

Preparation of substituted poly(vinylthiophene)s via lithiation of poly(vinylthiophene)

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2-Vinylthiophene was homopolymerized using benzoyl peroxide as initiator. The polymer was lithiated using *n*-butyllithium. The ^1H -n.m.r. spectrum of the deuterated product obtained by quenching the lithiated polymer with deuterium oxide indicated that 93% lithiation had occurred, and that it had occurred very largely, if not entirely, at the α -position of the thiophene ring. The lithiated polymer was reacted with a range of electrophiles to give products containing new bonds to carbon (in various oxidation levels), sulphur, iodine, boron, phosphorus, silicon, or mercury.

(Keywords: poly(vinyl thiophene); lithiation; functionalization; ^{13}C nuclear magnetic resonance; ^1H nuclear magnetic resonance; polymer-supported reactions)

INTRODUCTION

There has recently been considerable interest in applications of reactive polymers in organic chemistry, for example as reagents or as chromatographic stationary phases¹. The functionalized polymers are often prepared by the chemical modification of preformed polymers. Two of the most important methods for preparing polystyrene derivatives in this manner are the reactions of chloromethylated polystyrenes with nucleophiles¹, often under phase transfer conditions², and the reactions of lithiated polystyrene with electrophiles^{1,3,4,5}. Lithiated polystyrene is generally prepared either by treating polystyrene itself with *n*-butyllithium in the presence of tetramethylethylenediamine^{3,4,6}, or by treating brominated polystyrene with *n*-butyllithium^{3,5}. These methods are not ideal. Thus, results tend to be erratic⁷, often substantial excesses of *n*-butyllithium are required^{3,7}, and the former method at best results in only ca. 20% of the phenyl residues being lithiated^{3,6}.

n-Butyllithium reacts with thiophene far more easily than it reacts with benzene or bromobenzene, and this prompted us to carry out the work described here. We have prepared polymers using 2-vinylthiophene, lithiated these polymers, and reacted the lithiated polymers with a wide range of electrophiles. Although crosslinked polymers are preferred to linear polymers for most applications¹, linear polymers were used in this preliminary study because they are more easily characterized with the aid of ^{13}C -n.m.r. spectroscopy.

EXPERIMENTAL

Materials and spectra

n-Butyllithium (1.6 M solution in hexane) was obtained commercially, and 2-vinylthiophene was prepared as reported⁸. Tetrahydrofuran (THF) was dried by distilling over calcium hydride, and stored over molecular sieves. Unless otherwise indicated, polymeric products were dried overnight in a vacuum oven (2 mm Hg) at 60°C. Molecular weights (M_n) of the unsubstituted polymers

were determined with a Knauer membrane osmometer with toluene as the solvent at 37°C. Infra-red spectra were recorded on a Nicolet MX-1 FT-IR instrument for KBr discs. Proton n.m.r. spectra were recorded using a JEOL JNM-PMX60 spectrometer (unless stated otherwise), and ^{13}C -n.m.r. spectra were recorded using a JEOL FX100 FT NMR spectrometer operating at 25.05 MHz. The degree of substitution (*DS*) is the percentage of thienyl residues which have undergone substitution.

Preparation of poly(vinylthiophene) (PVT)

Benzoyl peroxide (40 mg) was added to 2-vinylthiophene (4.00 g, freshly prepared) under nitrogen, then the mixture was stirred at 90°C for 11 h. The mixture was cooled, dissolved in chloroform (20 ml), and the solution added dropwise to stirred methanol (400 ml). The precipitate was collected and suspended in fresh methanol (100 ml) for 1 h. The product was then collected and dried (2.30 g, 58% yield). It had $\bar{M}_n = 13\,000$. Analysis gave: *S* = 28.92% ($-\text{C}_6\text{H}_6\text{S}-$ requires 29.09%).

The ^1H -n.m.r. spectrum (measured using a JEOL FX100 FT NMR spectrometer operating at 99.6 MHz; see Figure 2) showed signals at 6.9–7.2 ppm (C_5 -proton), 6.6–6.9 (C_4 -proton), 6.1–6.5 ppm (C_3 -proton), 2.3–2.8 (methine proton), and 1.4–1.8 (methylene protons), and was identical to the previously reported spectrum⁹. The ^1H n.m.r. spectrum measured at 60 MHz (using a JEOL JNM-PMX60 n.m.r. spectrometer) was similar, but the signals overlapped.

Lithiation of PVT

A hexane solution of *n*-butyllithium (1.9 ml of 1.6 M solution, 3 mmoles) was added (using a syringe) to a three-necked flask fitted with a nitrogen inlet, septum cap, a drying tube, and magnetic stirrer bar, containing THF (5 ml). A solution of PVT (0.3 g, equivalent to 2.7 mmole monomer units) in THF (10 ml) was added dropwise over 10–15 min at 0°C. The mixture was heated for 30 min at 40–50°C, and then stirred for 1 h at room temperature.

The resulting mixture (which was a faint yellow fine suspension), was then reacted further, as described below.

Reactions of lithiated poly(vinylthiophene) (PVT) with various electrophiles

Procedure A. The reagent (either as the pure liquid, or, for a solid, in THF solution) was added dropwise to the solution of lithiated PVT (prepared as above from 0.3 g PVT) at 0°C in a three-necked round bottom flask (100 ml) fitted with a separating funnel and nitrogen inlet, a reflux condenser and drying tube, and a magnetic stirrer bar. After addition was complete, the mixture was stirred for several hours (see Table 2) at room temperature under dry nitrogen. The mixture was then added dropwise to methanol (or water) to degrade any intermediates and to precipitate the polymer. The product was filtered off, and (typically) washed successively with water (400 ml), methanol (100 ml), and ether (100 ml). The product was then dried (*in vacuo*) at 60°C and weighed, the i.r. ¹H-n.m.r. and ¹³C-n.m.r. spectra measured (where the product was sufficiently soluble), and an elemental analysis obtained (when useful). *DS* values were calculated from the integration of the ¹H-n.m.r. spectra, and/or the elemental analysis. Details of ¹³C-n.m.r. spectra are summarized in Table 3.

The above procedure was used for reactions of lithiated PVT with the following reagents.

Deterium oxide (3 ml): The dried product (0.1 g) had the following ¹H-n.m.r. spectrum (CDCl₃); δ1.65 (methylene protons), δ2.49 (methine proton), δ6.1–6.5 (C₃-proton), δ6.6–6.9 (C₄-proton), and a small signal at δ6.9–7.2 (residual protons at C₅) (see Figure 2). The value of *DS* was based on the integration of the ¹H-n.m.r. spectrum = 93%.

Dimethyl sulphate (3 ml): The product (0.28 g) had the following ¹H-n.m.r. spectrum; 1.4–1.9 (methylene protons), δ2.4–2.7 (a sharp signal from –CH₃ superimposed on broader methine signal), δ6.0–7.0 (protons in thiophene ring). *DS* based on n.m.r. spectrum integration = 74%.

Quinoline (0.5 g in 3 ml THF): The product (0.27 g) had the following ¹H-n.m.r. spectrum (CDCl₃); δ1.4–1.8 and δ2.3–2.7 (methylene and methine protons) and δ6.1–8.2 (broad, protons of thiophene and quinoline rings); there was no signal at δ8.7 corresponding to the proton on the carbon adjacent to the nitrogen. *DS* based on n.m.r. spectrum integration = 34%. Analysis; N = 2.4% indicating that *DS* = 24%.

Dimethylformamide (3 ml): The product (0.28 g) had ν_{\max} 1667 cm⁻¹ (CO), and the following ¹H-n.m.r. spectrum; δ1.2–1.8 and 2.0–2.7 (methylene and methine protons), δ6.0–6.9 (thiophene protons), and δ9.4–9.7 (aldehydic proton). The value of *DS* based on n.m.r. spectrum integration = 25%. A sample (0.2 g) of the product in THF (2 ml) was heated under reflux with hydroxylamine hydrochloride (0.3 g) in pyridine (3 ml) for 2.5 h. The precipitate formed on cooling was filtered off and washed successively with water, aqueous THF, and methanol. The dried product (0.15 g) had a value of ν_{\max} = 3320 cm⁻¹ (OH), but showed no carbonyl absorption at 1667 cm⁻¹. Analysis gave; N = 4.21%, indicating *DS* = 38%.

Phenylisocyanate (3 ml): The dried product (0.27 g) had ν_{\max} 1641 cm⁻¹ (CO), 3285 and 3360 cm⁻¹ (NH) and the following ¹H-n.m.r. spectrum (DMSO-d₆): broad signal

1.6–2.5 (methylene and methine protons, partly obscured by DMSO signal), 6.1–6.9 (thiophene ring), 6.9–7.5 and 7.5–7.9 (benzene ring). Analysis gave; N = 5.47%, indicating *DS* = 80%.

Dimethyl disulphide (3 ml): The product (0.31 g) had the following ¹H-n.m.r. spectrum (CDCl₃): 1.4–1.9 (methylene protons), 2.4–2.5 (sharp signal from CH₃ protons superimposed on broader signal from methine proton), and 6.1–6.9 (thiophene protons; clear absence of signal due to C₅-proton at 6.9–7.2). *DS* based on n.m.r. spectrum integration = 67%. Analysis gave; S = 36.86%, indicating that *DS* = 57%.

Benzophenone (0.7 g): The product (0.5 g) had ν_{\max} 3580 cm⁻¹ (–OH), and no absorption due to a carbonyl group, and the following ¹H-n.m.r. spectrum (CDCl₃); δ1.2–1.8 and 2.2–3.0 (methylene, methine, and hydroxyl protons), δ6.0–6.6 (thiophene protons), and δ6.6–7.6 (phenyl rings). The value of *DS* based on n.m.r. spectrum integration = 50%.

Iodine (0.9 g): Analysis of product (0.46 g), I = 35.82%, indicating that *DS* = 48%.

Diphenylchlorophosphine (2.8 ml): The product (0.4 g) had ¹H-n.m.r. spectrum (CDCl₃); 1.2–1.8 and 2.1–2.7 (methylene and methine protons), 6.0–6.9 (thiophene protons), and 7.0–7.1 (sharp, phenyl protons). *DS* based on n.m.r. spectrum integration = 47%. Analysis gave; P = 6.85%, indicating *DS* = 41%.

Trimethylchlorosilane (3 ml): The product (0.29 g) had ν_{\max} 1249 cm⁻¹ (Si–C), and the following ¹H-n.m.r. spectrum (CDCl₃); 0.24 (sharp, –CH₃), 1.3–1.9 and 2.2–2.8 (methylene and methine protons), and 6.0–6.9 (thiophene protons, no signal at 6.9–7.2 due to the C₅-proton). The value of *DS* based on n.m.r. spectrum integration = 58%. Analysis gave; Si = 7.5%, indicating *DS* = 37%. The polymer was found to have \bar{M}_n = 19 830.

Mercury(II) chloride (0.8 g): The product (0.7 g) had ν_{\max} = 340 cm⁻¹ (Hg–Cl). Analysis gave; Hg = 55.1% and 56.3%, indicating *DS* = 87%. (In this experiment the precipitated polymeric product was washed with water until the washings showed no positive test for mercury(II) ions⁹.)

Procedure B. The reagent (as a liquid or, for a solid, in THF solution) was added dropwise to the solution of lithiated PVT at 0°C, and then the reaction mixture was stirred at room temperature for a period, as in 'Procedure A'. Two layers formed. The organic layer was separated, and the aqueous layer extracted with chloroform (2 × 25 ml). The combined organic layers were reduced in volume (to approx. 25 ml), and then added dropwise to methanol. The precipitated product was then filtered off and treated as in Procedure A.

The above procedure was used in the reactions of lithiated PVT with the following reagents.

Benzyl bromide (1 ml): The product (0.34 g) had the following ¹H-n.m.r. spectrum (CDCl₃); 1.2–1.8 and 2.2–2.8 (methylene and methine protons), 6.1–6.8 (thiophene protons), and 7.2 (sharp, phenyl protons). The value of *DS* based on n.m.r. spectrum integration = 68%. Analysis gave; S = 17.85%, indicating that *DS* = 77%.

p-Bromobenzyl bromide (0.7 g): The product had the following ¹H-n.m.r. spectrum (CDCl₃); 1.2–1.8 and 2.2–2.8 (methylene and methine protons), 6.0–6.9 (thiophene protons), and 6.9–7.1 and 7.5–7.8 (both doublets, *p*-substituted phenyl system). The value of *DS* based on

n.m.r. spectrum integration = 54%. Analysis gave; Br = 22.75%, indicating DS = 60%.

Acetaldehyde (3 ml): The product (0.35 g) had ν_{\max} 3430 cm^{-1} (OH). A sample (0.2 g) of the product was heated under reflux with *p*-chlorobenzoyl chloride (3 ml) in dry pyridine (10 ml) for 3 h, and the mixture added dropwise to a mixture of water/ethanol (1:1, 400 ml). The precipitated product was filtered off and washed successively with water, methanol, and ether, and then stirred first with dioxan, and then with ether. After filtration, and washing (with ether), the dried product (0.17 g) had ν_{\max} 1718 cm^{-1} (CO), but no absorption at 3430 cm^{-1} . Analysis gave; Cl = 9.43%, indicating that DS = 57%.

The procedures used for the remaining preparations are as follows.

Carbon dioxide

The solution of PVT was poured onto a slurry of dry-ice in THF (approx. 30 ml), the mixture was stirred for 3 h at room temperature, and then water (10 ml) was added. The mixture was acidified (with a small volume of conc. HCl) and stirred for a further 30 min, and then extracted with chloroform (2 × 25 ml). The chloroform extracts were reduced in volume (to 25 ml) and added dropwise to petroleum ether (b.pt. 40°–60°C). The precipitated polymer was filtered off and washed with water and petroleum ether. The dried product (0.25 g) had ν_{\max} 2900–3500 cm^{-1} (broad, carboxyl group) and 1678 cm^{-1} (carbonyl group).

A sample (0.1 g) of the polymer was heated under reflux for 2 h with sodium hydroxide solution (5 ml of 1 M), and then left overnight stirring at room temperature. Titration of this solution with standard hydrochloric acid indicated DS = 100%.

Borane

A solution of borane in THF (7 ml, 0.87 M) was added, using a syringe and septum cap, to a solution of lithiated PVT (prepared from 0.5 g PVT), and the solution was stirred for 2 h at room temperature. Water (20 ml) was added cautiously, the mixture stirred for a further 2 h, and then acidified with 1 M HCl. The precipitated polymer was filtered off, washed with water, and then transferred to a beaker and stirred with water (80 ml) at 70°C for 2 h. The solid was again filtered off and washed with water, methanol and ether. The dried polymer (0.51 g) had ν_{\max} 3500 cm^{-1} (OH-group) and 1342 cm^{-1} (B–O group). Analysis gave; B = 1.63%, indicating that DS = 18%.

Trimethyl borate

Dry trimethyl borate (0.7 g) in THF (5 ml) was added dropwise to lithiated PVT at –15°C, the mixture was stirred for 6 h at room temperature, and then cooled and cautiously acidified with 10% sulphuric acid (27 ml). After stirring for a further 2 h the organic layer which had formed was separated and the aqueous layer extracted with chloroform (2 × 25 ml). The combined organic layers were added dropwise to methanol (250 ml), and the precipitate formed washed as described above. The dried product (0.2 g) had ν_{\max} 3480 cm^{-1} (OH group) and 1338 cm^{-1} (B–O group). Analysis gave; B = 1.25%, indicating that DS = 13%.

RESULTS AND DISCUSSION

2-Vinylthiophene was prepared from thiophene and acetaldehyde by the method of Emerson and Patrick⁸,

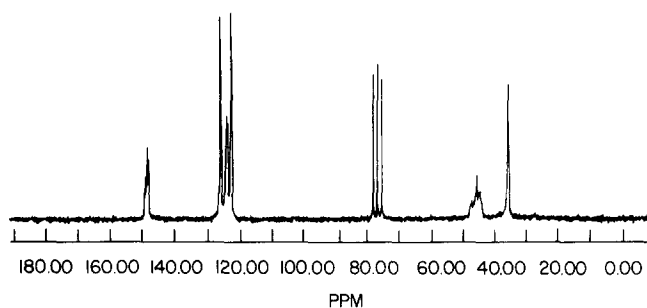


Figure 1 ^{13}C -n.m.r. spectrum (in CDCl_3) of poly(vinylthiophene)

Table 1 Chemical shifts in ^{13}C -n.m.r. spectra^a of poly(vinylthiophene) and α -methylthiophene^b

	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇
	(148.1–149.2)	(123.6–124.5)	126.1	122.7	36.1	(44.0–48.0)
	139.2	125.5	127.0	123.2	14.8	

^a For solution in CDCl_3

^b Taken from ref. 4

and was homopolymerized using benzoyl peroxide as the initiator. The product (**1a**) had a ^1H -n.m.r. spectrum virtually identical to that previously reported¹⁰. The ^{13}C -n.m.r. spectrum (see Figure 1 and Table 1) was consistent with the expected structure; assignments were made by reference to 2-methylthiophene¹¹ and polystyrene¹². The overall similarity of the spectra of poly(vinylthiophene) and polystyrene suggests that the signals at 36.1 and 44.0 to 48.0 ppm in the spectrum of the former polymer correspond to the methine and methylene carbon atoms respectively*, and this was confirmed using a DEPT technique.

The poly(vinylthiophene) in THF was treated at 0°C with a 10% excess of commercial *n*-butyllithium in hexane. The mixture was heated to 40°C for 30 min, then after a further hour stirring at room temperature the reaction was quenched with deuterium oxide, and the polymer isolated. The ^1H -n.m.r. spectrum of this product (see Figure 2) showed only a small signal at δ 7.0 (i.e. the expected position of the signal from the proton on carbon atom C₅ of the thiophene ring), indicating that the lithiation had occurred to at least 93% and, as expected¹⁴, at the α -position. The lithiated product, therefore, contained residues (**1b**).

Samples of poly(vinylthiophene) were lithiated under similar conditions, and then reacted with a range of electrophiles (Table 2). The isolated products were characterized by their infrared spectra, ^1H and ^{13}C -n.m.r. spectra (when sufficiently soluble), and in some cases, by elemental analysis. The ^1H -n.m.r. signals, although

* The analogous signals in the spectrum of polystyrene (at 40.4 and 42.0 to 47.0 ppm for –CH– and –CH₂– respectively) have not always been assigned correctly. See, for example references 12 and 13.

Table 2 Products (1) of reaction of lithiated poly(vinylthiophene) with various reagents

Entry	Reagent	Reaction time (h) ^b	Substituent (X) in formula (1)	DS% ^a	mmoles substituent g ⁻¹ polymer
1	D ₂ O	1	-D	93 ^b	8.4 ^b
2	(CH ₃) ₂ SO ₄	1	-CH ₃	74 ^b	6.1 ^b
3	C ₆ H ₅ CH ₂ Br	6	-CH ₂ ·C ₆ H ₅	68 ^b 77 ^c	4.3 ^c
4	pBrC ₆ H ₄ CH ₂ Br	14	-CH ₂ C ₆ H ₄ Br	54 ^b 60 ^c	2.8 ^c
5	CH ₃ ·CHO	4	-CH(OH)CH ₃	57 ^{c,e}	4.2
6	Quinoline	2	2-Quinolyyl	34 ^b 24 ^c	1.7 ^c
7	HCON(CH ₃) ₂	5	-CHO	25 ^b 38 ^{c,f}	3.1 ^c
8	CO ₂	3	-CO ₂ H	100 ^g	6.5 ^g
9	C ₆ H ₅ NCO	1	-CONHC ₆ H ₅	80 ^c	3.9 ^c
10	CH ₃ SSCH ₃	1.5	-SCH ₃	67 ^b 57 ^c	4.2 ^c
11	I ₂	2	-I	48 ^c	2.8 ^c
12	BH ₃	2	-B(OH) ₂ ^d	18 ^c	1.5 ^c
13	B(OCH ₃) ₂	6	-B(OH) ₂ ^d	13 ^c	1.1 ^c
14	(C ₆ H ₅) ₂ PCl	2.5	-P(C ₆ H ₅) ₂	47 ^b 41 ^c	2.2 ^c
15	(CH ₃) ₃ SiCl	1.5	-Si(CH ₃) ₃	58 ^b 37 ^c	2.7 ^c
16	HgCl ₂	3	-HgCl	87 ^c	2.8 ^c

^a DS = Degree of substitution, i.e. % of thieryl groups which contain new functional group

^b Determined by integration of ¹H-n.m.r. spectrum

^c Determined by elemental analysis

^d Obtained after hydrolysis of intermediate organoboron compound

^e Based on analysis (for chlorine) of derivative prepared from *p*-chlorobenzoyl chloride

^f Based on analysis (for Nitrogen) of the oxime derivative

^g Based on titration with alkali

^h Reactions carried out at room temperature

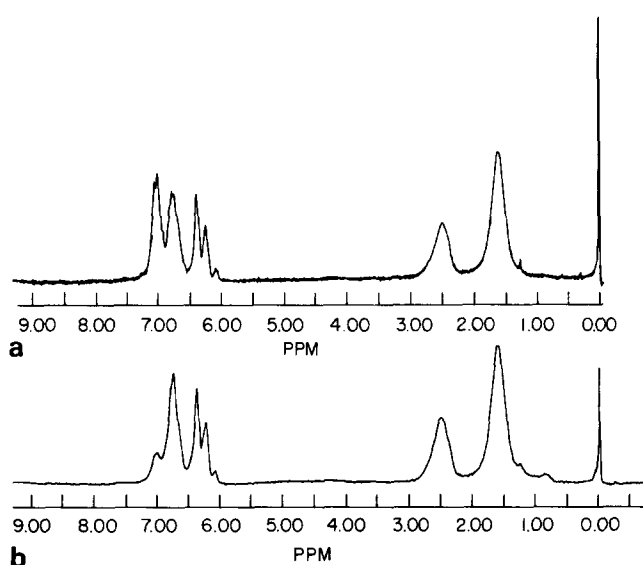
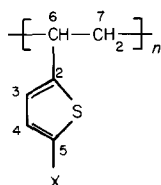


Figure 2 ¹H-n.m.r. spectra (in CDCl₃) of (a) poly(vinylthiophene) and (b) deuterated poly(vinylthiophene)

frequently broad, showed the expected shifts. A significant feature in many of the spectra was the absence, or diminution, in the absorption at δ6.9–7.2, indicating that the substituent was in the α-position (i.e. C₅) of the thiophene ring. This region of the spectrum was however, obscured in the products containing phenyl groups, since this moiety absorbs in the same region. The ¹³C-n.m.r. spectra of the various products showed clear signals



(1a), X = H
(1b), X = Li

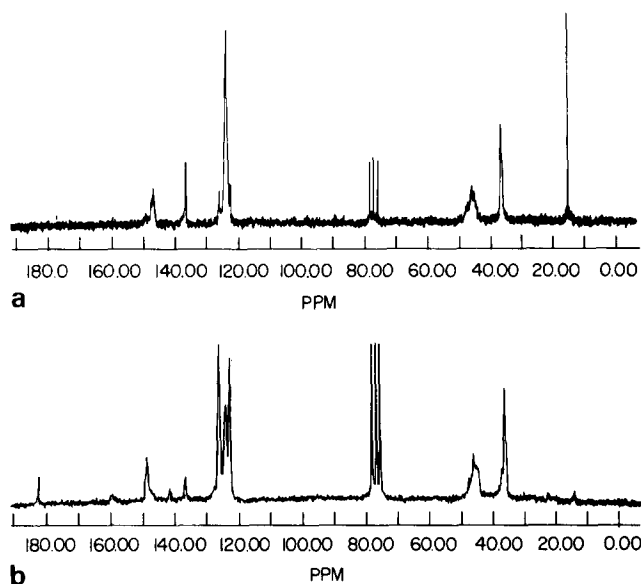


Figure 3 ¹³C-n.m.r. spectra (in CDCl₃) of poly(vinylthiophene) containing (a) -CH₃ groups and (b) -CHO groups (compound 1b, X = CH₃ or CHO)

which could be assigned to the particular substituent group (X in compound 1), and to the carbon atom of the thiophene ring bearing the substituent (C₅). Typical spectra are shown in Figure 3, and chemical shifts and assignments are summarized in Table 3. It is clear that the present method of introducing functional groups is versatile and allows bonds to be formed to carbon (in various oxidation levels), sulphur, iodine, boron, phosphorus, silicon, and mercury.

CONCLUSIONS

Poly(vinylthiophene), unlike polystyrene, readily undergoes direct lithiation (in the α-position of the thiophene

Table 3 Chemical shifts in ^{13}C -n.m.r. spectra of partially substituted poly(vinylthiophene)s^a (in CDCl_3)

C-atom number	H	Substituent group, X, and numbering system											
		$^8\text{-CH}_3$	$^8\text{-CHO}$	$^8\text{-CO-NH-}$	$^8\text{-CH}_2\text{-}$	$^8\text{-P-}$	$^8\text{-CH}_2\text{-}$	$^8\text{-CH}_2\text{-}$	$^8\text{-CH}_2\text{-}$	$^8\text{-SCH}_3$	$^8\text{-Si(CH}_3)_3$	Quinoline ring	
2	148.7	146.9	148.2 -148.8	148.0	148.3	148.0 -149.0 ^b	147.0 -149.0 ^b	148.0 -149.5 ^b	148.6	148.0 -149.5 ^b	148.0	147.0 -149.5	
3,4	124.2 126.1	122.4, 124.2 126.1 ^c	122.6, 124.1 126.0, 136.5 ^c	122.0 -126.4 ^{b,c}	124.2, 126.3	122.6 -126.2 ^{b,c}	122.5 -126.3 ^{b,c}	126.5 -127.6 ^c	122.5 126.5 130.8, 137.2	122.8 124.0, 126.5 133.2, 137.1	122.0 125.5	122.0 125.5	
5	122.7	136.7	141.8	153.0 -155.0 ^b	147.5	155.0 -157.0 ^b	147.0 -149.0	146.3 (141.6-142.5)	151.8	154.2 -154.8	147.0 -149.5 ^b	147.0 -149.5 ^b	
6	35.9 -36.2 ^b	36.0 -37.0 -37.5 ^b	35.5 -37.5 ^b	35.8 -37.4 ^b	36.2	35.8 -37.4 ^b	36.1	36.1	36.6	36.2	36.1	36.1	
7	44.5 -46.5 ^b	44.0 -48.0 ^b	44.0 -48.0 ^b	44.0 -48.0 ^b	43.0 -47.0 ^b	44.0 -48.0 ^b	44.0 -48.0 ^b	44.0 -48.0 ^b	44.0 -48.0 ^b	44.0 -48.0 ^b	44.0 -48.0 ^b	44.0 -48.0	
8	15.5	182.5	159.9	133.4	133.4	133.4	36.9	51.9	22.2	0.5	157.6	157.6	
9			138.7	132.6	140.5	132.6	139.4 -140.3	141.6-142.5 (146)			142.3	142.3	
10			120.5	128.2		128.2	130.4	127.6			125.5	125.5	
11			128.6	128.6		128.6	131.4	129.5 130.4			-130.0 ^f	-130.0 ^f	
12							120.3	130.4			136.4	136.4	

^a Numbering system as in Figure 1

^b Broad signal

^c Several signals with similar shifts, arising from substituted and unsubstituted thiophene residues

^d In DMSO-d_6 solvent

^e Includes other signals from quinoline ring

^f Hidden by signals from DMSO

^g Obscured by methine (C_6) signal

residue) on reaction with n-butyllithium. A high degree of metallation can be achieved without using catalysts (such as tetramethylethylenediamine) or a large excess of the organolithium reagent.

The lithiated polymer can be reacted with a wide range of electrophiles to give polymers containing a functional group on the α -position of the thienyl residue. Usually a relatively high degree of functionalization can be obtained. The present work has been deliberately limited to a linear system in order to facilitate spectroscopic characterization of the products, but it is reasonable to assume that polymers with a low degree of crosslinking will behave in a similar manner. Polymers prepared using vinylthiophene may, therefore, prove to be useful materials in the preparation of various polymer supported reagents.

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