylphosphine and NiBr_2 bipy in *N,N*-dimethylacetamide (DMA) generally leads to low polymerization degree oligomers⁵ on the contrary to bis(1,5-cyclooctadiene)nickel(0). If the short length of the polymer chain is actually a drawback for most of the chemical polymerizations, it can be an advantage for poorly soluble materials like PEDOT. By this method, we synthesized from 2,5-dibromo-3,4-ethylenedioxythiophene a fully undoped oligomer which is soluble in particular in DMA.

From HPLC analysis, we have clearly detected three main signals corresponding to three populations of variable low polymerisation degree (Fig. 1). To confirm this result, we studied the optical spectroscopy of the material in solution in DMA. As shown in Fig. 2, we can observe three main peaks located at 423, 451 and 482 nm which correspond to the three main oligomers present in the material.

3.1 Electrochemical and optical properties of thin films

Electroactivity of the material was investigated in a 0.1 M NBu_4BF_4 - CH_2Cl_2 medium. A film was deposited onto a Pt electrode by casting a soluble fraction from DMA solution. Cyclic voltammetry was carried out between -0.8 and +0.8 V vs. SCE. As shown in Fig. 3A, the material is oxidized with a main anodic peak centered at +0.5 V with a shoulder around +0.15 V during the initial anodic scan at a scan rate of +0.1 V s^{-1} . On the cathodic scan, only one well-defined reduction peak at +0.3 V is observed. Compared to the 2,5-dibromo-3,4-ethylenedioxythiophene monomer which exhibits an irreversible oxidation peak at +1.7 V vs. Ag/AgCl (curve not shown), the electroactivity of the deposited material is lowered, showing an enhancement of the conjugation which stabilizes the oxidized species. By comparison, Fig. 3B shows the cyclic voltammogram of the anodically synthesized PEDOT. Only one anodic peak at +0.22 V vs. SCE is observed while there is no well defined reduction peak at +0.3 V in what

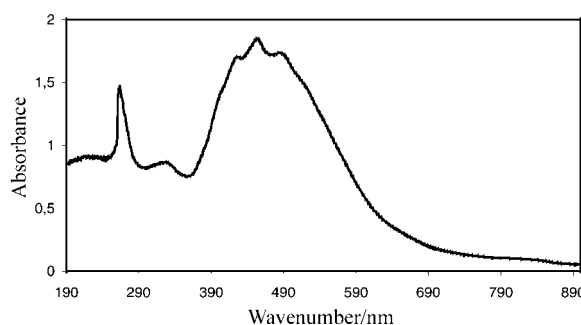


Fig. 2 Absorption spectrum of fully undoped oligomers in DMA solution.

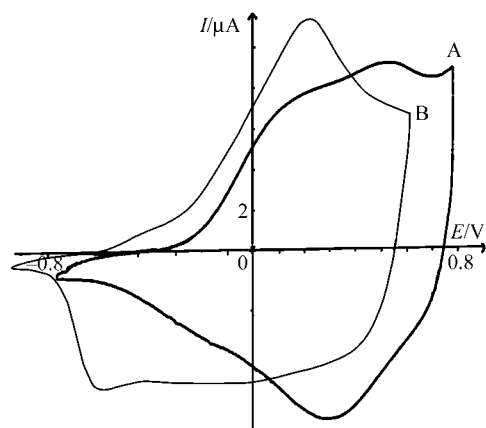


Fig. 3 Cyclic voltammograms in $\text{CH}_2\text{Cl}_2\text{-NBu}_4\text{BF}_4$ 0.1 M of a thin film of fully undoped oligomers (curve A) and PEDOT obtained by oxidative electropolymerization (curve B).

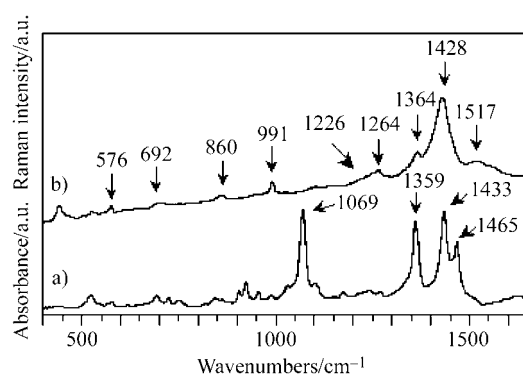


Fig. 5 a) FTIR and b) Raman ($\lambda_{\text{exc}} = 1064$ nm) spectra of undoped oligomers in the 400–1650 cm^{-1} range.

is a mainly capacitive feature. Compared to electrosynthesized PEDOT, the electroactivity of the soluble material is shifted towards more positive potentials which could indicate a decrease of the electronic delocalization of the EDOT segments.

Fig. 4 shows the UV-Visible characterization of a thin film deposited on a SnO_2 electrode. Compared to the spectrum obtained in solution, absorption of the three oligomers is less visible. Moreover, one can notice a red shift of the maximum absorption wavelength, in agreement with a more planar conformation in the solid state. Undoped material exhibits an electronic band gap (E_g) defined as the onset for the $\pi\text{-}\pi^*$ absorbance, of approximately 1.7 eV. If we compare this to PEDOT obtained by electro-oxidation (absorption band around 700 nm and band gap around 1.6 eV; ref. 2), we

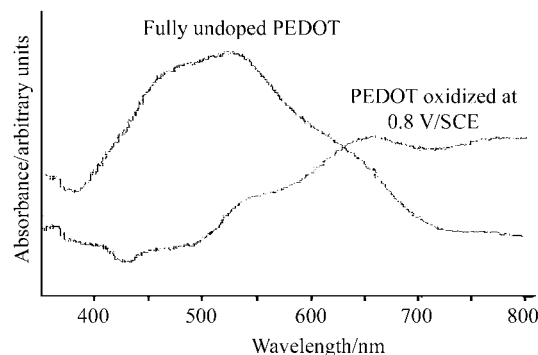


Fig. 4 Absorption spectrum of a thin film of fully undoped oligomers deposited by evaporation on SnO_2 electrode and after oxidation at +0.8 V/SCE.

observe a significant blue shift of the absorption. This is due to a decrease of the conjugation length when the electronic delocalization decreases. These results are in agreement with the formation of short oligomers compared to the compound obtained by electro-oxidation.

After oxidation at a potential of +0.8 V vs. SCE, a very broad band centered in the near IR grows to the expense of the 525 nm strong band. This behavior has been already reported for PEDOT films,^{2,14} leading to oxidized films with a sky blue color.

Therefore, electrochromic properties of this oligomer are similar to the ones of the polymer, and its processability is improved.

3.2 Raman and infrared spectroscopy

3.2.1 Vibrational assignment. Raman spectra of the oligomer were recorded for different excitation wavelengths. In Fig. 5, Raman ($\lambda_{\text{exc}} = 1064$ nm) and IR absorption spectra of the undoped material are respectively shown. The Raman spectrum is very similar to that of reduced electrochemical PEDOT.¹⁵ It is very interesting to note that, with $\lambda_{\text{exc}} = 457.9$ nm, we are in resonance with the short chains. Indeed, we observe a distribution of the conjugation length with two bands located at 1458 and 1440 cm^{-1} (see Fig. 7). A

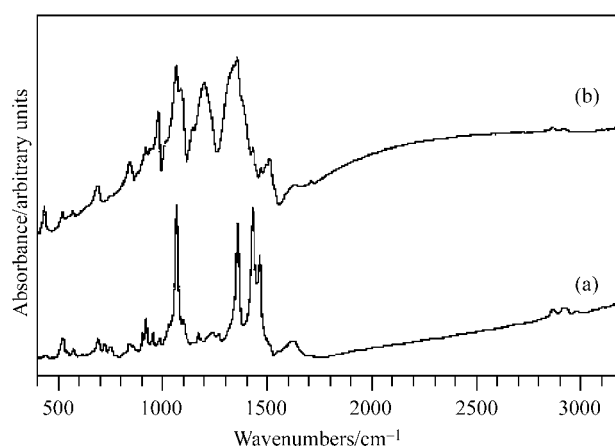


Fig. 6 FTIR spectra of a) EDOT oligomers and b) PEDOT obtained by chemical oxidation by FeCl_3 and partially dedoped with ammonia 2 M.

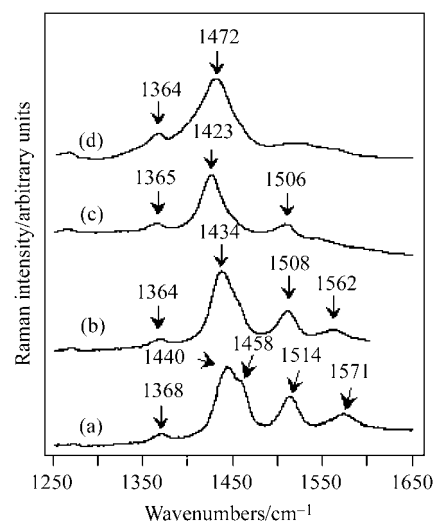


Fig. 7 Dependence of the position of the Raman band due to the $\text{C}_\alpha\text{=C}_\beta$ symmetric stretching on the excitation wavelength: a) 457 nm, b) 514 nm, c) 676 nm, d) 1064 nm for the undoped oligomers.

Table 1 Comparison between the observed frequencies of this neutral material and the calculated frequencies of reduced PEDOT (vw: very weak, w: weak, m: medium, sh: shoulder and s: strong)

Type of vibrations	IR Activity	Raman Activity	Experimental frequencies/cm ⁻¹	Calculated frequencies/cm ⁻¹	Approximate description of vibrations
Thiophene in plane modes	—	w	1517	1509	C=C stretching (antisym.)
	—	s	1428	1444	C=C stretching (sym.)
	—	m	1364	1366	C-C stretching
	—	w	1264	1267	C-C inter-ring stretching
	—	vw	1226	1228	C-C inter-ring stretching
	—	w	692	691	C-S-C deformation
	—	w	440	440	
	s	—	1465	1468	C=C stretching (antisym.)
	s	—	1433	1408	C=C stretching (sym.)
	s	—	—	1350	C-C stretching
	m	—	1029	1015	Cycle deformation
	w	—	955	962	C-S stretching
	m	—	921	911	C-S stretching
Oxyethylene ring modes	w	—	2972		CH ₂ symmetric stretching
	w	—	2923	2932	CH ₂ asymmetric stretching
	w	—	2862	—	CH ₂ symmetric stretching
	—	w	1570–1548 ^b	—	CH ₂ bending
	s	sh	1458–1465 ^b	—	—
	s	—	1359	—	CH ₂ bending
	w	w	1267	—	—
	w	vw	1240	—	—
	m	w	1105	1110	C-C stretching
	s	—	1069	1070	C-O stretching
	w	vw	1029	1061	C-O stretching
	—	m	991	988	Oxyethylene ring deformation
	w	w	860	865	O-C-C deformation
	vw	—	816	802	Oxyethylene ring breathing
	vw	w	780	788	Oxyethylene ring deformation
	w	—	722	—	CH ₂ rocking
	w	w	576	565	C-O-C deformation
	w	vw	522	525	—
	—	w	440	440	C-O-C deformation

^a1064 nm. ^b457 nm.

resolution of about 8 cm⁻¹ is too low to allow more contributions to be identified. In the same way, we observe 2 bands due to the C=C asymmetric stretching vibration, around 1571 and 1517 cm⁻¹. They correspond to the thiophene rings at the end and in the middle of the chains, respectively. The band in the vicinity of 1428–1440 cm⁻¹ (R) is due to the symmetric C_α=C_β stretching deformation. The band at 1364 cm⁻¹ (R) is due to the C_β-C_β stretching deformation in the aromatic thiophene ring. Two bands at lower wavenumbers (1264 cm⁻¹ and 1226 cm⁻¹, more clearly separated in another spectrum not presented here) are ascribed to the inter-ring C_α-C_α stretchings. Finally, the broad band at around 692 cm⁻¹ (R) is due to C-S-C ring deformation.

The CH₂ stretchings of the oxyethylene ring, which are expected in both Raman and infrared spectra, are assigned to the medium infrared bands at about 2800–3000 cm⁻¹ (Fig. 6a). At 1465 cm⁻¹ (IR), the CH₂ bending is observed. In the same way, the strong bands observed at 1069 and 1359 cm⁻¹ (IR) are also assigned to the oxyethylene ring. The C_α=C_β stretching of the thiophene ring is assigned to the 1433 cm⁻¹ (IR) band. A complete set of experimental Raman and IR bands for the oligomer is presented in Table 1.

One can notice that in comparison with the spectrum of PEDOT obtained by chemical oxidative polymerization (Fig. 6b) and then reduced by ammonia (10% v/v in water), the bands of the oligomer (from polycondensation) were much sharper, and much better defined. Yamamoto *et al.* showed that complete dedoping of PEDOT did not seem possible even with a treatment using a strong reductive agent and that 2% of chlorine (FeCl₄⁻) was still present, which explains the broad absorption bands characteristic of *p*-doped polythiophene.¹² Some new bands, absent in unsubstituted polythiophene, can be assigned to the oxyethylene ring deformations, carbon-oxygen and CH₂ vibration groups (see Table 1).

We were therefore tempted to compare these experimental results to a vibrational analysis of the reduced polymer previously published.¹⁵ The detailed description of the methodology used can be found elsewhere.¹⁶ A good agreement between the calculated and experimentally observed frequencies is found (Table 1), for Raman bands as well as for infrared bands. This fact clearly confirms previous results obtained for undoped electrochemical PEDOT.¹⁵

3.2.2 Study of the conjugation length dispersion. The conjugation length distribution is generally reflected not only in the UV-Vis spectra but also in Raman spectroscopy. The position of the Raman bands which are associated with the existence of the π -bonding system (C=C stretching) usually depends on the excitation wavelengths. Vibrations from the segments involving smaller conjugation length will be enhanced by shorter excitation lines (λ_{exc} =457.9 nm) whereas those from longer conjugated segments will be in resonance with the red (λ_{exc} =676.4 nm) or nir (λ_{exc} =1064 nm) excitation wavelengths. For regioregular poly(3-decylthiophene), where the chain length is more homogeneous, the position of the main band (due to C_α=C_β stretching) is weakly dependent on the excitation wavelength.¹⁷

In Fig. 7 the C_α=C_β symmetric stretching band for the oligomer is presented for different excitation wavelengths. It is noteworthy that changes in the peak positions are observed. Between blue and infrared, this shift is only 17 cm⁻¹, which is relatively weak. By comparison, the dispersion observed for electrochemical PEDOT is *ca.* 11 cm⁻¹. We can then conclude that the conjugation lengths in this material are less homogeneous by comparison to the “electrochemical” or “chemical” PEDOT, in agreement with the distribution of the short length of the oligomers.

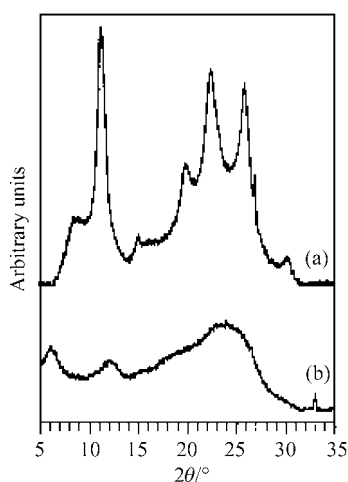


Fig. 8 XRD diffractograms of a) EDOT oligomers and b) PEDOT obtained by chemical oxidation by FeCl_3 and partially dedoped with ammonia 2 M.

Table 2 Correlation between position and interatomic distance, from XRD peaks

Angle/°	8.3	11.2	15.1	20.0	22.5	25.9	30.3
$d/\text{\AA}$	10.52	7.87	5.88	4.44	3.95	3.43	2.95

3.3. XRD experiment

The XRD experiments were carried out during approximately 16 hours and are shown in Fig. 8, where the undoped oligomers are compared with the partially dedoped PEDOT. We can see that this material possesses more crystalline parts than the homopolymer obtained by chemical oxidation, and then reduced by ammonia 2 M. This is evidenced by the rather sharp peaks that are present. These peaks are probably due to the contribution of short segments of the material. Since we are in the presence of a mixture of oligomers, we are not able to fully interpret this X-ray diffraction pattern. However, we can see in Table 2 the correspondence between the position (angle) of these peaks and the interatomic distances that can thus be calculated. It was not possible to perform refinements on these peaks, but we can notice that the most intense peak, located at 11.2° , gives rise to an interatomic distance of $7.87 \text{ \AA}$, which was previously found to be the c parameter (polymer repeat distance, along the chain) of the PEDOT/Tosylate orthorhombic structure.¹⁸ We could therefore assume that the first peak should correspond to one of the other parameters of the unit cell, *i.e.* $10.52 \text{ \AA}$. Aasmundtveit *et al.*¹⁸ found the following lattice parameters: $a = 14.0 \text{ \AA}$, $b = 6.8 \text{ \AA}$, $c = 7.8 \text{ \AA}$. Extrapolation of these results led us to suppose that this parameter could be the a parameter, where the shorter length can be explained by the absence of dopant ion layers between the polymer chain stackings.

4. Conclusions

We synthesized fully undoped oligoethylenedioxythiophene from polycondensation of EDOT dihalide. The resulting compound is mainly constituted of three oligomers which are soluble in DMA giving a good opportunity to improve its

processability. Electrochemical study and UV-Visible spectroscopy confirm that we have formed oligomers of EDOT.

In this work we also present the first Raman studies of fully undoped derivatives of PEDOT. From our results the following conclusions can be drawn:

(1) Similarly to non-regioregular poly(3-decylthiophene), the position of the main band in this oligo-PEDOT (due to $\text{C}_\alpha=\text{C}_\beta$ stretching) is dependent on the excitation wavelength proving its low homogeneity in conjugated length, due to the presence of different oligomers.

(2) A good agreement between the experimentally observed Raman frequencies and general vibrational calculations performed on PEDOT was found.

Studies are in progress in the laboratory to determine the length of each oligomer present in the material and to isolate them by sublimation under vacuum.

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