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## Raman spectroscopy of neutral and doped poly(3-methyl thienylene) and poly(3-methyl thienylene)–heteropolyanion complexes

J L Sauvajol†, J P Lère-Porte‡, C Chorro‡ and G Poussiguet†

†Groupe de Dynamique des Phases Condensées, UA CNRS 233, Université Montpellier II: Sciences et Techniques du Languedoc, Place E Bataillon, 34095 Montpellier Cédex 5, France

‡Laboratoire de Chimie Générale, Université Montpellier II: Sciences et Techniques du Languedoc, Place E Bataillon, 34095 Montpellier Cédex 5, France

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**Abstract.** In the first part of this paper is reported a Raman study performed on several electrochemically prepared poly(3-methyl thienylene) (P3MeT) films. The sample dependence of the Raman spectra is analysed. A correlation between the intensity, the frequency and the width of the Raman lines and the nature of the films under consideration (defined in terms of thickness, conjugation length, amount of structural defects and level of doping) is shown. Some Raman criteria are defined and used in order to characterize P3MeT samples from Raman spectroscopy. These Raman results are used to characterize a class of materials that are attracting much interest in electrochemistry, electrocatalytic and analytical chemistry: the poly(3-methyl thienylene)–heteropolyanion (P3MeT-PHA) complexes, with PHA =  $(\text{SiW}_{12}\text{O}_{40})^{4-}$  or PHA =  $(\text{PMo}_{12}\text{O}_{40})^{3-}$ . Two results can be emphasized: (i) the strong increase of the structural disorder of the P3MeT chain related to the intercalation of the PHA; (ii) the low value of the doping level or, in other words, the poor charge transfer between the PHA and the P3MeT chain. These results question the high value of the conductivity measured in this class of compound ( $\sigma$  around  $10 \text{ S cm}^{-1}$ ) and suggest that the role of the heteropolyanions in the conductivity process cannot be ignored.

### 1. Introduction

Polythienylene (PT) and poly(3-methyl thienylene) (P3MeT) (figure 1) are representative of stable conducting polymers with a non-degenerate ground state. Among the class of

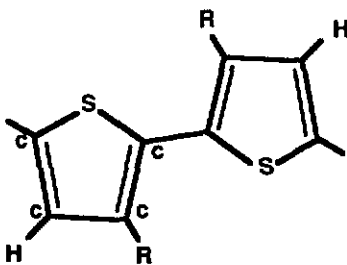


Figure 1. Centro-symmetric cell of the PT and P3MeT chain: for PT, R = H; for P3MeT, R =  $\text{CH}_3$ .

conductive polymers, polythienylene and poly(3-methyl thienylene) appear particularly attractive owing to their high chemical and electrochemical stability (Tourillon 1985). Strong evolution of the morphology and electrical conductivity of PT and P3MeT films as a function of their thickness, e.g. of the degree of advancement of the electro-polymerization reaction, has already been shown (Yassar *et al* 1989). Furthermore, it has been shown that P3MeT exhibits the highest electrical conductivity among the thienylene-derived polymers. This effect has been attributed to the presence of the methyl group, which statistically reduces the possibility of  $\alpha$ - $\beta$  coupling between thienylene units and thus leads to a more stereoregular polymer (enhancement of  $\alpha$ - $\alpha$  coupling) (Tourillon and Garnier 1983). Recently, some studies have been devoted to the analysis of the sample dependence of the Raman and photoluminescence spectra of electrochemically prepared polythienylene films (Sauvajol *et al* 1990). Significant modifications of the spectra have been observed and were discussed in relation to the 'quality' of the films under consideration. In these studies the film 'quality' was defined in terms of degree of polymerization  $N_{dp}$ , conjugation length  $N_c$  and amount of C=O defects. Especially, a strong correlation between the intensity, the frequency and the width of the Raman lines and the value of the conjugation length has been established (Sauvajol *et al* 1991). From these studies, Raman and photoluminescence spectroscopies appear to be efficient tools to characterize samples of polythienylene. The same kind of study does not exist in P3MeT, and only a few results concerning the vibrational properties of P3MeT have been reported (Steigmeier *et al* 1987). In the first part of this paper we report a Raman study performed on several electrochemically prepared films of poly(3-methyl thienylene). Correlations between the structure of the Raman spectrum and the features of the samples are investigated.

On the other hand, it is known that the formation of complexes between heteropolyanions of Keggin type such as  $(SiW_{12}O_{40})^{4-}$  and  $(PMo_{12}O_{40})^{3-}$  and various monomers such as poly(3-methyl thienylene) may contribute to the excellent polymerization that provides materials of higher density and good conductivity (Bidan *et al* 1989). This class of materials is attracting much interest in electrochemistry, electrocatalytic and analytical chemistry (Lapkowski *et al* 1991). Because of the large size of heteropolyanions (diameter of about 10 Å), the structure of the P3MeT chain in the complexes can be changed. In the second part of this paper we report a Raman study performed on complexes between poly(3-methyl thienylene) and heteropolyanions. By using the results derived in the first part of this study, we attempt to characterize from Raman spectroscopy the modifications of the structure of the polymeric chain related to the intercalation of the heteropolyanions.

## 2. Experimental details

### 2.1. Samples

Oxidized ( $PF_6^-$ -doped) poly(3-methyl thienylene) films were electrochemically prepared. The electrochemical synthesis was performed in a one-compartment cell using an EG&G PAR potentiostat model 363 under computer control. The working and counter-electrodes were platinum sheets (2 cm  $\times$  2.5 cm) placed at 1.8 cm and the anodic potential was measured versus an Ag/AgNO<sub>3</sub> ( $10^{-2}$  M) electrode. The platinum sheets were carefully polished with Al<sub>2</sub>O<sub>3</sub> before the synthesis. Oxygen was excluded from the

**Table 1.** Information about the P3MeT films used in this work.

Film	State	Thickness ( $\mu\text{m}$ )	Electrolyte
Film 1	Undoped	1.5	NBu <sub>4</sub> ClO <sub>4</sub>
Film 2	Undoped	0.6	NBu <sub>4</sub> PF <sub>6</sub>
Film 3	Heavily PF <sub>6</sub> <sup>-</sup> doped	0.6	NBu <sub>4</sub> PF <sub>6</sub>
Film 4	Lightly PF <sub>6</sub> <sup>-</sup> doped	1.2	NBu <sub>4</sub> PF <sub>6</sub>

electrochemical cell by using a nitrogen flow. Electropolymerization of 3-methylthiophene (0.2 M) dissolved in nitrobenzene containing an electrolytic salt (0.02 M) was performed at 5 °C. The working electrode was anodically polarized at 1.2 V versus the Ag/AgNO<sub>3</sub> (10<sup>-2</sup> M) electrode. The integrated charge  $Q$  passed during film growth was used to monitor the thickness of the deposited film; the following relation was used

$$e (\mu\text{m}) = 2.5Q (\text{C cm}^{-2}).$$

The heavy PF<sub>6</sub><sup>-</sup>-doped films obtained by this procedure were initially electrochemically reduced at 0.0 eV (versus the Ag/AgNO<sub>3</sub> (10<sup>-2</sup> M) electrode) until the current reached a negligible value (reduced film, lightly PF<sub>6</sub><sup>-</sup>-doped film) and then fully undoped (neutral film) by immersion in methanol for 48 h. At the end of this treatment we used infrared (IR) spectroscopy to estimate the amount of dopant; it was negligible and no chemical degradation could be attributed to this treatment. Some information about the films used in this work are given in table 1. Other characteristics of these films, like the average molecular weight and the conjugation length, have not been determined, essentially because: (i) these films cannot be dissolved in any solvent and the techniques used for soluble polymers in order to determine the molecular weight cannot be used; (ii) no correlation analogous to those evidenced in PT between the intensity ratio of IR lines and the value of the conjugation length (Furakawa *et al* 1987) has been found in P3MeT. The main object of this study is to show that, despite the poor characterization of the films, the significant differences between the Raman spectra from the different samples can be related to changes in the characteristics of the films under consideration. In this sense Raman spectroscopy appears to be an efficient tool to characterize electropolymerized films.

Poly(3-methyl thienylene) doped by (SiW<sub>12</sub>O<sub>40</sub>)<sup>4-</sup> and (PMo<sub>12</sub>O<sub>40</sub>)<sup>3-</sup> Keggin-type heteropolyanions were electrochemically prepared using the procedure described by Bidan *et al* (1989). We have verified that the infrared spectra of the complexes present broad absorptions characteristic of (SiW<sub>12</sub>O<sub>40</sub>)<sup>4-</sup> (1012, 968, 916 and 788 cm<sup>-1</sup>) and (PMo<sub>12</sub>O<sub>40</sub>)<sup>3-</sup> (1058, 954, 856 and 786 cm<sup>-1</sup>) heteropolyanions (Rocchiccioli-Deltcheff and Thouvenot 1974, Thouvenot *et al* 1974).

## 2.2. Experimental set-up

Raman spectra were recorded using a 'Coderg T800' triple-monochromator spectrometer. The 5145 and 4880 Å lines of an argon-ion laser were used as the light sources. In order to avoid local heating and degradation of the samples, the incident light power was limited to below 5 mW and the beam was defocused. A backscattering configuration was used and the instrumental resolution was about 6 cm<sup>-1</sup>. All the measurements at room temperature have been performed with samples under secondary vacuum. For the

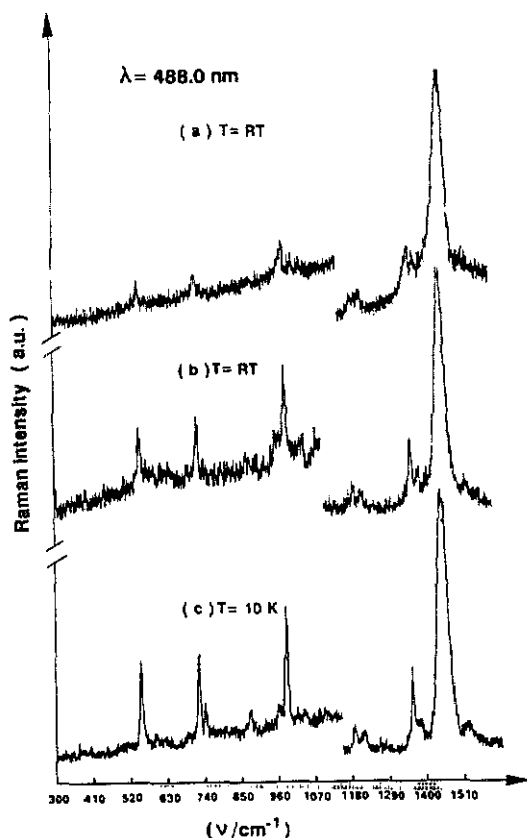


Figure 2. Raman spectra at  $\lambda_L = 4880 \text{ \AA}$  given by: (a) a thick film of P3MeT (film 1 in table 1) at room temperature; (b) a thin film of P3MeT (film 2 in table 1) at room temperature; (c) a thin film of P3MeT (film 2 in table 1) at  $T = 10 \text{ K}$ . The intensity scale in the frequency range 200–1100  $\text{cm}^{-1}$  is smaller (about two times) than that in the frequency range 1100–1700  $\text{cm}^{-1}$ .

measurements at low temperature, the sample was mounted in a cryostat in which the sample is cooled by cold helium gas.

In order to increase the intensity of the Raman lines, both VV and VH polarized components have been recorded at the same time (no analysis of the polarization of the scattered light is made). To justify this procedure, we recall that the main goal of this kind of study is to relate the changes of the Raman spectrum with the features of the films under consideration, and for that it is necessary to have the best signal possible. In addition, on the assumption that the point group of the infinite P3MeT chain is  $C_{2h}$  (next section), all the in-plane Raman modes have the  $A_g$  symmetry and are active in both the VV and VH polarizations. In consequence, the recording of polarized Raman spectra carried out from unoriented samples does not give any important additional information.

### 3. Raman spectra of neutral and doped poly(3-methyl thienylene)

#### 3.1. Neutral poly(3-methyl thienylene)

In figures 2(a) and (b) are displayed the Raman spectra obtained at room temperature from two different films of P3MeT. The Raman spectrum shown in figure 2(a) has been recorded on a thick film of P3MeT (film 1 in table 1); the conductivity of this film is small,  $\sigma = 50 \text{ S cm}^{-1}$ . The two other Raman spectra (figures 2(b) and (c)) have been obtained

from a very thin film of P3MeT (film 2 in table 1) at room temperature and low temperature ( $T = 10$  K) respectively. These spectra exhibit significant sample and temperature dependences.

A recent analysis of the sample dependence of the Raman spectrum of polythienylene has already shown a strong correlation between the parameters of the Raman lines (intensity, frequency and width) and the value of the conjugation length. The main results of this study can be summarized as follows. When the value of the conjugation length increases: (i) the intensity of the  $1222\text{ cm}^{-1}$  Raman line (mixture of ring deformation and C—C inter-ring stretching) increases; (ii) the  $1462\text{ cm}^{-1}$  Raman line (the C=C stretching mode; the most intense line of the spectrum) narrows; (iii) a Raman line at  $1476\text{ cm}^{-1}$  emerges in the wing of the previous line; (iv) the shape of the  $1500\text{ cm}^{-1}$  Raman line drastically changes—for large  $N_c$  values it appears as a narrow peak, and for weak  $N_c$  values a significant broadening of this peak occurs. We have proposed that in the  $1500\text{ cm}^{-1}$  region a normal mode of the chain (of  $B_g$  symmetry) overlaps with a defect mode, and that this latter becomes predominant when  $N_c$  decreases (Sauvajol *et al* 1991). Owing to the high intensity of the Raman spectrum (especially in the range  $1300$ – $1700\text{ cm}^{-1}$ ) these previous results concerning the  $N_c$  dependence of the intensity and width of the Raman lines were unambiguously established. In this analysis of the Raman spectra, each line has been fitted to a Gaussian shape and the frequency, the width and the intensity of each Raman line have been derived from this fit. In this paper the same kind of treatment of the poly(3-methyl thienylene) Raman data has been performed.

As shown in figure 2, the Raman spectra displayed by P3MeT are strongly temperature-dependent. However, more important changes appear between room temperature and 80 K. In consequence, comparison between spectra recorded at 80 and 10 K is straightforward. A significant increase of the intensity of the spectrum is observed when the temperature decreases; in particular, several weak lines emerge at low temperature at  $596$ ,  $692$ ,  $744$ ,  $1018$  and  $1041\text{ cm}^{-1}$ . The frequencies of the Raman lines do not change significantly with the temperature. Owing to the strong intensity of the Raman spectrum at low temperature, the frequencies of all the Raman lines may be determined with a good accuracy. These frequencies are reported in table 2. In the same table comparison with the frequencies of the Raman lines measured by Steigmeier *et al* (1987) at  $T = 80$  K and  $\lambda_L = 4416\text{ \AA}$  is given. Good agreement between the two sets of data is observed. The changes of the frequency with the laser excitation is slight compared with the strong change observed in *trans*-polyacetylene (Mulazzi *et al* 1983). On the other hand, in the same table the frequencies of the Raman lines measured at the same temperature from a 'high-quality' film of polythienylene (large  $N_c$  value) are also given. It is obvious that the number of active Raman modes is greater in P3MeT than in PT; in addition some Raman lines in PT seem to give two components in P3MeT. If we consider the centrosymmetric primitive cell of the polymeric chain displayed in figure 1, and if we take the  $\text{CH}_3$  group as a point mass (called R), the  $k = 0$  in-plane vibrational optic modes of PT (factor group  $D_{2h}$ ) and P3MeT (factor group  $C_{2h}$ ) respectively are represented by

$$\Gamma(\text{PT}) = 7A_g + 7B_g + 6B_{2u} + 6B_{3u}$$

$$\Gamma(\text{P3MeT}) = 14A_g + 12B_u.$$

The reduction of the symmetry in P3MeT explains the multiplication of the lines in the Raman spectrum. Especially in PT, the frequencies of  $B_g$  Raman lines have been calculated at  $738$ ,  $1296$  and  $1498\text{ cm}^{-1}$  (Poussiguet and Benoit 1989); these modes appear in the spectrum of P3MeT at  $725$ ,  $1363$  and  $1525\text{ cm}^{-1}$  respectively. On the other hand,

**Table 2.** Frequencies ( $\text{cm}^{-1}$ ) of the Raman-active vibrational modes in the range 200–1600  $\text{cm}^{-1}$ .

P3MeT <sup>a</sup>	P3MeT <sup>b</sup>	PT <sup>c</sup>
		292 w
390 vw	388 vw	
	432 vw	
	460 vw	
500 vw	486 vw	
551 s	550 s	
596 vw	595 w	
625 vw	632 w	652 w <sup>d</sup>
692 w		682 w <sup>d</sup>
		701 s
725 s	722 s	
744 m		740 w
		791 w
878 m	880 m	
962 m		
986 s	986 s	1000 vw
1018 vw	1020 w	
1041 vw		
		1047 s
1100 vw		
		1176 m
1187 m	1205 s	
1216 m		
		1221 m
1363 s	1360 s	
1382 m		
1449 s		
	1470 s	1462 s
1473 m		
		1476 m
		1500 m
1525 m		

<sup>a</sup> In P3MeT,  $T = 10$  K,  $\lambda_L = 4880$  Å (this work).

<sup>b</sup> In P3MeT,  $T = 80$  K,  $\lambda_L = 4416$  Å (from Steigmeier *et al* 1987).

<sup>c</sup> In PT,  $T = 10$  K,  $\lambda_L = 5145$  Å (from Sauvajol *et al* 1991).

the Raman spectrum given by poly(3-hexyl thienylene) exhibits the same features in the frequency range 1150–1600  $\text{cm}^{-1}$  as that by P3MeT (Zagorska and Sauvajol 1991). This implies that the vibrational motions of the atoms of the substituent R (except the carbon,  $C_R$ , directly connected to the cycle) do not contribute to the Raman intensity in this frequency range.

By analogy with our previous study on the sample dependence of the Raman spectrum of polythienylene, and in order to define Raman criteria to characterize poly(3-methyl thienylene) samples, we have turned our attention to the sample dependence of several Raman lines.

*3.1.1. Raman lines in the frequency range 1280–1600  $\text{cm}^{-1}$ .* The 1280–1600  $\text{cm}^{-1}$  frequency range of the Raman spectra is shown in figure 3. It is necessary to take five

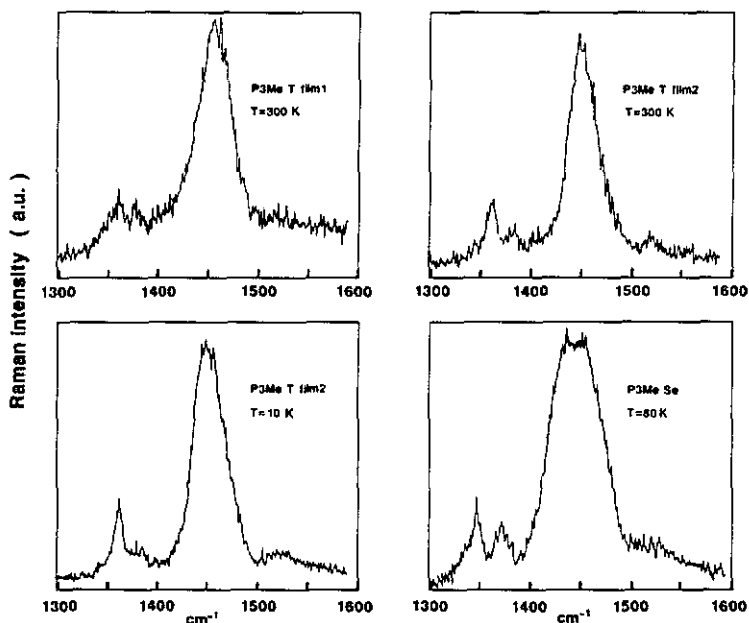


Figure 3. Comparison between the profiles of the Raman spectra given by different films in the frequency range 1300–1600  $\text{cm}^{-1}$ .

bands into account in order to reproduce the profile of the Raman spectrum. The non-symmetric profile of the strongest Raman band arises from the overlap of two neighbouring peaks. This double-peak structure is more evident in the Raman spectrum of another polymer of the same class, poly(3-methylselenophene) ( $\text{P3MeSe}$ , figure 3(d)). The intensities, the widths and the frequencies of these five Raman components derived from the fit of the Raman spectrum are reported in table 3. The best fit is obtained by a Lorentzian rather than a Gaussian profile (as for PT) for each Raman line. Usually a Lorentzian profile is expected for a Raman line in an ordered system, whereas a Gaussian profile is more characteristic of a disordered or inhomogeneous system. Then it is attractive to assign the Lorentzian shape of the Raman line in  $\text{P3MeT}$  to an increase of the conjugation order in  $\text{P3MeT}$ . However, the improvement of the fit by using a Lorentzian profile rather than a Gaussian profile for the Raman lines is too small to allow us to give a definitive explanation in these terms. All the Raman lines are narrowed in the thin film of  $\text{P3MeT}$ . Similar behaviour has been observed in PT with the increase of the conjugation length. In PT we have shown that an important contribution to the linewidth results from the inhomogeneous broadening related to the breaking of the translational symmetry in chains of finite length. Indeed, for finite chains, several components with neighbouring frequencies have a Raman activity and each Raman band displays an envelope of all these components. When  $N_c$  increases, the symmetry of the chain must be close to that of the infinite chain, the number of Raman components decreases and the lines become narrower (Sauvajol *et al* 1991, Poussiguet *et al* 1991). We think that the sample dependence of the width of the Raman lines is the signature of the 'dispersion effect' related to the distribution of the conjugation length in polythiophene and its derivatives. From this statement and with regard to the sample dependence of the linewidths of the Raman lines in  $\text{P3MeT}$  films, we conclude that the value of the conjugation length is better in film



**Table 3.** Intensity,<sup>a</sup> frequency and width of the Raman lines in the range 1250–1600 cm<sup>-1</sup>.

Room temperature				T = 10 K	
Film 1 (cm <sup>-1</sup> )	Film 2 (cm <sup>-1</sup> )	L <sub>1</sub> (%)	L <sub>2</sub> (%)	Film 2 (cm <sup>-1</sup> )	L <sub>2</sub> (%)
$\nu_1 = 1451$ (2)	1451 (2)	100	100	1449 (2)	100
$\Gamma_1 = 37$ (2)	28 (2)			31 (2)	
$\nu_2 = 1465$ (2)	1468 (2)	46	24	1473 (2)	26
$\Gamma_2 = 25$ (3)	20 (3)			20 (3)	
$\nu_3 = 1359$ (2)	1362 (2)	13	22	1362 (1)	25
$\Gamma_3 = 18$ (2)	13 (2)			12 (2)	
$\nu_4 = 1381$ (3)	1384 (3)	23	9	1386 (2)	8
$\Gamma_4 = 20$ (fixed)	20 (4)			20 (3)	
$\nu_5 = 1515$ (5)	1520 (4)	15	7	1523 (3)	7
$\Gamma_5 = 50$ (8)	25 (5)			24 (4)	

<sup>a</sup> Intensities of films 1 and 2 are denoted  $I_1$  and  $I_2$ .

2 than in film 1 or, in other words, that the increase of the film thickness leads to a decrease of the conjugation length as expected from the conductivity measurements (Yassar *et al* 1989). Changes in the relative intensities of the Raman lines are also observed; especially, the 1450 and 1363 cm<sup>-1</sup> Raman lines are stronger in the thin film of P3MeT. On the other hand, the intensity of the 1470 cm<sup>-1</sup> Raman line is higher for small  $N_c$  values. This increase, coupled with the broadening of the Raman lines, leads to an overlapping of the two lines at 1450 and 1470 cm<sup>-1</sup>, explaining why, in some experiments, only one peak at 1460 cm<sup>-1</sup> was observed (Steigmeier *et al* 1987, Soma *et al* 1987).

**3.1.2. Raman lines in the frequency range 300–1300 cm<sup>-1</sup>.** Near the strong and medium Raman lines at 551, 725 and 986 cm<sup>-1</sup> appear other peaks that exhibit a clear sample dependence. For instance, the lines at 744, 878 and 962 cm<sup>-1</sup> are significantly stronger in the thin film of P3MeT (and especially at low temperature) than in the thick film of P3MeT. The opposite behaviour is observed for the Raman lines at 692 and 1010 cm<sup>-1</sup>. With regard to these behaviours and with respect to the statement that an increase of thickness leads to a decrease of conjugation length (previous section), the first group of lines may be assigned to normal modes of a chain with a large conjugation length and the second group to defect modes related to vibrational motion in a non-planar structure of the chain. A double-peak structure of the band around 1187–1216 cm<sup>-1</sup> clearly appears. The intensity of the low-frequency component of the doublet relative to the intensity of the high-frequency component of the doublet (compare the spectra displayed in figures 2(a)–(c) and figure 5(b)) increases with the conjugation length. All these behaviours have been observed from the study of P3MeT samples synthesized by other procedures (Nicolau and Sauvajol 1991).

In conclusion, the low-temperature Raman spectrum given by a thin film of P3MeT (large  $N_c$  value) shows unknown features at this time, especially the Raman line at 878 cm<sup>-1</sup> and the double-peak structure of the 1216, 1360 and 1460 cm<sup>-1</sup> bands. It may

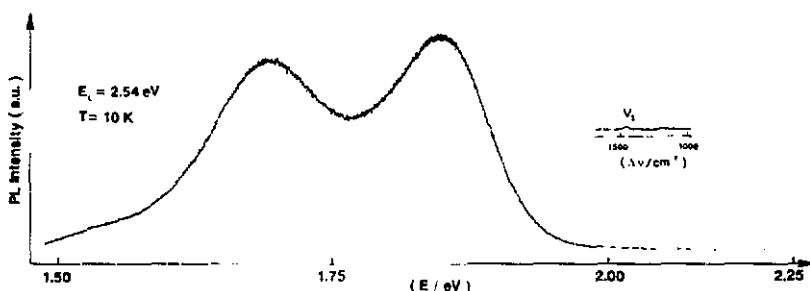


Figure 4. Photoluminescence band given by a thin film of P3MeT at low temperature. The photoluminescence band and the  $\nu_1$  Raman line ( $1450 \text{ cm}^{-1}$ ) are displayed at the same scale.

be necessary to take these lines into account to calculate the lattice dynamics and the vibrational spectrum of polythienylene and its derivatives. The unambiguous evidence for these modes questions some explanations of the vibrational properties of PT and P3MeT, for which these Raman lines are not taken into account (Faulques *et al* 1989, Lopez-Navarrete and Zerbi 1991a). In this paper we have analysed the dependence of the intensity and width of the Raman lines with the features of films. As in PT the profile and intensity of the Raman spectrum are essentially dependent on the conjugation length value. This analysis gives some possibilities to characterize P3MeT samples from Raman experiments.

In PT, strong changes of the photoluminescence (PL) band with respect to the value of the conjugation length have already been studied (Sauvajol *et al* 1990). With the increase of the conjugation length the following have been shown: (i) a strong increase of the intensity of photoluminescence (with respect to the intensity of the most intense Raman band at  $1450 \text{ cm}^{-1}$ ); (ii) the appearance of well defined peaks equally spaced ( $\Delta E = 0.17 \text{ meV}$ ) and assigned to a phonon replica of the PL emission. The photoluminescence measured from the thin film of P3MeT at  $T = 10 \text{ K}$  is displayed in figure 4. It shows the same features as a 'good' film of PT (note especially the strong intensity of the PL band with respect to the  $\nu_1$  mode). This result emphasizes the high conjugation of this sample.

### 3.2. Doped poly(3-methyl thienylene)

In figure 5 we compare the Raman spectra obtained at the same temperature ( $T = 85 \text{ K}$ ) from a doped ( $\text{PF}_6^-$ ) thin film of P3MeT (film 3 in table 1) and from a lightly doped ( $\text{PF}_6^-$ ) P3MeT film (film 4 in table 1). We observe a drastic decrease of the Raman intensity upon doping of the film (note the drop of the signal-to-noise ratio between the two spectra; also compare the same ratio for the spectrum displayed in figure 2(c)). The main effects of doping on the structure of the Raman spectrum can be summarized as follows:

- (i) All the Raman lines are broadened.
- (ii) The resonant Raman scattering (RRS) lines around  $553, 725, 986$  and  $1187\text{--}1216 \text{ cm}^{-1}$  are slightly shifted to lower frequency.
- (iii) The relative intensities of these lines are less affected than the intensity of the  $878 \text{ cm}^{-1}$  line, and lines in the  $1300\text{--}1700 \text{ cm}^{-1}$  frequency range.

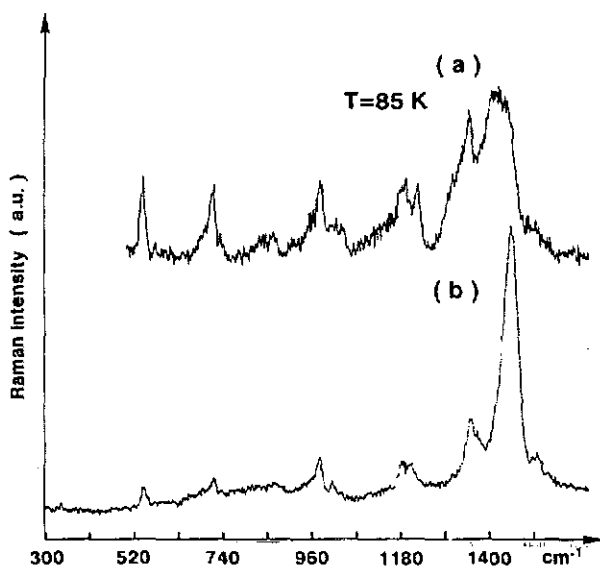


Figure 5. Raman spectra at  $\lambda_L = 5145 \text{ \AA}$  and  $T = 85 \text{ K}$ : (a) given by a heavily  $\text{PF}_6^-$ -doped  $\text{P3MeT}$  film (film 3 in table 1); (b) given by a lightly  $\text{PF}_6^-$ -doped  $\text{P3MeT}$  film (film 4 in table 1).

From points (ii) and (iii) we propose assigning this group of lines to vibrational modes for which the force constants involved are unchanged when the  $\pi$  electron distribution is altered upon doping. By reference to the assignment of the lines in polythienylene and related compounds, we propose to assign the  $990 \text{ cm}^{-1}$  line to C—H bending, the  $729$  and  $553 \text{ cm}^{-1}$  lines to a ring vibration and C—S deformation. The assignment of the  $1194$ – $1220 \text{ cm}^{-1}$  lines is not clear at this time. With regard to the  $1222 \text{ cm}^{-1}$  line, which appears in PT and is attributed to the inter-ring C—C stretch (Wallnöfer *et al* 1989), the  $1194$ – $1220 \text{ cm}^{-1}$  lines could be assigned to the same kind of motion (with an admixture of C—C and C=C intra-ring stretching modes). However, it is surprising, with regard to the kind of motion involved, that these lines do not significantly change upon doping. On the other hand, we can note that C—C<sub>R</sub> stretching modes may also occur in the same frequency range.

(iv) The most significant changes in the Raman spectrum occur for the lines in the frequency range  $1300$ – $1700 \text{ cm}^{-1}$  and for the Raman line around  $880 \text{ cm}^{-1}$ . This last band disappears in the doped film and a large and weak structure develops at about  $850 \text{ cm}^{-1}$ . An analogous structure has already been observed in the resonant Raman spectrum of  $\text{P3MeT}$  absorbed on  $\text{Cu}^{2+}$ -montmorillonite, this last species appearing to be an oxidized product (Soma *et al* 1987). As in PT, the bands in the frequency range  $1300$ – $1700 \text{ cm}^{-1}$  for which the C—C and C=C intra-ring stretching and C—C inter-ring stretching are involved exhibit a significant dependence upon doping. The shift of these lines in  $\text{P3MeT}$  (of about  $30 \text{ cm}^{-1}$ ) is more important than those observed in PT (of about  $15 \text{ cm}^{-1}$ ). The high-frequency component of each doublet, occurring at  $1352$  and  $1443 \text{ cm}^{-1}$  respectively, becomes predominant. All these behaviours are the signature of the aromatic  $\rightarrow$  quinoid transition along the polymeric chain upon doping.

In conclusion to this section, we have shown a significant sample dependence of the Raman spectrum of poly(3-methyl thienylene); these changes can be related to an

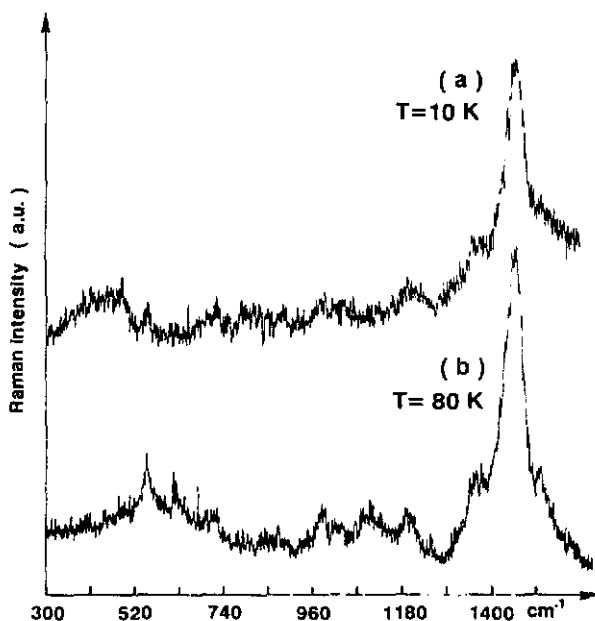
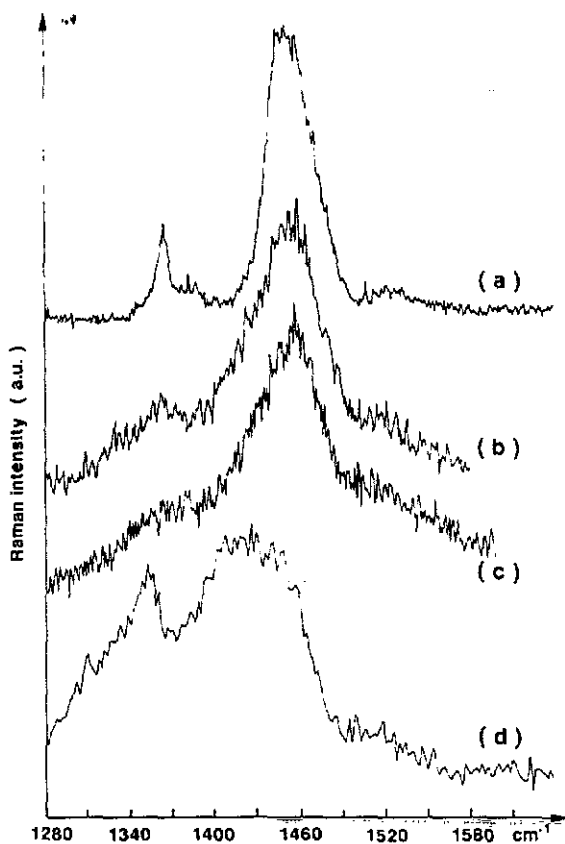


Figure 6. Raman spectra at  $\lambda_L = 5145 \text{ \AA}$  given by: (a) a  $\text{P3MeT-PHA}$  complex,  $\text{PHA} = (\text{SiW}_{12}\text{O}_{40})^{4-}$ , at  $T = 10 \text{ K}$ ; (b) a  $\text{P3MeT-PHA}$  complex,  $\text{PHA} = (\text{PMo}_{12}\text{O}_{40})^{3-}$ , at  $T = 80 \text{ K}$ .

increase of the structural disorder with thickness of film, in agreement with scanning electron microscopy (SEM) results (Tourillon and Garnier 1984). The increase of the film thickness leads to a drop of the observed value of the conjugation length and consequently to a decrease in the conductivity as observed experimentally (Yassar *et al* 1989). Raman experiments appear to be an appropriate method of studying the evolution of the conjugation length of the  $\text{P3MeT}$  chain under various factors including: the synthesis procedure, chemical degradation of the films, exposure to air and doping. A strong dependence of the Raman spectrum upon doping has been shown, and was assigned to the aromatic  $\rightarrow$  quinoid transition along the polymeric chain; in particular, the doping effect is clearly demonstrated by the behaviour of the modes in which the  $\text{C}=\text{C}$  and  $\text{C}-\text{C}$  stretching motions are involved. In the next section of this paper we use these previous results in order to characterize the  $\text{P3MeT-PHA}$  complexes.

#### 4. The Raman spectra of poly(3-methyl thienylene)-heteropolyanion complexes

In figure 6 the Raman spectra performed at low temperature from  $\text{P3MeT-(PMo}_{12}\text{O}_{40})^{3-}$  and  $\text{P3MeT-(SiW}_{12}\text{O}_{40})^{4-}$  complexes are displayed. A comparison with the spectra given by neutral  $\text{P3MeT}$  (figure 2) shows a strong reduction of the Raman intensity. Also, a significant broadening of all the Raman lines occurs, especially the double-peak structure of the bands around 1200, 1370 and  $1460 \text{ cm}^{-1}$  is no longer observed. In addition, the relative intensities of the lines at 1018 and  $692 \text{ cm}^{-1}$ , assigned to defect modes in our previous analysis of the dependence of the Raman spectrum with the 'quality' of  $\text{P3MeT}$  sample, increase. All these results lead to the proposal that the conjugation length along the polymer segments in the  $\text{P3MeT-PHA}$  complexes is decreased. To have an idea of the



**Figure 7.** Comparison between the shapes of Raman spectra in the frequency range 1280–1640  $\text{cm}^{-1}$  ( $\lambda_L = 5145 \text{ \AA}$ ): (a) neutral thin film of P3McT (film 2 in table 1) at  $T = 10 \text{ K}$ ; (b) P3McT-(SiW<sub>12</sub>O<sub>40</sub>)<sup>4-</sup> complex at  $T = 10 \text{ K}$ ; (c) P3McT-(PMo<sub>12</sub>O<sub>40</sub>)<sup>3-</sup> complex at  $T = 80 \text{ K}$ ; (d) heavily PF<sub>6</sub><sup>-</sup>-doped P3McT film (film 3 in table 1) at  $T = 85 \text{ K}$ .

charge transfer between the heteropolyanion and the polymer chain, it is interesting to compare the parameters (intensity, frequency and width) of the Raman lines in the frequency range 1250–1700  $\text{cm}^{-1}$  for neutral P3McT, doped P3McT and P3McT-PHA complexes. Indeed, we have previously observed a significant change of the Raman spectrum in this frequency range, related to the aromatic  $\rightarrow$  quinoid transition, which occurs upon doping. The comparison of the Raman spectra is given in figure 7. The maxima of the two strongest bands (around 1370 and 1460  $\text{cm}^{-1}$  occur at the same frequency in P3McT (mean frequency of the envelope of the double-peak structure) and in P3McT-PHA complexes. However, broadening of these bands occurs and the two peaks of each band cannot be deconvoluted. These results mean that in the complexes the conjugation length and the structural order are strongly affected. On the other hand, a shoulder appears on the low-frequency side of the 1460  $\text{cm}^{-1}$  band at a frequency close to that measured in doped P3McT. This shoulder is the 'signature' of the charge transfer between the heteropolyanion and the polymer. However, with regard to the low intensity of this structure, the doping level of the P3McT chain is obviously small. The conductivity values in these kinds of complexes then appear surprisingly high ( $\sigma \sim 30 \text{ S cm}^{-1}$ ) in view of the

strong degradation of the structural order and of the long inter-chain distances (Bidan *et al* 1989), and our results suggest that the role of the HPA in the conductivity process cannot be ignored.

## 5. Discussion and conclusions

From this Raman study performed on neutral P<sub>3</sub>MeT, doped P<sub>3</sub>MeT and P<sub>3</sub>MeT-PHA complexes, several unambiguous features of the Raman lines with respect to the nature of the samples under consideration have been shown.

In agreement with other experiments (Tourillon and Garnier 1983, 1984, Yassar *et al* 1989), we claim that a decrease in the conjugation length is related to an increase in the film thickness. For a comparison between Raman spectra performed on thin and thick films, we can state the following:

(i) When the conjugation length decreases, all the Raman lines are broadened and the Raman intensity becomes weak. At the same time, the intensity of several peaks (for instance the Raman lines at 1018 and 692 cm<sup>-1</sup>) is increased and these lines can be assigned to defect modes. By analogy with the behaviour of the defect modes in PT, we can assign these peaks to vibrational motion in a non-planar structure (ring torsion) of the P<sub>3</sub>MeT chain.

(ii) The more significant and interesting results of this study concern the dependence of the Raman spectrum in the frequency range 1300–1700 cm<sup>-1</sup>. In neutral P<sub>3</sub>MeT, the lines at 1473 and 1382 cm<sup>-1</sup> are clearly separated from the lines at 1450 and 1362 cm<sup>-1</sup> respectively. This double-peak structure is also clearly observed in poly(3-methylselenophene). We suggest that this result is the equivalent of those observed in PT, where two peaks at 1462 and 1476 cm<sup>-1</sup> could be deconvoluted (Sauvajol *et al* 1991). When the conjugation length increases, the intensity of the high-frequency components of each doublet increases and all the Raman lines are broadened; consequently, the double-peak structure of each band disappears and we observe experimentally an envelope of the doublet with mean frequencies at 1460 and 1370 cm<sup>-1</sup> respectively. It is important to note that in previous Raman experiments and in various calculations of the vibrational properties of PT and P<sub>3</sub>MeT, only the average frequencies have been taken into account and the Raman lines at 1476 cm<sup>-1</sup> in PT and 1472 and 1384 cm<sup>-1</sup> in P<sub>3</sub>MeT were ignored (Lopez-Navarrete and Zerbi 1991b). This double-peak structure also appears upon doping with a low-frequency shift of about 30 cm<sup>-1</sup>. In the doped sample, the intensity of the high-frequency component of each doublet is high.

Other Raman results can be emphasized and question some results previously published: In all our Raman spectra the line at 1520 cm<sup>-1</sup> is very weak and this frequency is not sensitive to the sample 'quality'. The frequency of this line is higher than those measured in a 'bad' film of polythienylene (1500 cm<sup>-1</sup>). On the other hand, it is known from other experiments that the regularity in the  $\alpha$ - $\alpha$  coupling is enhanced in P<sub>3</sub>MeT and that it leads to a value of the conjugation length higher in P<sub>3</sub>MeT than in PT (Tourillon and Garnier 1983), and the high value of the conductivity in P<sub>3</sub>MeT has been attributed in part to this effect (Yassar *et al* 1989). So it is certainly incorrect to deduce the number of thienylene rings in P<sub>3</sub>MeT (and in other derivatives) from a comparison with the sample dependence of the 1500 cm<sup>-1</sup> line in PT as suggested by Zerbi *et al* (1991). (In PT a correlation is made between the increase of this frequency and the decrease of the number of cycles.) The model of the 'effective coordinate R' developed in the same

reference (see also Castiglioni *et al* 1988) in order to explain the dynamics of polythienylene could be in agreement with our results if the  $\nu_1$  mode of this model (the R mode) is assigned to the line at  $1473\text{ cm}^{-1}$  ( $1476\text{ cm}^{-1}$  in PT) and not to the line at  $1520\text{ cm}^{-1}$  ( $1500\text{ cm}^{-1}$  in PT) as suggested by Zerbi *et al* (1991). Following the predictions of this model, the intensity of the  $\nu_1$  mode decreases on increasing the conjugation length with a barely appreciable increase of the other modes. This effect is explained in terms of coupling of the  $\nu_1$  mode with the other modes (and especially with the neighbouring modes at  $1450\text{ cm}^{-1}$  in P3MeT and  $1462\text{ cm}^{-1}$  in PT) when the conjugation length increases. The broadening of the lines with decreasing conjugation length is not taken into account in this model.

On the other hand, molecular dynamics calculations using a powerful new computing process, the spectral moments method, have been able to display the dependence of the shape of the Raman spectra of PT with the conjugation length (Poussiguet *et al* 1991). In this explanation, the lines at  $1462$  and  $1476\text{ cm}^{-1}$  have  $A_g$  symmetry in an infinite chain model and are strongly coupled. For small  $N_c$  values, or in other words in chains of finite length, the breaking of the translational symmetry gives Raman activity of some components that have neighbouring frequencies and the spectrum displays an envelope of all these contributions. On the other hand, the calculation shows that the intensities of the  $1476$  and  $1460\text{ cm}^{-1}$  bands are close. When  $N_c$  increases, the system behaves like an infinite chain, and the number of Raman-active components decreases, leading to a narrowing of the two bands. In addition, the relative intensity of the  $1460\text{ cm}^{-1}$  component becomes stronger than that of the  $1476\text{ cm}^{-1}$  line and the two peaks can be easily resolved. The same kind of explanation is also able to describe the sample dependence of the Raman spectra of poly(3-methyl thienylene).

In summary, when  $N_c$  increases, the narrowing of the Raman linewidth (the width of the Raman line and the distribution of conjugation length are correlated) and the change of the intensity of the Raman lines explain all the dependences in the profile of the Raman spectra shown in this study.

Concerning the Raman study of P3MeT-PHA complexes, it is clear that the characterization of these samples is possible from Raman spectroscopy by comparison between the different Raman spectra obtained on doped, undoped complexed and uncomplexed samples. The analysis of the Raman data from these kinds of compounds shows that: (i) on the one hand, an increase of the structural disorder of chains related to the intercalation of the heteropolyanion in the polymer host is established, leading to a significant decrease of the conjugation length; (ii) on the other hand, the doping level or, in other words, the charge transfer between the heteropolyanion and the P3MeT chain is low.

With regard to the strong interest in this kind of complex, these results can be emphasized. To our knowledge it is the first time that characterization of this class of materials has been made using Raman spectroscopy.

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