

# Regiochemistry characterization of poly(3-hexanoyloxyethyl-2,5-thienylene) through proton and carbon nuclear magnetic resonance spectroscopy

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The poly(3-hexanoyloxyethyl-2,5-thienylene) was studied by means of mono- and bidimensional nuclear magnetic resonance spectroscopy. The regiochemistry of the polymer is assigned on the basis of the  $^{13}\text{C}$  chemical shifts, which are easily obtained through inverse detection experiments, utilizing a triad-based model.  
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## INTRODUCTION

The grafting of relatively long alkyl-chains onto the polythiophene backbone has led to a significant improvement in solubility and fusibility; the polymers are easily processed while retaining a high level of electrical conductivity<sup>1</sup>. Moreover, novel and interesting properties, such as solvatochromic, thermochromic, piezochromic, and ionochromic effects, have also been observed with the introduction of flexible side chains<sup>2-7</sup>. All the above properties, together with good chemical and thermal stability, make substituted polythiophenes excellent candidates for practical applications.

Since the incorporation of substituents strongly influences the electronic structure, which is coupled to the main-chain conformation<sup>6,7</sup>, it is possible, in principle, to achieve structure-property control through side-chain functionalization. With regards to 3-substituted polythiophenes, only the incorporation of a few groups, notably ether<sup>1,7-11</sup> and ester<sup>12-17</sup>, has been studied. The ester linkage is particularly attractive since it can lead to materials processable into films as well as acting as an active site for further modification; for example, it can be hydrolysed to hydroxy function<sup>16</sup>.

It is of fundamental importance for these studies to know the microstructure of the polymers, for conjugation length and one-dimensional charge transport are affected by structural defects such as head-to-head (HH) couplings. In this respect, it has been shown that n.m.r. spectroscopy, in its one- and two-dimensional version, appears to be a very useful tool in determining the substitution pattern and regiochemistry of polymers obtained with different polymerization methods<sup>18-21</sup>.

Many reports are concerned mainly with the proton and carbon results obtained from monodimensional<sup>22-25</sup> techniques and only a few papers report applications of bidimensional<sup>22,24</sup> ones. Inverse-detected  $^1\text{H}$ ,  $^{13}\text{C}$  two-dimensional n.m.r. spectroscopy has been applied to the study of poly(3-hexylthiophene)<sup>26,27</sup> to determine polymerization defects, and the importance of the triad-based model in the assignment of the regiochemistry of polythiophenes with alkyl side-chains has been underlined<sup>19</sup>.

In this paper we report a  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. study on the poly(3-hexanoyloxyethyl-2,5-thienylene) (P3HET) and its monomer (3-thienyl)ethyl hexanoate (TEH).  $^{13}\text{C}$  chemical shifts are easily obtained and assigned through inverse-detected heteronuclear multiple-quantum (HMQC)<sup>28</sup> and multiple-bond (HMBC)<sup>29</sup> correlation experiments. Total correlation spectroscopy (TOCSY)<sup>30</sup> and the one-dimensional nuclear Overhauser effect (1D-NOE)<sup>31</sup> are also applied to the polymer study. The results shed light on the effect of the alkylester substituent on the chemical shifts of the aromatic proton and enable the structure of the polythienylenes 3-substituted with alkyl ester side-chains to be interpreted.

## EXPERIMENTAL

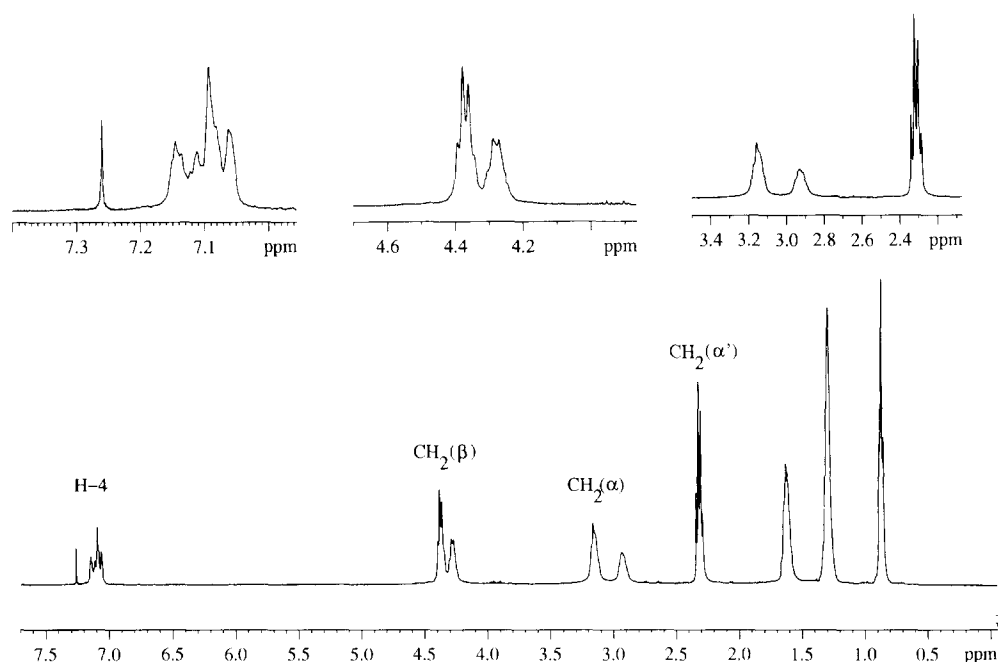
### Samples

The synthesis of 2-(3-thienyl)ethyl hexanoate (TEH) has already been reported<sup>12</sup>. The polymer P3HET was prepared by polymerization of TEH with  $\text{FeCl}_3$  in chloroform for 5 h, as previously described<sup>14</sup>.

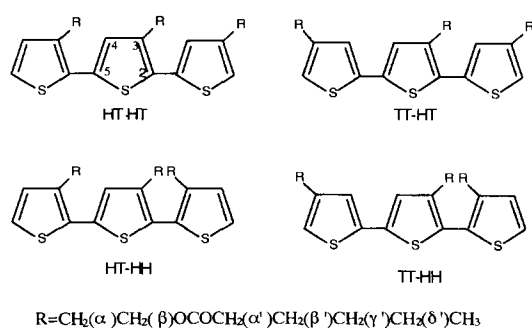
### N.m.r. measurements

The  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra of TEH and P3HET in  $\text{CDCl}_3$  solution, were recorded at 300 K with a Bruker

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**Figure 1**  $^1\text{H}$  n.m.r. spectrum of P3HET (lower trace). Expanded regions (upper trace) correspond, from left to right, to H-4,  $\text{CH}_2(\beta)$ ,  $\text{CH}_2(\alpha)$  and  $\text{CH}_2(\alpha')$  protons



**Scheme 1**

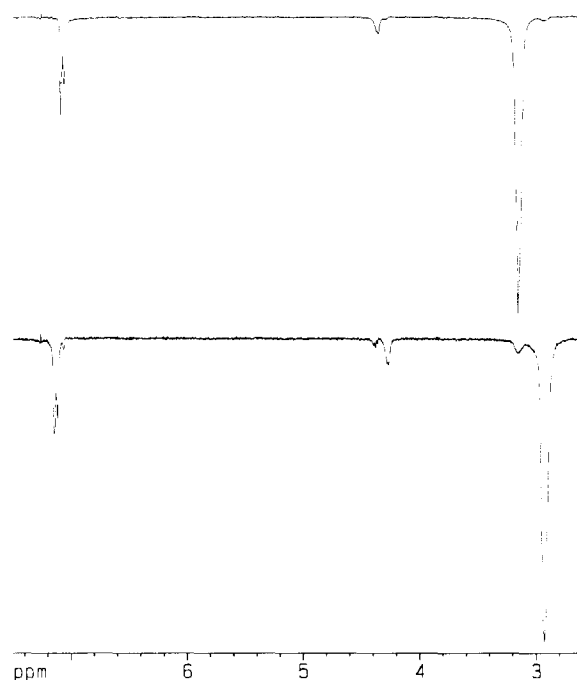
spectrometer AMX-400 WB operating at 400.13 and 100.61 MHz, respectively.

The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts ( $\delta$  in ppm) are quoted with respect to the  $\text{CHCl}_3$  signal at 7.26 ppm (for  $^1\text{H}$ ) and 77.0 ppm (for  $^{13}\text{C}$ ).

HMQC<sup>28</sup> parameters for aromatic and aliphatic region: spectral width (f2) = 3–5 ppm, 2048 complex points; spectral width (f1) = 40–80 ppm, 256 t1 increments with 8 scans per t1 value; relaxation and evolution delays = 0.5–1 s and 2.78–4.00 ms, respectively. Zero filling in f1 and f2, sine function in f1 was applied before Fourier transformation. HMBC<sup>29</sup> parameters: as for HMQC<sup>28</sup>, but spectral width (f1) = 180 ppm, 32 scans per t1 value and delay for long-range coupling constant evolution = 100 ms.

One-dimensional proton-decoupled  $^{13}\text{C}$  spectra were acquired with standard pulse sequences. Typical parameters were: pulse width =  $40^\circ$ , digital resolution = 3 Hz per point, relaxation delay = 5 s, 1–2k scans.

The TOCSY-TPPI<sup>30</sup> experiment was performed with a standard pulse sequence. Parameters: spectral width (f2) = 8.5 ppm, 4096 complex points; spectral width (f1) = 8.5 ppm, 512 t1 increments with 8 scans per t1 value; relaxation delay = 1 s; spin-lock field of 4 kHz applied for 141 ms. Zero filling in f1 was applied before Fourier transformation.



**Figure 2** 1D-NOE difference spectra of P3HET.  $\text{CH}_2(\alpha)$  at 2.93 ppm (lower trace) and  $\text{CH}_2(\alpha')$  at 3.15 ppm (upper trace) were irradiated

A differential steady-state NOE experiment<sup>31</sup> on P3HET was performed, acquiring 128 + 128 transients in groups of 8, alternately irradiating on- and off-resonance, with a presaturation time of 1 s.

## RESULTS AND DISCUSSION

### *N.m.r. characterization of poly(3-hexanoyloxyethyl-2,5-thienylene)*

The  $^1\text{H}$  n.m.r. spectrum of P3HET (Figure 1) displays four signals in the aromatic region at 7.15, 7.11, 7.09 and 7.06 ppm with an abundance of 19, 14, 45 and 21%,

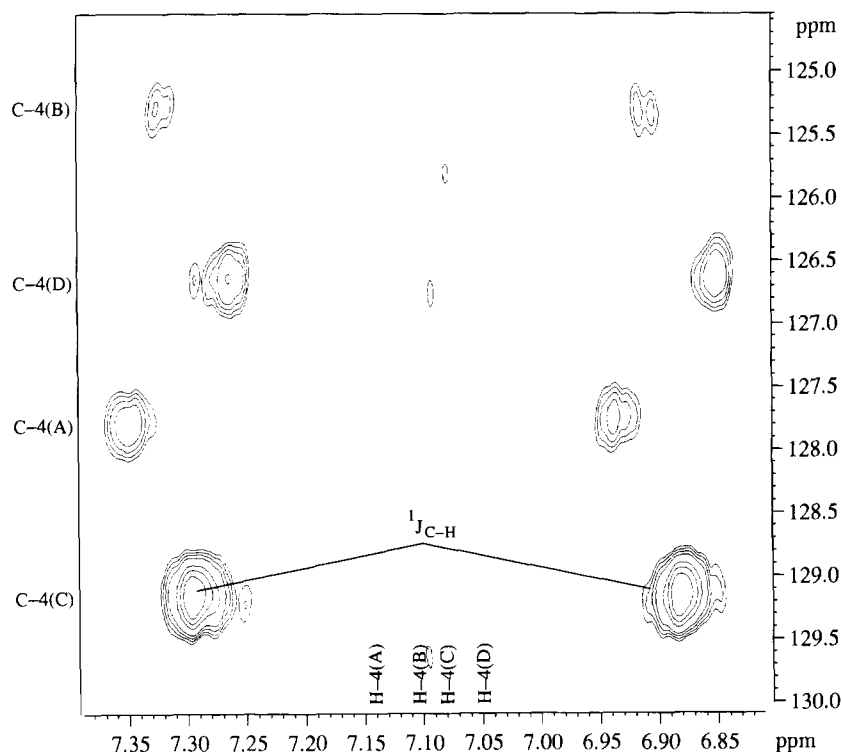
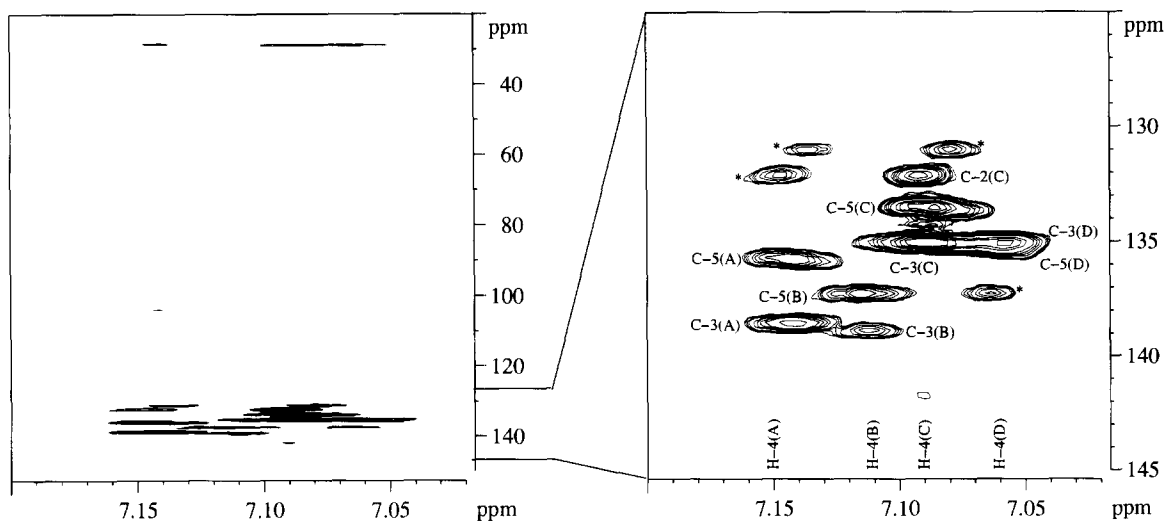
**Table 1**  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts ( $\delta$  in ppm) of configurational triads of P3HET

Triad	H-4	C-2	C-3	C-4	C-5	$\text{CH}_2(\alpha)$	$\text{CH}_2(\alpha)^a$	$\text{CH}_2(\beta)$	$\text{CH}_2(\beta)$	$\text{CO}^b$	$\text{CH}_2(\alpha')^c$
A	7.15	129.6	138.5	127.8	135.8	2.94	28.4	4.29	63.59	173.61	2.30
B	7.11	128.1	138.8	125.4	137.4	2.92	28.4	4.27	63.57	173.59	2.30
C	7.09	132.3	135.2	129.2	133.6	3.16	28.7	4.38	63.49	173.66	2.32
D	7.06	131.1	135.4	126.7	135.8	3.14	28.7	4.36	63.43	173.64	2.32

<sup>a</sup> The two carbons signals for A, B and C, D triads are indistinguishable from the directly acquired  $\{^1\text{H}\}-^{13}\text{C}$  spectrum

<sup>b</sup> The assignment of  $^{13}\text{C}$  chemical shifts of CO, directly acquired, is based on the observation that the signal at 173.66 ppm is the more abundant one

<sup>c</sup> The assignment of  $\text{CH}_2(\alpha')$  protons to the related chains is based on their abundance, only one signal at 34.24 ppm is observed for the corresponding carbons


**Figure 3** Coupled HMQC spectrum of the aromatic region of P3HET. Four doublets corresponding to the C-4 carbons were detected

**Figure 4** HMBC spectrum of P3HET detected through the aromatic protons and performed with an evolution delay of 100 ms. On the left the spectrum relative to the global carbon region, on the right the expanded aromatic region. The symbols \* denote not assigned signals

respectively. These resonances are described<sup>14</sup> as being due to the H-4 protons of the four configurational triads (depicted in *Scheme 1*). The correctness of this

assignment is confirmed by the values of  $^1J_{\text{C-H}} = 169$  Hz (values obtained by direct inspection of the  $^1\text{H}$ -coupled HMQC spectrum, *Figure 3*), which is characteristic

of  $\beta$ -(C, H) fragments and very different from the same coupling in  $\alpha$ -(C, H) fragments (189 Hz) of the thiophene ring<sup>32</sup>.

The presence of four aromatic protons requires, in principle, the presence of four different aliphatic chains, but different groups of resonances for each type of chain are detected only for  $\text{CH}_2(\alpha)$ ,  $\text{CH}_2(\beta)$  and  $\text{CH}_2(\alpha')$ , in the aliphatic region, at 400 MHz. The remaining methylene protons are not distinguishable as belonging to different chains. The  $\text{CH}_2(\alpha)$  appear as two broad quartets centered at 3.15 and 2.93 ppm; these are due to the superimposition of two methylene resonances, each being a triplet at 3.16 and 3.14 ppm and at 2.94 and

2.92 ppm, respectively. Analysis of the  $\text{CH}_2(\beta)$  signals centred at 4.37 and 4.28 ppm shows that they are due to the superimposition of two triplets at 4.38 and 4.36 ppm and at 4.29 and 4.27 ppm, respectively. The  $\text{CH}_2(\alpha')$  signal is actually due to two superimposed triplets at 2.32 and 2.30 ppm, even though it might be perceived as a sharp quartet at 2.31 ppm.

In order to assign each chain to the proper ring, we performed a 1D-NOE experiment (Figure 2). The irradiation of the  $\text{CH}_2(\alpha)$  signals at 3.15 ppm generates a NOE at H-4 protons at 7.09 and 7.06 ppm, whereas the irradiation of  $\text{CH}_2(\alpha)$  signals at 2.93 ppm produces a NOE at H-4 protons at 7.15 and 7.11 ppm. Finally, the TOCSY<sup>30</sup> experiment enables the related H-4,  $\text{CH}_2(\alpha)$  and  $\text{CH}_2(\beta)$  protons belonging to the central unit of each triad to be found. The results of 1D-NOE and TOCSY experiments are summarized in Table 1.

The H-4 proton chemical shifts do not allow the regiochemistry of P3HET to be ascertained. In fact, the major peak at 7.09 ppm, tentatively assigned to the head-to-tail-head-to-tail (HT-HT) couplings (this being the main configuration of all poly(3-alkylsubstituted)thiophenes), does not fit, as regard position, the H-4 pattern of poly(3-hexylthiophene) (PHT), where the H-4 belonging to the HT-HT connection is the more shielded one. This different behaviour is ascribable to the influence, dependent on distance, of the ester linkage on the H-4 chemical shift, as already observed<sup>17</sup>.

Useful information for the assignment of the polymer regiochemistry can be obtained from  $^{13}\text{C}$  chemical shifts. The  $^{13}\text{C}$  n.m.r. data of P3HET (Table 1) are obtained and assigned through inverse detection experiments; a HMQC<sup>28</sup> experiment was performed with the modulation of the coupling constant C4-H4 in order to find the C-4 of each configurational triad.

The remaining aromatic carbon resonances were detected and assigned by means of an HMBC<sup>29</sup> experiment

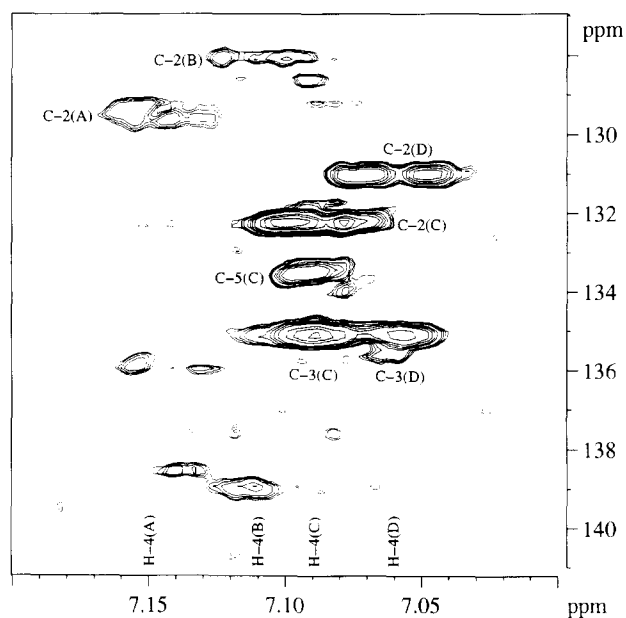


Figure 5 HMBC spectrum of P3HET detected through the aromatic protons and performed with an evolution delay of 50 ms

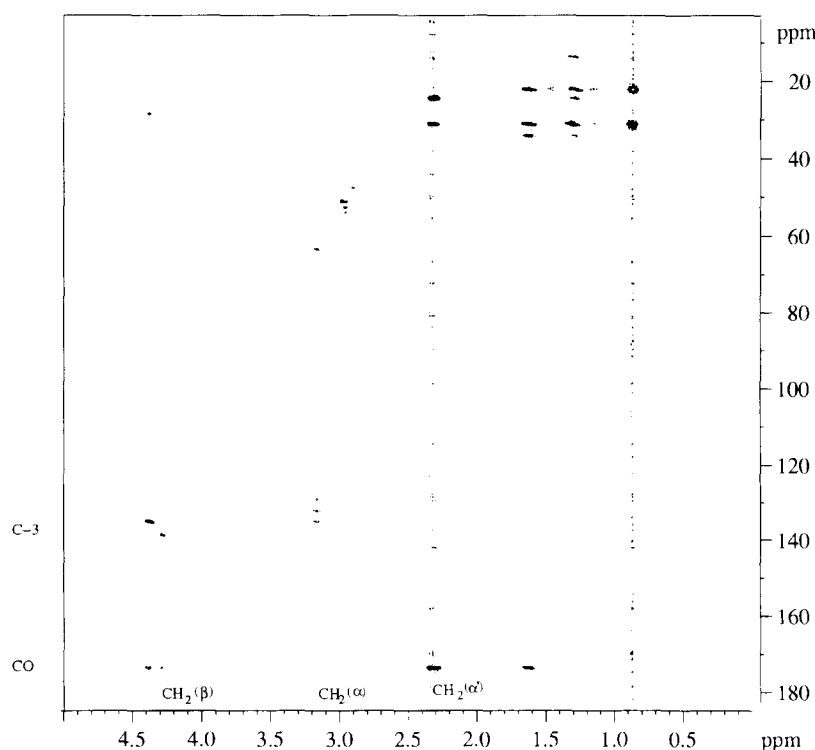


Figure 6 HMBC spectrum of P3HET detected through the aliphatic protons. The global carbon region is displayed

with an evolution delay of 100 ms, corresponding to a 5 Hz coupling constant. In these experimental conditions, each H-4 proton shows a long-range correlation with almost all the relayed aromatic carbons, and the correct assignment of each carbon is based on the value of the measured long-range proton-carbon coupling constant. The detection and assignment of the other aromatic carbons, requires an additional HMBC experiment with an evolution delay corresponding to a 10 Hz coupling constant. The HMQC<sup>28</sup> and HMBC<sup>29</sup> experiments for P3HET are reported in Figures 3, 4 and 5.

The  $\text{CH}_2(\alpha)$  and  $\text{CH}_2(\beta)$  protons, as previously pointed out on PHT<sup>26,27</sup>, are a useful probe for the detection of the chemical shifts of the carbons C-3 and C-2, owing to the long-range coupling constants with C-3 and C-2, and enable each chain to be connected to the proper ring. The HMBC<sup>29</sup> experiment performed in the aliphatic region (Figure 6) displays the long-range connected carbons and protons.

#### Assignment of $^1\text{H}$ and $^{13}\text{C}$ signals to the four configurational triads

In order to assign each group of carbon and proton signals to the proper triad, we adopted a treatment which takes into account the fact that the variation in the  $^{13}\text{C}$  chemical shifts of the central unit of each triad, with respect to the monomer, is due to the different type of adjacent connectivities. The parameters to be used in this approach were obtained from the  $^{13}\text{C}$  chemical shifts of four configurational trimers of 3-hexylthiophene. The  $\Delta\delta$  values of the carbons of the central unit of each trimer of PHT, with respect to the monomer, are reported in Table 2. The reliability of the approach based on trimers is supported by the fact that the difference between the calculated chemical shifts for the trimers of PHT and those observed for the triads is no more than 0.5 ppm<sup>26</sup>.

The  $^{13}\text{C}$  chemical shifts of (3-thienyl)ethyl hexanoate reported in Table 3, together with the values  $\Delta\delta$  ( $\Delta\delta = \delta_{\text{trimer}} - \delta_{\text{monomer}}$ ) reported in Table 2, give the data for the central unit of the four configurational triads of P3HET.

Comparison of the calculated data for the triads of P3HET (Table 4) with those experimentally determined

**Table 2**  $\Delta\delta^a$  values for the carbons of the central unit of each configurational trimer of PHT with respect to the monomer

Trimer	C-2	C-3	C-4	C-5
HT-HT	11.0	-3.7	0.4	8.8
TT-HT	10.1	-3.3	-2.0	10.2
HT-HH	8.9	-0.6	-0.9	10.9
TT-HH	7.8	-0.1	-3.3	12.3

<sup>a</sup> Obtained from  $^{13}\text{C}$  chemical shifts:  $\Delta\delta = \delta_{\text{trimer}} - \delta_{\text{monomer}}$

**Table 3**  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts<sup>a,b</sup> ( $\delta$  in ppm) of (3-thienyl)ethyl hexanoate<sup>c</sup>

H-2 <sup>d</sup>	H-4 <sup>d</sup>		H-5 <sup>d</sup>	$\text{CH}_2(\alpha)$	$\text{CH}_2(\beta)$	$\text{CH}_2(\alpha')$	$\text{CH}_2(\beta')$	$\text{CH}_2(\gamma')$	$\text{CH}_2(\delta')$	$\text{CH}_3$	
7.03	6.97		7.25	2.97	4.29	2.29	1.61	1.29	1.28	0.89	
C-2	C-3	C-4	C-5	$\text{CH}_2(\alpha)$	$\text{CH}_2(\beta)$	$\text{CH}_2(\alpha')$	$\text{CH}_2(\beta')$	$\text{CH}_2(\gamma')$	$\text{CH}_2(\delta')$	$\text{CH}_3$	CO
121.47	138.09	128.21	125.52	29.61	64.0	34.28	24.61	31.25	22.28	13.85	173.76

<sup>a</sup> The  $^1\text{H}$  and  $^{13}\text{C}$   $\delta$  values are for 0.1 mol dm<sup>-3</sup> solution in  $\text{CDCl}_3$  and refer to  $\text{CHCl}_3$  at 7.26 and 77.0 ppm

<sup>b</sup> The  $^{13}\text{C}$  were assigned on the basis of HMQC<sup>28</sup> and HMBC<sup>29</sup> experiments

<sup>c</sup> For the numbering, see Scheme 1

<sup>d</sup> The values of the proton-proton coupling constants are:  $J(2, 4) = 1.30$ ,  $J(2, 5) = 2.96$ ,  $J(4, 5) = 4.92$  Hz. The protons of  $\text{CH}_2(\alpha)$  show a long-range coupling constant with H-2 ( $J = 0.88$  Hz) and with H-4 ( $J = 0.40$  Hz)

(Table 1) shows a very good correspondence, with differences in chemical shifts not exceeding 1 ppm. This correspondence allows the triad A of P3HET to be identified at HT-HH, B as TT-HH, C as HT-HT, and D as TT-HT and also enables the chemical shifts to be assigned to the corresponding protons. This correspondence is further born out by the fact that the predominant triad of P3HET effectively corresponds to HT-HT, as generally expected for polythiophene.

This procedure can be generally adopted for the assignment of the regiochemistry of different polymers, by utilizing the  $^{13}\text{C}$  n.m.r. data of monomer and the connectivity parameters of Table 2. Table 1 reports  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts identified as belonging to the four different triads, whereas the fully proton-decoupled  $^{13}\text{C}$  spectrum also shows one set of signals for the carbons of  $\text{CH}_2(\alpha')$ ,  $\text{CH}_2(\beta)$ ,  $\text{CH}_2(\gamma')$ ,  $\text{CH}_2(\delta')$  and  $\text{CH}_3$ ; these were assigned to the related proton through inverse detection experiments. The  $\text{CH}_2(\alpha')$  protons found at 2.32 and 2.30 ppm are directly connected with carbon at 34.24 ppm, and the protons of  $\text{CH}_2(\beta')$  at 1.62,  $\text{CH}_2(\gamma')$  at 1.29,  $\text{CH}_2(\delta')$  at 1.28 and  $\text{CH}_3$  at 0.87 ppm are connected with carbons at 24.61, 31.28, 22.88 and 13.86 ppm, respectively.

It is interesting to note that all the carbons are regiochemical-dependent; however, C-4 and C-3 are found to be more convenient for the configurational assignment of the polymer, thanks to the easy detection and assignment of their chemical shifts.

The  $^{13}\text{C}$  chemical shift of C-3 is the same as that of the monomer when it belongs to an HH connection, whereas it is shielded by about 3 ppm when it belongs to an HT connection. The C-4 chemical shift is similar to that of the monomer when it belongs to an HT connection and is shielded by 2-3 ppm when it belongs to a TT connection.

The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts of the aliphatic chains show a characteristic trend, parallel to that observed for the methylene group in the hexyl chain of PHT. The  $\text{CH}_2(\alpha)$  protons are deshielded (0.18 ppm) with respect to the monomer when they belong to an HT connection, whereas they are only slightly shielded (-0.04 ppm) in the HH connection. The corresponding carbons are more shielded in HT than in HH connections.  $\text{CH}_2(\beta)$  also shows a regiochemical-dependent chemical shift:  $\text{CH}_2(\beta)$  is shielded in HT connections, and only slightly shielded or unchanged in HH connections. The corresponding carbons are all shielded, but the more shielded ones are those belonging to HT connections.

## CONCLUSIONS

The inverse-detection experiments, HMQC and HMBC, are valuable in that they allow us to find and assign the

**Table 4** Calculated <sup>13</sup>C chemical shifts of the central unit of the four configurational triads of P3HET

Triad	C-2	C-3	C-4	C-5
HT-HT	132.5	134.4	128.6	134.3
TT-HT	131.6	134.8	126.2	135.7
HT-HH	130.4	137.5	127.3	136.4
TT-HH	129.3	138.0	124.9	137.8

<sup>13</sup>C chemical shifts. Their regiochemical-dependence can be used as a key in establishing the regiochemistry and the defects of a polymer, mainly those of C-3, C-4, and CH<sub>2</sub>(α). To this end, the triad-based model appears to be generally applicable, and the assignment of the triads can be performed from the <sup>13</sup>C chemical-shift values of monomers incremented by the variations due to the different types of connectivities. Finally, the knowledge of the regiochemistry and the defects of a polymer should enable us to rationalize the influence of regiochemistry on the physical and chemical properties of these materials.

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