

# <sup>1</sup>H-<sup>13</sup>C NMR inverse detection of poly(3-hexylthiophene): characterization of the structural defects

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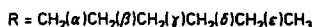
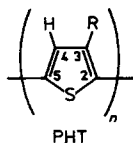
## SUMMARY:

NMR inverse detection was applied to the study of regiochemistry of a highly *head to tail* (HT)-regioregular poly(3-hexylthiophene) (PHT). It proved to be a valuable tool in the characterization of polymerization defects not directly revealable or assignable by inspection of the one-dimensional <sup>13</sup>C spectrum. Almost all the <sup>13</sup>C chemical shifts of the four configurational triads of PHT were derived by utilizing the aromatic protons, whereas through the  $\alpha$ -protons of the aliphatic chain only carbons belonging to HT-HT connections were detected, owing to the high regiospecificity of the PHT under study and to the high multiplicity of aliphatic proton signals. The correctness of the model of the interpretation of PHT structure based on the four trimers of 3-hexylthiophene was confirmed.

## Introduction

Polythiophenes are synthetic conducting materials with a wide range of applications<sup>1–4</sup>. Alkyl chains in  $\beta$  position enhance their solubility in organic solvents and facilitate their characterization in solution by different spectroscopic techniques (NMR, IR, UV)<sup>5–13</sup>. The <sup>1</sup>H and <sup>13</sup>C chemical shifts are useful probes for the characterization of the substitution pattern<sup>5–13</sup> and have mainly been derived from the one-dimensional spectra. Applications of two-dimensional techniques have also been reported<sup>6, 7, 12</sup>.

The characterization of the structural defects of poly(3-hexylthiophene) (PHT) through the analysis of the proton chemical shifts of the aromatic region has led to contradictory interpretations<sup>10, 11</sup>. A recent study<sup>13</sup> underlined the importance of the aromatic <sup>13</sup>C chemical shifts of the central unit of the four trimers of 3-hexylthiophene as a key to the interpretation of PHT structure, but an unambiguous correlation between the proton and the four carbon aromatic signals belonging to the same triad of PHT has not yet been demonstrated.



This work reports an application to PHT of proton-detected chemical shift correlation spectroscopy, based on multiple-quantum coherence (HMQC<sup>14</sup>) and HMBC<sup>15</sup>) experiments, and demonstrates the high level of information afforded by these techniques: not only the major *head to tail* (HT) regioregular part of PHT but also the three minor triads are characterized.

## Experimental part

The PHT sample used in this work (85% HT regioregular) was a gift from Dr. G. Barbarella. The synthesis is reported in ref. <sup>13</sup>)

NMR spectra were obtained at 300 K using a Bruker AMX-400 WB operating at 400.13 and 100.61 MHz, for <sup>1</sup>H and <sup>13</sup>C, respectively, on a CDCl<sub>3</sub> saturated solution. <sup>1</sup>H and <sup>13</sup>C  $\delta$  values are quoted to internal CHCl<sub>3</sub> at 7.26 and 77.0 ppm, respectively.

<sup>13</sup>C  $\delta$  were assigned from inverse-detected heteronuclear multiple-quantum coherence (HMQC)<sup>14</sup>) and heteronuclear multiple-bond coherence (HMBC)<sup>15</sup>) shift-correlation experiments, performed with standard pulse sequences.

HMQC parameters: spectral width ( $f_2$ ) = 1 ppm, 512 complex points; spectral width ( $f_1$ ) = 30 ppm, 256  $t_1$  increments with 32 scans per  $t_1$  value; relaxation and evolution delays, 0.5 s and 2.97 ms, respectively. Zero filling in  $f_1$  and  $f_2$ , sine function in  $f_1$  and sensitivity function in  $f_2$  (LB = 1) were applied before Fourier transformation.

HMBC parameters: as for HMQC, but spectral width ( $f_1$ ) = 150 ppm, 128 scans per  $t_1$  value, and delay for long-range coupling constant evolution = 100 ms.

## Results and discussion

The directly acquired proton-decoupled <sup>13</sup>C NMR spectrum of our PHT consists of only four signals in the aromatic region (at  $\delta$  = 139.89, 133.71, 130.51 and 128.61 ppm) even after 8000 scans, corresponding to the major HT component. The <sup>1</sup>H spectrum, on the other hand, reveals structural defects: in the aromatic region three minor signals are present<sup>13</sup>) downfield with respect to the major one, and a similar but more complex situation is found in the aliphatic region<sup>16</sup>). The resonances in the aromatic region have been assigned<sup>10, 13</sup>) to the four triads of PHT: *head to tail-head to tail* (HT-HT), *tail to tail-head to tail* (TT-HT), *head to tail-head to head* (HT-HH) and *tail to tail-head to head* (TT-HH).

The signals of the three minor triads were not detected in the directly-acquired <sup>13</sup>C NMR spectrum owing to the low receptivity of the nucleus involved (<sup>13</sup>C was at natural abundance) and to the high HT-regioregularity of our PHT. These problems were overcome by acquiring the more receptive <sup>1</sup>H nucleus<sup>17</sup>) and obtaining the <sup>13</sup>C chemical shifts in the second dimension of selected shift-correlated experiments. Inverse-detected <sup>1</sup>H-<sup>13</sup>C two-dimensional NMR spectroscopy is a widely-applied technique in the study of natural products<sup>18</sup>), porphyrins and polysaccharides<sup>19</sup>), and oligonucleotides<sup>20, 21</sup>); and its application to the configurational assignments for poly(methacrylonitrile)<sup>22</sup>) and to the study of poly(3-octylthiophene)<sup>12</sup>) have recently been reported.

The carbon directly bonded to the aromatic proton of each triad was found through a coupled HMQC experiment (Fig. 1). The numerical results are similar to those

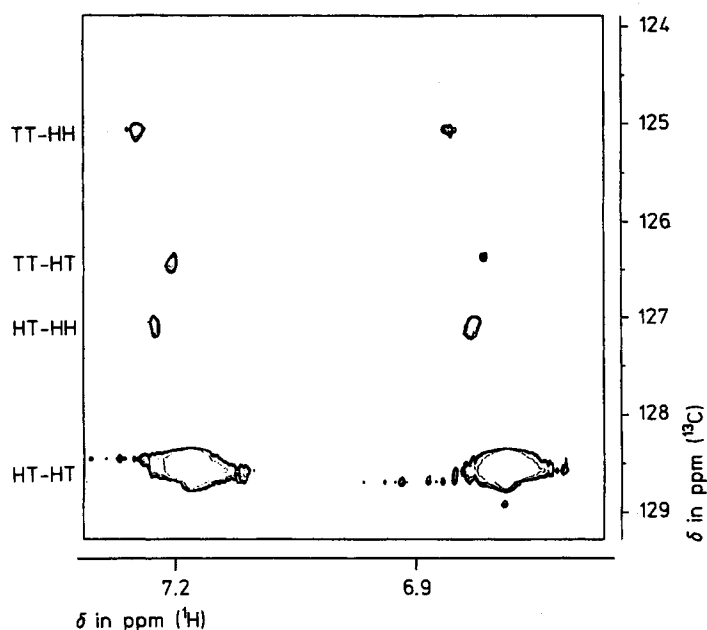


Fig. 1. Coupled HMQC spectrum of the aromatic region of PHT. Four doublets corresponding to the C-4 carbons are detected for the four triads

obtained by Sato<sup>6a)</sup> with a decoupled heteronuclear chemical-shift correlation experiment ( $^{13}\text{C}$  directly acquired) on poly(3-dodecylthiophene). We opted for a coupled experiment for two reasons: firstly, to avoid the problems of interpretation of decoupled HMQC spectra, in which signals of very low intensity can be lost if  $^1\text{H}$ - $^{12}\text{C}$  major signals are poorly suppressed; secondly, to verify that the three minor signals were actually due to H-4 protons and not to H-2 or H-5 coming from small amounts of  $\alpha,\beta$ -coupling paths. The direct proof that these proton signals are really H-4's are the numerical values of  $^1\text{H}$ - $^{13}\text{C}$  one-bond coupling constants (in the range 163 to 165 Hz in our PHT) typical of  $\beta$ -(C,H) fragments of the thiophene ring and very different from the same coupling in  $\alpha$ -(C,H) fragments (189 Hz in thiophene)<sup>23)</sup>.

In principle, the aromatic and, alternatively, the  $\alpha$ -aliphatic chain protons can be used as probes for the detection and assignment of the remaining aromatic  $^{13}\text{C}$  signals through selected HMBC experiments. Both types of protons exhibit long-range coupling constants with the carbons of the thiophene ring<sup>16,23)</sup>. The HMBC experiment in which the aromatic protons were detected, reported in Fig. 2, enables the remaining aromatic carbons and the C- $\alpha$  of the aliphatic chain of the regioregular HT part to be detected. This second experiment suffers more from sensitivity problems than the HMQC experiment because long-range coupling constants of low entities are involved. Nevertheless, nearly all the possible aromatic carbons are detected even for

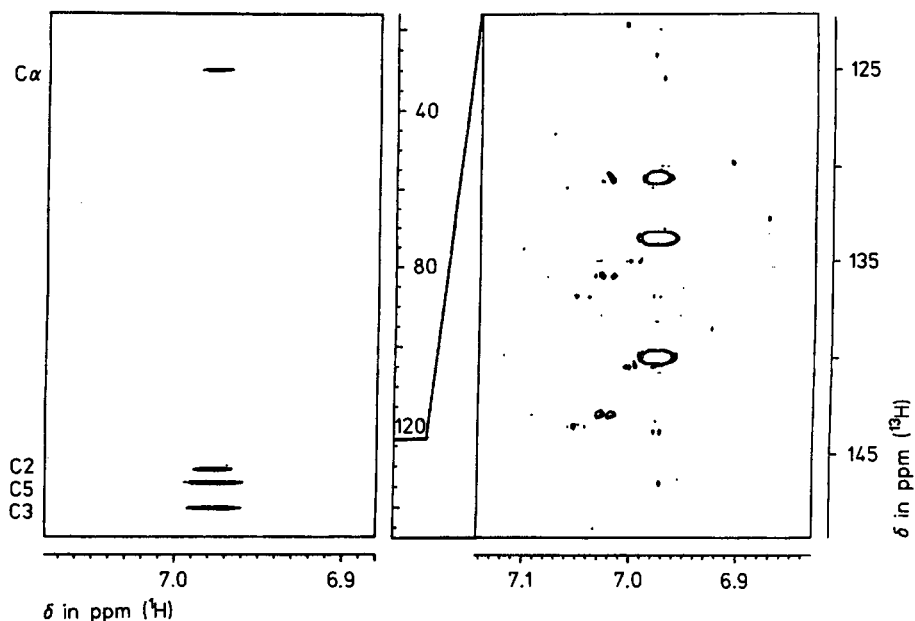
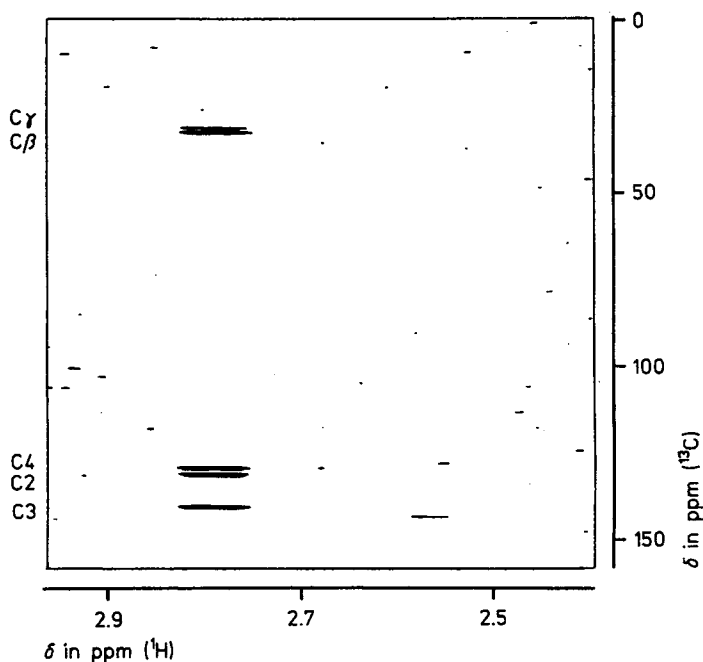


Fig. 2. HMBC spectrum of PHT detected through the aromatic protons. On the left the spectrum relative to the global carbon region, on the right the expanded aromatic region with increased intensity

the three minor triads, except C-2 and C- $\alpha$ , whose responses are weakened in the experimental conditions adopted<sup>15</sup>). In fact, the evolution delay was selected in order to maximize the correlations relative to long-range coupling constants of about 5 Hz (see Exptl. part).

An analogous result can be achieved by using the aliphatic  $\alpha$ -protons for the inverse detection of the relayed aromatic and aliphatic carbons (Fig. 3). The proton aliphatic region of PHT presents two groups of signals at  $\delta = 2.80$  (major) and 2.56 (minor) ppm which can be assigned to the  $\alpha$ -protons of hexyl chains in HT and HH connections, respectively. The carbons C-2, C-3, C-4, C- $\beta$  and C- $\gamma$  were easily detected for the major regioregular PHT but this approach was less effective in detecting long-range correlations in the three minor triads owing to the higher signal multiplicity. Only the long-range correlations between the multiplet at  $\delta = 2.56$  ppm and carbons at  $\delta = 142.8$  ppm and 127.3 ppm were detected. Despite the problems involved in the present case, a carefully set-up HMBC experiment based on aliphatic protons can be a valuable alternative tool in the regiochemical assignment of poly(3-alkylthiophene)s, especially when the aromatic approach is, for any reason, not feasible.

The chemical shifts of aromatic protons and carbons of the four triads of PHT are reported in Tab. 1 in comparison with those of the central units of the four trimers of

Fig. 3. HMBC spectrum of PHT detected through the  $\alpha$ -aliphatic protonsTab. 1. Aromatic  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts ( $\delta$  in ppm) of the central unit of triads of PHT and of trimers of 3-hexylthiophene<sup>a)</sup>

	H-4	C-2	C-3	C-4	C-5
PHT:					
major	6.98	130.7	139.9	128.6	133.9
	7.00	—	140.4	126.5	135.0
	7.02	—	142.8	127.1	135.7
	7.05	—	143.6	125.0	137.0
Central unit of					
trimers:					
HT-HT	6.92	130.7	139.5	128.6	133.9
TT-HT	6.96	129.8	139.9	126.2	135.2
HT-HH	6.98	128.6	142.6	127.3	135.9
TT-HH	7.00	127.5	143.1	124.9	137.3

<sup>a)</sup> The  $^{13}\text{C}$  data for trimers are those of ref.<sup>13)</sup>; the numbering of the central unit of trimers was adapted to that of PHT.

3-hexylthiophene<sup>13</sup>). The matching of the two sets of data is singular: the highest differences, found for carbons bearing the hexyl chain, do not exceed 0.5 ppm. In our opinion, this is an important piece of evidence in favour of the widely used interpretative model of PHT structure based on the four configurational triads.

The numerical values of the <sup>13</sup>C chemical shifts (Tab. 1) are consistent with those of the regio-random (1:1:1:1, HT-HT:TT-HT:HT-HH:TT-HH) PHT<sup>9</sup>), but the present assignment is not in accordance with that reported by Rieke<sup>9</sup>). Previous assignments of all <sup>1</sup>H aromatic signals<sup>10, 13</sup>) and of the <sup>13</sup>C aromatic signals of the HT part of PHT<sup>13</sup>) are confirmed and the characterization of the three minor triads is completed.

The advantages of <sup>1</sup>H-<sup>13</sup>C inverse detection in analysing the substitution pattern and the presence of structural defects of a polymer are here amply demonstrated. The technique can, in principle, be applied to all those polymers whose degree of stereospecificity enables the <sup>1</sup>H signals of the structural features to be detected, irrespective of the presence of the <sup>13</sup>C counterpart in the directly-acquired spectrum.

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