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Regiochemical Analysis of Water Soluble Conductive Polymers: Sodium Poly(ω-(3-thienyl)alkanesulfonates)

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ABSTRACT: The first regiochemical analysis of self-doped polythiophenes is presented. Regioregularity is assigned based on the ^{1}H and ^{13}C NMR spectra of sodium poly(3-(3-thienyl)propanesulfonate) **(1)** and sodium poly(6-(3-thienyl)hexanesulfonate) **(2)** to particular configurational diads and triads, using one- and two-dimensional nuclear Overhauser effect (NOE), double quantum filtered homonuclear correlational spectroscopy (DQF-COSY), and heteronuclear multiple-quantum coherence (HMQC) experiments. Excellent resolution enhancement of peaks is obtained with a Gaussian multiplication. An estimate of the relative populations of the configurational triads in these polymers is thereby obtained. The ratio of HT to HH diads in both **1** and **2** is 4:1, based on the areas associated with the aromatic NMR signals.

Introduction

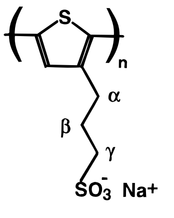
Polythiophenes have been the subject of a great deal of research from the applied and the fundamental point of view.[1−3] The parent polythiophene is intractable but substituents at the 3-position of the thienyl ring can yield materials which are soluble in organic solvents.[4−6] The electrical and optical properties of materials composed of poly(3-alkylthiophenes) are largely controlled by configurational and stereochemical factors.[7−11]

NMR spectroscopy has played an invaluable role in the characterization and quantitation of configurational structures in these polymers. Sato and co-workers[12] have presented a comprehensive study on the configurational structures of poly(3-alkylthiophenes). Two resonances are observed for the α-CH_2 unit and they are assigned to the head-to-head (HH) and head-to-tail (HT) configurational diads. Moreover, the aromatic proton at the 4-position was found to yield four resonances that correspond to the four possible configurational triads. It has been shown[7] that poly(3-alkylthiophenes) containing a high percentage of HT diads ($>95\%$) exhibit electrical conductivities 60-fold higher than $FeCl_3$- or electrochemically-prepared polymers. Much attention has been paid to the regioregularity of the associated polymers.

Following the discovery that derivatization of polythiophenes with alkyl substituents yielded soluble polymers, the synthesis of water soluble derivatives, poly(ω-(*3*-*t*hienyl)*a*lkane*s*ulfonates) (*P3TASs*) was reported.[13,14] In addition to providing water solubility, the sulfonate groups serve as charge balancing counter ions when the polymers are oxidatively doped. This led to the concept of “self-doped” conductive polymers.[13,14] Furthermore, the sulfonic acid form of the polymers was found to protonate the π-conjugated backbone, thus resulting in “auto-doped” conducting polymers.[13,14]

Since this discovery, the synthesis and properties of self-doped polythiophenes,[15−21] and self-doped conducting polymers in general,[22−27] have been actively pursued. However, in contrast to the detail of the regiochemistry of nonsulfonated P3ATs, little attention has been given to the regiochemistry of P3TASs because of difficulties in obtaining high resolution NMR spectra of aqueous polymer solutions. The ^{1}H NMR spectrum of a sulfonated polypyrrole has been reported,[23] but little information could be extracted as a result of broad signals. NMR spectra of polymers in solution are often characterized by broad lines due to short transverse relaxation times (T_2). This is ultimately determined by slow molecular tumbling which is quantified by a single parameter, the correlation time (τ_c), assuming isotropic motion.[28]

In this report we describe the regiochemical analysis of sodium poly(ω-(3-thienyl)alkanesulfonate), the alkyl group being propyl **(1)** and hexyl **(2)**. Regiochemical analysis was achieved by NMR spectroscopic analysis, employing one- and two-dimensional nuclear Overhauser effect (NOE), double quantum filtered homonuclear correlational spectroscopy (DQF-COSY),[29−32] and heteronuclear multiple quantum coherences (HMQC)[33−35] techniques. The latter proved to be a valuable tool in the assignment of both ^{1}H and ^{13}C NMR spectra since it provided enhanced sensitivity over direct detection in the acquisition of the ^{13}C NMR spectra. The low sensitivity associated with the spectra of these polymers is a particular problem due to the high molecular weight.



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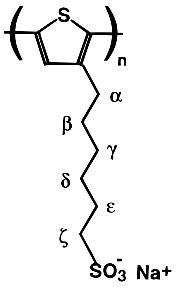

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Resolution enhancement with Gaussian multiplication was used to decrease the line width of signals and to change the shape of the Lorentzian lines to a Gaussian line shape[36] (Gaussian lines are much narrower at the base than Lorentzians for equivalent width at half height). This resolution enhancement protocol allowed an estimation of the relative populations of the configurational diads and triads in the polymers. To the best of our knowledge, this is the first regiochemical analysis and NMR spectroscopic characterization of sulfonated polythiophenes.

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Experimental Section

The synthesis of sodium poly(ω-(3-thienyl)alkanesulfonates) via oxidative coupling of the corresponding monomers with ferric chloride in water, using a modification of the method of Ikenoue,[18] together with their physical characterization were described in detail in our previous paper.[20] Polymer samples were dried under vacuum for at least 12 h at 100 °C. NMR samples were prepared by partially dissolving the polymer in acetonitrile-d_3 or DMSO-d_6, followed by the addition of a minimum amount of D_2O to effect complete dissolution. **1** and **2** were dissolved in mixtures of D_2O:DMSO-d_6 (1:1.33) and D_2O:acetonitrile-d_3 (1:1.12) to give concentrations of 19.9 mg/mL and 15.7 mg/mL, respectively. Solutions were subsequently deoxygenated by 3 freeze-pump-thaw cycles and then sealed under nitrogen.

Chemical shifts are referenced to tetramethylsilane ($\delta = 0$ ppm). All NMR experiments, unless otherwise stated, were acquired on an AMX400 Bruker instrument operating at 400.13 MHz at 25 °C. Suppression of water was achieved through presaturation during the relaxation delay of 2 or 4 s for 2-D or 1-D experiments, respectively. T_1 values for the aromatic and aliphatic protons (average) in both polymers were determined to be of the order of 0.8 and 0.5 s, respectively. Typically, 1-D experiments were acquired on a 8K data set with a sweep width of 9.05 ppm, an acquisition time of 1.130 s and 64 scans. Two-dimensional NOE experiments were acquired with the standard phase sensitive NOESY[37] pulse sequence using time proportional phase increments (TPPI).[38] For the correlation of the aromatic with the aliphatic signals, mixing times of 15 and 10 ms gave the best results in terms of minimizing spin diffusion and J-coupling effects for **1** and **2**, respectively. In a typical NOESY experiment, 1024 1K spectra were acquired using a sweep width of 10.24 ppm in both dimensions, an acquisition time of 0.125 s, 24 scans, and 4 dummy scans. Processing was performed in a 1K × 1K array using QSine shifted by 90° as the apodization function in both dimensions. One-dimensional transient-NOE experiments were performed using Gaussian-shaped pulses.[39] Gaussian pulses of 155 ms were constructed from 1024 step increments. Difference spectra were obtained through phase cycling subtraction of the FIDs of the on- and off-resonance spectra in an alternating sequence. These 1-D transient-NOE experiments were acquired on a 4K data set using a sweep width of 10.33 ppm, an acquisition time of 0.496 s, 512 scans, and 4 dummy scans. Inverse-detected correlation (HMQC) experiments were obtained via zero and double quantum coherences using standard pulse sequences. The HMQC spectrum of the aliphatic region of **1** was acquired on a Bruker AMX600 spectrometer using a gradient-enhanced HMQC pulse program.[40] HMQC spectra of **2** were obtained with a variation of HMQC that employs the Bird pulse sequence.[35] In a typical HMQC experiment, 256 2K spectra were acquired employing an acquisition time of 0.248 s, 64 scans, 32 dummy scans, and a sweep width of 10.33 ppm and 190 ppm in the ^1H and ^{13}C dimension, respectively. Processing was performed in a 2K × 512 matrix using a QSine shifted by 90° apodization function in both dimensions. A phase sensitive DQF-COSY[29−32] spectrum was acquired on a Bruker AMX600 spectrometer using TTPI. In this experiment, 512 8K spectra were acquired using a sweep width of 4.21 ppm in both dimensions, an acquisition time of 1.622 s, 56 scans, and 4 dummy scans. Processing was accomplished in a 8K × 512 matrix which was apodized with a QSine 90° shifted function in both dimensions.

Resolution enhancement of the ^1H NMR spectra was performed with a Gaussian multiplication using FELIX version 2.0. The first point of the Gaussian function was normalized to 1. The optimum processing parameters for the aromatic signals in **1** were found to be a line broadening factor of −10 Hz and a Gaussian factor of 0.1 with a truncated 4K data set. Enhancement of the aliphatic signals was performed on a spectrum that had been acquired at 100 °C, using the same parameters except that the line broadening factor was set to −15 Hz.

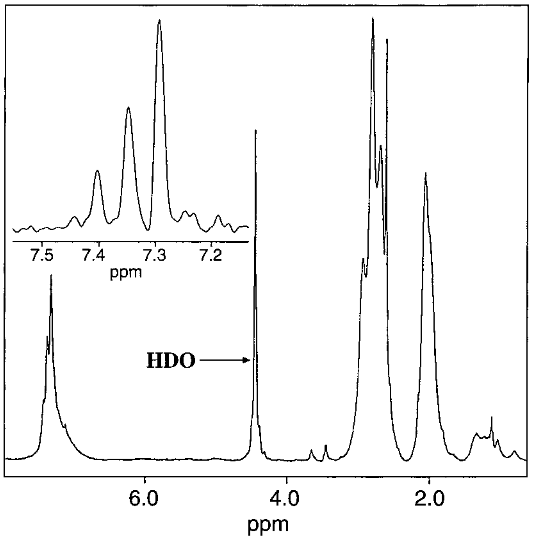

Figure 1. ^1H NMR spectrum of sodium poly(3-(3-thienyl)-propanesulfonate) **1** in a mixture of DMSO-d_6 and D_2O. The inset shows the aromatic region after resolution enhancement.

Results and Discussion

The ^1H NMR spectra of the sulfonated polymers **1** and **2** in D_2O are virtually featureless. We therefore considered the use of aprotic solvents to avoid hydrogen bonding interactions with the polymer, with the expectation that the increased molecular tumbling rate would lead to the decreased NMR line widths. Indeed, a dramatic improvement in resolution was observed. Increasing the temperature to 100 °C led to a very small improvement in resolution in the spectrum of **1**. This spectrum was used for resolution enhancement. However, in the case of **2**, we saw little advantage in acquiring spectra at higher temperatures, and the spectrum at 25 °C was used for resolution enhancement.

Variable temperature ^1H NMR studies indicated no changes in the spectra, suggesting that multiple sets of peaks in the spectra are not due to conformational exchange that is slow in the NMR time scale, but rather to the different configurations that result from coupling thiophene monomers. The assignment of the spectra to configurational diads and triads follows.

The ^1H NMR spectrum of **1** shows a broad peak at δ 2.06 with a shoulder (see Figure 1) which can be assigned to the β-CH_2 protons in two configurational isomers. In an analysis of configurational diads, one ring can be considered as a substituent on the second ring. Therefore, the chemical shift of the β-CH_2 group under consideration is affected by the different chemical environments provided by the substituent in the two different configurations (see Figure 2). The major component of the peak at 2.06 ppm is assigned to the β-CH_2 group in the HT configuration and the shoulder to the HH configuration. This is based on the relative magnitudes of these two peaks and on the putative assignment of the α-CH_2 signals. The latter signals in the HH configuration appear upfield from the HT signals in poly(3-alkylthiophene);[9] for example, the chemical shift of the α-CH_2 unit in poly(3,4-dihexylthiophene) is upfield compared to that of the HT regiochemically pure poly(3-hexylthiophene).[7,41]

The peak at δ 2.67 is assigned to the overlapping signals from the α- and γ-CH_2 groups in the HH configurations. This is readily seen from an HMQC spectrum in which the overlapping ^1H NMR signals are separated in the ^{13}C dimension (see Figure 3). Further

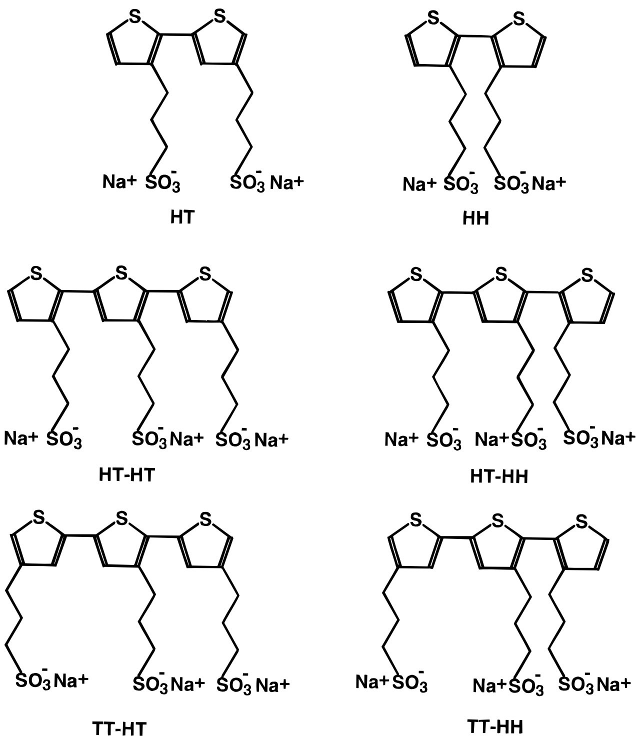

Figure 2. Configurational diads and triads for sodium poly(3-(3-thienyl)propanesulfonate) **1**.

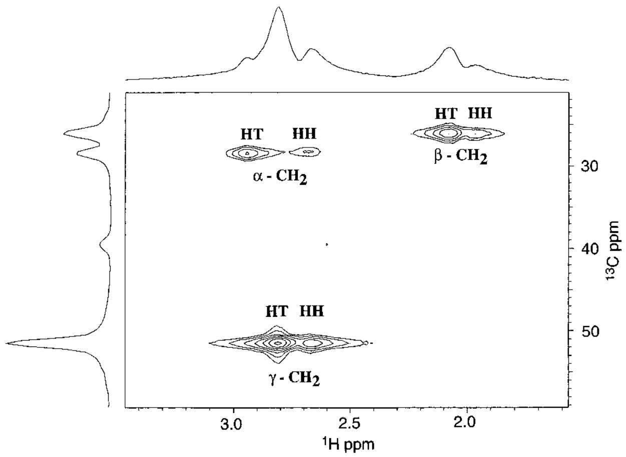

Figure 3. ^1H-^{13}C HMQC spectrum of sodium poly(3-(3-thienyl)propanesulfonate) **1**, illustrating the aliphatic region.

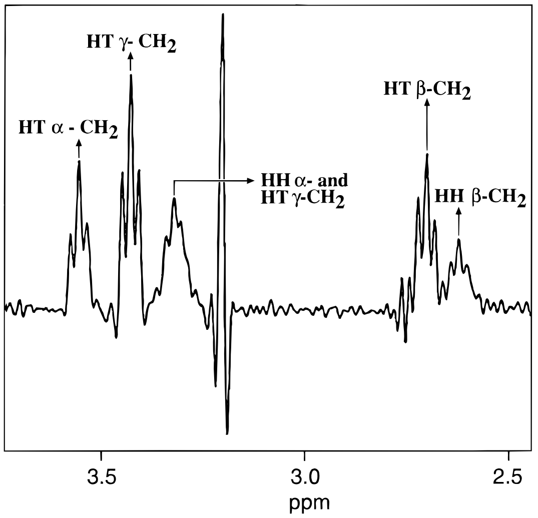

Figure 4. ^1H NMR spectrum of sodium poly(3-(3-thienyl)propanesulfonate) **1** after resolution enhancement. Note that the chemical shifts are different since this spectrum was acquired at 100 °C.

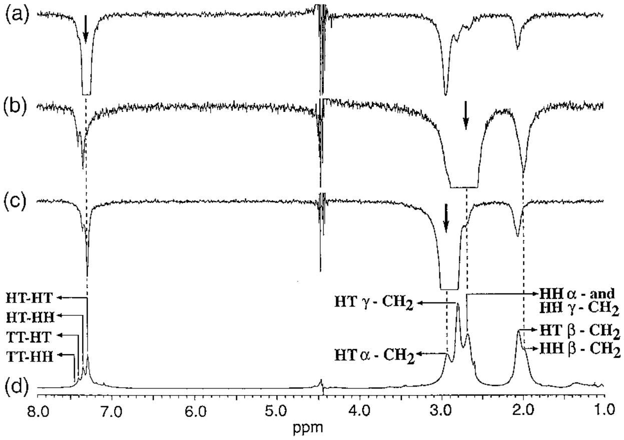

Figure 5. One-dimensional transient-NOE difference spectra a−c and the normal ^1H NMR spectrum (d) of sodium poly(3-(3-thienyl)propanesulfonate) **1**. Arrows indicate the signal that was inverted with a Gaussian-shaped pulse.

evidence was obtained from a resolution-enhanced ^1H NMR spectrum in which the peak in question gives the expected multiplets (see Figure 4). 1-D Transient NOE experiments also corroborate this assignment since irradiation of the peak at 2.67 ppm leads to an enhancement of the signal of the β-CH_2 group in the HH configuration (see Figure 5b), and irradiation of the latter gives an enhancement of the signal at 2.67 ppm (not shown).

The peak at δ 2.80 is assigned to the γ-CH_2 group in the HT configuration since this signal correlates with a ^{13}C peak at δ 51.68 which is the typical chemical shift for a methylene unit next to a sulfonic acid group.[42] The peak at δ 2.92 is assigned to the HT configuration of the α-CH_2 group. Moreover, these two peaks appear as triplets in the resolution-enhanced ^1H NMR spectrum, as expected (see Figure 4).

The aromatic proton at the 4-position in the thiophene ring gives rise to four peaks (see inset of Figure 1) which correspond to the four possible triads (see Figure 2). In these triads, the proton under observation is located in the central unit and the other rings are treated as substituents. The highest intensity peak (δ 7.29) is assigned to the HT-HT triad since oxidative coupling of monomers is known to yield mainly HT coupling of alkyl substituted thiophenes. Moreover, the resonance signal for this triad also appears upfield from the other triads in poly(3-alkylthiophene) analogues.[12] Since there is a preference for HT coupling, the lowest intensity peak (δ 7.44) may be assigned to the TT-HH triad. Further assignment is made using the general concept that the rate of growth of NOE enhancement is inversely proportional to the sixth power of the interproton distance.[43] Examination of Figure 2 indicates that inversion of the α-CH_2 resonance in the HT configuration should lead to an intra-ring enhancement of the aromatic proton resonance in the HT-HT, TT-HT, and HT-HH triads. In addition, an inter-ring enhancement is possible in the HT-HT and HT-HH triads. A 1-D-transient NOE experiment clearly shows that inversion of the HT α-CH_2 peak (δ 2.92) leads to a stronger enhancement of the aromatic signal of the major HT-HT isomer (δ 7.29) and the signal next to it at δ 7.34 (see Figure 5c). Therefore, the peak at δ 7.34 can be assigned to the HT-HH triad. The peak at δ 7.40 is

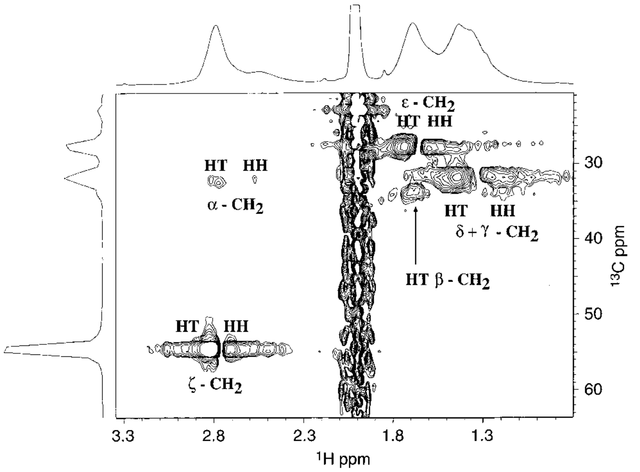

Figure 6. ^{1}H$-^{13}$C HMQC spectrum of sodium poly(6-(3-thienyl)hexanesulfonate) **2**, illustrating the aliphatic region.

assigned to the TT-HT triad by the process of elimination. A NOESY experiment also corroborates this assignment by showing two strong cross-peaks between the HT α-CH$_2$ peak and both HT-HT and HT-HH aromatic peaks (see Figure S1, supporting information).

An HMQC spectrum shows three cross-peaks at δ (7.29, 130.58), (7.35, 128.61), and (7.41, 126.71) which correspond to the HT-HT, HT-HH, and TT-HT triads, respectively. The signal for the TT-HH triad could not be observed as a result of poor signal to noise ratio. This spectrum indicates that the ^{13}C chemical shift of C-4 for the different triads decreases monotonically as the corresponding H-4 ^{1}H chemical shift increases (see Figure S2). This trend is not observed in the alkyl-substituted analogues. In the latter case, the carbon chemical shift of the HT-HH triad appears at a higher field than that of the TT-HT triad.[12]

The NMR spectra of **2** were obtained using a mixture of acetonitrile-d_3 and D$_2$O as a solvent since the residual signal of DMSO-d_6, which was used in the previous example, overlaps with the signals of interest. The acquisition of the NMR spectra of this polymer presented some problems owing to its lower solubility. Shorter T$_2$s associated with the hydrogens were encountered and the sensitivity of the NOE and HMQC experiments was generally lower.

The ^{1}H NMR spectrum of **2** shows a broad signal at δ 2.79 that overlaps with a lower intensity broad peak at δ 2.53 (see ^{1}H NMR projection of Figure 6). The higher intensity signal is made up of three overlapping peaks: HT and HH ζ-CH$_2$ and HT α-CH$_2$ signals. This is illustrated by the decoupled HMQC spectrum which shows two sets of cross-peaks at 55.12 ppm and 32.33 ppm in the ^{13}C dimension (see Figure 6). The first set is assigned, based on its ^{13}C chemical shift, to the carbon in the methylene unit that is adjacent to the sulfonate group (ζ-CH$_2$). The major and minor cross-peaks in this set are located at δ 2.82 and δ 2.71 in the ^{1}H dimension and are assigned to the HT and HH configurations, respectively, by analogy with the corresponding assignments in **1**. The second set gives two cross-peaks at δ 2.77 and δ 2.57 in the ^{1}H dimension and are associated with the HT and HH configurations, respectively, of the α-CH$_2$ group. The latter assignment is corroborated by a NOESY spectrum (see Figure S3) with a mixing time of 10 ms which shows a strong cross-peak that correlates the HT-HT resonance (δ 6.88) of the broad aromatic peak with the HT α-CH$_2$ resonance which is located in the upfield shoulder of the peak at δ 2.79. The line width of the signal due to the α-CH$_2$ protons in the ^{1}H NMR spectrum is much larger than that from the ζ-CH$_2$ protons. This implies that the transverse magnetization of the α-CH$_2$ protons decays much faster (shorter T$_2$). This may explain the weak intensity of the cross-peaks for the α-CH$_2$ protons in the HMQC spectra when compared to those from the ζ- CH$_2$ protons.

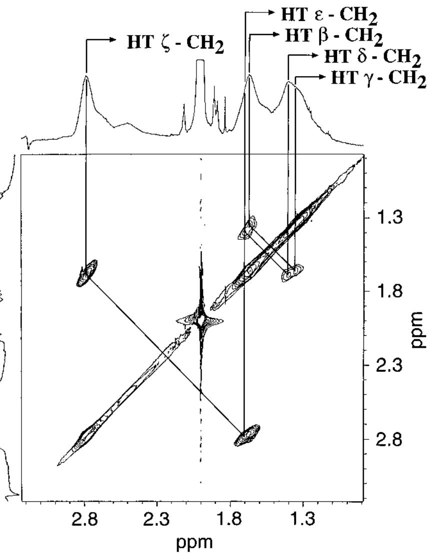

Figure 7. Double quantum filtered COSY spectrum of sodium poly(6-(3-thienyl)hexanesulfonate) **2**, illustrating the aliphatic region.

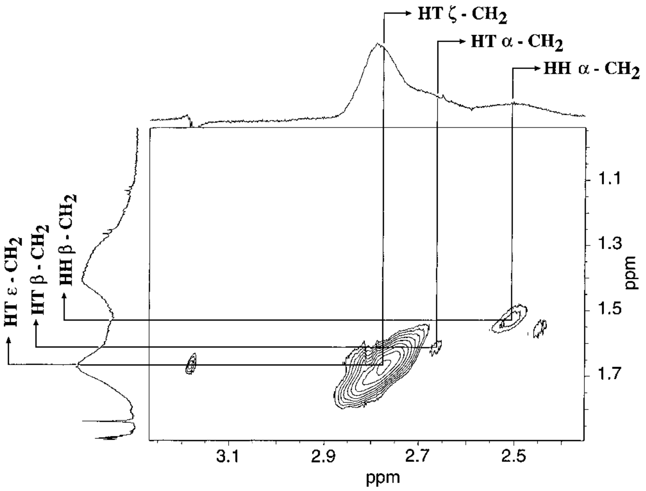

Figure 8. Expansion of the double quantum filtered COSY spectrum of sodium poly(6-(3-thienyl)hexanesulfonate) **2** using a lower threshold value. Cross peaks that relate HT α-CH$_2$ to HT β-CH$_2$, HT ζ-CH$_2$ to HT ϵ-CH$_2$, and HH α-CH$_2$ to HH β-CH$_2$ are indicated.

A double quantum filtered COSY spectrum (see Figure 7) shows a strong correlation between the HT ζ-CH$_2$ protons and the HT ϵ-CH$_2$ signal which is located in the downfield shoulder of the broad peak at δ 1.69. The HT ϵ-CH$_2$ protons are also correlated with the HT δ-CH$_2$ resonance at δ 1.40. A weak cross-peak is observed (see Figure 8) for the correlation of the HT α-CH$_2$ protons and the HT β-CH$_2$ protons whose signals are present in the broad peak at δ 1.69. A strong cross-peak is also observed between the HT β-CH$_2$ protons and the HT γ-CH$_2$ protons. The cross-peaks correlating the HT γ-CH$_2$ protons and the HT δ-CH$_2$ protons are not observed since they should appear next to the diagonal peak at δ 1.35. A correlation is also observed

Table 1. Relative Population of the Triads in 1 and 2

	relative area under the aromatic ^{1}H NMR signals	
configuration	sodium poly(3-(3-thienyl)-propanesulfonate) **1**	sodium poly(6-(3-thienyl)-hexanesulfonate) **2**
TT-HH	1.0	1.0
TT-HT	4.3	3.0
HT-HH	9.8	3.5
HT-HT	13.6	5.0

between the HH α-CH_2 protons and the HH β-CH_2 resonance which occurs at δ 1.55.

Based on the analysis of the DQF-COSY spectrum, further assignment of the cross-peaks in the decoupled HMQC spectrum is now possible (see Figure 6). The cross-peak at δ 34.43 in the ^{13}C dimension is assigned to the HT β-CH_2 group. The corresponding HH component is not visible as a result of overlap with a strong cross-peak at δ 1.44, 32.02. This strong cross peak is assigned to both the δ- and γ-CH_2 groups of the HT configuration. Therefore, the corresponding cross-peak at δ 1.27, 32.02 is assigned to the HH configuration of both δ- and γ- CH_2 groups. The remaining sets of cross-peaks at δ 1.74, 27.45 and δ 1.60, 27.78 are assigned to the ϵ-CH_2 group in the HT and HH configurations, respectively.

A configurational assignment of sulfonated polythiophenes possessing longer side chains, e.g., sodium poly(8-(3-thienyl)octanesulfonate), was not successful due to its lower solubility in aprotic solvents.

Resolution enhancement of the ^{1}H NMR signals of both polymers, **1** and **2**, permitted an estimation of the relative population of the configurational isomers (see Table 1). The ratio of HT to HH diads in both **1** and **2** is 4:1, based on the areas of the resonances in the aromatic region. Knowledge of the regiochemistry of substituted polythiophenes is important since a high content of HT diads in poly(3-alkylthiophenes) results in materials that exhibit superior electrical conductivities.[7] On the other hand, a low percentage of HT diads leads to materials which possess higher luminescence efficiency.[8]

Conclusions

Assignment of the ^{1}H and ^{13}C NMR spectra of sodium poly(3-(3-thienyl)propanesulfonate) **(1)** and sodium poly(6-(3-thienyl)hexanesulfonate) **(2)** has been achieved. The solvent system played a major role in the resolution of the ^{1}H NMR spectra. Refinement of the spectra was obtained by resolution enhancement. The areas under the peaks were not affected. One- and two-dimensional NOE, HMQC, and DQF-COSY experiments were employed successfully for the configurational assignment of diads and triads in these sulfonated polymers. The ^{1}H chemical-shift pattern of the triads was found to be the same as in poly(3-alkylthiophene). This was not the case with the ^{13}C chemical shifts which decrease monotonically as the ^{1}H chemical shift increases. The difference in ^{13}C chemical shift of the CH_2 groups for HT or HH configurations is small. The ^{1}H chemical shift of the CH_2 group next to the sulfonate group in both polymers exhibits a large configurational dependence. This is in contrast to the case of poly(3-alkylthiophene) in which the difference in ^{1}H chemical shift for the HT and HH configurations decreases as the methylene unit is located further away from the thiophene ring. The ratio of HT to HH diads in both **1** and **2** is 4:1 based on the areas of the resonances in the aromatic region. This ratio is comparable with that found in poly(3-alkylthiophenes) when polymerized via oxidative coupling with ferric chloride.[20]

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support.

Supporting Information Available: Figure S1: Partial NOESY spectrum of **1** using a mixing time of 15 ms; figure S2: ^{1}H$-^{13}$C HMQC spectrum of **1** illustrating the aromatic region; figure S3: NOESY spectrum of **2** obtained with a mixing time of 10 ms (S3) (4 pages). Ordering information for these 4 pages is given on any current masthead page.

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