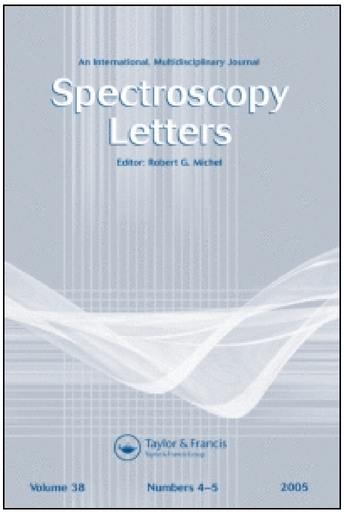

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Application of Surface-Enhanced Raman Scattering for *ex Situ* and *in Situ* Investigations of Polythiophene Derivatives

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Application of Surface-Enhanced Raman Scattering for *ex Situ* and *in Situ* Investigations of Polythiophene Derivatives

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Abstract: Polythiophene derivative films have been synthesized on electrochemically roughened silver, gold, and copper electrodes by anodic oxidation of the corresponding monomers. Surface-enhanced Raman scattering (SERS) analyses of these coatings led to high-quality spectra with high signal-to-noise ratios. In contrast with platinum, the use of SERS-active metals allowed the observation of important changes in the positions, widths, and relative intensities of the Raman bands during the polymer

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doping-dedoping process. *In situ* SERS investigations revealed that the modifications in the spectral features, when the polymer oxidation degree is progressively increased, are due to a transition from the aromatic to the quinoid structure and to an increase of structural defects along the polymer chains. Moreover, in the case of soluble polyalkylthiophene films, SERS analyses were also carried out using colloidal silver solutions. Despite the very low polymer concentration and the mild experimental conditions used in these experiments, a large amplification of the Raman signal took place. Two other methods for obtaining polybithiophene–silver composite films are reported. In these cases, thanks to the silver particles, the polymer displays a SERS effect, which greatly improves the signal-to-noise ratio of the Raman spectra, thus allowing a much better vibrational analysis of both doped and undoped states.

Keywords: Electrochemical polymerization, *in situ* and *ex situ* SERS, micellar solution, polythiophene derivatives, SERS-active colloid, SERS-active electrode, surface-enhanced Raman scattering

INTRODUCTION

Surface-enhanced Raman scattering (SERS) has been proved to be a powerful technique to provide high-quality Raman spectra. Ideed, it has been shown[1–3] that some metals like silver, gold, and copper, under appropriate mechanical or electrochemical roughening treatments, can produce a huge enhancement of Raman spectra for molecules adsorbed onto their surface. The two mechanisms commonly considered to account for SERS are connected either to a molecular enhancement of the polarizability of the molecule due to its adsorption onto the metal surface or to an intensification of the electromagnetic field induced by the resonance of the metal surface plasmons. It seems that the electromagnetic mechanism always occurs in SERS, whereas the molecular one can manifest itself only if the molecule is specifically adsorbed onto the surface.

SERS has opened up new perspectives in Raman spectroscopy and could be an efficient tool in the study of thin polymer films.[4–7] Indeed, this spectrocsopic method enabled us to obtain not only selective structural insights into polythiophenes but also information concerning the orientation and the anchorage mode of the polymer rings during the first stages of the electropolymerization. In this context, during the past few years, some interesting SERS investigations have been reported for either polythiophenes obtained by electrochemical polymerization on various metal working electrodes[8–10] or thiophene oligomers adsorbed on silver surfaces.[11–13] In this latter case, the adsorption process and the resulting vibrational changes were studied by means of SERS and other spectroscopic techniques. The SERS spectra of adsorbed terthiophene molecules for thick adsorbate layers were found to be similar to those of bulk polythiophene films and were interpreted in terms of adsorption-induced[12] or photoinduced[13] polymerization of the oligomers.

In this paper, we report *ex situ* and *in situ* SERS studies of polythiophene and polythiophene derivatives performed under various experimental conditions. Three approches were considered. In the first, suitably roughened silver, copper, and gold massive plates were used as working electrodes to electrosynthesize thin polymer films by direct anodic oxidation of the monomers. Detailed vibrational analyses of the polymers were obtained from SERS spectra recorded during the doping-dedoping process. In the second approach, the use of silver colloids to analyze traces of soluble polyalkylthiophenes gives rise to a very strong SERS effect. The obtained SERS spectra are compared with those recorded for the same polymers electrodeposited onto SERS-active gold electrodes. Finally, in the third approach, we report SERS experiments performed using other SERS-active systems. Especially, we describe an electrochemical procedure for obtaining SERS spectra of polythiophene on platinum, which consists of using silver dodecylsulfate (AgDS) micellar aqueous solution to electrosynthesize polythiophene with SERS-active silver particles embedded within the polymer film. Nonelectrochemical methods for preparing multilayer SERS-active systems in which the polymer is sandwiched between an iron support and a thin layer of a SERS-active metal are also briefly described.

MATERIALS AND METHODS

The electrochemical experiments were performed in a one-compartment cell with three electrodes connected to an EG&G PAR model 373A potentiostat/galvanostat (USA). The working electrode was massive silver, copper ($8 \times 40\ \mathrm{mm}^2$), or gold ($8 \times 15\ \mathrm{mm}^2$) plates. A platinum grid was used as auxiliary electrode, and all potentials were measured either with respect to Ag/AgCl electrode or to a saturated calomel electrode (SCE).

Before electropolymerization, the massive Ag, Cu, and Au working electrodes were mechanically polished with abrasive paper (1200) and diamond pastes (6, 3, and 1 μm; Reichert Jung, Germany), washed twice with distilled water under ultrasonic stirring, and roughened by three electrochemical oxidation–reduction cycles between -0.4 and $+0.15$ V versus *vs*. SCE for Ag and between -0.6 and $+0.15$ V versus SCE for Cu, with 10 mV s^{-1} scan rate in 0.1 M KCl aqueous solution. In the case of gold, an effective roughening procedure to generate an intense and stable SERS effect consists in applying to the electrode 25 successive potential scans between -0.3 and $+1.2$ V versus SCE with a scan rate of 500 mV s^{-1} and polarization times of 30 s at -0.3 V and 1.3 s at $+1.2$ V in the same electrolytic medium as Ag and Cu.

In some cases, SERS-active metallic layers were deposited using nonelectrochemical procedures: by thermal deposition in the case of Ag or by cathodic sputtering (60–90 s, 50 W) using a Dressler Cesar RF (Germany) power generator equipped with Au or Cu target in a Pfeiffer PLS 500 (Germany) vacuum chamber. The thickness of the SERS-active layers was estimated to be approximately 5–10 nm.

The experimental protocol for the preparation of the so-called Creighton silver colloid is based on the reduction of silver nitrate by sodium borohydride. This method consists in adding drop by drop a solution of sodium borohydride (30 mL of 2×10^{-3} M) into an aqueous silver nitrate solution (10 mL of 10^{-3} M). The obtained colloid is maintained under stirring at ambient temperature for approximately 1 hr; it is of a golden-yellow color and consists of almost spherical silver particles the radius of which ranges from 7 to 12 nm.

Raman spectra were recorded using two exciting laser lines: $\lambda_e = 514.5$ nm from a Spectra-Physics model 165 argon ion laser (USA) in the case of silver and $\lambda_e = 632.8$ nm from a Spectra-Physics model 207B helium–neon laser for gold and copper substrates. The scattered beam, collected at 180 degrees from the incident beam (retro-Raman), was focused onto the entrance slit of a Dilor XY spectrometer (France). This apparatus consists of a double monochromator used in subtractive mode (i.e., with no dispersion) to select a given spectral range, followed by a spectrograph to complete the dispersion and by a 1024 × 256 Jobiin-Yvon CCD matrix multichannel detector (France), cooled by thermoelectronic effect. With the slits used (100 μm), the spectral resolution was typically 2 cm^{-1}.

RESULTS AND DISCUSSION

SERS with Massive Metal Electrodes

Polybithiophene onto Roughened Silver and Copper Electrodes

Thin polybithiophene (PbT) films of 50 Å thickness were obtained by electrochemical oxidation of bithiophene onto roughened silver and copper electrodes. SERS spectra of the oxidized and reduced samples are displayed in Fig. 1 with the Raman spectra of PbT films obtained onto platinum, under the same electrosynthesis conditions, for comparison.

In the case of classical platinum electrodes, the only significant difference observed between the oxidized and reduced PbT spectra concerns the overall intensity of the reduced sample, which is about five times greater than that of the oxidized one. This intensity difference is due to a larger resonance effect of the reduced film, which is associated with a stronger UV-visible absorption near the laser excitation wavelength (514.5 nm), resulting from the π-π^* electronic transitions.

The electrodeposition of PbT films onto roughened silver or copper plates, instead of classical platinum one, is of double interest when analyzing the polymer Raman spectra. First, all the Raman bands observed when PbT films are deposited onto platinum are found again when SERS-active

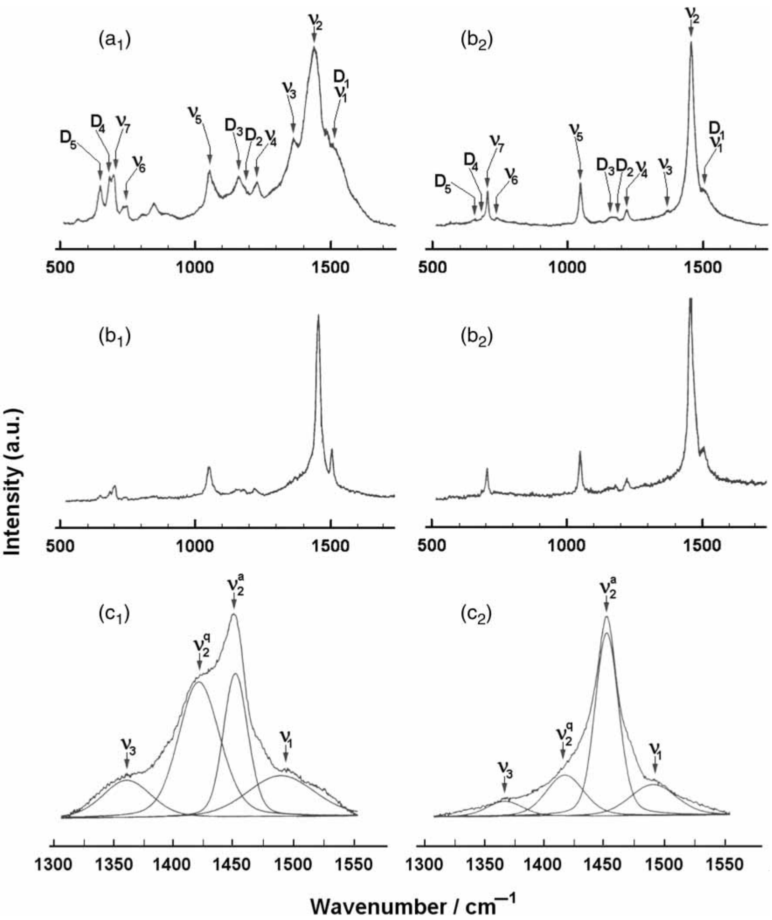

Figure 1. *Ex situ* SERS spectra of oxidized (a_1) and reduced (a_2) PbT films electrodeposited onto roughened silver electrodes compared with Raman spectra of oxidized (b_1) and reduced (b_2) PbT samples electrosynthesized onto platinum electrodes. The 1450 cm^{-1} SERS spectral region has been subjected to a decomposition procedure into components with Voigt profiles for oxidized (c_1) and reduced (c_2) PbT films electrodeposited onto roughened copper electrodes. Excitation wavelengths and laser powers: 514.5 nm, 0.5 mW for Ag; 514.5 nm, 5 mW for Pt; and 632.8 nm, 12 mW for copper. Intensities are normalized.

electrodes are employed. However, owing to the SERS effect, the signal-to-noise ratio is considerably increased when using SERS-active metals, allowing an accurate vibrational characterization. Second, significant differences are pointed out between spectra of the reduced and the oxidized PbT films deposited onto silver electrodes, whereas almost no difference is observed in the case of platinum.

The aim of this work is not to discuss the quite well-established band assignments of polythiophene Raman spectrum, but rather to analyze several key bands and to relate some spectral features to different physicochemical parameters such as the polymer doping yield.

The ν_2 symmetric C=C stretching band is particularly affected by oxidation. It becomes broader and its maximum is shifted toward low frequencies. A similar behavior is observed when roughened copper electrodes are used and SERS spectra recorded with 632.8 nm laser excitation (Fig. 1). With copper, the difference between the oxidized and reduced films is much more pronounced because the oxidized PbT sample displays a pre-resonance effect due to a significant absorption band in the red region, which slightly overlaps with the laser excitation wavelength, 632.8 nm. After a band decomposition of the 1450 cm^{-1} spectral region has been performed, it appears that the ν_2 band consists of two components originating from the aromatic (ν_2^a: upper wavenumber side component) and quinoid (ν_2^q: lower wavenumber side component) thiophene rings in the PbT chains. As shown in Fig. 1, the increase of the intensity ratio $I(\nu_2^q)/I(\nu_2^a)$ translates the transformation of some thiophene rings from the aromatic to the quinoid structures when the polymer is oxidized.

The very weak ν_3 band in the reduced sample, associated with C-C ring vibration, is strongly enhanced in the oxidized state. On the basis of the SERS selection rules,[14,15] this suggests that the polymer rings make a significant angle with respect to the working electrode. Indeed, because the SERS selection rules predict that the vibrations belonging to the same irreducible representation as α_{zz} polarizability tensor component are the most enhanced, the vibrations occurring perpendicular to the SERS-active surface should be more intense than those parallel to it. The C-C ring bond in the reduced form is parallel to the surface whatever the orientation of the thiophene ring plane is with respect to the electrode surface, thus leading to a weak band. When the polymer is oxidized, the C-C ring bonds of the doped units makes an important angle with respect to the metal surface, thus leading to a rather important variation of the α_{zz} component and then allowing a significant intensity enhancement.

The Raman spectrum of PbT displays, in addition to normal modes, defect bands (*kinks*) denoted D_1 to D_5, which appear in the oxidized form with fairly strong intensity. These bands have been used in previous studies to evaluate the quality of the polymer.[16–18] The 700 cm^{-1} spectral zone displays the ν_6 and ν_7 normal modes assigned to in-plane ring deformations and two defect modes D_4 and D_5. In order to evaluate the amount of structural defects in the polymer chains for the different samples, the intensity ratios $I(D_4)/I(\nu_7)$ and $I(D_5)/I(\nu_7)$, estimated from the integrated intensity of the individual bands, are reported in Table 1. By comparison of these values, it appears that the amount of defects and distorted parts in the polymer skeleton increases in the oxidized samples.

Table 1. $I(D_4)/I(\nu_7)$ and $I(D_5)/I(\nu_7)$ are used as indicators of the amount of defects within the PbT chains[a]

	Reduced PbT		Oxidized PbT	
	$I(D_4)/I(\nu_7)$	$I(D_5)/I(\nu_7)$	$I(D_4)/I(\nu_7)$	$I(D_5)/I(\nu_7)$
Silver electrode	0.80	0.40	1.25	1.10
Copper electrode	0.64	0.46	0.99	0.62
Platinum electrode	0.35	0.35	0.55	0.40

[a] These intensity ratios increase with the oxidation degree of the polymer and are more enhanced in the case of SERS-active metals (Ag and Cu).

Moreover, the defect bands exhibit a noticeable SERS effect, implying that the defects are close to the electrode surface and probably indicate that the oxidized PbT films are bound to the surface through these defects, which act as anchor points.

In order to analyze in more detail the structural changes appearing during the doping-dedoping process, we developed an *in situ* experimental setup[19] that enables us to study the film electroactivity by recording the SERS spectra while the applied potential is varied. After PbT films had been electrodeposited onto roughened Ag and Cu electrodes, SERS spectra were recorded in CH_2Cl_2 with 0.1 M $Nu(Bu)_4PF_6$ as supporting electrolyte, at applied potentials varying from -0.4 to $+0.8$ V versus Ag/AgCl. This potential range was chosen to cover the polymer electroactivity domain. Special attention was paid to the $1450\,cm^{-1}$ spectral region where Raman lines originating from both aromatic and quinoid rings can be detected. The *in situ* variations in the SERS spectra with the applied potential recorded for PbT films deposited onto Ag (excited at 514.5 nm) and Cu (excited at 632.8 nm) are very similar to those observed in the *ex situ* SERS experiments. The most striking result concerns the splitting of the ν_2 band into its two aromatic (ν_2^a) and quinoid (ν_2^q) components, the relative intensities of which depend closely on the applied potential value and thus on the oxidation level of the polymer. A band decomposition procedure (Fig. 2) enables us to determine the relative amount of aromatic and quinoid species, and as expected, during the doping process, the number of quinoid rings increases at the expense of aromatic ones. When the logarithm of the intensity ratio $I(\nu_2^q)/I(\nu_2^a)$ is plotted versus the applied potential, a linear behavior of the curve is observed (Fig. 2) and obeys the Nernst equation, $E = E^0 + (0.059/n)\log[I(\nu_2^q)/I(\nu_2^a)]$, with a small number of transferred electrons ($n = 0.08$) per thiophene unit. This low n value, comparable with that reported for polymethylthiophene from UV-visible experiments,[20] is probably due to the fact that the redox species are in the solid state and therefore not really in equilibrium.

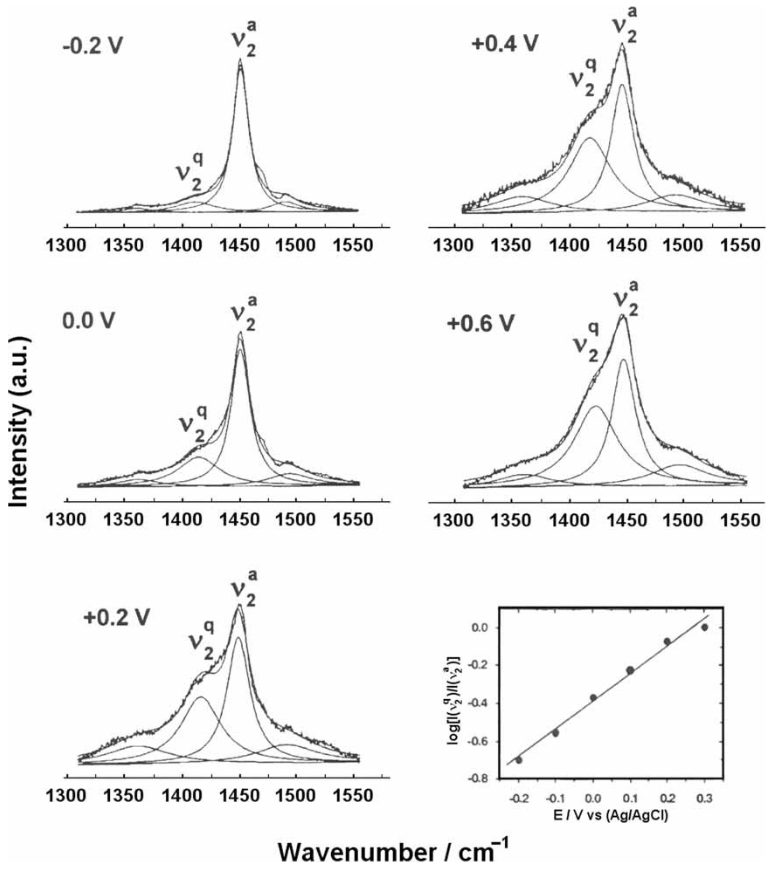

Figure 2. Plot of $\log[I(\nu_2^q)/I(\nu_2^a)]$ as a function of the applied potential. The intensity ratios are evaluated by decomposition of the 1450 cm^{-1} spectral region into four bands for applied potentials varying between -0.2 and $+0.6$ V versus Ag/AgCl. The *in situ* SERS spectra of PbT are obtained using a roughened copper working electrode, and the experiment is performed in dichloromethane (CH_2Cl_2) in the presence of 0.1 M $N(Bu)_4PF_6$ as supporting electrolyte. Excitation wavelength λ_e, 632.8 nm; laser power, 12 mW.

Polyalkylthiophenes onto Roughened Gold Electrodes

Oxidized and reduced polyoctylthiophene (POcT), polybutylthiophene (PBuT), and polymethylthiophene (PMeT) films have been electrosynthesized onto roughened gold electrodes and onto platinum for comparison. The similarity between the peak wavenumbers and relative intensities for the spectra recorded on either substrate is clearly visible (Fig. 3). However, owing to a SERS effect, the spectra obtained onto roughened gold electrodes are approximately 160 times more intense than those onto platinum. There is probably

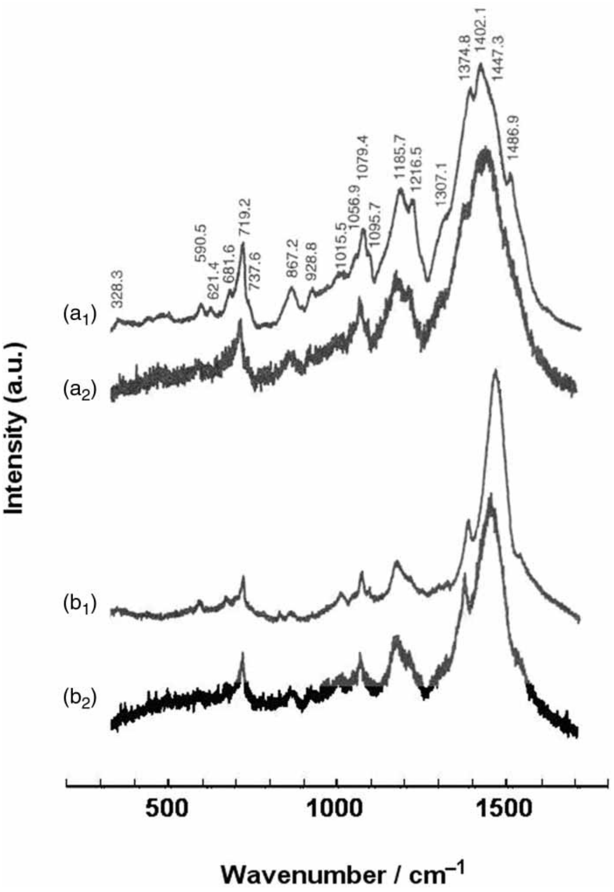

Figure 3. Comparison between SERS spectra of oxidized (a$_1$) and reduced (b$_1$) PBuT films electrodeposited onto roughened gold electrodes and Raman spectra of the same oxidized (a$_2$) and reduced (b$_2$) films electrosynthesized onto platinum electrodes. Excitation wavelength λ_e, 632.8 nm; laser power, 4 mW; counting time, 10 s for gold and 100 s for platinum. Intensities are normalized.

also a resonance effect that enables the detection of the species deposited on platinum, which otherwise could not be observed on account of the very small film thickness.

Polyalkylthiophene Raman spectra exhibit a greater number of bands than polythiophene, because the symmetry of thiophene is broken by the alkyl groups.[21–24] The ν_2 band, at approximately 1400 cm^{-1} assigned to the symmetric stretching mode of the C=C double bond of the ring, is very sensitive to the polymer oxidation degree. A significant broadening and a downward shift of approximately 40 cm^{-1} on, going from the reduced to the oxidized samples, should be pointed out.

As in the case of PbT deposited onto Ag and Cu electrodes, *in situ* experiments were performed to elucidate this behavior. SERS spectra of POcT films were recorded in 0.1 M $LiClO_4$ aqueous solution at potentials increasing from -0.2 to 1.0 V versus Ag/AgCl by 0.2 V steps. Despite difficult *in situ* experimental conditions, the spectra are of very good quality with high signal-to-noise ratio. A band decomposition procedure was performed in order to determine the relative amount of the aromatic and quinoid species (Fig. 4, left column). When the applied potential is increased, the strongest line (ν_2^a) shifts toward higher wavenumbers on account of a change in the polymer conjugation length brought about by the presence of quinoid rings.[19] Therefore, this shift may be used as an indicator of the oxidation level of the polymer. As it was previously observed for PbT electrodeposited onto SERS-active Ag and Cu electrodes, a linear curve is obtained when the logarithm of the intensity ratio $I(\nu_2^q)/I(\nu_2^a)$ is plotted versus the applied potential in the case of polyalkylthiophene films electrosynthesized onto SERS-active gold electrodes according to the aforementioned Nernst equation.

By analogy with PbT, the SERS spectra of the polyalkylthiophene films display, in addition to normal modes, defect modes. Particularly, in the 700 cm^{-1} spectral region, two normal modes ν_6 and ν_7, assigned to in-plane ring deformations, and two defect modes D_4 and D_5 are observed. Using a band decomposition procedure, we determined the intensity ratios of these defect modes relative to the ν_7 band (Fig. 4, right column). The increase in this ratio with the potential reflects the doping along with the growth of the film disorder.

The ν_3 band at approximately 1375 cm^{-1}, assigned to the C-C single bond stretching of the ring, does not shift when going from the reduced to the oxidized samples; however, for the investigated polyalkylthiophenes, its relative integrated intensity is significantly greater in the oxidized state. On the basis of the SERS selection rules, this suggests that the polymer rings make a significant angle with respect to the gold substrate, as previously proposed for PbT on silver and copper electrodes.

SERS with Metallic Colloidal Solutions

During the past three decades, the use of silver and gold colloids to generate strong SERS effects has opened up new perspectives, and multiple applications have been developed. This technique has been widely used in the fields of analytical chemistry and bio-organic chemistry, particularly for the detection of traces of pollutants, hydrocarbons, antibiotics, antitumorals, and so forth.

The important potentialities of this method prompted us to extend our investigations to the characterization of soluble conducting polymers by the use of silver colloids and to compare the obtained SERS spectra to those recorded onto roughened gold electrodes.

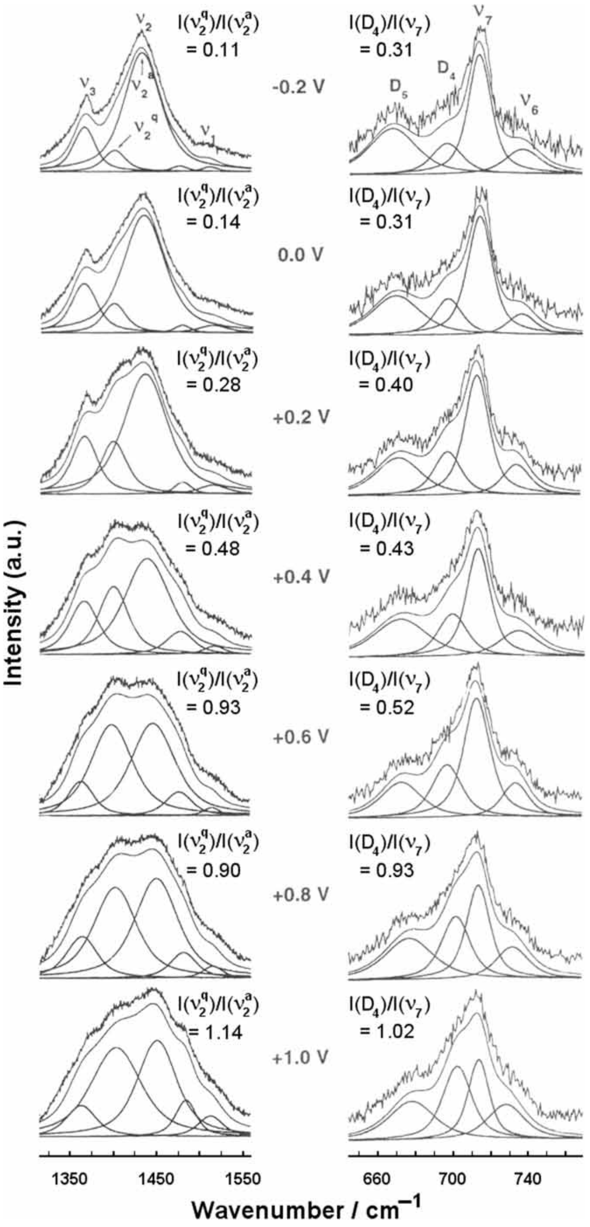

Figure 4. Decomposition of the 700 (right column) and 1450 cm^{-1} (left column) spectral regions into components with Voigt profiles for applied potentials varying between -0.2 and 1.0 V versus Ag/AgCl. The *in situ* SERS experiment is performed in a 0.1 M aqueous solution of $LiClO_4$; the working electrode being a POcT film coating roughened gold electrode. Excitation wavelength λ_e, 632.8 nm; laser power, 4 mW; counting time, 60 s.

In this context, oxidized and reduced PMeT, PBuT, and POcT films were electrochemically prepared and dissolved in THF. The obtained solutions are orange for the reduced PBuT and POcT samples and green for the oxidized ones. Owing to its poor solubility, PMeT gives light-yellow solution in the reduced state and colorless solution in the oxidized form.

The samples for SERS analyses are prepared by dropping 5 μL of the polyalkylthiophene solution into 500 μL of silver colloid. Then, when 15 μL of 1 M sodium nitrate in water was introduced, the colloid color turned from yellow to dark-blue. This color change is due to the partial aggregation of the silver particles into clusters of any size and shape. There is no precipitation of the colloid but a drastic change in its absorption spectrum because of the emergence of new plasmon resonances that are at the origin of the SERS effect.

Figure 5 shows the SERS spectra recorded with 514.5 nm excitation wavelength and 30 mW laser power. Despite the very low polymer

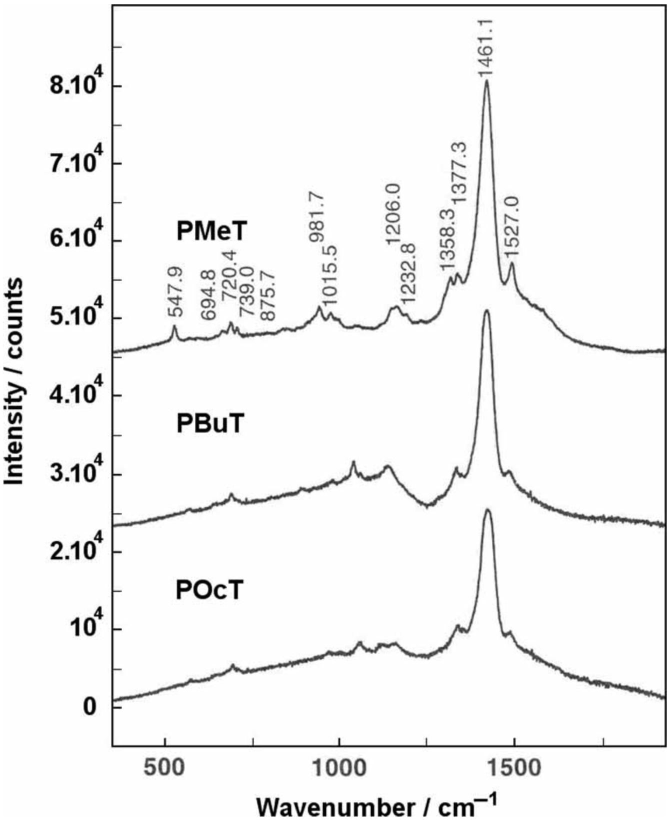

Figure 5. SERS spectra of PMeT, PBuT, and POcT traces (10^{-7} to 10^{-10} M) deposited on silver colloids. Excitation wavelength λ_e, 514.5 nm; laser power, 30 mW.

concentrations and the mild experimental conditions, the spectra exhibit high signal-to-noise ratios with well-resolved Raman bands. The slight intensity decrease when going from PMeT to POcT is due to the effect of increasing length of the aliphatic side chain, which prevents the thiophene rings coming close to the surface of the silver aggregates. On the other hand, it must be emphasized that contrary to the massive electrodes, the spectra of the two oxidation states obtained in the colloid are similar. Indeed, in the oxidized films, the inner layers close to the electrode contain more oxidized motifs than the outer layers.[25] Because the undoped state is much more soluble than the doped one, only the outer layers of oxidized samples are dissolved, leading to THF solutions containing polymer chains with small amounts of oxidized units. Thus, the SERS spectra of the oxidized polyalkylthiophenes in the silver colloid are, in fact, spectra of nearly completely reduced species. In the case of roughened electrodes, as the electromagnetic field decays exponentially when going away from the surface, the polymer inner layers, which are closer to the SERS-active surface, are much more enhanced than the outer ones. This is the reason why the vibrational modes of the oxidized species appear clearly on gold electrodes.

The spectra obtained in silver colloid solutions are rather similar to those reported on metal electrodes, and the Raman bands have been well-established previously.[26] Only some interesting vibrational features of the PMeT SERS spectrum are presented below. The ring C-C stretching mode is split into two components at 1377.3 and 1358.3 cm^{-1} because of the symmetry break introduced by the methyl group in the β-position of the ring. For the same reason, the C-C interring band appears as a doublet at 1232.8 and 1206.0 cm^{-1}. The band at 1191.1 cm^{-1} is assigned to the angular deformation of C-H in the β-position. The stretching modes of C-Me bond are observed at 981.7 and 875.7 cm^{-1}. Finally, the modes that appear at 739.0, 720.4, and 547.9 cm^{-1} are attributed to the vibrations of the C-S-C groups.

Other SERS Procedures

In this section, we succinctly describe two other electrochemical and nonelctrochemical procedures for obtaining SERS-active substrates that lead to an easy vibrational characterization of polythiophene in both oxidized and reduced states. The enhancement effect is produced by the presence of metallic islands scattered onto the film surface or embedded within the polymer matrix.

AgDS Micellar Solutions

The electropolymerization of 5×10^{-3} M bithiophene was performed in water–butanol (9:1) mixture, in the presence of 7×10^{-2} M silver dodecylsulfate (AgDS) and 0.1 M $\mathrm{LiClO_4}$ as supporting electrolyte. When scanning the potential between −0.2 and 1.2 V versus SCE, bithiophene within the micelle is carried toward the platinum working electrode and undergoes anodic oxidation. A thin and homogeneous PbT film grows on the electrode surface, and at the same time, some Ag^+ cations arising from the AgDS surfactant are entrapped between the polymer chains. During the cathodic process, these Ag^+ ions are reduced, leading to Ag^0 metallic particles embedded within the PbT film. The aggregated silver islands, analyzed by scanning electron microscopy (Fig. 6d), appear to grow as fractal objects. These silver islands allow the observation of a SERS effect for both doped and undoped PbT films.

The SERS effect was confirmed by comparison of the spectra of these samples recorded using the 514.5-nm laser excitation with those of PbT electrosynthesized under the same conditions but in a sodium dodecylsulfate (SDS) micellar solution (i.e., without Ag^+ cations) (Fig. 6). In these conditions, the intensity enhancement factor is about 40 and can increase up to 200 for very thin films owing to better organization of the polymer, which leads to sharper peaks.

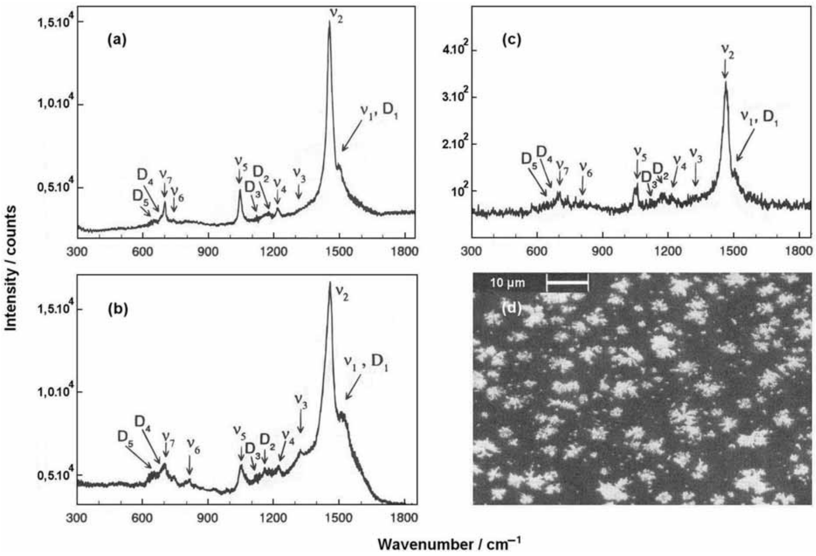

Figure 6. SERS spectra of reduced (a) and oxidized (b) PbT films electrodeposited onto platinum electrodes in an AgDS aqueous micellar solution compared with the Raman spectrum of the polymer obtained in an SDS aqueous micellar solution (c). All these spectra were recorded under identical experimental conditions: 514.5-nm excitation wavelength, 1 mW laser power, and 25 accumulations of 2 s counting time. The plate (d) shows an SEM micrograph of PbT obtained in the AgDS solution. The aggregated silver particles, responsible for the SERS effect, are clearly visible in white and appear to grow as fractal objects.

All the results previously obtained in the case of massive silver electrodes (broadening of normal modes, growth of defect bands, enhancement of ν_1 and ν_3 modes, and splitting of ν_2 band into two components) are reproduced for these PbT films containing silver islands, prepared in AgDS micellar solutions on platinum electrodes.

These results show clearly that the SERS spectrum of PbT consists of three main contributions: (i) the vibrational normal modes arising from the aromatic rings of the reduced undoped PbT, which is the most abundant species; (ii) the vibrational normal modes of the quinoid rings, the intensity of which depends on the oxidation level, and increase to ca. 30% in the oxidized, fully doped PbT form; (iii) the vibrational modes from structural defects, which appear and increase with the polymer oxidation degree.

Multilayer Systems

Thin layers of Ag, Au, and Cu were deposited on PbT films previously electrosynthesized onto iron electrodes. The samples were analyzed as prepared or after they had been subjected to a thermal treatment at 120°C for 5 min. This treatment produces metallic islands hundreds of nanometers in size and consequently leads to a roughening of the outer metallic layer.[27–29]

In situ SERS experiments were performed on these samples by varying progressively the potential of the working electrode from -0.2 (reduced state) to $+0.8$ V (oxidized state); This results in a broadening of the main PbT bands attributed to normal modes ν_1 to ν_7 and in intensity amplification of the defect modes D_1 to D_5. These observations demonstrate that the transition from the undoped to the doped forms is accompanied by an increase of disorder and the appearance of structural defects, such as distorted parts in the polymer skeleton. The change in the electronic configuration of some thiophene rings from aromatic to quinoid is also confirmed by the splitting of the ν_2 band into two components as already emphasized above.

Moreover, the effect of the thermal treatment on the SERS enhancement factor can be estimated by comparing the SERS intensities of the samples before and after the thermal treatment with that of PbT on iron (i.e., in the absence of the SERS-active metal). The enhancement factors are ca. 13 and 7 for Ag/PbT/Fe and Cu/PbT/Fe before treatment and increase to 100 and 30, respectively, after treatment.

The observed improvement of the enhancement factor is essentially due to changes in the morphology of the outer metallic layer. Indeed, the SERS effect is closely linked to the surface state of the SERS-active metal; particularly, the magnitude of the enhancement factor depends on the shape and the size of the surface asperities. As the thermal treatment produces metallic islands leading to a roughening of the metal surface, a huge intensification of the electromagnetic field occurs because of a better resonance of the metal surface plasmons.

CONCLUSIONS

In this paper, we have proved that SERS spectroscopy is among the most sensitive and efficient analytical techniques available for the characterization of organic conducting polymers and could be developed as an *in situ* tool in monitoring the redox process of these organic materials. In summary, we have presented different procedures for generating SERS spectra of some polythiophene derivatives, based on the use of massive metal electrodes, metal colloid solutions, or metal islands.

The use of suitably activated Ag, Au, or Cu as massive working electrodes has allowed the observation of SERS spectra of polythiophene derivatives. The spectra of the oxidized and the reduced samples are quite different and can be considered as arising from vibrations of aromatic rings, quinoid cycles, and defect modes. We have shown, by means of *in situ* experiments, that the relative intensities of the aromatic and quinoid components depend closely on the oxidation level, as proved by the intensity ratio $I(\nu_2^q)/I(\nu_2^a)$ of the quinoid to aromatic C═C ring stretching mode, which obeys a Nernst equation. In addition, the defect bands exhibit a significant SERS effect when the doping yield is increased, indicating that the structural defects are close to the SERS-active surface or even act as anchorage points of the polymer to the metallic support. The strong enhancement of the C-C ring stretching mode suggests that polymer cycles make a significant angle with the electrode surface.

Taking advantage of polyalkylthiophene films solubility in organic solvents, we have shown that the SERS spectra of these polymers adsorbed on silver colloids at very low concentrations (10^{-7} to 10^{-10} M) exhibit features similar to those obtained on roughened gold electrodes but with huge signal amplification; this later result underlines the capacity of SERS for trace detection.

Finally, we have succinctly described two other methods for obtaining PbT–Ag composite films. In these cases, thanks to the silver islands, the polymer films display a SERS effect that greatly improves the signal-to-noise ratio of the Raman spectra, thus allowing a much better vibrational analysis of both doped and undoped states.

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