In Situ Spectroelectrochemical Raman Studies of Poly(3,4-ethylenedioxythiophene) (PEDT)

S. Garreau,* G. Louarn, J. P. Buisson, G. Froyer, and S. Lefrant

Laboratoire de Physique Cristalline, Institut des Matériaux de Nantes, B.P. 32229, 44322 Nantes Cedex 3, France

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ABSTRACT: The vibrational properties of poly(3,4-ethylenedioxythiophene) (PEDT) have been studied by means of UV−vis−NIR optical absorption spectroscopy and resonance Raman scattering (RRS) spectroscopy with two excitation lines: green (514 nm) and infrared (1064 nm). The two-step oxidative doping process does not induce a drastic change for the Raman bands, but the changes that occur are clearly evidenced. During doping, new bands appear, indicating a modification of the electronic structure of the polymer. Vibrational calculations were carried out using a symmetrized dynamical matrix model and the results were compared with experimental data, especially in the $1200-1600 \text{ cm}^{-1}$ range, where the $C_\alpha{=}C_\beta$ and $C_\beta{-}C_\beta$ stretching vibrations are active. It appears that PEDT seems to have an intermediate electronic structure, between the quinoid and benzoid structures.

Introduction

In the last 20 years, conducting polymers gave rise to a great amount of researches. Among the promising family of polythiophenes, the poly(3,4-ethylenedioxythiophene) (PEDT) showed remarkable stability.[1,2] It can be synthesized both chemically and electrochemically, even in aqueous medium,[3] and its transparency in the doped state makes it suitable for electrochromic devices.[4] Although it is infusible and insoluble, it is commercially available as a dispersion in aqueous poly-(styrenesulfonic acid) (PSSA).[5] It is industrially utilized as an antistatic coating on photographic films, and its potential applications are as various as a capacitor,[6] through-hole plating of printed circuit boards,[7] or radioactive source support.[8]

Raman scattering and infrared absorption spectroscopies are very useful and complementary techniques which, coupled with group theory, allow one to reach the normal vibration modes and, subsequently, the structure of molecules. Moreover, it is known that Raman spectroscopy is a very useful tool for studying the doping process in conjugated polymers.[9,10]

As far as we know, one study during doping of PEDT was realized by means of FTIR internal reflection,[11] and one brief Raman study was made by Sakmeche et al.[3]

In this paper, we report the spectroelectrochemical study of the oxidative doping of poly(3,4-ethylenedioxythiophene). We tried to take advantage of the resonance Raman effect using two excitation lines: 514 nm (green) and 1064 nm (near-infrared). Indeed, despite the fact that the resonance effect complicates the spectra for the conjugated polymers, the use of different excitation lines may provide spectroscopic and chemical information unobtainable by other spectroscopic methods. We finally propose a coherent set of force constants related to the assignment of the Raman bands and an estimation of the polymer chain modification occurring upon doping.

* To whom correspondence should be addressed. E-mail: Sebastien.Garreau@cnrs-imn.fr.

Experimental Section

The 3,4-ethylenedioxythiophene monomer was provided from Bayer AG, and used as received.

Electropolymerization was carried out potentiostatically using an EG&G PAR 273 potentiostat−galvanostat in a three-electrode single-compartment cell equipped with platinum plates as working and counter electrodes and an $Ag/AgNO_3$ reference electrode. The electrolyte was an acetonitrile (ACN) solution with 0.2 M EDT and 0.1 M tetrabutylammonium tetrafluoroborate ((TBA)BF$_4$). The potential scanning was performed between −1.0 V and +0.8 Vvs Ag/AgNO$_3$.

In situ resonance Raman spectra were performed using a three-compartment electrochemical cell connected to a LINSEIS LY 1400 plotter. The electrolyte was the monomer-free acetonitrile solution described above, and the electrodes are the same as for polymerization. A multichannel Jobin-Yvon T64000 spectrophotometer connected to a CCD detector was used in the visible range with the following excitation lines: 457.9 nm (blue), 514.5 nm (green), 676.4 nm (red), and FT Raman spectra were recorded with a RFS 100 Bruker spectrometer (excitation wavelength 1064 nm).

UV−vis−NIR optical absorption was performed with a Varian CARY 5G spectrophotometer on galvanostatically prepared poly(3,4-ethylenedioxythiophene) films on ITO coated glass (current density = 0.5 mA/cm^2) with the same electrodes and electrolyte system described above.

Infrared ATR experiments were carried out with a NICO-LET Magna IR 560 FT spectrometer.

Results

The cyclic voltammograms of electrochemically prepared poly(3,4-ethylenedioxythiophene) are shown in Figure 1. We can see two rather broad oxidation peaks with maxima at −0.1 and +0.55 V. A further experiment showed that for potentials above +0.8 V the redox cycles were quite reproducible, but the peak located at −0.1 V was shifted toward lower potentials. We assumed that this shift was due to the beginning of degradation (i.e., overoxidation) of the polymer.

UV−vis−NIR spectroelectrochemical results are presented in Figure 2. The spectra obtained for neutral poly(3,4-ethylenedioxythiophene) ($E < -0.3$ V) show a broad absorption peak covering the visible range, with a maximum at 600 nm (2.1 eV), corresponding to the
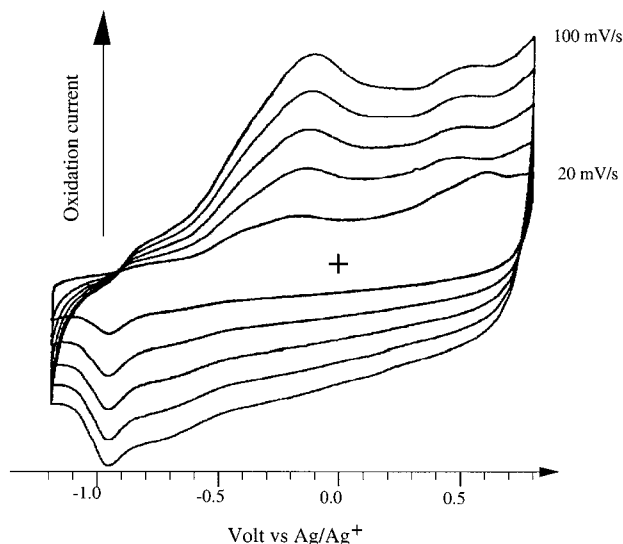
Figure 1. Cyclovoltammograms of the redox process occurring in poly(3,4-ethylenedioxythiophene) recorded in 0.1 M (TBA)-BF$_4$ in ACN, between -1.0 and $+0.8$ V vs Ag/AgNO$_3$ (sweep rate increased from 20 to 100 mV/s).
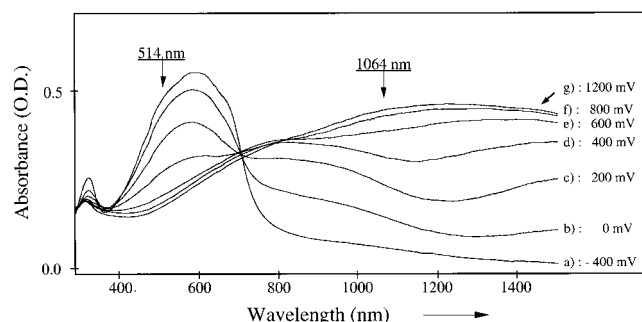

Figure 2. In situ optical absorption spectra recorded in 0.1 M (TBA)BF$_4$ in ACN at different potentials vs Ag/AgNO$_3$ on ITO-coated glass electrodeposited polymer films.

Figure 3. Spectroelectrochemical Raman study of poly(3,4-ethylenedioxythiophene) with an excitation wavelength of 514 nm in 0.1 M (TBA)BF$_4$/ACN (the asterisks indicate the solvent bands).

Figure 4. Spectroelectrochemical Raman study of poly(3,4-ethylenedioxythiophene) with an excitation wavelength of 1064 nm in 0.1 M (TBA)BF$_4$/ACN (the asterisks indicate the solvent bands).

$\pi-\pi^*$ transition. As well as previous studies on regioregular polythiophenes,[12,13] the two-step oxidation observed on the cyclovoltammograms is confirmed by UV–vis–NIR optical absorption. Up to -0.1 V, we only observe this peak at 600 nm. Between the two oxidation potentials, i.e., between -0.1 and $+0.55$ V, it decreases monotonically while two other broad bands grow in the near-infrared range, at around 850 nm (1.5 eV) and 1800 nm (0.7 eV), respectively.

These absorbances grow until the applied potential reaches the one of the second oxidation peak. Above this potential, only one very large band around 1200 nm (1 eV) appears. It is worth noting that the isosbestic point corresponding to an entire conversion between doped and undoped polymer without any secondary reaction does not seem to be valid anymore above $+0.8$ V. This confirms our previous assumption of the degradation of poly(3,4-ethylenedioxythiophene) when the applied potential goes beyond $+0.8$ V.

We then realized in situ resonance Raman study with different excitation wavelengths. Here we present the result for two typical wavelengths: 514 and 1064 nm (Figures 3 and 4). The intensities of the bands of the concerned structures are enhanced due to the resonance effect; that means that the excitation wavelength corresponds to an electronic transition occurring in the studied material. As seen in Figure 2, the green line is in resonance with the neutral form of poly(3,4-ethyl-
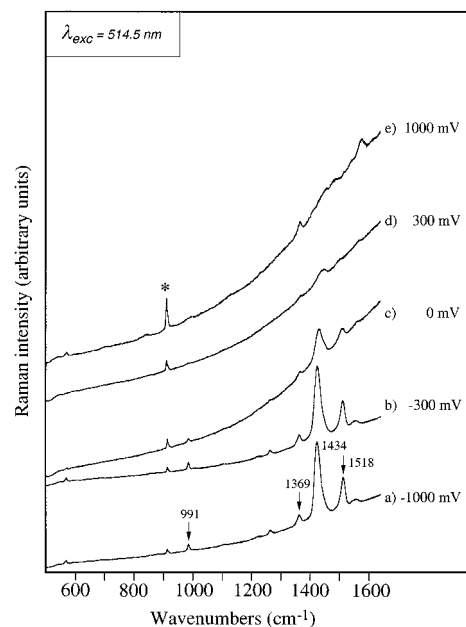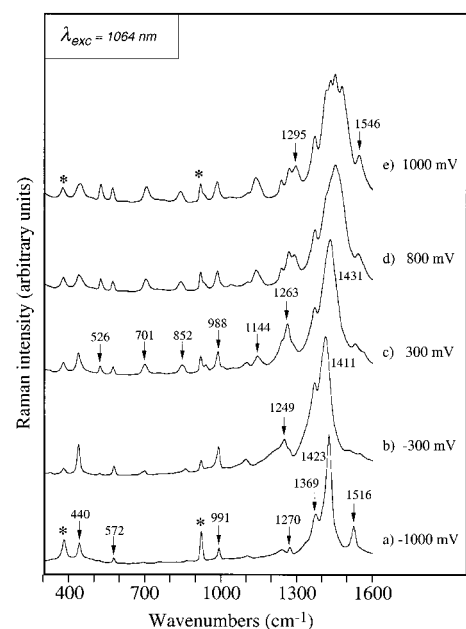
enedioxythiophene), and the infrared (1064 nm) line is in resonance with the doped structure.

At 514 nm, we observe a decrease of the intensity of the peaks. The principal peak is broadened and shifted from 1434 cm^{-1} (at -1.0 V) to 1453 cm^{-1} (at $+0.3$ V) during doping. We can notice that the spectrum recorded at $+1.0$ V is mainly that of the solvent (ACN). The enhancement of the intensity of the neutral polymer bands due to the resonance effect explains why the bands of the doped structures do not appear and why the collected signal is less and less intense with increasing potentials.

In Table 1 are listed the principal Raman lines, the comparison with parent compounds, and their assign-

Table 1. Observed and Calculated Frequencies of Neutral Poly(3,4-ethylenedioxythiophene) and Parent Compounds, with Assignment of the Principal Bands[a]

| polythiophene | | | | poly(3,3′-dibutoxy-2,2′-bithiophene) | | poly(ethylenedioxythiophene) | | | | approximative description of vibrations |
| Raman | | infrared | | Raman | | Raman | | infrared | | |
exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	
							2931	2934	2933	CH_2 str
1497	1498	1488	1504	1522	1512	1520	1509	1488	1468	asym C=C str
1455	1460	1441	1429	1451	1456					sym C_α=C_β(−H) str
				1415	1401	1431	1444	1427	1408	sym C_α=C_β(−O) str
1365	1359	- - -	1338	1375	1300	1369	1366	1366	1350	C_β-C_β str
						1270	1267			C_α−$C_{\alpha'}$(inter-ring) str
1220	1210	1224	1225	1190	1201	1226	1228			C_α−$C_{\alpha'}$(inter-ring) str + C_β-H bend
- - -	1197			1170	1163					
1045	1039	1065	1055		1004					C_β−H bend
				1112	1108	1111	1110	1051	1070	C−O−C def
							1061			C−O−C def
							964		911	oxyethylene ring def
									961	sym C−S−C def
						991	988	892	866	oxyethylene ring def
							806		802	oxyethylene ring def
740	746	737	747	754	757					asym C−S−C def
700	696	590	587	699	676	692	691			sym C−S−C def
- - -	522				523	571	577		565	oxyethylene ring def
							486		525	
							440			

[a] Key: str, stretching; asym asymmetric; sym, symmetric; bend, bending; def, deformation.

ment based on the work of Louarn et al.[14] and Snyder et al.[15]

At 1064 nm, the spectrum of the reduced form of poly-(3,4-ethylenedioxythiophene) is similar to that at 514 nm. The most important change is the frequency of the main peak that we assign to the C_α=C_β stretching: it is pointed at 1423 cm^{-1}, indicating that this vibration mode is sensitive to the excitation line. When the first oxidation peak is attained, we can see that new bands appear, which we did not observe with the green line.

We are able to make some interesting remarks:

•The symmetric C_α=C_β peak continuously broadens and its maximum shifts from 1423 to 1411 cm^{-1} for −0.3 V and then moves to higher frequencies, to reach 1431 cm^{-1} at +0.3 V and even 1450 cm^{-1} at +0.8 V.

•The asymmetric C_α=C_β band is splitted into two bands located at 1503 and 1545 cm^{-1} which shift up to 1528 and 1562 cm^{-1}, respectively, for +0.3 V. At +0.8 V, only one broad peak is observed, with a maximum at 1539 cm^{-1}. At this potential, the second peak is not observed.

•The initial band located at 1271 cm^{-1} (C_α−$C_{\alpha'}$ stretching) seems to be overlapped by the broadening of the band at 1238 cm^{-1}, which shifts to 1249 cm^{-1} (−0.3 V) and finally to 1263 cm^{-1} (+0.3 V). It seems to split into three bands at 1239, 1268, and 1289 cm^{-1} for +0.8 V.

In the rest of the spectra, new bands grow at 1143, 1045, 1017, 945, 866 (shifts down to 847), 699 (shifts up to 703), 527, and 310 cm^{-1} with no particular broadening.

Methodology and Discussion

Infrared and Raman spectroscopies combined with careful calculations of vibrational spectra are known to provide valuable information for electronic structure. The experimental data obtained are compared with values calculated using a symmetrized dynamic matrix model. The calculation method used in this research has been successfully applied to polyaniline[16] and other conjugated polymers.[17] The detail of this methodology can be found elsewhere.[16] Here we just outline the most important points.

All chemical and structural changes occurring upon poly(3,4-ethylenedioxythiophene) doping should give rise to modification of force constants. We therefore attempted to carry out a vibrational analysis, for undoped and doped poly(3,4-ethylenedioxythiophene). For the calculations, we made some preliminary hypotheses.

•We considered a planar geometry of the rings, which permits the separation between in-plane and out-of-plane vibration modes.

•In our simulation, we defined a perfectly regular and infinitely long chain. Such a polymer chain cannot actually exist, but in poly(3,4-ethylenedioxythiophene) the conjugation is sufficiently long to consider the translation as a symmetry operation to a first approximation. The data should also be useful in the estimation of the reliability of the final set of force constants and the normal vibration modes.
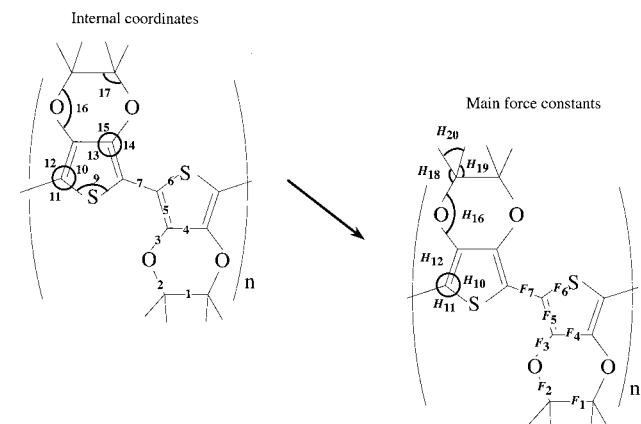
•It must be additionally assumed that some force constants must be fairly local (only dependent on the position and the type of few nearest neighbors), and for this reason they can be transferred from other compounds of appropriate chemical structure. Hence, force constants corresponding to common groups were expected to be transferable among these molecules.

The calculations of the force field and frequencies are carried out using Fourier's dynamical matrix. Since the chain of poly(3,4-ethylenedioxythiophene) possesses translational symmetry, one can restrict the calculations to one repeat unit. These calculations require the knowledge of the force constants and the bond lengths and bond angles. An internal coordinate system consisting of 16 bonds and 25 bond angles was used to compute the fundamental vibrations of poly(3,4-ethylenedioxythiophene), it is presented in Figure 5. The local redundancies were handled by suitable symmetry coordinates.

The calculations start from minimal set of force constants expressed in terms of internal coordinates and defined by

Table 2. Main Force Constants for A$_g$ and B$_{3g}$ Modes (Defined in Figure 5) and Their Contribution (P.E.D.) to the Raman Bands, Where Only Contributions Superior to 5% Are Presented

| | P.E.D. (%) for force constants (values in mdyn/Å or mdyn/Å/rad²) | | | | | | | | | | | | | | | | |
F_1 (4.23)	F_2 (5.00)	F_3 (5.05)	F_4 (6.29)	F_5 (6.81)	F_6 (4.63)	F_7 (5.23)	H_9 (2.28)	H_{10} (0.99)	H_{11} (0.69)	H_{12} (1.08)	H_{13} (1.32)	H_{16} (1.05)	H_{17} (0.93)	H_{18} (0.54)	H_{19} (0.51)	H_{20} (0.40)
calcd freq																
1510														21	54	28
1509				70	9				6	12	14					
1444		23	18	20						11				15	18	
1368			49	61		27	5	7								
1268			20		29	50				10						
1228				18	20	86		14		12	8					
1117	60	64										5		8		
989	10		48			9	11	8		9	5					
857	28	54													5	
688			9		5	7	15				12		22			
577	6		27		7	20		9				25	5			
440						19		9			6	35	7			
230				5	11		13			17	27	7				

Figure 5. Poly(3,4-ethylenedioxythiophene) unit with the principal internal coordinates and force constants.

$$F_{RR} = \left(\frac{\partial^2 \phi}{\partial R \partial R'}\right)_0 \quad (1)$$

where F, R, and R' are the harmonic potential energy and two internal coordinates, respectively.

For the planar oscillations, the valence force field chosen as a model for the sexithiophene and polythiophene by Louarn et al.[14] was first adopted. We therefore tried to minimize the number of force constants utilized in the subsequent step. The interaction constants for which no value was available from related system were taken initially at 0. This procedure enables to reduce significantly the number of independent constants, which becomes much lower than the number of observed frequencies.

The force constants are finally adjusted from experimental and calculated frequencies with a least-squares root procedure in which we minimize the standard deviation X, defined by

$$X = \left[\frac{1}{N}\sum_{i=1}^{N}(\varpi_i^{\text{exp}} - \varpi_i^{\text{calc}})^2\right]^{1/2} \quad (2)$$

where ϖ_i^{exp} and ϖ_i^{calc} are the experimental and calculated frequencies of the ith vibration and N is the number of experimental frequencies. The iterative process is stopped when the deviation between calculated and observed mode wavenumbers reaches a minimum. Changes in the force constants must be limited
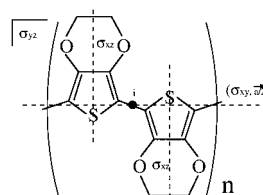
Figure 6. Symmetry elements of the D_{2h} point group for poly-(3,4-ethylenedioxythiophene).
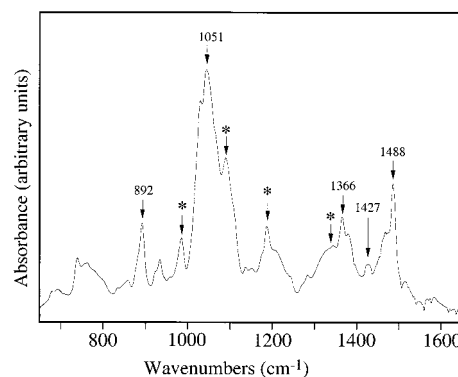
Figure 7. ATR spectrum of PEDT in the 650−1650 cm⁻¹ frequency range (an asterisk indicates residual doped segments).

in order to control the wrong evolution that may lead to nonphysical values at the end of iterations. In our study, the refinement converged smoothly under these conditions with an average error of 7 cm⁻¹ between the observed and calculated frequencies. Finally, a clear assignment of the vibration modes is obtained by the study of the potential energy distribution (P.E.D.), which permits us to see the fractional part of the potential energy of a normal mode contributed by each force constant. For all of the calculations, we supposed that the geometry of the polymer was that of neutral polythiophene, i.e., the benzene form of the thiophene cycles. The geometrical parameters used in this research were taken as follows: $r(\text{C}-\text{C}) = 1.45$ Å, $r(\text{C}-\text{H}) = 1.08$ Å, $r(\text{C}_\alpha-\text{S}) = 1.70$ Å, $r(\text{C}_\alpha-\text{C}_\beta) = 1.38$ Å, $r(\text{C}-\text{O}) = 1.52$ Å, $r(\text{C}_\alpha-\text{C}_{\alpha'}) = 1.44$ Å, $\text{C}-\text{S}-\text{C} = 95°$, $\text{C}_\beta-\text{C}_\alpha-\text{S} = 111°$, and $\text{C}_\beta-\text{C}_\alpha-\text{C}_{\alpha'} = 124°$, and the C−C−O and C−O−C angles of the oxyethylene ring were chosen to be equal to 120°.

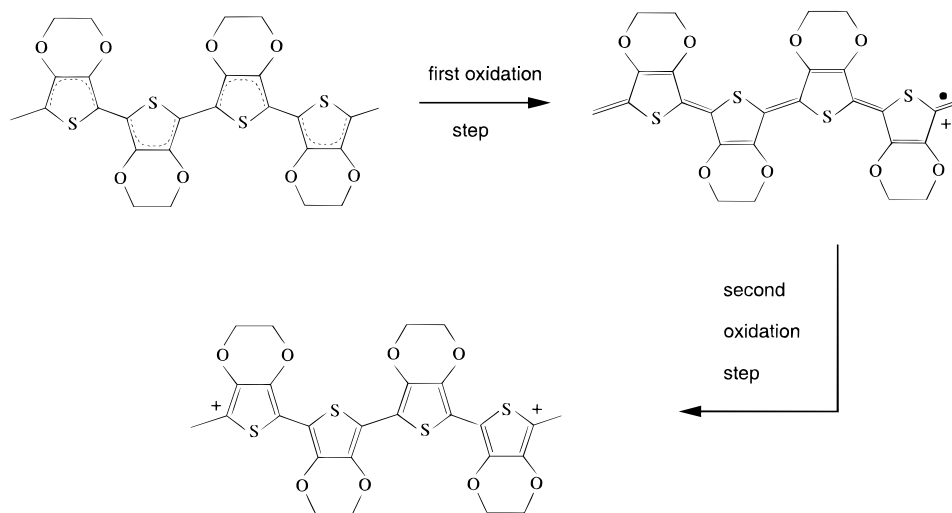Group theory is a very useful tool for the prediction of the Raman and infrared activity of the modes. With

Figure 8. Scheme of the proposed structure modification during the doping process of PEDT.

the hypotheses we made, poly(3,4-ethylenedioxythiophene) belongs to the D_{2h} point group, as seen in Figure 6. It possesses 78 fundamental modes. The 48 in-plane vibrations are separated into 12 A_g, 12 B_{3g}, 12 B_{1u}, and 12 B_{2u} vibrations. The exclusion rule due to the presence of a center of symmetry induces a separation between the activities of the modes. The "gerade" symmetry modes are active in Raman, and the "ungerade" symmetry modes are infrared active. So, we expect 24 in-plane Raman active modes and 24 in-plane infrared active modes. The results obtained for neutral poly(3,4-ethylenedioxythiophene) (-1.0 V) with the green line were used for the calculations. For the refinement on infrared modes, an in situ experiment was not realizable here. So we used the following method: the poly(3,4-ethylenedioxythiophene) film was exposed over 30 min to a potential of -1 V and rinsed with $CHCl_3$ before recording an ATR spectrum. We assumed that the time between when we got the film out of the solution and when we measured the reflection was short enough to consider this spectrum as that of neutral poly(3,4-ethylenedioxythiophene). The results of this ATR experiment may differ from classical transmittance experiments by some reciprocal centimeters (Figure 7). The results are presented in Table 1. For a better refinement of the force constants, we made the calculations at the same time on the monomer and the polymer, but we only present the results obtained for the polymer in this paper. The potential energy distributions and the final set of the main force constants for poly(3,4-ethylenedioxythiophene) are presented in Table 2. The whole set of force constants is reported in Table 3.

During the doping process, the force constants that are expected to change are as follows: F_3 relative to the $C_\beta-O$ bonds, F_4 relative to the $C_\beta-C_\beta$ bonds, F_5 relative to the $C_\alpha=C_\beta$ bonds, F_6 relative to the $C-S$ bonds, and F_7 relative to the $C-C$ inter-ring bonds.

The valence force field calculated for neutral poly(3,4-ethylenedioxythiophene) was taken and recalculated for these force constants for two different potentials, i.e. -0.3 and $+0.8$ V. The variation of the values of the force constants is very slight (maximum 5%), so we cannot interpolate these calculations with a sufficient reliability. However, on the basis of these results combined with the observation of the experimental Raman spectra, we can propose a mechanism for the modification of the electronic structure of PEDT, which is depicted

Table 3. Definition of the Internal Coordinates and Values of the Related Force Constants[a]

Diagonal Force Constants					
coord no.	atomic corresp	force const value	coord no.	atomic corresp	force const value
1	C−C	4.23	12	$C_\beta=C_\alpha-C_{\alpha'}$	1.08
2	C−O	5.00	13	$C_\beta-C_\beta=C_\alpha$	1.32
3	$C_\beta-O$	5.05	14	$C_\alpha=C_\beta-O$	0.27
4	$C_\beta-C_\beta$	6.29	15	$C_\beta-C_\beta-O$	0.27
5	$C_\alpha=C_\beta$	6.81	16	C−O−C	1.05
6	$C_\alpha-S$	4.63	17	C−C−O	0.93
7	$C_\alpha-C_{\alpha'}$	5.23	18	H−C−O	0.54
9	C−S−C	2.28	19	H−C−C	0.51
10	$S-C_\alpha=C_\beta$	0.99	20	H−C−H	0.40
11	$S-C_\alpha-C_{\alpha'}$	0.69	21	C−H	4.71

Nondiagonal Force Constants					
coord no.	force const value	coord no.	force const value	coord no.	force const value
1−2	0.39	1−19	0.28	5−12	0.09
2−3	0.62	1−17	0.37	5−13	0.31
3−4	0.37	2−16	0.62	5−14	0.11
3−5	0.54	2−17	0.71	6−9	0.65
4−5	0.84	2−18	0.45	6−10	0.77
5−5	−0.45	3−14	0.85	6−11	0.51
5−6	0.55	3−15	0.98	7−11	0.70
5−6[b]	−0.16	3−16	0.85	7−12	0.33
5−7	1.00	4−13	0.06	17−18	−0.19
6−6	0.22	4−15	0.47	17−19	−0.08
6−7	0.73	5−10	0.23	18−18	−0.06

[a] Units are mdyn Å^{-1}, mdyn rad^{-1}, mdyn Å rad^{-2}. [b] Key: inter-ring interaction.

in Figure 8. This scheme was mainly "deduced" from the behavior of the band assigned to the $C_\alpha=C_\beta$ stretching vibration: this band, located at 1424 cm^{-1} for -1.0 V with the infrared line, is shifted to 1410 cm^{-1} for -0.3 V and then to 1450 cm^{-1} for $+0.8$ V. It should be stressed that the bands at 1369 and 1270 cm^{-1} remain unchanged. The highly doped poly(3,4-ethylenedioxythiophene) seems to tend to return to the conformation that it had in the neutral state. Assuming a behavior similar to that of polythiophene, polarons should appear on the first oxidation peak and bipolarons on the second step. The deformation of the backbone during the first oxidative process should correspond to a rearrangement in quinoid structure, and an inverse rearrangement should go along with the appearance of bipolarons

(Figure 8). It should be mentioned that the structures depicted in this scheme are exaggerated. It only expresses tendencies we observed from experimental data and calculations.

This behavior should indicate that for poly(3,4-ethylenedioxythiophene), the usual scheme, benzoid structure → quinoid structure, is not suitable and that the structure of the neutral polymer is intermediate. This could explain the high stability of poly(3,4-ethylenedioxythiophene). To confirm these results, complementary studies on poly(5-tetradecyldioxeno[2,3-c]thiophene), also called PEDT-C14, are in progress.

Conclusion

In this work, we have presented a comparative analysis of theoretical and experimental vibrational spectra in which the fundamental vibrations of PEDT have been assigned. The dynamical calculations based on the symmetrized dynamical matrix have been used to calculate the frequencies of the vibration modes, the potential energy distributions and the Cartesian displacements. We can notice that for some bands the calculation of the P.E.D. was very useful for the description of the vibrations.

During doping, the changes in the Raman spectra are interpreted in terms of modification of electronic distribution along the chain. On the basis of these spectra and the calculations, we propose a mechanism for this modification and we show that the behavior of PEDT is different from that of the parent polythiophene.

Finally, we believe this work provides a good basis for calculations of force constants and coordinates of the perturbed structure created by doping. This will result in a better understanding of the spectra, structure, and optical effects in PEDT and similar compounds.

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