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Routes towards three-dimensional fully conjugated conducting polymers: 1. Preparation of the kit of monomers

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We have prepared and characterized several trithienylbenzenes. These compounds are used as reticulation points in poly(3-n-octylthiophene). It was necessary to study the reactivity of the reticulation points with regard to 3-n-octylthiophene. That is the reason why we have prepared copolymers starting from very high percentages of deuterated reticulation points (> 10%) and monitored their reactivities following the evolution of the =C–D band in the infra-red spectra of the copolymers. The copolymers thus obtained contain from 10% to 30% of reticulation points. They swell in apolar solvents whereas the poly(reticulation point) (100% of reticulation points) does not swell. A low molar doping level ($FeCl_3 \cdot 6H_2O$, <9%) leads to a non-negligible conductivity (0.1 to 0.2 S cm^{-1}) of these copolymers. In the same conditions, the poly(reticulation point) cannot be doped and thus remains insulating.

(Keywords: trithienylbenzene; poly(3-alkylthiophene); conjugated conducting polymers)

INTRODUCTION

It is well known that the structure of a conducting polymer determines its electrical and optical properties[1–13]. So, it is of great interest to control the architecture of a polymer in order to study the structure–properties relationship. Among the conducting organic polymers, poly(3-alkylthiophenes) have been extensively studied because of their stability, solubility and fusibility[14–19] and because of the novel characteristics they demonstrate, such as thermochromism, photochromism, anomalous temperature and alkyl-chain-length dependence of luminescence[20–22] and solvatochromism[22–24]. Nevertheless, 'thermal undoping' is a fatal problem for poly(3-alkylthiophene) application[25–27].

These polymers are generally one-dimensional but some 'gels' of poly(3-alkylthiophenes) may also be obtained by four methods[28]. In the first and second methods, the insoluble fraction obtained after the chemical (via $FeCl_3$) or electrochemical polymerization of 3-alkylthiophene is assumed to be a gel able to swell in different solvents[28–32]. The third method consists of preparing poly(3-alkylthiophene) by radical initiator[33,34] and, finally, the fourth method consists of γ-ray irradiation of soluble poly(3-alkylthiophene)[35]. These gels are not well defined: some amount of crosslinking between the chains has been assumed but the nature of the crosslinking has so far not been determined.

Some papers dealing with the structure–properties relationship in poly(3-alkylthiophenes) have been published recently[7–11]. The authors show that regioregular one-dimensional poly(3-alkylthiophenes) exhibit higher conjugation length, higher electronic conductivity and higher degree of structural order than the non-regioregular ones. Our aim is to prepare xerogels of poly(3-alkylthiophenes) with well defined conjugated crosslinks (reticulation points), with random or regioregular structure. The main interest in this kind of gel may be, first, to give information on the conductivity of polyconjugated systems of dimension $D>2$ and, secondly, to present a quick dopage–dedopage phenomenon. We present in this first paper the preparation of the different compounds required for the elaboration of these gels and the preliminary results concerning the oxidative (via $FeCl_3$) copolymerization of the reticulation points with 3-n-octylthiophene.

METHOD

Among the different possible ways of elaboration of these kinds of polymers, we have decided to perform the copolymerization of 3-n-octylthiophene with fully conjugated reticulation points containing several thienyl groups. Different chemical coupling methods will be used (leading to the obtention of more or less regioselective polymers). In each case, we shall observe the influence of

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the relative concentration of the reticulation point with regard to 3-n-octylthiophene.

CHOICE OF THE MONOMERS

Polymerization of thiophene may be performed according to three main methods.

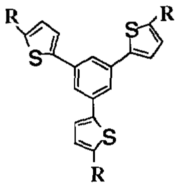
The first method consists of an oxidative coupling using oxidants such as $FeCl_3$ or $Cu(ClO_4)_2$ (refs. 36–41). This method allows us to obtain poly(3-alkylthiophenes) with 50–80% head-to-tail couplings[7,8]. In this case, 3-n-alkylthiophene reacts directly with unfunctionalized reticulation points or with labelled reticulation points (in order to get information on the reactivity of the reticulation points).

The second method consists of a nickel-catalysed Grignard coupling[43–46] according to the method described by Tamao *et al.*[42]. The regioselectivity of the poly(3-alkylthiophene) obtained by this method was investigated by Mao *et al.*. They found that the molecular weights, the molecular-weight distribution and the nature of the terminal groups of the resultant polymers depend on the initial polymerization conditions[44]. Some authors report that the stereoregularity of the polymers thus obtained is higher than that observed in the polymers prepared with $FeCl_3$ (ref. 47). Furthermore, this method has the advantage of avoiding *β* linkages but requires the preparation of functionalized reticulation points.

The third method consists of the 'cross-coupling' according to the method described by MacCullough *et al.*[8]. This method, like the previous one, allows us to avoid *β* linkages and also presents the great advantage of leading to the regiochemically well defined poly(3-alkylthiophene) with 97% of head-to-tail–head-to-tail (HT–HT) couplings[9]. This method also requires the preparation of functionalized reticulation points. We have chosen to use only the first and third methods, because the first one allows us to get imperfect 'random' copolymers, contrary to the third one, which gives regiospecific *β*-linkage-free copolymers. Therefore, we have chosen to prepare the following reticulation points.

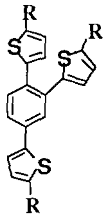
Unfunctionalized reticulation points

The reticulation points we have chosen are 1,3,5-tri(2'-thienyl)benzene **1** (*Figure 1a*), 1,2,4-tri(2'-thienyl)benzene **2** (*Figure 2a*), 1,3,5-tri(3'-thienyl)benzene **3** (*Figure 3a*) and 1,2,4-tri(3'-thienyl)benzene **4** (*Figure 4a*). Comparison of **1** and **2** with **3** and **4** respectively will give information on the influence of the substitution positions on the benzene ring (*meta* in the first case and *ortho* and *para* in the second). Comparison of **1** and **3** with **2** and **4** respectively will give information on the influence of the polymerization site number on the reticulation point (three in the first case and six in the second).



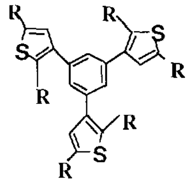
a)R=H : 1
b)R=D : 5
c)R=Br : 9

Figure 1 Different 1,3,5-tri(2'-thienyl)benzene reticulation points



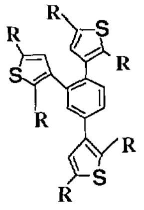
a) R=H : 2
b) R=D : 6

Figure 2 Different 1,2,4-tri(2'-thienyl)benzene reticulation points



a) R=H : 3
b) R=D : 7

Figure 3 Different 1,3,5-tri(3'-thienyl)benzene reticulation points



a) R=H : 4
b) R=D : 8

Figure 4 Different 1,2,4-tri(3'-thienyl)benzene reticulation points

Labelled reticulation points

We need to obtain information on the reactivity of the reticulation points in the oxidative copolymerization reaction and, thus, answer the question: 'Do the thienyl groups of the reticulation point react with 3-alkylthiophene?' We have therefore labelled the three free α positions of the thiophene groups (with regard to sulfur) of **1** and **2** with deuterium and the six related positions of **3** and **4**. We expected that the out-of-plane =C–D deformation band characteristic of the thiophene group would substitute the related =C–H deformation bands[48]. This =C–D band would be a probe for testing the reactivity of the ramification point because it is in a region where no significant bands of the poly(3-n-octylthiophene) or of unfunctionalized reticulation point appear. Consequently, we have prepared 1,3,5-tri(5'-deutero-2'-thienyl)benzene **5** (*Figure 1b*), 1,2,4-tri(5'-deutero-2'-thienyl)benzene **6** (*Figure 2b*), 1,3,5-tri(2',5'-dideutero-3'-thienyl)benzene **7** (*Figure 3b*) and 1,2,4-tri(2',5'-dideutero-3'-thienyl)benzene **8** (*Figure 4b*).

Functionalized reticulation points

At this moment, we have only obtained 1,3,5-tri(5′-bromo-2′-thienyl)benzene **9** (*Figure 1c*).

CHEMICAL ROUTES USED FOR THE PREPARATION OF THE RETICULATION POINTS AND THE RELATED REAGENTS

Unfunctionalized reticulation points: 1, 2, 3, 4

Cyclization of acetyl compounds (*Figure 5*). This reaction has been extensively studied[49–56]. It was adapted by Wirth *et al.* for acetyl compounds with aromatic R groups[57]; Buu-Hoï *et al.* have prepared **1** in this way[58] with a yield of 50%, but they only report the elemental analysis. More recently, Elmorsy *et al.*[49] have studied the reaction of acetophenone with tetrachlorosilane in ethanol: they prepared 1,3,5-triphenylbenzene with a yield of 86%.

We have tested these two routes with 2-acetylthiophene. We have obtained **1** with a yield of 25% in both cases. In the first case (HCl, ethylorthoformate), we observed the unexpected formation of 1,3-di(2′-thienyl)benzene **10** (*Figure 6*); with tetrachlorosilane, we did not observe this compound.

This first method has three disadvantages: first, only 1,3,5-tri(2′-thienyl)benzene (not 1,2,4-tri(2′-thienyl)benzene) can be obtained; secondly, the yield is not high enough; and thirdly, the obtained crude product contains a mixture of oligomers and the purification of **1** is not easy. In addition, we did not succeed in preparing 1,3,5-tri(3′-thienyl)benzene starting from 3-acetylthiophene (we obtained solid products insoluble in every solvent, difficult to characterize; they look like polymers). So, we decided to test another method.

Cyclization of arylacetylenes catalysed by halides of tantalum (*Figure 7*). Masuda *et al.*[59] have performed the cyclization of phenylacetylene catalysed by halides of tantalum ($TaCl_5$ is the precursor of the catalytic species $TaCl_3$) or of niobium. After a short reaction time, they have obtained 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene and insoluble polymers. In order to test this method, we have had to prepare 2-ethynylthiophene **b1** and 3-ethynylthiophene **b3**. Starting from **b1**, we succeeded in preparing at 25°C with a yield of 80% a mixture of 40% of **1** and 60% of **2** (according to n.m.r. data). The remaining 20% of the crude product consisted of insoluble polymers. Starting from **b3**, we have obtained **3** and **4** with the same yield and approximately 40% of **3** and 60% of **4**.

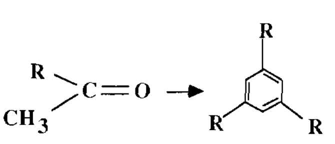
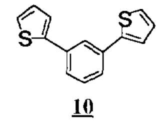


Figure 5 Chemical route for the obtention of 1,3,5-trithienylbenzene



10

Figure 6 1,3-Di(2′-thienyl)benzene

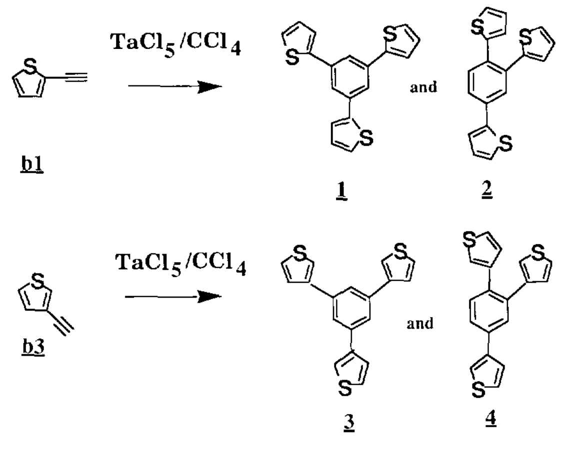


Figure 7 Chemical route for the preparation of 1,3,5- and 1,2,4-tri(2′-thienyl)benzene and 1,3,5- and 1,2,4-tri(3′-thienyl)benzene

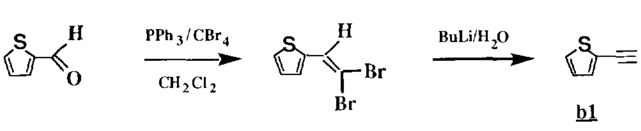


Figure 8 Chemical route for the obtention of 2-ethynylthiophene

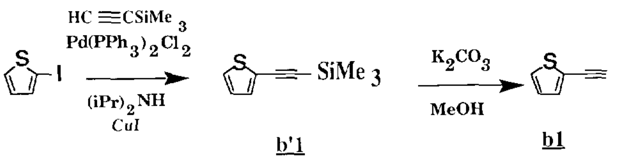


Figure 9 Alternative preferred chemical route for the obtention of 2-ethynylthiophene

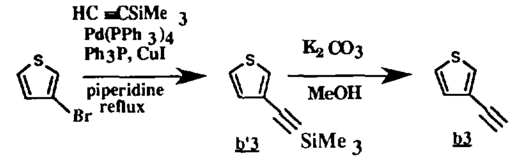


Figure 10 Chemical route for the preparation of 3-ethynylthiophene

*Preparation of 2-ethynylthiophene **b1** and 3-ethynylthiophene **b3***. Compound **b1** has already been prepared[60,61] according to the method of Corey *et al.*[62] (*Figure 8*). Although this method gives an overall good yield (65%), we have preferred to adapt the method using the palladium-catalysed ethynylation[63–68] (*Figure 9*). Indeed, in our opinion, it is easier to prepare **b1** or **b3** in this way especially because it is not necessary to isolate **b′1** or **b′3** before further use, and thereby this reaction may be considered as a 'one-step reaction', contrary to the first one. We have obtained **b1** with 81% yield.

As 3-iodothiophene is not commercially available, **b3** was not obtained in the same way as **b1**. Compound **b3** was prepared from the less reactive 3-bromothiophene according to the method described by Brandsma *et al.*[69] (*Figure 10*). We have obtained **b3** with 81% yield (in this case, we have used 1.2 mol of trimethylsilylacetylene per mole of 3-bromothiophene).

D-labelled reticulation points: 5, 6, 7, 8

We have performed the lithiation of **1** and **2** (in THF, tetrahydrofuran) and of **3** and **4** (in TMEDA, *N,N,N′,N′*-tetramethylethylenediamine) with butyllithium followed by the action of D_2O. The deuteration reaction was observed by mass spectrometry, by ^1H n.m.r. and by i.r. spectroscopy.

The percentages of the different deuterated compounds have been obtained (see *Table 1*) via mass spectrometry. *Figure 11* presents the mass spectra of the reticulation points **1**, **2**, **3** and **4** before and after deuteration. We have performed the mass spectrometry experiments with a low potential (10 eV) in order to avoid the formation of compounds resulting from deprotonation and thus to obtain an accurate value of the percentage of deuteration.

The selectivity of the deuteration has been observed by ^1H n.m.r. spectrometry. ^1H n.m.r. results are summarized in *Table 2*: they show that the deuteration is selective and only concerns the free α positions of the thiophene groups (with regard to sulfur). *Figures 12a, 14a, 16a,* and *18a* respectively present the ^1H n.m.r. spectra of **1**, **2**, **3** and **4** before and after deuteration.

I.r. spectrometry results concerning the deuteration of **1**, **2**, **3** and **4** are summarized in *Table 3*. We observed the appearance of out-of-plane =C–D deformation bands and the vanishing of related =C–H bands. *Figures 13, 15, 17* and *19* respectively present the i.r. spectra of **1**, **2**, **3** and **4** before and after deuteration.

Table 1 Deuteration: results from mass spectrometry

Deuteration of	Deuteration (%)						
	di	tri	tetra	penta	hexa	hepta	octa
1	4	95	0.5	0.5			
2	7	91	1.5	0.5			
3			2	17	78	2	1
4			2	11	82	4	1

Table 2 Selectivity of deuteration: results from ^1H n.m.r

Deuteration of	Deuterated positions[a]
1	5
2	5, 14, 20
3	2, 5
4	2, 5, 11, 14, 17, 20

[a] Enumeration refers to *Figures 12b, 14b, 16b* and *18b* as far as **1**, **2**, **3** and **4** respectively are concerned

Table 3 Deuteration: results from i.r. spectrometry

Deuteration of	Band (cm^{-1})	
	Out-of-plane =C–H deformation band vanishing	Out-of-plane =C–D deformation band appearing
1	698	561
2	701, 710	557, 570
3	772	577
4	777, 780	577, 588

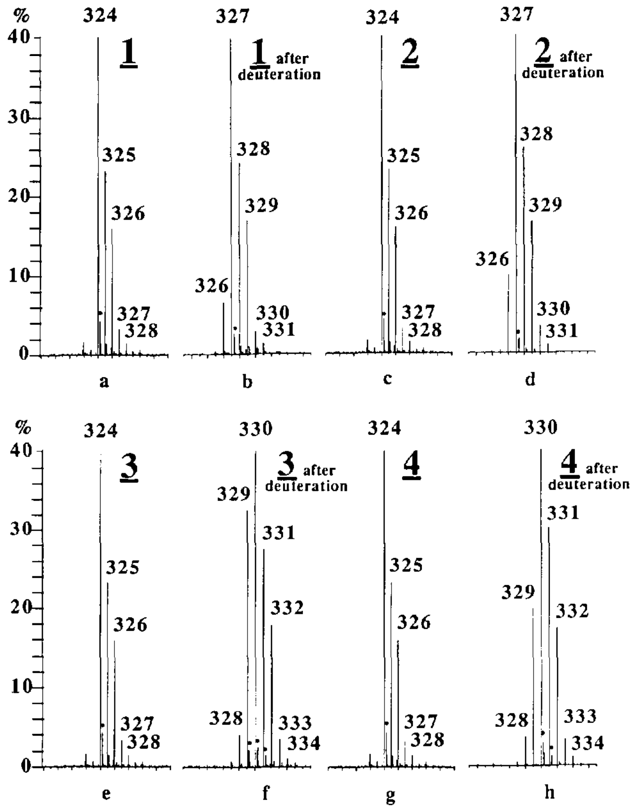


Figure 11 Mass spectra of (a) **1**, (b) **1** after deuteration, (c) **2**, (d) **2** after deuteration, (e) **3**, (f) **3** after deuteration, (g) **4**, (h) **4** after deuteration; (*) satellite peak due to a peak foot

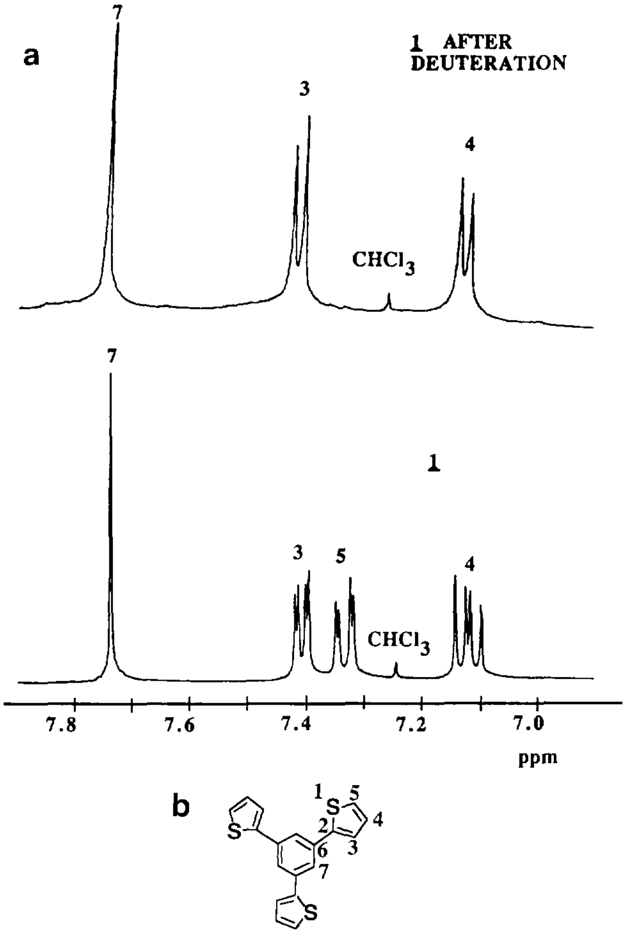


Figure 12 (a) ^1H n.m.r. spectra of **1** before and after deuteration. (b) Enumeration of the different positions of **1**

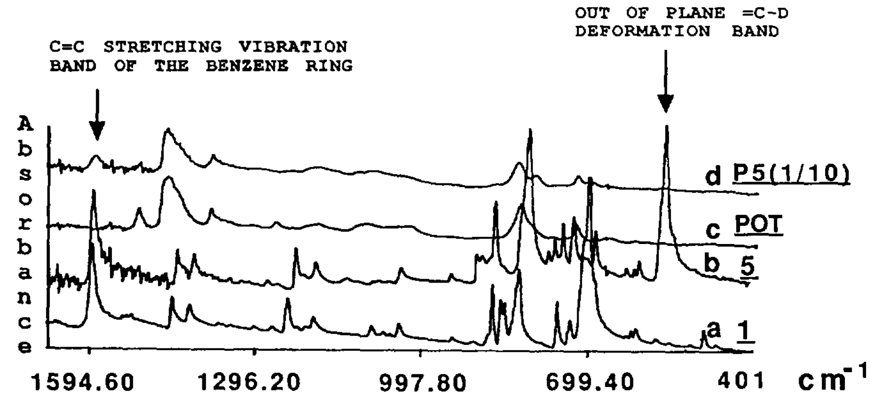


Figure 13 I.r. spectra of (a) **1**, (b) **5**, (c) POT and (d) P5(1/10)

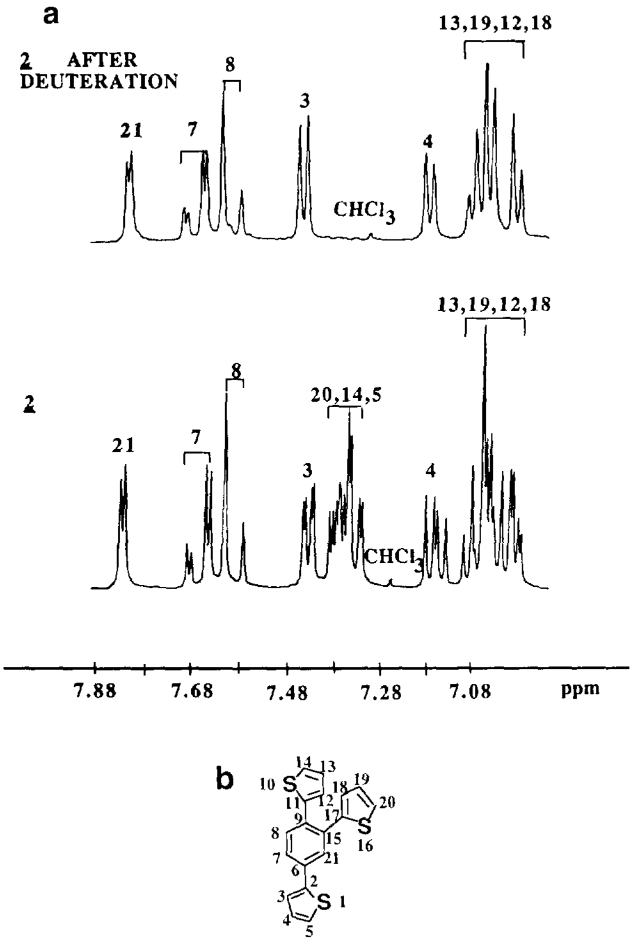


Figure 14 (a) ^{1}H n.m.r. spectra of **2** before and after deuteration. (b) Enumeration of the different positions of **2**

Table 4 The R_i and resulting R_f values of four copolymers

Copolymer obtained with the reticulation point	R_i	R_f
1	1/10	1/4.5
2	1/5	1/3
3	1/12	1/8
4	1/12	1/9

Functionalized reticulation point: 1,3,5-tri(5′-bromo-2′-thienyl)benzene 9

Cyclization of acetyl compounds. The route we have chosen consists of the cyclization of the related bromo-acetyl compound. The reaction performed on 5-bromo-2-acetylthiophene in the presence of dry hydrogen chloride and ethylorthoformate[57,58] has led to the colourless crystalline 1,3,5-tri(5′-bromo-2′-thienyl)benzene **9** (20% yield) after recrystallization in acetone. This crystalline product also contains less than 10% of 1,3-di(5′-bromo-2′-thienyl)-5-(5′-chloro-2′-thienyl)benzene **11** (*Figure 20*). The same reaction in the presence of tetrachlorosilane[59] does not allow one to obtain **9**: we only observe the formation of a yellow crystalline compound, which we have characterized as being one of the two dimers **12a** and **12b** (*Figure 21*). This compound precipitates, thus checking the reaction (we assume that the observed dimer is more probably **12a**). In this case, too, the crystals contain less than 10% of molecules with one thiophene ring substituted by a chlorine atom.

The obtention of **9** in this way requires the preparation of 5-bromo-2-acetylthiophene (**a9**), which has been prepared like the related iodo compound[70]. This reaction of 'crotonization–cyclization' allows one to obtain easily 1,3,5-tri(5′-bromo-2′-thienyl)benzene **9**, contrary to the related iodo compound (during the formation of which deiodation occurs).

TEST OF THE REACTIVITY OF THE RETICULATION POINTS IN THE COPOLYMERIZATION WITH 3-n-OCTYLTHIOPHENE

In order to test the reactivity of the reticulation points **1**, **2**, **3** and **4** in the oxidative copolymerization with 3-n-octylthiophene in the presence of $FeCl_3$, we have performed the copolymerization of the related D-labelled reticulation points (**5**, **6**, **7** and **8**). Let us define the following ratio:

$$R = [\text{reticulation point}]/[\text{3-n-octylthiophene}]$$

R_i is the initial ratio in the reaction medium and R_f the final ratio in the obtained copolymer. In order to avoid the dilution of information related to the reticulation points, we have chosen high R_i ratios. *Table 4* presents the R_i used and the resulting R_f of the four copolymers.

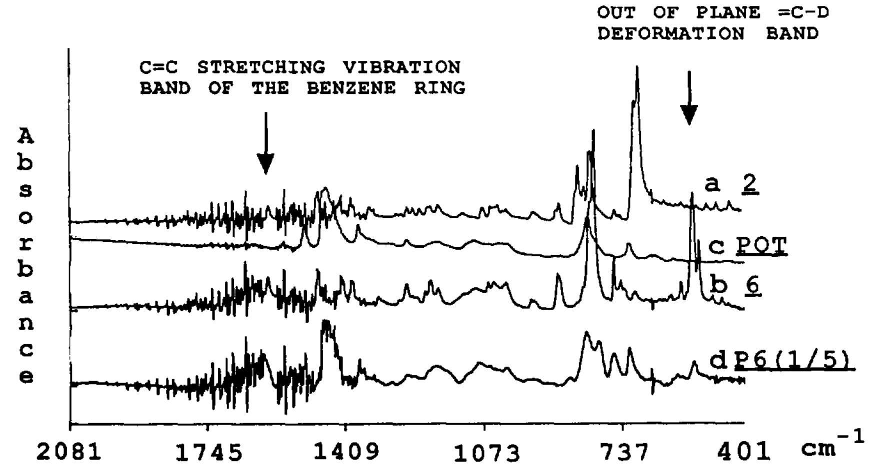


Figure 15 I.r. spectra of (a) **2**, (b) **6**, (c) POT and (d) P6(1/5)

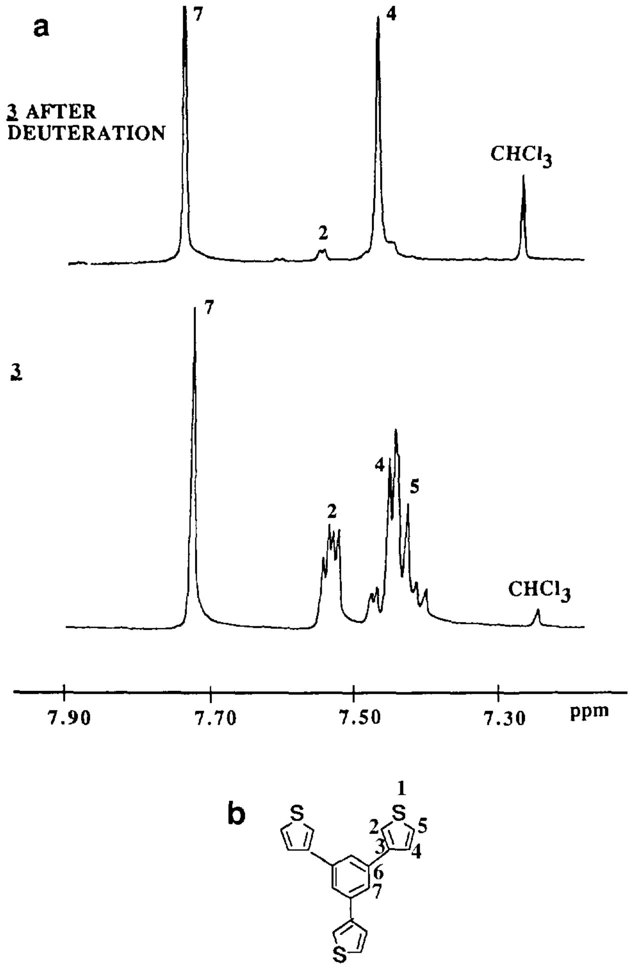


Figure 16 (a) ^{1}H n.m.r. spectra of **3** before and after deuteration. (b) Enumeration of the different positions of **3**

We have observed the copolymers by i.r. spectroscopy. These copolymers were prepared according to the method of Sugimoto[37], which we have optimized in order to obtain fully soluble poly(3-n-octylthiophene); actually, it was necessary to be sure that the insoluble copolymer did not contain any insoluble poly(3-n-octylthiophene) in order to be able to get an accurate final ratio R_f.

Reactivity of the reticulation point 5

We have performed the copolymerization with an initial ratio R_i equal to 1/10. We obtained a copolymer, which we name P5(1/10), with a final ratio $R_f = 1/4.5$ (see the 'Experimental' part). *Figures 13a, b, c* and *d*, respectively, present the i.r. spectra of the reticulation point **1**, of the reticulation point **5**, of the poly(3-n-octylthiophene) (POT) and of the copolymer P5(1/10). We observed, first, that the reticulation points (labelled or not) have a 'fingerprint': the band at 1590 cm^{-1} (C=C stretching vibration band of the benzene group). Secondly, we observed that the out-of-plane =C–D deformation band in the i.r. spectrum of the deuterated reticulation point **5** (561 cm^{-1}) is approximately twice as intense as the one related to the C=C band of the benzene ring. If the C=C band is observable in the spectrum of the copolymer, that means that at least one of the thiophene groups of the reticulation point has reacted. So, if the two other thiophene groups have not reacted, the intensity of the residual =C–D band will be approximately equal to 4/3 of the one of the C=C band. In the P5(1/10) copolymer i.r. spectrum, the presence of the C=C band (1590 cm^{-1}) is obvious despite the dilution of **5**; on the contrary, no =C–D band is observable. A first explanation of these results is that all the thiophene groups of the reticulation point have reacted with 3-n-octylthiophene (according to i.r. spectroscopy precision). Another explanation may be that a dedeuteration reaction may have happened during the copolymerization reaction because of the acidic reaction medium. Actually, with these results, we cannot exclude this hypothesis, but we shall see later that with the reticulation point **6** we observe a residue of the =C–D band: this result is in favour of the first explanation.

Reactivity of the reticulation point 6

We have performed the copolymerization with an initial ratio R_i equal to 1/5. We obtained a copolymer that we named P6(1/5). *Figures 15a, b, c* and *d*, respectively, present the i.r. spectra of the reticulation point **2**, of the reticulation point **6**, of the poly(3-n-octylthiophene) (POT) and of the copolymer P6(1/5). We observed, first, that the reticulation points (labelled or not) had a 'fingerprint': the band at 1598 cm^{-1} (C=C

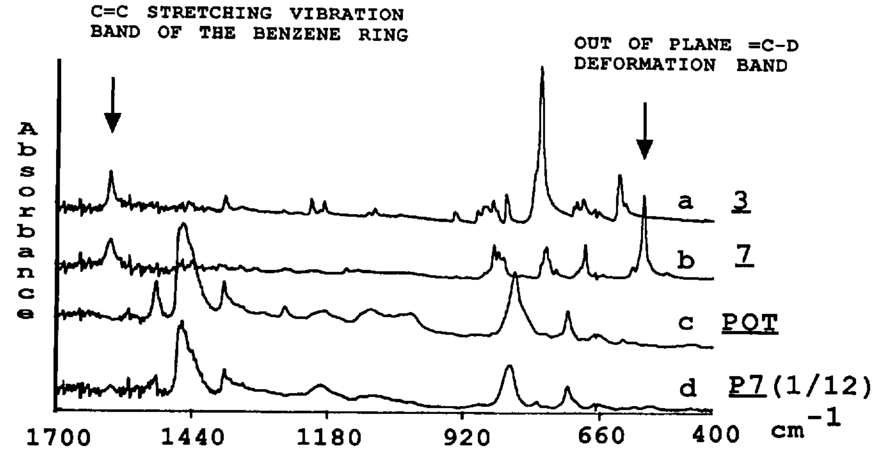


Figure 17 I.r. spectra of (a) 3, (b) 7, (c) POT and (d) P7(1/12)

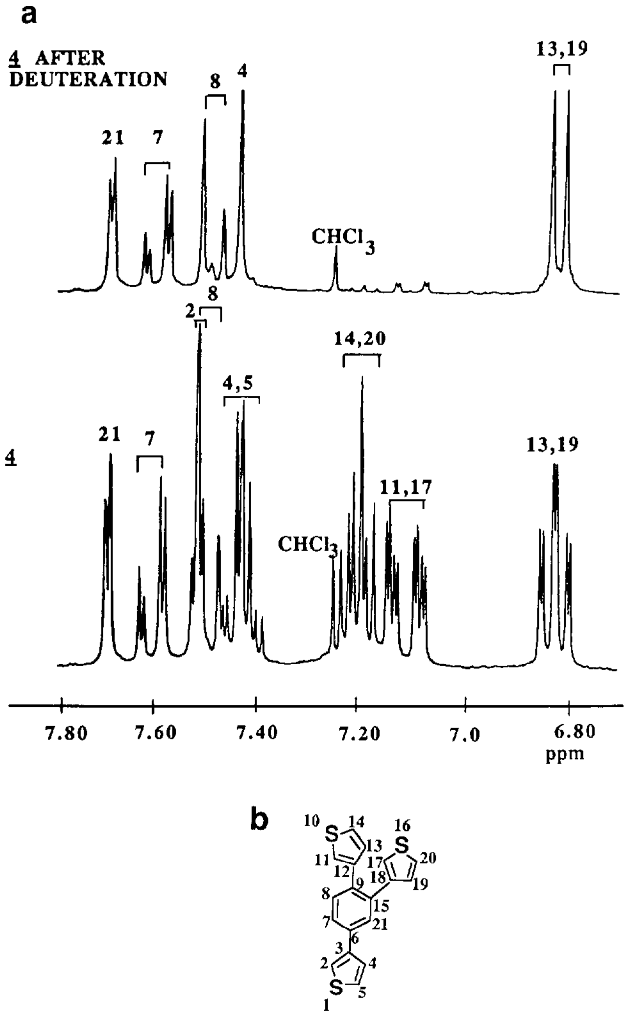


Figure 18 (a) ^{1}H n.m.r. spectra of 4 before and after deuteration. (b) Enumeration of the different positions of 4

stretching vibration band of the benzene group). Secondly, we observed that the intensity of the out-of-plane =C–D deformation band in the i.r. spectrum of the deuterated reticulation point **6** (at 570 cm^{-1}) was approximately six times as intense as the one related to the C=C band of the benzene ring. In the spectrum of P6(1/5), we observed that the =C–D out-of-plane deformation band (570 cm^{-1}) intensity was approximately equal to half that of the C=C band; so, as previously, we can assume that less than 20% of all the thiophene groups of the reticulation points have not reacted. We stress the fact that the remaining presence, in this case, of the =C–D band is an indication that the observed dedeuteration is not due to the acidic medium but to a polymerization reaction.

Reactivity of the reticulation point 7

In this case, we have had to decrease the initial ratio R_i because of the six reactive positions present in the reticulation point: we have chosen $R_i = 1/12$. *Figures 17a, b, c* and *d*, respectively, present the i.r. spectra of **3**, **7**, POT and P7(1/12). The initial ratio R_i leads to a final ratio R_f equal to 1/8. So, in this case, it is more difficult to obtain information about the reticulation point in the copolymer because of its dilution. Nevertheless, if we assume that the reticulation point has not been dedeuterated, according to the relative percentages of the C=C band and of the =C–D band in **7** and in P7(1/12), we can conclude that at least 50% of the reactive positions of the reticulation point have reacted with 3-n-octylthiophene (assuming that no dedeuteration is due to the medium acidity).

Reactivity of the reticulation point 8

Figures 19a, b, c and *d*, respectively, present the i.r. spectra of **4**, **8**, POT and P8(1/12). As previously, we have chosen an initial ratio R_i equal to 1/12, which gives a final ratio R_f equal to 1/9. In the case of **8**, the C=C band is less intense than the one observed in the spectrum of **7**; so, it is difficult to come to a conclusion about the percentage of reactive sites of the reticulation point which are concerned by the polymerization.

EXPERIMENTAL PART

3-n-Octylthiophene (97% purity according to g.c. analysis) was provided by Solvay. THF (Merck, $H_2O < 0.1\%$) was distilled under argon in the presence of CaH_2 and sodium + benzophenone (in order to detect the eventual presence of water). Ethanol (Carlo Erba, $H_2O < 0.1\%$) and $CHCl_3$ (Carlo Erba, $H_2O < 0.03\%$) were distilled

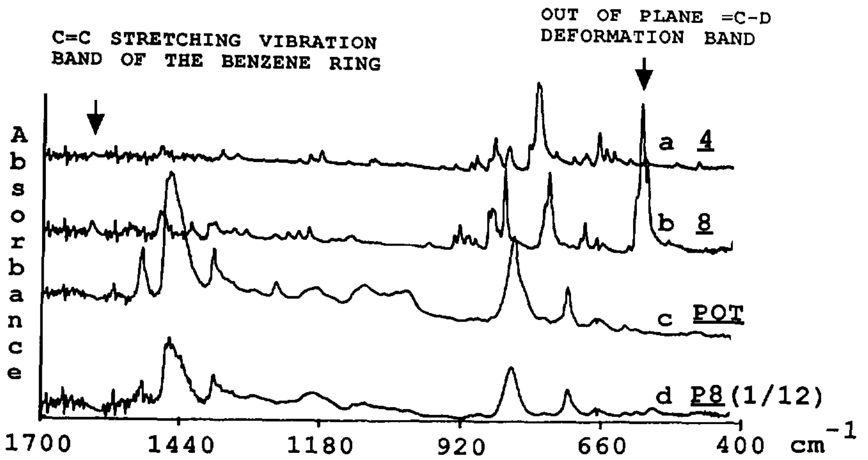
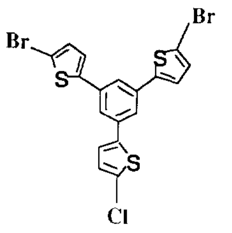
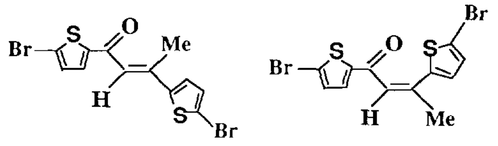


Figure 19 I.r. spectra of (a) **4**, (b) **8**, (c) POT and (d) P8(1/12)



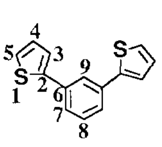
11

Figure 20 1,3-Di(5′-bromo-2′-thienyl)-5-(5′-chloro-2′-thienyl)benzene **11**



12a 12b

Figure 21 Dimers **12a** and **12b** obtained during the preparation of **9**



10

Figure 22 1,3-Di(2′-thienyl)benzene **10**

under argon on $CaCl_2$; CCl_4 (Prolabo, $H_2O < 0.01\%$) was distilled under argon in the presence of P_2O_5; TMEDA (Aldrich) was distilled under argon on KOH. All other reagents, unless otherwise indicated, were commercially available (Aldrich) and were used without further purification.

Instrumentation

Melting points were determined with a Koffler apparatus. I.r. spectra were obtained on KBr discs as far as solid compounds are concerned; liquids were observed between two KBr discs using a Brucker IFS 25 spectrophotometer and are reported as ν (cm^{-1}). U.v.-visible spectra were taken on solutions in $CHCl_3$ using a Hewlett–Packard 8452A diode-array spectrophotometer and are reported as λ (nm). The 200 MHz ^1H n.m.r. spectra were recorded on an AC 200 Brucker spectrometer using the 7.24 ppm chloroform resonance or the 2.03 ppm acetone resonance of the solvent as an internal reference and are reported as δ (ppm) downfield from tetramethylsilane (TMS). J values have been attributed by referring to the values generally obtained in the case of 2-substituted thiophenes ($J_{4\text{-}5} \sim 5$ Hz, $J_{3\text{-}5} \sim 1$ Hz, $J_{3\text{-}4} \sim 3.5$ Hz) and of 3-substituted thiophenes ($J_{2\text{-}4} \sim 1.5$ Hz, $J_{2\text{-}5} \sim 3$ Hz, $J_{4\text{-}5} \sim 5$ Hz). All 200 MHz ^{13}C spectra (^1H-decoupled) were recorded on a AC 200 spectrometer using the 76.9 ppm chloroform resonance or the 204.1 ppm acetone resonance of the solvent as an internal reference (acetone presents the advantage of allowing a better separation of the doublets of doublets related to the aromatic protons of the ethynylthiophenes) and are reported as δ (ppm) downfield from TMS. We have used the 2DXHCORR and COSY programs for n.m.r. characterization when it was necessary. Mass spectra were measured on a Fisons-VG Instrument mass spectrometer of the type ZAB-SEQ working at medium resolution with an e.i.c.i. (electron impact chemical ionization) source at 200°C, 70 eV for all the compounds except the D-labelled ones. As far as the D-labelled compounds are concerned, it is necessary to avoid the formation of fragments resulting from deprotonation; actually, the presence of these fragments induces a bad evaluation of the percentage of deuteration. So, the experiments were performed with a potential of 10 eV at 150°C.

Preparation of 1,3,5-tri(2′-thienyl)benzene 1

Method 1. According to the preparation of Buu-Hoï[58], we have stirred at room temperature a solution of 2-acetylthiophene (6.3 g, 50 mmol) and ethylorthoformate (11.1 g, 75 mmol) in 100 ml of toluene for 1 h, while bubbling dry hydrogen chloride (obtained by adding drop by drop 50 ml of concentrated hydrochloric acid onto concentrated sulfuric acid). HCl bubbling was stopped after 1 h but stirring remained for a further 15 h. The reaction was stopped by adding very slowly a solution of sodium carbonate (10%) until neutralization was reached. The reaction mixture was washed twice with water and finally dried ($MgSO_4$). Insoluble products present in the reaction mixture (polymerization products) were removed by filtration. Evaporation of the toluene afforded the crude product, which was chromatographed on silica gel with hexane as eluant. The first eluted product was 1,3-di(2′-thienyl)benzene **10** (colourless crystalline product) with 5% yield. The second eluted product was the colourless crystalline 1,3,5-tri(2′-thienyl)-benzene **1** (3.95 mmol, 25% yield).

Characterization of 10. Mass spectrometry: found $m/e=242$; required 242. Melting point 86°C.

^{1}H n.m.r. ($CDCl_3$): 7.93 (m, H9); 7.59 (m, H7); 7.40 (t, H8, $J_{7\text{-}8}=7.7$ Hz; we do not detect a coupling between H8 and H9 the J value of which should be around 0.5 Hz); 7.39 (dd, H3, $J_{3\text{-}4}=3.6$ Hz, $J_{3\text{-}5}=1.1$ Hz); 7.33 (dd, H5, $J_{4\text{-}5}=5.1$ Hz); 7.13 (dd, H4) (see *Figure 22*).

^{13}C n.m.r. ($CDCl_3$): 143.8 (assigned to C2); 134.9 (assigned to C6); 129.3 (C8); 127.9 (C4); 124.9 (2 C: C5 and C7); 123.4 (2 C: C3 and C9) (see *Figure 22*).

The characterization of this compound has been reported in the literature[71] but the resolution of the ^{1}H n.m.r. spectrum was bad and ^{13}C n.m.r. data were not reported.

Method 2. According to the method of Elmorsy *et al.*[49], we have added 6 ml of $SiCl_4$ (8.5 g, 50 mmol) at room temperature to a stirred solution of 6.3 g (50 mmol) of 2-acetylthiophene in 50 ml of distilled ethanol (on $CaCl_2$) under argon. The mixture remained stirred for 6 h and was then poured in 100 ml of water. The mixture was extracted three times with 50 ml of dichloromethane and the dichloromethane layer was dried over sodium sulfate. The solution was filtered and the solvent removed under vacuum. The crude product was purified by chromatography (silica gel, hexane; 30 g of silica gel per gram of crude product). The first eluted product was the colourless crystalline **1** (1.35 g, 3.95 mmol, 25% yield).

Preparation of 1,3,5-tri(2′-thienyl)benzene 1 and of 1,2,4-tri(2′-thienyl)benzene 2

According to the method of Masuda *et al.*[59], we have added drop by drop at 20°C 1.08 g (10 mmol) of 2-ethynylthiophene **b1** (first dried over $MgSO_4$) to a suspension of 36 mg (0.1 mmol) of $TaCl_5$ in 10 ml of CCl_4 under argon. The reaction was very exothermic and a rapid darkening of the solution was observed. The mixture was stirred for 1 h and then checked by adding 10 ml of a 1/4 NH_3–methanol solution. The mixture was extracted three times with 50 ml of dichloromethane. The dichloromethane layer was washed with water and then dried over magnesium sulfate. The dichloromethane layer was filtered, the solvent was removed under vacuum and the crude product was purified by chromatography (silica gel, hexane, 30 g of silica gel per gram of crude product). The first eluted product was 1,2,4-tri(2′-thienyl)benzene **2**; the second one was **1**. Beautiful colourless crystals of **2** were obtained under vacuum in toluene (good solvent) with the diffusion of a non-solvent (methanol). The mechanism of this exothermic reaction has been studied by Lachmann *et al.*[72]. We stress the fact that no reaction will occur if the reaction medium is not completely free of water and oxygen (H_2O reacts with $TaCl_5$, which is the precursor of the catalytic species $TaCl_3$; as for $TaCl_3$, it may be oxidized by O_2). At this temperature, we obtained a yield of 80% of dark brown product containing only **1** and **2** with a relative percentage of 40% **1** and 60% **2**. We stress the fact that the separation of **1** and **2** was not easy and the yields of perfectly pure **1** and **2** are respectively 15% and 20%.

Characterization of 1. Analysis: found—C 66.68%, H 3.61%, S 29.32%; required—C 66.67%, H 3.61%, S 29.63%. Mass spectrometry (e.i.): found $m/e=324.0106$; required $m/e=324.010116$. Melting point 160°C.

^{1}H n.m.r. ($CDCl_3$): 7.73 (s, H7); 7.41 (dd, H3, $J_{5\text{-}3}=1.1$ Hz, $J_{4\text{-}3}=3.5$ Hz); 7.33 (dd, H5, $J_{5\text{-}4}=5.1$ Hz); 7.12 (dd, H4) (see *Figures 12a* and *12b*).

^{13}C n.m.r. ($CDCl_3$): 143.5 (assigned to C2); 135.6 (assigned to C6); 127.8 (C4); 125.3 (C5); 123.8 (C3); 122.7 (C7) (see *Figures 12a* and *12b*).

U.v.-vis.: $L_{max}=294$ nm.

I.r. (cm^{-1}): 3098 (=C–H5 (see *Figure 12b*) stretching vibration of thiophene ring); 3069 (=C–H stretching vibration of aromatic rings); 1590 (C=C stretching vibration of benzene); 1446, 1414 (bands assigned to C=C in-plane stretching vibration); 1237, 1191, 1086, 1036, 869, 855, 847, 822, 753, 730 (not assigned); 698 (=C–H5 out-of-plane deformation band; this band has been assigned by comparison with the spectrum of the deuterated compound **5**); 617, 613, 491.

Characterization of 2. Mass spectrometry: found $m/e=324$; required $m/e=324$. Melting point 88°C.

^{1}H n.m.r. ($CDCl_3$): 7.83 (dd, H21, $J_{8\text{-}21}=0.4$ Hz, $J_{7\text{-}21}=1.9$ Hz); 7.66 (dd, H7, $J_{7\text{-}8}=8.0$ Hz); 7.58 (dd, H8); 7.42 (dd, H3, $J_{5\text{-}3}=1.1$ Hz, $J_{4\text{-}3}=3.6$ Hz); 7.36 (dd, H20 or H14, $J_{20\text{-}19}=J_{14\text{-}13}=5.1$ Hz, $J_{20\text{-}18}=J_{14\text{-}12}=1.1$ Hz); 7.34 (dd, H5, $J_{5\text{-}4}=5.1$ Hz); 7.32 (dd, H20 or H14); 7.14 (dd, H4); 7.06 (dd, H19 or H13, $J_{19\text{-}18}=J_{13\text{-}12}=3.5$ Hz); 7.03 (dd, H12 or H18); 7.02 (dd, H13 or H19); 6.97 (dd, H12 or H18) (see *Figures 14a* and *14b*). A COSY experiment has allowed us to ascertain that each group of protons, the chemical shifts of which are (7.36, 7.06, 7.03) and (7.32, 7.02, 6.97), belong to the same thiophene group. We have assumed that the chemical shifts of H3, H4, H5 were the most similar to those of the symmetric isomer.

^{13}C n.m.r. ($CDCl_3$): 143.2 (1 C), 142.2 (2 C assumed) (quaternary carbons probably related to the thiophene groups[73]); 134.1, 133.9, 132.9 (quaternary carbons probably related to the benzene group); 131.3 (C8); 128.4 (C21); 128.1 (C4); 127.3 (1 C: C12 or C18); 127.0 (1 C: C12 or C18); 126.9 (2 C: C13 and C19); 126.1 (1 C: C14 or C20); 126.0 (1 C: C14 or C20); 125.2 (2 C: C5 and C7); 123.6 (C3) (*Figures 14a* and *14b*). The attributions have been made thanks to a 2DXHCORR experiment but we cannot attribute all the signals because it has not been possible to attribute the related protons without any ambiguity.

I.r. (cm^{-1}): 3100, 3094 (=C–H5, 14, 20 stretching vibration of the thiophene rings (see *Figure 14b*)); 3067, 3034 (=C–H stretching vibration); 1598 (C=C stretching vibration of the benzene group); 1477, 1419, 1396 (bands assigned to C=C in-plane stretching vibration); 844, 829, 817 (not assigned); 710, 701 (assigned without ambiguity to the out-of-plane =C–H deformation of the 5, 14, 20 positions of the thiophene groups by comparison with the spectrum of **6**).

*Preparation of 1,3,5-tri(3′-thienyl)benzene **3** and of 1,2,4-tri(3′-thienyl)benzene **4***

According to the method of Masuda *et al.*[59], these two compounds have been obtained in the same way as **1** and **2**; we obtained a yield of 80% of dark brown product containing only **3** and **4** with a relative percentage of 40% **3** and 60% **4**. We stress the fact that the separation of **3** and **4** was not easy and the yields of perfectly pure **3** and **4** are respectively 15% and 20%.

*Characterization of **3**.* Mass spectrometry: found $m/e = 324$; required $m/e = 324$. Melting point 141°C.

^{1}H n.m.r. ($CDCl_3$): 7.72 (s, H7); 7.53 (dd, H2, $J_{2\text{-}5} = 3$ Hz, $J_{2\text{-}4} = 1.3$ Hz); 7.46 (dd, H4, $J_{4\text{-}5} = 5$ Hz); 7.42 (dd; H5) (see *Figures 16a* and *16b*).

^{13}C n.m.r.: 142.4 (assigned to C3); 137.2 (assigned to C6); 126.6 (C5); 126.5 (C4); 123.8 (C7); 120.9 (C2) (see *Figures 16a* and *16b*).

I.r. (cm^{-1}): 3103, 3082 (=C–H2, 5 stretching vibration of the thiophene groups (see *Figure 16b*)); 3059 (=C–H stretching vibration); 1596 (C=C stretching vibration of the benzene group); 1375 (band assigned to C=C in-plane stretching vibration); 772 (assigned to the out-of-plane =C–H deformation of the 2 and 5 positions of the thiophene groups by comparison with the spectrum of **7**); 625 (not assigned).

*Characterization of **4**.* Mass spectrometry: found $m/e = 324$; required 324. Melting point 130°C.

^{1}H n.m.r. ($CDCl_3$): 7.68 (d, H21, $J_{21\text{-}7} = 2$ Hz); 7.59 (dd, H7, $J_{7\text{-}8} = 7$ Hz); 7.50 (dd, H2, $J_{2\text{-}4} = 1.3$ Hz, $J_{2\text{-}5} = 3$ Hz); 7.48 (d, H8); 7.44 (dd, H4, $J_{4\text{-}5} = 5$ Hz); 7.41 (dd, H5); 7.21 (dd, H14 or H20, $J_{11\text{-}14} = J_{17\text{-}20} = 3$ Hz, $J_{13\text{-}14} = J_{19\text{-}20} = 5$ Hz); 7.19 (dd, H14 or H20); 7.13 (dd, H11 or H17, $J_{11\text{-}13} = J_{17\text{-}19} = 1.3$ Hz); 7.08 (dd, H11 or H17); 6.83 (dd, H13 or H19); 6.81 (dd, H13 or H19) (see *Figures 18a* and *18b*). A COSY experiment has allowed us to ascertain that each group of protons, the chemical shifts of which are (7.21, 7.13, 6.83) and (7.19, 7.08, 6.81), belong to the same thiophene group. We have assumed that the chemical shifts of H2, H4, H5 were the most similar to those of the symmetric isomer.

^{13}C n.m.r. ($CDCl_3$): 142.1, 141.6 (2 C assumed) (quaternary carbons probably related to the thiophene groups[73]); 135.7, 135.0, 134.1 (quaternary carbons probably related to the benzene group); 130.5 (C8); 128.9 (C19 or C13); 128.8 (C19 or C13); 128.2 (C21); 126.3 (C5); 126.2 (C4); 125.4 (C7); 124.8 (C20 or C14); 124.6 (C20 or C14); 122.9 (C17 or C11); 122.8 (C17 or C11); 120.4 (C2) (see *Figures 18a* and *18b*).

I.r. (cm^{-1}): 3097 (=C–H2, 5, 11, 14, 17, 20 stretching vibration of the thiophene rings (see *Figure 18b*)); 3082, 3034 (=C–H stretching vibration); 1602 (C=C stretching vibration of the benzene group); 1475 (bands assigned to C=C in-plane stretching vibration); 859, 832 (not assigned); 780, 777 (assigned without ambiguity to the out-of-plane =C–H deformation of the 2, 5, 11, 14, 17, 20 positions of the thiophene groups by comparison with the spectrum of **8**); 667 (not assigned).

*Preparation of 1,3,5-tri(5′-deutero-2′-thienyl) **5** and of 1,2,4-tri(5′-deutero-2′-thienyl)benzene **6***

Under an inert atmosphere, 1.62 g (5 mmol) of trithienylbenzene were dissolved in 25 ml THF. At 0°C, 6.6 ml of butyllithium in hexane (2.5 M, 16.5 mmol) were added dropwise. The solution became green coloured and some salts appeared gradually. The mixture was left under stirring at room temperature for 2 h. Then, 0.4 g of deuterium oxide (99.8%, 20 mmol) were added at 0°C. The solution became yellow-brown and was poured into 200 ml of water. The mixture was neutralized with dilute HCl and extracted three times with 50 ml of ether. The joined organic extracts were dried over anhydrous magnesium sulfate, filtered and the solvents were distilled off. We obtain **5** and **6** as slightly brown solids with 99% yield after two successive deuteration reactions.

*Characterization of **5**.* Mass spectrometry: see *Table 1*.

^{1}H n.m.r. ($CDCl_3$): 7.73 (s, H7); 7.40 (d, H3, $J_{4\text{-}3} = 3.6$ Hz); 7.11 (d, H4) (see *Figures 12a* and *12b*).

^{13}C n.m.r. ($CDCl_3$): 143.4 (C2); 135.6 (C6); 127.7 (C4); 125.1 (t, C5, $J_{C5\text{-}D} = 28$ Hz); 123.8 (C3); 122.7 (C7) (see *Figure 12b*).

I.r. (cm^{-1}): 3066 (=C–H stretching vibration); 2312 (=C–D stretching vibration); 1590 (C=C in-plane stretching vibration of benzene); 1436, 1406 (bands related to C=C in-plane stretching vibration); 1224, 1189, 1034, 866, 806, 758, 744, 725, 686 (not assigned); 561 (=C–D out-of-plane deformation bands of thiophene (strong)).

*Characterization of **6**.* Mass spectrometry: see *Table 1*.

^{1}H n.m.r. ($CDCl_3$): 7.83 (dd, H21, $J_{8\text{-}21} = 0.4$ Hz, $J_{7\text{-}21} = 1.9$ Hz); 7.66 (dd, H7, $J_{7\text{-}8} = 8.0$ Hz); 7.58 (dd, H8); 7.42 (d, H3, $J_{3\text{-}4} = 3.5$ Hz); 7.13 (d, H4); 7.05 (d, 1 H, $J = 3.5$ Hz); 7.01 (d, 2 H, $J = 3.5$ Hz); 6.96 (d, 1 H, $J = 3.5$ Hz) (these four last non-assigned chemical shifts are related, of course, to H12, H13, H18 and H19) (see *Figures 14a* and *14b*).

^{13}C n.m.r. ($CDCl_3$): 143.1 (1 C), 142.1 (2 C assumed) (quaternary carbons probably related to the thiophene groups[73]); 134.1, 133.9, 132.9 (probably related to the benzene ring); 131.3 (C8); 128.4 (C21); 128.0 (C4); 127.3 (1 C: C12 or C18); 127.0 (1 C: C12 or C18); 126.8 (2 C: C13 and C19); 123.6 (C3); the triplets of C5, C14, C20 have not been observed because of insufficient accumulation (see *Figure 14b*).

I.r. (cm^{-1}): 3070, 3030 (=C–H stretching vibration); 2315 (=C–D stretching vibration); 1598 (C=C stretching vibration of the benzene ring); 1475, 1418, 1392 (C=C stretching vibration of the thiophene group); 894, 817, 807, 758 (not assigned); 570, 557 (out-of-plane =C–D deformation band).

*Preparation of 1,3,5,-tri(2′,5′-dideutero-3′-thienyl)benzene **7** and of 1,2,4-tri(2′,5′-dideutero-3′-thienyl)benzene **8***

Under an inert atmosphere, 100 mg (0.31 mmol) of trithienylbenzene were dissolved in 10 ml of TMEDA[74]. At room temperature, 5 ml of butyllithium in hexane (1.6 M, 8 mmol) were added dropwise. The solution became slightly orange coloured and some salts appeared gradually. The mixture was left under stirring at room temperature for 20 and 44 h as far as **7** and **8** are respectively concerned. Then, 2 ml of deuterium oxide (99.8%, 111 mmol) were added at room temperature. The solution was poured into 100 ml of water. The mixture was neutralized with dilute HCl and extracted three times with 50 ml of ether. The joined organic extracts were dried over anhydrous magnesium sulfate, filtered and the solvents were distilled off. We obtained **7** and **8** as slightly brown solids with 99% yield.

Characterization of 7. Mass spectrometry: see *Table 1*.

^{1}H n.m.r. ($CDCl_3$): 7.72 (s, H7); 7.45 (s, H4) (see *Figures 16a* and *16b*).

I.r. (cm^{-1}): 3059 (=C–H stretching vibration); 2321 (=C–D stretching vibration); 1596 (C=C stretching vibration of benzene); 862, 854, 843, 761, 690 (not assigned); 577 (out-of-plane =C–D deformation band).

Characterization of 8. Mass spectrometry: see *Table 1*.

^{1}H n.m.r.: 7.68 (d, H21, $J_{7\text{-}21}=2$ Hz); 7.59 (dd, H7, $J_{7\text{-}8}=7$ Hz); 7.48 (d, H8); 7.43 (s, H4); 6.82 (s, H13 or H19); 6.80 (s, H13 or H19) (see *Figures 18a* and *18b*).

I.r. (cm^{-1}): 3084, 3034 (=C–H stretching vibration); 2314 (=C–D stretching vibration); 1602 (C=C stretching vibration of benzene); 1477, 1420, 1374 (probably related to C=C stretching vibration); 869, 863, 839, 758, 691 (not assigned); 588, 577 (out-of-plane =C–D deformation).

Preparation of 1,3,5-tri(5′-bromo-2′-thienyl)benzene 9

Method 1. According to the preparation method of Buu-Hoi *et al.*[58], we have prepared **9** like the unfunctionalized compound **1**. We have purified **9** by recrystallization in acetone. The colourless crystalline **9** was obtained with a yield of 20%. According to mass spectrometry and ^{1}H n.m.r. analysis, the crystals contain less than 10% of **11**.

Characterization of 9. Mass spectrometry: found $m/e=361$; required $m/e=361$. Melting point 183°C.

^{1}H n.m.r. ($CDCl_3$): 7.50 (s, H7); 7.10 (d; H3 or H4; $J_{3\text{-}4}=3.9$ Hz); 7.05 (d, H3 or H4) (see *Figure 12b*).

^{13}C n.m.r. ($CDCl_3$): 144.3; 135.2; 130.7; 124.1; 122.1; 112.3 (see *Figure 12b*).

I.r. (cm^{-1}): 3095, 3077, 3049 (=C–H stretching vibration); 1592 (C=C stretching vibration of the benzene group); 1449, 966, 854, 786 (not assigned); 488 (=C–Br).

Method 2. According to the method of Elmorsy *et al.*[49], we have added 6 ml of $SiCl_4$ (8.5 g, 50 mmol) at room temperature to a stirred solution of 10.24 g (50 mmol) of 5-bromo-2-acetylthiophene in 50 ml of distilled ethanol under argon. The mixture was refluxed for 6 h, leading to the formation of pale yellow crystalline **12** with a yield of 20%. According to mass spectrometry and ^{1}H n.m.r. analysis, the crystals contain less than 10% of molecules one thiophene ring of which has been substituted with a chlorine atom.

Characterization of 12. Mass spectrometry: found $m/e=392$; required $m/e=392$. Melting point 104°C.

^{1}H n.m.r. ($CDCl_3$): 7.44 (d, 1 H, $J=4.0$ Hz); 7.15 (d, 1 H, $J=4.0$ Hz); 7.09 (d, 1 H, $J=4.0$ Hz); 7.04 (d, 1 H, $J=4.0$ Hz) (these four signals are assigned to the protons of the two thiophene groups); 6.94 (m, 1 H) (assigned to the proton of the double bond); 2.59 (d, 3 H, $J=1.1$ Hz) (assigned to the CH_3 group).

I.r. (cm^{-1}): 3106, 3090, 3074 (=C–H stretching vibration); 2955, 2922 (stretching vibration of the CH_3 group); 1630 (C=O); 1584 (C=C); 1521; 1411.

Preparation of 2-trimethylsilylethynylthiophene b′1

At room temperature, in a flask containing 400 ml of degassed diisopropylamine were added successively under an inert atmosphere while stirring 21 g (0.1 mol) of 2-iodothiophene, 10.8 g (0.11 mol) of trimethylsilylacetylene, 0.23 g (0.33 mmol) of bis(triphenylphosphine)-palladium dichloride ($Pd(PPh_3)_2Cl_2$) and 0.19 g (1 mmol) of copper iodide. The salts of amine then precipitated gradually. Half an hour later, exothermicity was observed. The reaction was complete after 2 h (no more adduct observed by n.m.r. analysis). The diisopropylamine was then removed under vacuum. The residue was treated with 500 ml of water and extracted three times with 100 ml of dichloromethane. The organic extracts were then dried over anhydrous magnesium sulfate and filtered over a short alumina column to remove the catalyst. The dichloromethane was then removed under vacuum. We obtained 17.1 g (95% yield) of a brown oil containing 98% of **b′1** (according to gas chromatography analysis). It is not necessary to purify the product by distillation before using it in the following reactions.

Characterization of b′1. Boiling point 104°C/15 mmHg (in agreement with the literature[75]).

^{1}H n.m.r. (C_3D_6O): 7.43 (dd, H4, $J_{4\text{-}5}=5.1$ Hz, $J_{4\text{-}3}=3.6$ Hz); 7.25 (dd, H3, $J_{3\text{-}5}=1.1$ Hz); 7.00 (dd, H5); 0.22 (s, 9 H_{SiMe_3}) (see *Figure 23*).

^{13}C n.m.r. (C_3D_6O): 131.5, 126.6, 126.0, 121.8 (assigned to the thiophene group); 97.0, 96.5 (assigned to C6 and C7); −1.9 ($SiMe_3$) (see *Figure 23*).

I.r. (cm^{-1}): 3105, 3078 (=C–H stretching vibration of thiophene); 2960, 2898 (–C–H stretching of the $SiMe_3$ group); 2146 (triple bond elongation); 1250 (symmetrical deformation vibration of the CH_3 group in $SiMe_3$); 759 ($Si(CH_3)_3$). This type of reaction has been widely used to prepare acetylenes derivatives[63–69,75,76]. Compound **b′1** has already been prepared by a similar method[65], but it has never been described in detail previously.

We stress the fact that it is important to work under an inert atmosphere to prevent coupling leading to the diacetylene 1,4-dithienylbutadiyne[76]. A mechanism for the understanding of this reaction has already been proposed[77].

Sometimes, diethylamine has been used for this type of reaction[64] but the use of this amine was unsuccessful in this case.

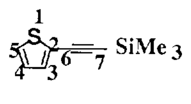
Preparation of 3-trimethylsilylethynylthiophene b′3

We have prepared **b′3** from the less reactive 3-bromothiophene[64] according to the method developed by Brandsma *et al.*[69], the only difference being that we have engaged a slight excess of trimethylsilylacetylene (1.1 mol per mole of 3-bromothiophene). The desired product **b′3** was obtained as a colourless oil with 86% yield after distillation (purity of more than 98% (g.c. analysis)).

Characterization of b′3. Boiling point 74°C/4 mmHg.

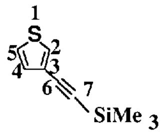
^{1}H n.m.r. (C_3D_6O): 7.62 (dd, H2, $J_{2\text{-}5}=3.0$ Hz, $J_{2\text{-}4}=1.1$ Hz); 7.42 (dd, H5, $J_{4\text{-}5}=5.0$ Hz); 7.12 (dd, H4); 0.21 (s, 9 H_{SiMe_3}) (see *Figure 24*).

^{13}C n.m.r. (C_3D_6O): 129.1, 129.0, 125.0, 121.8 (assigned to the thiophene group); 99.7, 92.6 (assigned to C6 and C7); −1.8 ($SiMe_3$) (see *Figure 24*).



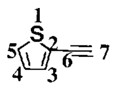
b'1

Figure 23 2-Trimethylsilylethynylthiophene **b'1**



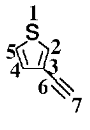
b'3

Figure 24 3-Trimethylsilylethynylthiophene **b'3**



b1

Figure 25 2-Ethynylthiophene **b1**



b3

Figure 26 3-Ethynylthiophene **b3**

I.r. (cm^{-1}): 3108 (=C–H stretching vibration of thiophene); 2958, 2897 (–C–H stretching of the $SiMe_3$ group); 2170, 2153, 2106 (triple bond elongation); 1249 (symmetrical deformation of the CH_3 group in $SiMe_3$); 760 ($Si(CH_3)_3$).

*Preparation of 2-ethynylthiophene **b1** and of 3-ethynylthiophene **b3***

Compounds **b1** and **b3** were prepared in the same way from **b'1** and **b'3** respectively: in 200 ml of methanol at room temperature was added 0.7 g (5 mmol) of K_2CO_3. The silylethynyl derivative was then added (0.1 mol) and the medium was left under stirring for 2 h and then poured in 400 ml of water. The mixture was extracted three times with 100 ml of dichloromethane. The joined organic extracts were dried over anhydrous magnesium sulfate and the whole dichloromethane was distilled off without vacuum. The resulting ethynyl derivative was then distilled under reduced pressure to give a colourless oil. The mechanism of this reaction has been studied[78]: it is not necessary to degas as has already been advised in the literature[63,75]. It is also possible to perform the desilylation of the acetylenic site with 1 M KOH in methanol.

Compound **b1** was obtained with a yield of 83% (purity of more than 99% (g.c. analysis)); **b3** was obtained with a yield of 83% (purity of more than 98% (g.c. analysis)).

*Characterization of **b1**.* Boiling point 43–44°C/15 mmHg (46°C/15 mmHg reported in the literature[60]).

^1H n.m.r. ($CDCl_3$): 7.33 (dd, H3, $J_{3\text{-}4} = 3.7$ Hz, $J_{3\text{-}5} = 1.1$ Hz); 7.25 (dd, H5, $J_{5\text{-}4} = 5.1$ Hz); 6.98 (dd, H4); 3.42 (s, H of the triple bond) (see *Figure 25*).

^{13}C n.m.r. ($CDCl_3$): 132.7 (C3); 127.2 (C5); 126.6 (C4); 121.7 (C2); 81.3 (C7); 76.8 (C6) (see *Figure 25*).

I.r. (cm^{-1}): 3293 (C–H elongation next to a triple bond); 3106, 3077 (=C–H stretching vibration of thiophene); 2105 (triple bond elongation).

*Characterization of **b3**.* Boiling point 44°C/15 mmHg (48–50°C/15 mmHg reported in the literature[60]).

^1H n.m.r. (C_3D_6O): 7.63 (dd, H2, $J_{2\text{-}5} = 3.0$ Hz, $J_{2\text{-}4} = 1.1$ Hz); 7.42 (dd, H5, $J_{4\text{-}5} = 5.0$ Hz); 7.13 (dd, H4); 3.48 (s, H7) (see *Figure 26*).

^{13}C n.m.r. (C_3D_6O): 128.6 (C2); 128.5 (C4); 124.6 (C5); 120.0 (C3); 76.9 (C6); 75.9 (C7) (see *Figure 26*).

I.r. (cm^{-1}): 3292 (C–H elongation next to a triple bond); 3107 (=C–H stretching vibration of thiophene); 2112 (triple bond elongation).

Preparation of poly(3-n-octylthiophene) (POT)

We have optimized the method of preparation of fully soluble POT[37] in order to avoid any contribution of insoluble POT in the insoluble copolymer and so to be able to reach R_f.

Under argon, we dissolved (partially) 6.61 g (40.8 mmol) of anhydrous $FeCl_3$ in 80 ml of distilled chloroform and we added drop by drop during 10 min a degassed solution of 2 g (10.2 mmol) of 3-n-octylthiophene in 20 ml of distilled chloroform while stirring vigorously. We stress the fact that the time used for the addition of 3-n-octylthiophene and the stirring rate have to be constant: these parameters have a great influence on the quality of the obtained polymer[40] (solubility as far as poly(3-n-octylthiophene) is concerned). The reaction medium became dark green as soon as 3-n-octylthiophene was added. The mixture remained stirring for 2 h. It was then poured in 300 ml of methanol and this mixture was stirred for 2 h. Insoluble components were filtered and extracted (Soxhlet) with methanol for 72 h. Solid product was dried until constant weight and further extracted (Soxhlet) with chloroform for 4 h. The poly(3-n-octylthiophene) thus obtained was fully soluble in chloroform. After evaporation we obtained 1.59 g of POT (80% yield; the other 20% consists of soluble oligomers and 3-n-octylthiophene). Notice that if the efficiency of the stirring is good enough, the crude doped polymer looks like a finely divided solid contrary to the solid obtained with bad stirring. In the case of bad stirring, the dedoping of the 'block' of polymer will be more difficult than the one of the finely divided solid leading to bad solubility of the POT.

Preparation of P5(1/10), P6(1/5), P7(1/12) and P8(1/12)

Concerning the preparation of these copolymers devoted to the study of the reactivity of the different reticulation points, we have adapted the method optimized for the preparation of fully soluble POT because of the small amounts of 3-n-octylthiophene used for the reaction. Another modification concerns the amount of added $FeCl_3$. In the presence of reticulation points, we had to take into account the number of polymerization sites. So, we had to add 6 and 12 mol respectively of $FeCl_3$ per mole of **5**, **6** and **7**, **8** in addition to the 4 mol related to 3-n-octylthiophene.

Table 5 Amounts of reactants used in preparation of copolymers

Reticulation points	3-n-Octylthiophene		Reticulation point		$FeCl_3$	
	mg	mmol	mg	mmol	mg	mmol
5	200	1.02	66.8	0.204	860	5.3
6	200	1.02	33.4	0.102	760	4.7
7	200	1.02	28.1	0.085	826	5.1
8	200	1.02	28.1	0.085	826	5.1

Table 6 Doping level and conductivity of copolymers

Copolymer	Doping level (mol%)	Conductivity (S cm^{-1})
P5(1/10), $R_f = 1/4.5$	9	0.7
P6(1/5), $R_f = 1/3$	7	0.2
P7(1/12), $R_f = 1/8$	10	0.6
P8(1/12), $R_f = 1/9$	8	2.0
Poly(**1**), $R_f = \infty$	Cannot be doped in this way	Non-conducting

Except for these two modifications, the method of preparation being the same, we only report in *Table 5* the amounts of 3-n-octylthiophene, reticulation points and $FeCl_3$.

Doping of the copolymers

Copolymers were doped using a solution of $FeCl_3 \cdot 6H_2O$ in a mixture of nitromethane (which dissolves the dopant) and chloroform (in which the copolymers swell). The poly(**1**) and the four copolymers P5, P6, P7 and P8 (40 mg) were first allowed to swell in chloroform (8 ml) at room temperature for a few minutes. Secondly, the solution of $FeCl_3 \cdot 6H_2O$ (55 mg in 6 ml of nitromethane, 3.4×10^{-3} M) was added and the sample remained without stirring at room temperature for 60 h. The doped samples were then washed with clean nitromethane and dried under vacuum at room temperature; they were reweighed to determine the amount of dopant uptake (*Table 6* gives the molar doping level).

Conductivity measurements

Doped samples are obtained as powder. Doped P5, P6, P7 and P8 have been pressed as pellets of respectively 0.79, 0.94, 0.36 and 0.64 mm depth. Doped poly(**1**) cannot be pressed and does not seem to be doped because its colour remains yellow (doped P5, P6, P7 and P8 became black). The conductivity was measured by the collinear four-point probe method[79]. The measured conductivity remained constant as the current density was varied over several decades. Conductivity values are reported in *Table 6*.

FIRST CHARACTERIZATION OF THE COPOLYMERS

The preliminary characterizations of the copolymers of high R_f deal with i.r. spectrometry, solvent swelling observation and conductivity measurements.

In order to study the evolution of the properties of the copolymers according to R_f, we have also prepared the poly(reticulation point **1**) for which $R_f = \infty$; the R_f of poly(3-n-octylthiophene) is equal to 0.

I.r. spectrometry

This has allowed us to point out the effective copolymerization between the different reticulation points and 3-n-octylthiophene.

Solvent swelling

We observe (qualitatively) that the four copolymers P5(1/10), P6(1/5), P7(1/12) and P8(1/10) swell in apolar solvent such as chloroform (the volume after swelling is at least four times the initial one); that is not the case for poly(**1**), which does not swell at all.

Conductivity

We only report preliminary experiments concerning P5(1/10), P6(1/5), P7(1/12) and P8(1/12). We have doped these copolymers with $FeCl_3 \cdot 6H_2O$. The obtained conductivities (see *Table 6*) are comparable to or even higher than those of poly(n-octylthiophenes) prepared in the same way[80]. Poly(**1**) could not be doped in this way. After doping, these four copolymers no longer swelled.

CONCLUSION

In order to get conducting polymers, the dimensionality of which is higher than 2, we have prepared fully conjugated reticulation points and copolymerized them with 3-n-octylthiophene. All the reticulation points have been characterized and their reactivity with 3-n-octylthiophene has been demonstrated thanks to their labelling with deuterium. The copolymers swell in apolar solvents even with a very high level of reticulation point (30 mol%), although the poly(reticulation point **1**) does not swell. Concerning the conductivity, we did not succeed in doping the poly(reticulation point **1**) whereas, in the same conditions, copolymers (30 mol% relative concentration of reticulation points) were doped and exhibit a conductivity comparable to that of poly(3-n-octylthiophene). Further characterization of such copolymers covering a range of R_f from 1/3 to 1/90 will be presented in the second paper of this series.

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