JOURNAL OF MATERIALS SCIENCE 20 (1985) 2687–2694

First evidence of crystalline structure in conducting polythiophene

F. GARNIER*, G. TOURILLON
Laboratoire de Photochimie Solaire, ER 241, CNRS, 2 Rue H. Dunant
94320 Thiais, France

J. Y. BARRAUD
Laboratoire de Marcoussis, CGE, Route de Nozay, 91460 Marcoussis, France

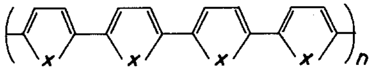
H. DEXPERT
Laboratoire des Eléments de Transition dans les Solides, CNRS, 1 Place Aristide Briand,
92190 Meudon, France

In order to optimize the properties of organic conducting polymers we analysed the effect of structure and dopant. The substitution of the β carbon atoms in thiophene leads to a higher regularity in the corresponding polymer, obtained by electrochemical oxidation. The trifluoromethylsulphonate anion appears to be the best fitting dopant, allowing a 1:2 doping level of the polymer. Transmission electron microscopy reveals crystal patterns for this highly doped polymer. The obtained electron diffraction and X-ray data are consistent with a hexagonal lattice. The discussion of these results lead us to propose a coil structure for this organic conducting polymer.

1. Introduction

Organic conducting polymers form a new class of interesting metal-like compounds and the improvement of their conductivity represents a very attracttive goal, to which many studies have already been devoted. The necessary factors have been discussed [1, 2] and, amongst them, the doping level has been shown to be critical. Polyacetylene and polyparaphenylene can be reversibly doped to about 6% and 20% respectively [3–5], whereas the electrochemically synthesized polypyrrole [6] and polythiophene [7] appear very promising, owing to their larger doping level of 25 to 30%. These latter polymers however are obtained in a fully amorphous state. Discussing the structural criteria for metallic behaviour, Baughman *et al.* [1] have pointed out that, although the planarity of the polymeric backbone is not a necessary condition for high conductivity, the regularity and the homogeneity of the chain structure is a determining factor.

Following our work on electrochemically synthesized polythiophenes [7], we analysed the structural factors which control polymer regularity. Five membered heterocycles, such as pyrrole, thiophene or furan, polymerize by an α–α' coupling, giving a highly conjugated chain, I, where x is O, S, NH. Among the structural defects which can affect conjugation, the most probable one is an α–β' coupling of the monomeric units. During the radical polymerization process, the reactivity of the β carbon atom is significant enough, compared to the α carbon atom, to allow this α–β' coupling. Thus, in the case of neutral polythiophene (x = S), no characteristic C_β – H vibration band can be observed in the i.r. spectrum at 3035 cm^{-1}, which indicates that this defect largely affects the polymer structure. In order to enhance the polymer regularity, we have analysed the effect of methyl substitution on the β carbon atoms of the thiophene monomer.



I

---

*To whom all correspondence should be sent.

0022–2461/85 $03.00 + .12

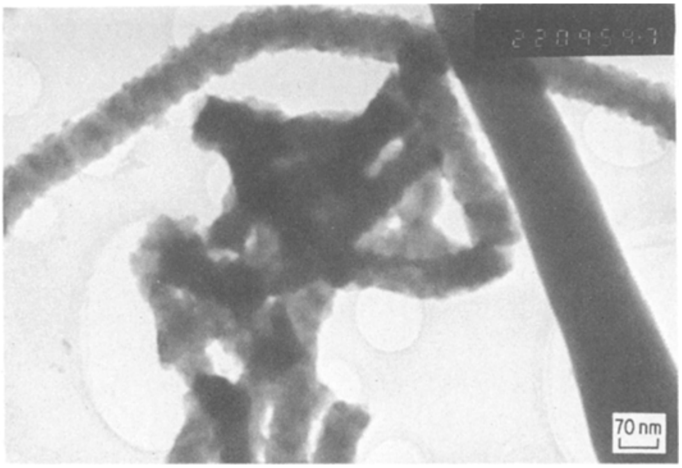
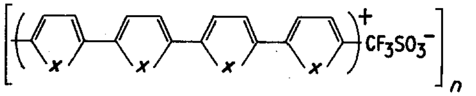


Figure 1 TEM picture of polythiophene–$CF_3SO_3^-$, doping level 30%.

In this paper, we report the first crystallographic patterns obtained on substituted polythiophene, which have been characterized by X-rays and electron diffraction, and which lead us to propose a coil structure for these polymers.

2. Experimental procedures

The electrochemical synthesis of polymers on a Pt electrode has been described previously [7]. The reaction medium involves CH_3CN, the monomer, and a counter anion, $CF_3SO_3^-$, which intercalates the polymer during polymerization and which plays the role of dopant. The synthesis thus directly affords the oxidized doped polymer II, which can thereafter be electrochemically reduced to its neutral undoped state, I.



II

The monomers, thiophene, 3-methylthiophene and 3, 4-dimethylthiophene were freshly distilled. The salt, $N(Bu)_4SO_3CF_3$ Fluka Purissimum was dried prior to the synthesis.

Elemental microanalyses were performed on powdered samples of the polymer, obtained by scratching off thick deposits from the electrode.

X-ray measurements were performed on a Philips PW 1130 with a Norelco goniometer. The generator power was 45 kV, 35 mA. A Co anticathode was used, with $K\alpha$ line at 1.788 65 μm. Due to the mainly amorphous nature of the sample, the observed peaks were of low intensity and required a scan rate of 1/8° per minute, and a high detector sensitivity (scintillation counter). The reticular distances were indexed with the aid of a computer.

Transmission electron microscope measurements were made on a JEOL 120 CX, with a magnification up to 700 000. The polymer suspended in an alcoholic medium, and this solution was evaporated on to an amorphous carbon grid.

3. Results

The doping level of the polymer by $CF_3SO_3^-$ was determined by elemental microanalysis. Polythiophene has been obtained with a 25 to 30% doping level, PT_{25-30}, and poly-3, 4-dimethylthiophene with 30 to 40% doping level, PMe_2T_{30-40}. The most interesting feature concerns poly-3-methylthiophene, which has a doping extent up to 50%, $PMeT_{50}$, with an intermediate stage of about 30%, $PMeT_{30}$.

The transmission electron microscope (TEM) analysis of these polymers shows a fibrillar structure for PT_{25-30}, with a fibril diameter of about 80 nm (Fig. 1). These fibrils are formed by packed polymer chains, the individual chain axes being distributed around the fibre axis. This polymer is however fully amorphous under TEM as well as under X-ray. When doped to 30%, $PMeT_{30}$ reveals the same fibrillar structure as PT_{25-30}, but some microcrystallites appear in the fibril (Fig. 2). As discussed for individual polymer chains, the microcrystallites do not appear to be ordered along a preferential axis. On the other hand, $PMeT_{50}$ and PMe_2T_{30-40} show compact masses (Fig. 3), as if the fibrils had aggregated together. At higher magnification, and only in the case of the highly doped $PMeT_{50}$, we were able to record, in some areas of the polymer sample, TEM

Figure 2 TEM picture of poly 3-methylthiophene – $CF_3SO_3^-$, doping level 30%. Fibrillar structure with crystallites.

pictures clearly displaying reticulations (Figs. 4a and b). In this particular case however, the crystallized areas were not large enough to allow us to record diffraction patterns. By the analysis of other zones of the polymer sample, we have been able to obtain the diffraction patterns shown in Fig. 5, which clearly reveal a six-fold symmetry.

X-rays measurements, performed on polymer powders, gave the following results (Fig. 6): Doped $PMeT_{30}$ and $PMeT_{50}$ exhibit two peaks, located at $2\theta = 17°$ and at $2\theta = 29.8°$. The peak intensities increase with the doping level, from 30 to 50, but it must be pointed out that even in the most favourable case of $PMeT_{50}$, the observed signals are weak and correspond to a low percentage of crystallinity, estimated at less than 5%. With undoped PMeT, the X-ray peak at $2\theta = 29.8°$ is still observed, but the second one at $2\theta = 17°$ is decreased very much in intensity. Under TEM, we were unable to record diffraction patterns for this undoped PMeT, but it may be argued that even for the doped $PMeT_{50}$, the crystallized areas were statistically rare and unstable under the electron beam. Doped $PMe_2T_{30\text{–}40}$ also displays two X-ray peaks. In order to discriminate from possible aggregation of the dopant anions in the polymer, we recorded the X-ray diffraction of the $N(Bu)_4SO_3CF_3$ salt and verified that it did not correspond to any of the two preceeding peaks.

These experimental results confirm the existence of crystallized areas in these polymers. The six-fold symmetry defined by the electron diffraction experiments can be related either to a cubic structure or to a hexagonal structure. Using the diffraction data determined on $PMeT_{50}$, the reticular distances have been indexed on a computer. No fit with a cubic structure could be realized. On the other hand, the indexation with a hexagonal structure led to a very good agreement with the X-ray diffraction as well as with the electron diffraction data (Table I). These results show that:

(a) the characteristic distances for the hexag-

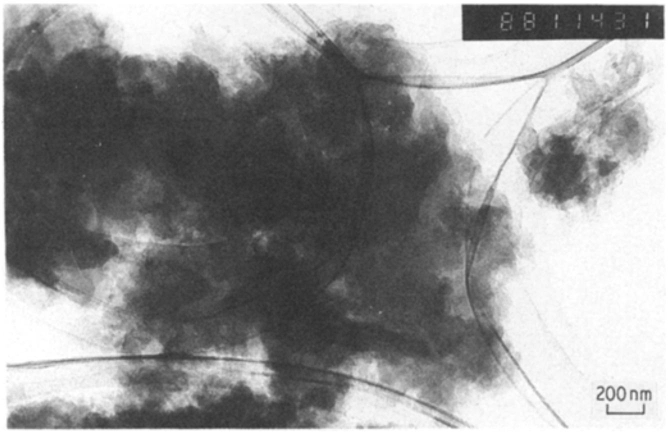


Figure 3 TEM picture of poly 3-methylthiophene – $CF_3SO_3^-$, doping level 50%. Compact masses.

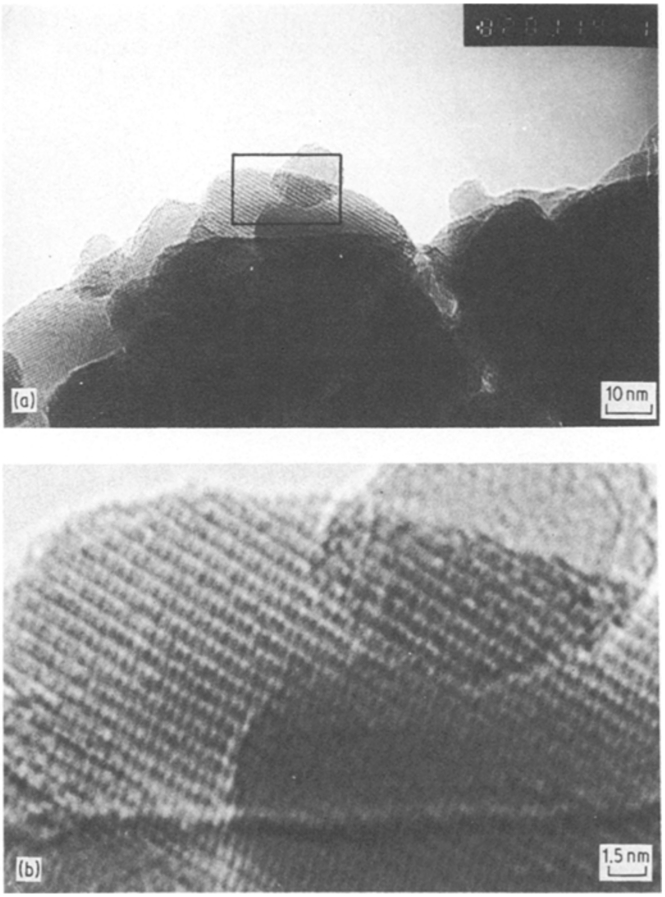


Figure 4 (a) TEM picture of crystallized areas of poly 3-methylthiophene doped with 50% $CF_3SO_3^-$. Reticulation planes. (b) Encircled area in (a), at higher magnification.

TABLE I Indexation of the electron and X-ray diffraction data of poly 3-methylthiophene doped with 50% $CF_3SO_3^-$.

h k l	*d* (nm) theoretical	*d* (nm) experimental		
		Electron diffn*	X-ray diffn	TEM†
1 0 0	0.823			
1 0 1	0.682			
0 0 2	0.610		0.605	0.62
1 0 2	0.490			
1 1 0	0.475	0.44		
1 1 2	0.375			
2 0 2	0.341		0.345	
2 1 0	0.311			
2 1 1	0.301			
2 1 2	0.277			0.28
3 0 0	0.274	0.26		
3 3 0	0.158	0.148		

*Hexagonal system. Accuracy: ± 5%. $a \sim 0.95$ nm, $c \sim 0.122$ nm.
†See Fig. 4b.

onal lattice are $a = 0.95$ nm and $c = 1.22$ nm, see Fig. 7.

(b) the most intense X-ray diffraction peaks are related to the [002] and [202] planes, and the most intense electron diffraction spots to the [110] [300] and [330] planes,

(c) the two main sets of atomic planes shown on Fig. 4b correspond to [0 0 2] separated by 0.61 nm (experimental value 0.62 nm), and [2 1 2] separated by 0.277 nm (experimental value 0.28 nm), the zone axis pattern being [1 2 0]. The measured angle between these two planes agrees fairly well with the one calculated from the proposed cell, i.e. 68° on the micrograph of Fig. 4b, and 63° for the calculated value,

(d) the diffraction patterns shown on Figs. 5a and b correspond to the [0 0 1] zone axis, with the [1 1 0] and [$\bar{1}$ 2 0] on the first ring.

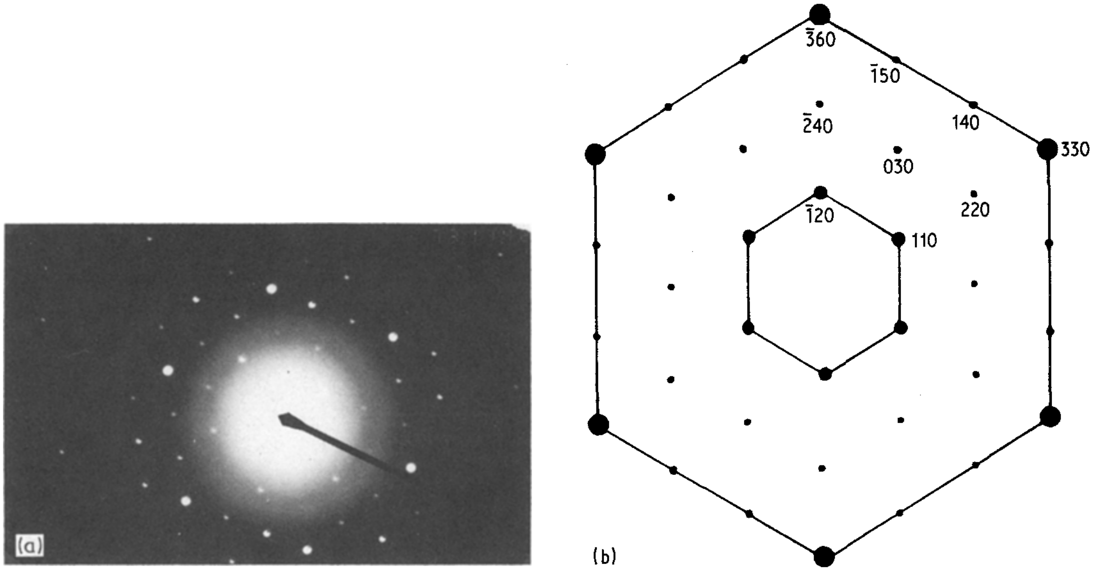


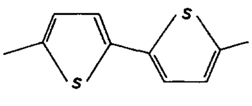
Figure 5 (a) Electron diffraction patterns of crystallized areas of poly 3-methylthiophene doped with 50% $CF_3SO_3^-$. (b) Indexation of the most important spots in a hexagonal system.

This result disagrees with the monoclinic lattice which has been proposed by Street [8] and Geiss [9] for polypyrrole solely on the basis of diffuse diffraction rings observed by electron microscopy. The experimental data reported here unambigously rule out this monoclinic structure hypothesis for polythiophene derivatives.

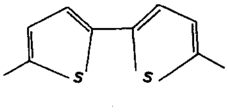
4. Discussion

The bond length and angle values given in the literature for thiophene [10] and for $CF_3SO_3^-$ [11] were used in the following discussion of the polymer chain structure.

The sequence of the thiophene units in the chain can be analysed by considering the already known dimer, α, α' bithiophene. Although the s trans (III) is the only conformer present in the crystal state, the s trans–s cis (IV) interconversion has been shown to occur in the liquid phase with a relatively low energy barrier [12]. These two conformations must thus be taken into account. Two extreme models for the polymer chain can be derived from an ideal ordering of the thiophene units, whether all s trans or all s cis.



III



IV

Sequence III would lead to a planar structure for the polymeric chain. On the other hand, Sequence IV would correspond to a coil structure. The diameter of the coil can be calculated on the basis of the angle between the two exocyclic α–α' bonds in the thiophene molecule, 147.6°.

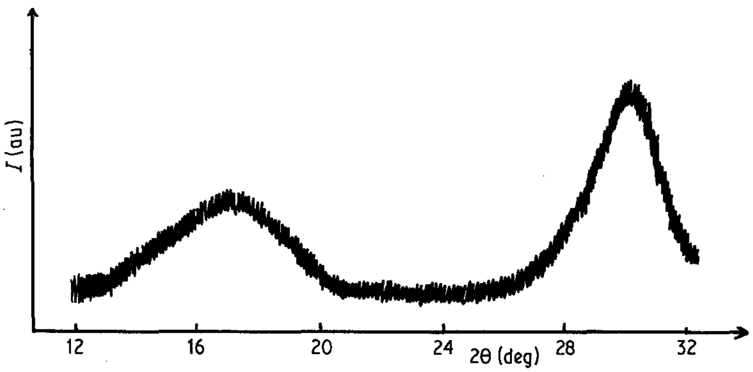


Figure 6 X-ray diffraction spectra of poly 3-methylthiophene doped with 50% $CF_3SO_3^-$.

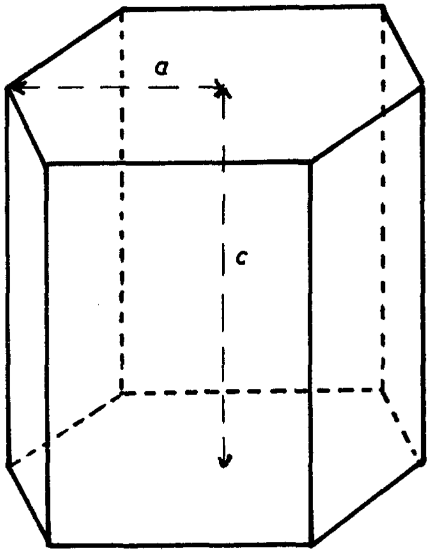


Figure 7 Hexagonal lattice parameters: $a = 0.95$ nm; $c = 1.22$ nm.

Each thiophene unit being bent with an angle of 32.4° to the preceeding one, one loop of the coil would involve 360°, i.e. 360/32.4 about 11 thiophene units. This coil should thus have an outer and inner diameter of respectively about 2.0 nm and 1.2 nm, taking account of the size of the 3 methylthiophene molecule.

Considering now the dopant, our results on PMeT–$CF_3SO_3^-$ indicate that 50% may represent an optimum doping level for these polymers, corresponding to one dopant anion for each two thiophene units. The position of the dopant $CF_3SO_3^-$ with respect to the thiophene molecular plane must be guided by positive charge delocalization in the polymeric chain. We have recently demonstrated, using ESR data [13], that these five membered polyheterocycles behave like polyacetylene, and involve an electron delocalization only along the carbon atom chain (and not the heteroatom) for the transport of charge. This conclusion agrees also with theoretical calculations made on the parent polymer, polypyrrole [14]. It can thus be proposed that the $CF_3SO_3^-$ dopant is most likely located above the thiophene molecular plane, anchored to one thiophene unit by two oxygen atoms of the sulphonate group, and to the other adjacent thiophene unit by two fluorine atoms of the electron withdrawing CF_3 group.

In this Sequence III hypothesis, the doped polythiophene should thus involve layers of linear planar polymeric chains, in which the backbones should be parallel throughout the structure, the dopant being intercalated between these layers. This structural hypothesis corresponds to the monoclinic cell unit already advanced by Street [8], Sequence IV on the other hand would lead to a coil structure, with 11 thiophene units per loop (Fig. 8), the dopant anions being intercalated between the thiophene molecular planes of two superposed loops, the inner hold of the coil remaining empty. This hypothesis corresponds to a hexagonal structure for the unit cell.

The indexation of our X-ray and electron diffraction data strongly support this coil structure, ruling out the monoclinic unit cell hypothesis. The calculated distances a and c for the hexagonal lattice can be attributed in the following way.

The calculated coil diameter, $2a = 1.9$ nm agrees with the expected diameter, d of the already discussed loop containing 11 thiophene units, $1.2 \lesssim d \lesssim 2.0$ nm. Taking account for the odd number of thiophene units in one loop, and also for the 1/2 doping level by $CF_3SO_3^-$, the periodicity along the c axis will involve two loops of this doped polymer. To calculate the coil pitch value, we will use the experimental diameter of $CF_3SO_3^-$ [11], 0.215 nm, and the distance of closest approach between acceptor and donor molecule, which has been shown to be between 0.18 and 0.32 nm [15]. The calculated coil pitch value is thus 0.71 ± 0.13 nm. The two loops in the hexagonal lattice will correspond to a distance of 1.42 ± 0.26 nm. This value agrees also with the experimental parameter c determined for the hexagonal cell, $c = 1.22$ nm.

The density of the doped polymer can be calculated, on the basis of the hexagonal cell (parameters $2a$ and c) contining 22 thiophene units and 11 $CF_3SO_3^-$ anions, as 1.62 g cm^{-3}. This calculated density lies reasonably close to the experimental value, 1.46 g cm^{-3}, which we determined for this doped polymer by the use of the floating method.

The case of undoped PMeT is more difficult to analyse, owing to the absence, up to now, of electron diffraction data, the interpretation of the X-ray results cannot be conclusive. It must be pointed out however that the peak at $2\theta = 29.8°$, related to the parameter a of the coil diameter, is retained. This can be expected from a deintercalation process, which does not alter the coil diameter. The attribution of the very weak second peak at $2\theta = 17°$ was however too uncertain.

PMe_2T_{30-40} did not show any electron diffraction pattern, but as for PMeT, the low level of

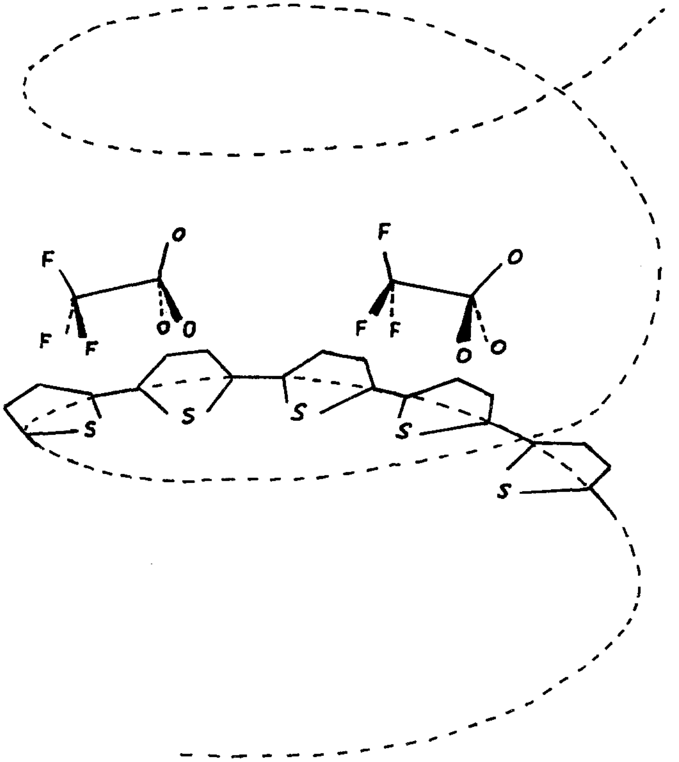


Figure 8 Helicoidal structure proposed for the highly doped, crystallized poly 3-methylthiophene – $CF_3SO_3^-$.

crystallinity and the instability of these polymers under the electron beam must be remembered. By X-ray diffraction however, peaks similar to those for $PMeT_{50}$ have been observed. The only difference is a slight decrease in c, the a parameter being almost constant. The shortening of 0.03 nm in c can be associated to an enhancement of the dopant–polymer interaction, due to the electronic effect of the methyl substituents. The variation is however very small.

This coil structure hypothesis has received a further confirmation from u.v.–visible spectra analysis [16]. As a matter of fact, the absorption spectrum of undoped PT and PMeT present a band maximum at 480 nm, which corresponds to the expected limit value for conjugated polythiophenes [17]. On the other hand, PMe_2T and also poly-3, 4-diethylthiophene absorption maximum lies respectively at 330 nm and 280 nm. This very important loss of conjugation, which increases with the bulkiness of the substituents, must be related to a large twist of each thiophene unit along the α–α' coupling bond in the undoped polymeric chain. Only the Sequence IV hypothesis agrees with such high steric hindrance between each two adjacent thiophene units.

The question of why $CF_3SO_3^-$ allows such a high doping level and has these crystallographic patterns is not easy to answer. But in this intercalation process, structural as well as electronic factors should intervene:

Structural factors – The effect of the dopant molecule size on the conductivity properties of such polymers has already been pointed out [19]. In the case of a 1:2 doping of polythiophene derivatives, the structural parameters of $CF_3SO_3^-$ appear to be suitable for an anchoring of the dopant on two adjacent thiophene units;

Electronic factors – The hard and soft acid base concept developed by Pearson [19] appears interesting for the interpretation of the polymer–dopant interaction. The large conjugated polymeric chain with highly delocalized positive charges can be considered as a soft acid. The most suitable dopant interaction. The large conjugated polymeric charge delocalization should also occur. In the dopant considered here, the electron withdrawing group CF_3 ensures this electronic effect. In the same way, the picryl anion has been shown to be also a very interesting dopant for these five membered polyheterocycles [20–22]. In this dopant too, the nitro groups induce an effective charge delocalization. This soft interaction between dopant and polymer can also be considered as a determining factor in order to avoid a positive charge localization in the polymeric chain, which would occur in the case of an interaction with a small hard charged dopant.

5. Conclusions

This attempt to improve the regularity of electrochemically synthesized polythiophenes, by substituting the carbon atoms, led us to put into evidence, for the first time, a crystal structure. The hypothesis, which up to now best fits with the crystallographic data, involves a coil structure in which the dopant intercalation determines the pitch. Steric interactions however appear in 3, 4-disubstituted polythiophenes, and lead to polymeric chain distortions. The geometry and the electronic characteristics of the dopant play also an important role for the charge delocalization in the polymers. Although the crystallization of the polymer is still low, about 5%, we reached a better understanding of the structural parameters which control the regularity of the polymeric chain structure.

References

1. R. H. BAUGHMAN, J. L. BREDAS, R. R. CHANCE, R. L. ELSENBAUMER and L. W. SHACKLETTE, *Chem Rev.* **82** (1982) 209.
2. G. WEGNER, *Angew. Chem.* **93** (1981) 352.
3. A. G. MacDIARMID and A. J. HEEGER, in "Molecular Metals", edited by W. E. Hatfield, (Plenum Press, New York, 1979) p. 161.
4. G. B. STREET and T. C. CLARKE, *IBM J. Res. Develop.* **25** (1981) 51.
5. L. W. SHACKLETTE, R. L. ELSENBAUMER and J. M. SOWA, in "Proceedings of the Spring Electrochemical Society Meeting", (1982), Montreal, p. 985.
6. K. K. KANAZAWA, A. F. DIAZ, W. D. GILL, P. M. GRANT, G. B. STREET, G. P. GARDINI and J. F. KWAK, *Synthetic Met.* **1** (1979) 329.
7. G. TOURILLON and F. GARNIER, *J. Electroanal. Chem.* **135** (1982) 173.
8. G. B. STREET, Proceedings of the 163rd Electrochemical Society Meeting (1983) San Fransico, p. 111C.
9. R. H. GEISS, Proceedings of the 38th Meeting of the Microscopy Society of America (1980) p. 238.
10. B. BAK, D. CHRISTENSEN, L. HANSEN-NYYGARD and J. RASTRUP-ANDERSEN, *J. Mol. Spectros.* **7** (1961) 58.
11. J. BROCK SPENCER and J. O. LUNDGREN, *Acta. Crystall.* **B29** (1973) 1923.
12. P. BUCCI, M. LONGERI, C. A. VERACINI and L. LUNAZZI, *J. Amer. Ceram. Soc.* **96** (1974) 1305.
13. G. TOURILLON, D. GOURIEZ, F. GARNIER and D. VIVIEN, *J. Phys. Chem.* **88** (1984) 1049.
14. W. K. FORD, C. B. DUKE and W. R. SALANEK, *idem.* **77** (1982) 5030.
15. R. FOSTER in "Organic Charge Transfer Complexes" (Academic Press, London 1969) p. 230.
16. G. TOURILLON and F. GARNIER, *J. Electroanal. Chem.* **161** (1984) 51.
17. J. W. SEASE and L. ZECHMEISTER, *J. Amer. Chem. Soc.* **69** (1947) 270.
18. E. K. SICHEL, M. KNOWLES, M. RUBNER and J. GEORGES, Jr. *Phys. Rev. B* **25** (1982) 5574.
19. R. G. PEARSON in "Hard and Soft Acids and Bases", edited by Dowden, Hutchinson and Ross (1973).
20. F. GARNIER, G. TOURILLON, M. GAZARD and J. C. DUBOIS, *J. Electroanal. Chem.* **148** (1983) 299.
21. A. F. DIAZ, unpublished data.
22. H. NAARMAN "Polyméres Electroactifs" (Font-Romeu, France, 1982).

Received 27 April
and accepted 2 July 1984.