

Review

Silyl substitution as an aid in polymerization reactions: oxidative coupling of silylthiophene, a route to highly conjugated polythiophene¹

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Abstract

Raman spectroscopic and photoluminescence studies have shown that the oxidative polymerization of silyl thiophene monomers leads to highly conjugated polythiophene. Soluble high molecular weight polymers have been obtained by use of silylated monomers. The role of silicon is suggested to involve the stabilization of intermediate cationic species.

Keywords: Silicon; Polythiophene; Oxidative coupling; Silylthiophene; Conducting polymer

1. Introduction

Conjugated polymers have attracted much interest in recent years owing to their potential applications in electronics, optoelectronics and as non-linear optical materials [1]. Efforts have been made to synthesize polymers with improved conjugation properties, and also to prepare new conjugated polymers containing novel chain units, from a variety of unsaturated monomers.

Silicon-directed reactions have been widely used in organic synthesis to improve the selectivity of carbon-carbon bond formation [2]. However, with the exception of the group transfer polymerisation reactions [3], little attention has been paid to the use of related methodology for selective polymerization reactions. Improved selective routes to polymeric materials would be of particular interest in the case of conjugated organic polymers, since the properties of the latter are strongly related to the structural properties of the conjugated chain.

We present below a brief review of the use of silylated monomers for the preparation of polythiophene. After the recent observation, based on electrochemical studies, that trimethylsilyl groups facilitate the α - α' oxidative coupling of thiophene [4], we [5] and others [6] reported the preparation of polythiophene films from various silylthiophene derivatives:



We were interested in defining the role of the silyl substituents during the oxidative polymerization and in characterizing changes in the structural properties that might result from the use of silyl monomers. The evaluation of this new route to polythiophene required a precise characterization of the conjugated materials produced. Therefore, we first summarize new criteria based on Raman and photoluminescence spectroscopy which allow a precise estimate of the conjugation properties. Then, the synthesis and characterization of polythiophene samples arising from the oxidative polymerization of silyl thiophene is described. We discuss both the electrochemical and chemical oxidation of a variety of

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¹ Dedicated to Professor Robert Corriu in recognition of his outstanding contribution to silicon chemistry.

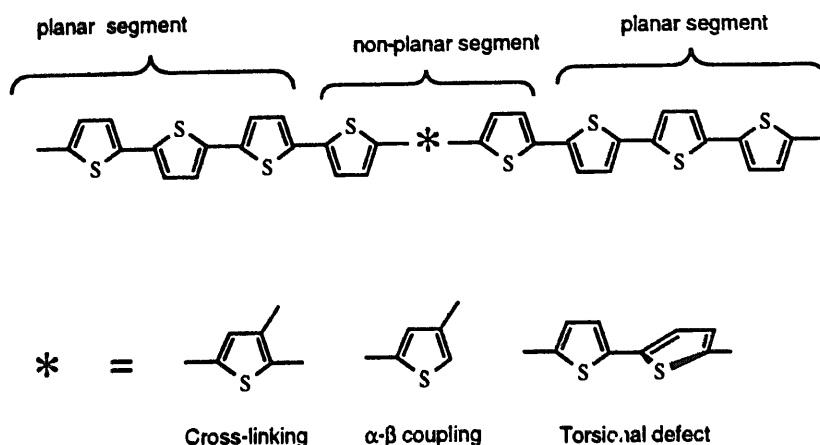


Fig. 1. Chain of polythiophene containing well conjugated (planar) segments and poorly conjugated (non-planar) segments.

silyl thiophene monomers. The polymerization of alkyl substituted monomers leading to high molecular weight soluble polythiophene is also discussed.

2. Characterization of polythiophenes by Raman spectroscopy and photoluminescence

For unsaturated polymers, the conjugation appears to determine the properties of the conjugated systems (electronic, non-linear optics, electroluminescent properties, etc.). Knowledge and control of the conjugation parameters, i.e. the mean value of the conjugation length L_c and the polydispersity ΔL_c of the conjugation length, are of particular importance.

Methods based on Raman spectroscopy and photoluminescence have been developed in order to evaluate the conjugation length in conjugated polymers. A detailed discussion of the various methods has been reported [5e]. Here, we only summarize the main criteria used to characterize and compare the conjugation properties of various polythiophene samples arising from the oxidative polymerization of a variety of thiophene monomers prepared in different ways.

2.1. Resonant Raman scattering

Polythiophene can be viewed as a chain of alternating planar highly conjugated segments and non-planar poorly conjugated segments. The highly conjugated segments consist of a chain of thienyl units exclusively 2,5-linked throughout (α, α' coupling) in a planar arrangement. The poorly conjugated segments are associated with the presence of conjugation defects arising from changes in the chain conformation by rotation around the C–C single bond, the presence of α – β coupling or cross-linking (Fig. 1).

A detailed analysis of the Raman spectrum of polythiophene (Fig. 2) allows us to define two kinds of Raman mode: the modes of the highly conjugated

coplanar chain and the defect modes. The defect modes vanish in highly conjugated polythiophene. More precisely, a strong correlation between the value of the conjugation length L_c and the ratio R of the intensities of the Raman lines at 682 and 700 cm^{-1} has been established. The 700 cm^{-1} band was assigned to the ring-deformation vibration in a coplanar chain and the 682 cm^{-1} one to the same kind of motion in a distorted conformation of the chain. Consequently, this last parameter R relates the value of the conjugation length to the distortion of the chain and gives a measure of the number of coplanar segments along the chain.

In addition, an increase in the conjugation length causes a large increase in the ratio ρ of the intensities of the Raman lines at 700 and 1045 cm^{-1} . The latter, assigned to the in-plane C–H bending mode, is not sample dependent and was chosen as an internal inten-

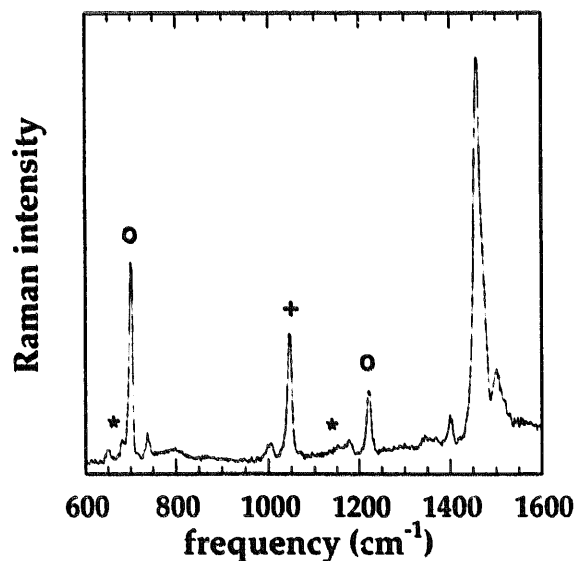


Fig. 2. Low temperature Raman spectrum of polythiophene (pTh(2-Si)) recorded at $\lambda_{\text{exc}} = 5145 \text{ \AA}$ and $T = 10 \text{ K}$. O, Raman lines of the planar conjugated segments; *, Raman lines of the non-planar poorly conjugated segments; +, C–H bending mode used as intensity reference.

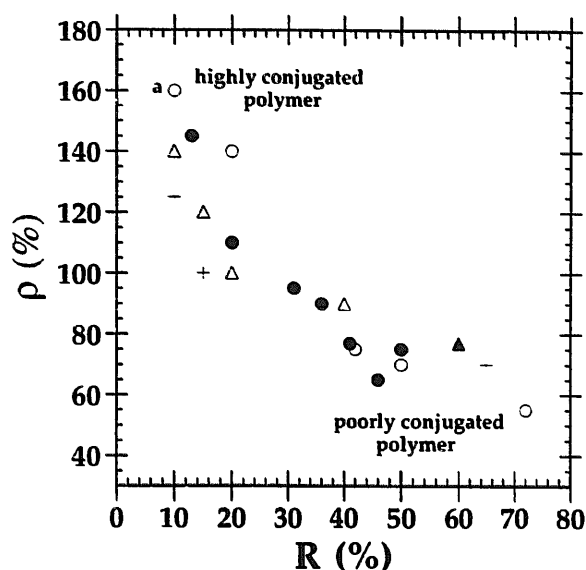


Fig. 3. $\rho(I_{700}/I_{1047})$ vs. $R(I_{682}/I_{700})$ dependence for polythiophene samples. a, pTh(2-Si) electrochemically prepared; \circ , pTh(n -Si) obtained by electrooxidation of monomers (n -Si), $n = 1, 2, 3$; \bullet , pTh(n) obtained by electrooxidation of monomers (n), $n = 1, 2, 3$; Δ , pTh(n -Si) prepared by chemical oxidation of monomers (n -Si), $n = 1, 2, 3, 4$; $+$, pTh(n) prepared by chemical oxidation of monomers (n), $n = 1, 2, 3, 4$; \blacktriangle , pTh(6-Si) obtained electrochemically.

sity reference. We established a clear correlation between the R and ρ parameters [5a,e]. Examples are shown in Fig. 3. The determination of the ratio ρ is significantly more precise and much easier than of the ratio R , especially for polymers with extended conjugation length. The ρ ratio appeared to be the most pertinent Raman criterion for defining the conjugation length and especially for distinguishing between different highly conjugated polythiophene samples.

2.2. Photoluminescence

Photoluminescence is observed in conjugated polymers with non-degenerate ground states, such as cis-polyacetylene [7], polythiophene [8] and polyphenylenevinylene [9]. Photoluminescence spectra are attributed to fluorescence due to their short lifetime and similarity to emission from the singlet state [10]. An energy diagram illustrating the fluorescence of polythiophene is shown in Fig. 4. The 'ideal' spectrum of emitted light exhibits vibronic structure (Fig. 5), i.e. a series of discrete peaks separated by optic phonon frequencies [5e,11].

From a detailed analysis of the photoluminescence properties of various oligomers and polymers, the following conclusions were reached [5e].

(i) The position of the photoluminescence band depends on the conjugation length. The photoluminescence shifts to lower energy when the conjugation length L_c is increased.

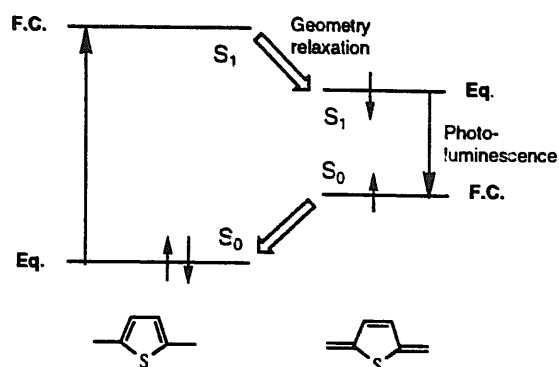


Fig. 4. Energy diagram illustrating the photoluminescence of polythiophene. S, singlet state; Eq., equilibrium electronic state; F.C., Frank-Condon electronic state.

(ii) The dispersion of the conjugation lengths leads to a dispersion of the emission energy. This results in a broadening of the photoluminescence. Assuming that the dispersion of the conjugation length is the main cause of broadening, the width of the peaks then gives a qualitative estimate of the polydispersity ΔL_c of the conjugation length.

(iii) With respect to the 'ideal' profile of the photoluminescence, additional peaks are observed in crystalline compounds.

From a quantitative point of view, measurement of the positions of the peaks and/or their relative intensities provides an estimate of the value of the confinement parameter γ [11], which is the pertinent parameter in the description of the electronic properties of conjugated polymers with non-degenerate ground states.

3. Electrochemical oxidation of α - and β -silylated thiophenes

3.1. α -Silylated thiophenes

Evidence for the influence of silyl substituents was first observed in electropolymerization experiments [4].

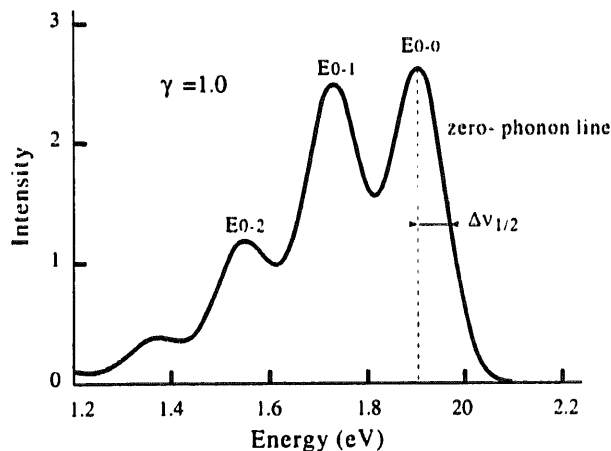


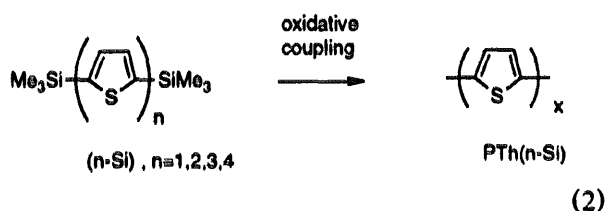
Fig. 5. "Ideal" photoluminescence spectrum calculated for a well conjugated polythiophene ($\gamma = 1$) (from Ref. [11]).

Table 1
R and ρ values (%) for polythiophene films prepared by electrochemical oxidation of silylated monomers

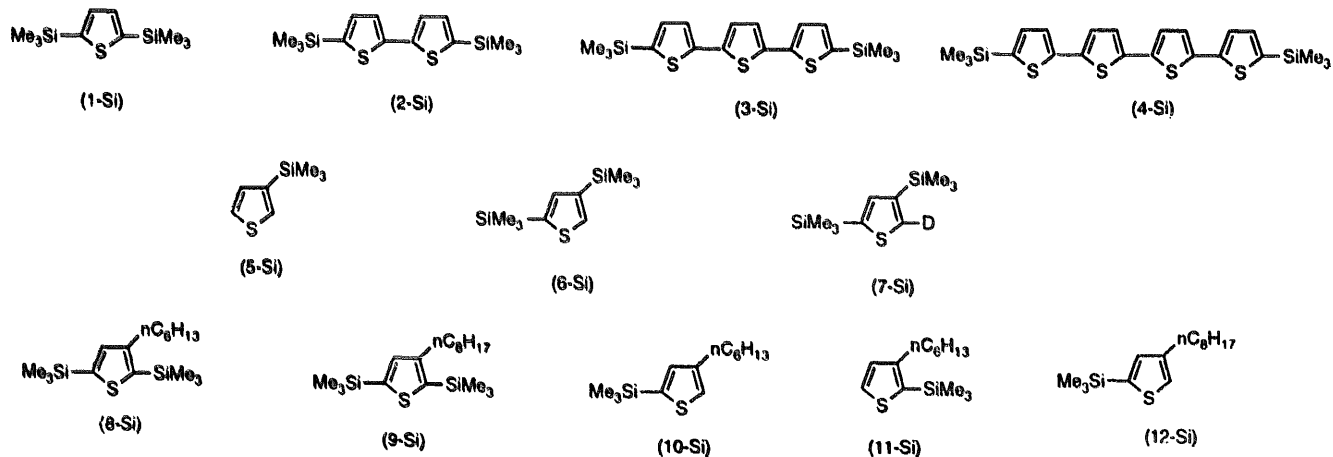
| Film | <i>R</i> | ρ |
|-----------|----------|--------|
| pTh(1-Si) | 40 | 75 |
| pTh(2-Si) | 10 | 160 |
| pTh(3-Si) | 20 | 140 |

In contrast with the electropolymerization of bithiophene which yields the polymeric material as a powder with low conductivity, the polymerization of bis α , α' -bis-silylated bithiophene leads to a free-standing polymer film with good conductivity. Moreover, the voltammogram of the film shows closer similarities with that of the material obtained upon polymerization of thiophene rather than that of the polymeric material arising from bithiophene.

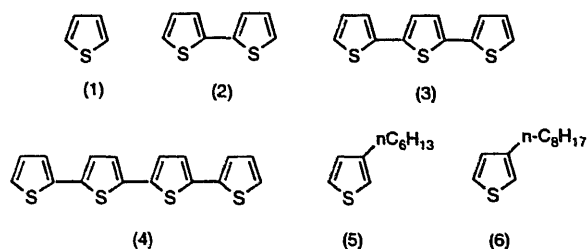
We prepared [5a] polymer films by oxidative polymerization of various bis-silylated monomers, 1-Si, 2-Si, 3-Si (Scheme 1). The resulting materials (pTh(1-Si), pTh(2-Si), pTh(3-Si); Eq. (2)) were scanned by IR and Raman spectroscopy.



The initial characterization of the films by FTIR spectroscopy led to the conclusion that electropolymerization occurs via α - α' coupling with elimination of the SiMe_3 groups. The characteristic bands of polythiophene were observed (strong absorption around 780 cm^{-1} , assigned to the C-H out-of-plane bending of the 2,5-disubstituted thiophenes), and the characteristic vibrations of the SiMe_3 groups were very weak. Moreover, EDAX analysis revealed very low Si/S ratios (less than 0.03) in the material produced.



Scheme 1. α - and β -silylated thiophenes used as monomers for oxidative polymerization. Abbreviations of monomers are quoted in parentheses.



Scheme 2. Non-silylated thiophenes used as monomers for oxidative polymerization.

The effect of the use of silyl monomers on the structural properties of polythiophene was assessed on the basis of Raman resonance scattering and photoluminescence criteria [5a].

The Raman spectra of the films pTh(1-Si), pTh(2-Si) and pTh(3-Si) were examined in the 600 – 720 and 1045 cm^{-1} regions to determine the *R* and ρ values. Each Raman line, 652 , 682 and 700 cm^{-1} , was fitted to a Lorentzian profile in order to obtain *R* with good accuracy. The *R* and ρ values obtained are listed in Table 1. With respect to the *R* and the ρ criteria, the film synthesized from α , α' -bis-silylated bithiophene monomer (pTh(2-Si)) appeared the more conjugated sample. Moreover, the narrowing of the Raman line at 1458 cm^{-1} is consistent with a highly conjugated material with low ΔL_c value.

The values of ρ for polythiophene films synthesized from silylated monomers 1-Si, 2-Si and 3-Si are plotted against *R* in Fig. 3, which for comparison also shows plots for the related non-silylated monomers (Scheme 2) thiophene (1), bithiophene (2) and terthiophene (3) respectively. The polymer pTh(2-Si) appears the most conjugated of this series. Comparison of the *R* and ρ factors for polymer films prepared under similar reaction conditions from silylated and non-silylated bithiophene monomers clearly shows that the use of silylated

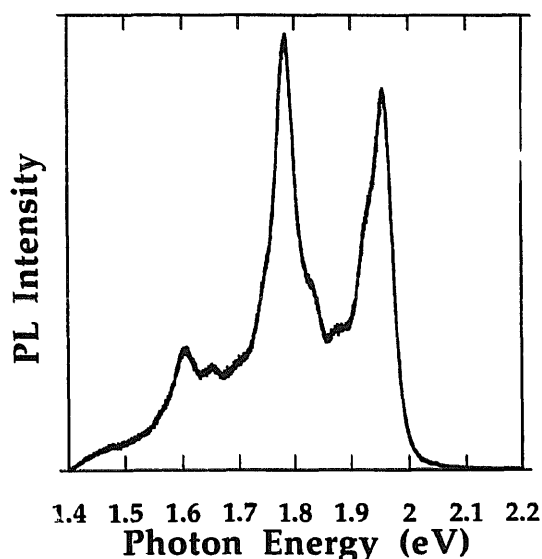


Fig. 6. Low temperature ($T = 10$ K) photoluminescence spectrum of pTh(2-Si) electrochemically prepared ($\lambda_{exc} = 5145$ Å).

monomers results in an increase in the mean conjugation length L_c of the polymeric chain.

In agreement with the Raman data, the photoluminescence from the pTh(2-Si) film shows the expected profile for a highly conjugated polymer: three narrow and well-defined peaks with an energy separation of 0.175 eV (Fig. 6). This shape is close to the calculated "ideal" profile (see Fig. 4).

The photoluminescence data for polythiophene samples prepared from bis-silyl thiophene monomer (pTh(2-Si)) and from non-silylated bithiophene (pTh(2)) are shown in Table 2. Compared with polythiophene prepared from bithiophene, the polymer arising from the silyl monomer (2-Si) showed a zero-phonon line at lower energy values and with a reduced line width. These observations are consistent with an increase in the mean conjugation length L_c and a decrease in the polydispersity ΔL_c of the conjugation length when using a silyl-substituted monomer.

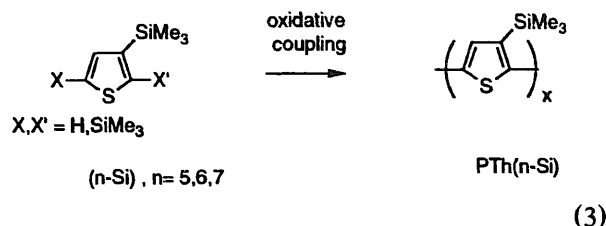
3.2. β -Silylated thiophenes

We also studied, for comparison, the use of monomers with silyl substituents at the β -position. The electropolymerization of the 3-trimethylsilylthiophenes (5-Si, 6-Si, 7-Si in Scheme 1) [5a] gave in all cases

Table 2
Photoluminescence data for polymers pTh(2) and pTh(2-Si)

| Polymer | "Zero-phonon" line | |
|-----------|-----------------------|------------------------------|
| | Energy value 0-0 (eV) | Line width $\Delta\nu_{1/2}$ |
| pTh(2-Si) | 1.95 | 0.02 |
| pTh(2) | 1.97 | 0.04 |

free-standing films which were deposited on Pt electrodes:



The FTIR spectra of the films are consistent with the formation of polythiophene. In addition, these spectra show strong absorption bands which can be assigned to vibrational modes of $(\text{CH}_3)_3\text{Si}$ groups. The electropolymerization of β -silylated thiophene led to polythiophene, in agreement with mainly α, α' coupling, though it contained numerous non-disilylated thiophene units (Eq. (3)).

However, partial desilylation occurred during polymerization. A quantitative estimate of this was obtained from X-ray fluorescence spectroscopy [5a]. The values of the Si/S ratio varied from 0.5 for pTh(5-Si), to 0.7 for pTh(6-Si) and 0.78 for pTh(7-Si). It showed that 50 to 80% of the silyl substituents were retained during the polymerization.

The partial desilylation does not seem to be associated with the formation of α - β linkages in the polymer chains. The IR absorption spectrum of neither pTh(5-Si) nor pTh(6-Si) shows a $\nu_{\text{C-H}}$ vibration at 3100 cm^{-1} characteristic of the presence of a hydrogen atom on the α -carbon of the thiophene ring. This was further confirmed by an examination of the infrared spectrum of the pTh(7-Si) polymer obtained from a monomer with a deuterium at the 2-position. No absorption associated with the $\nu_{\text{C-D}}$ vibration (2200 cm^{-1}) was observed. This, together with the absence of absorption at 569 cm^{-1} due to the $\gamma_{\text{C-D}}$ vibrational mode, is consistent with extensive electropolymerization through the 2,5-positions. The loss of SiMe_3 probably arises from competing protodesilylation of the monomer [12].

The Raman and photoluminescence spectra of pTh(6-Si) film are displayed in Fig. 7. The ρ/R value is indicative of a low conjugation length together with a large number of distorted segments (Fig. 3, symbol \blacktriangle). The photoluminescence profile is quite different from those previously recorded for highly conjugated polymers. The first maximum was observed at 2.02 eV, i.e. at a significantly higher energy than in highly conjugated samples. The band is broadened and the phonon replica structure is smoothed.

The above data are consistent with polymerization with a dominant α - α' coupling along the chain. The presence of an Me_3Si group at the β -position of the thiophene ring induces a large number of non-planar segments owing to steric interaction between neighbour-

ing thiophene units, and results in a decrease in the conjugation.

4. Chemical oxidation of α -silylated thiophenes

We also prepared polythiophene samples by chemical oxidation of α -silylated thiophene monomers and compared the material obtained with samples from non-silylated thiophenes [5f]. Evidence for a high mean conjugation length in the polythiophene chain prepared from silylated monomers was obtained by comparing Raman and photoluminescence data from polymers synthesized by chemical oxidation of silylated and non-silylated mono-, bi-, ter- and quaterthiophene monomers, according to the criteria previously defined.

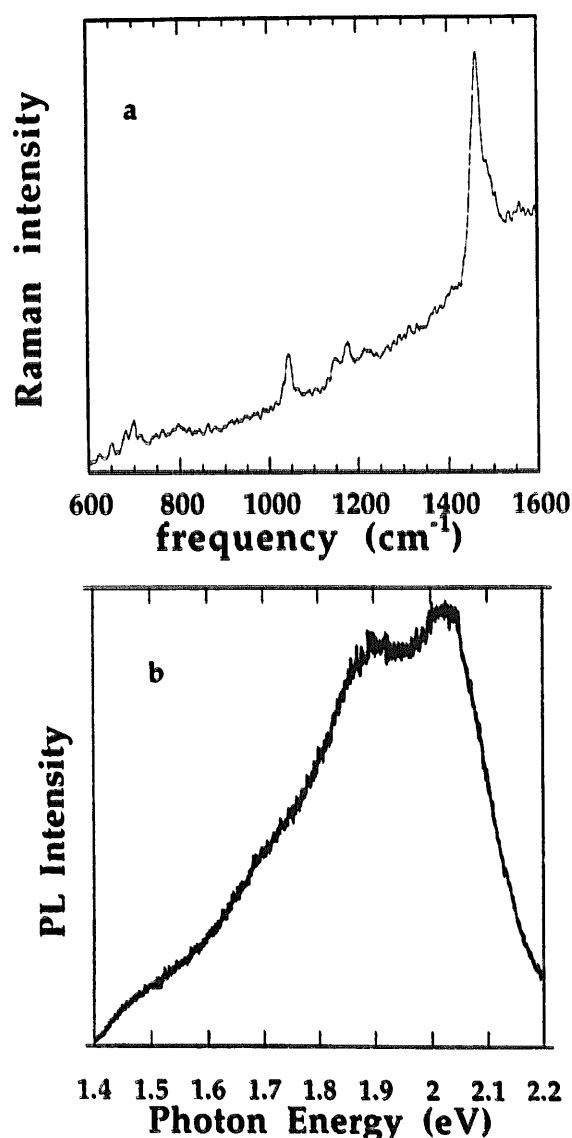


Fig. 7. (a) Low temperature ($T = 10$ K) Raman spectrum of pTh(6-Si) electrochemically prepared ($\lambda_{\text{exc}} = 5145$ Å); (b) low temperature ($T = 10$ K) photoluminescence of pTh(6-Si) recorded at $\lambda_{\text{exc}} = 5145$ Å.

Table 3

ρ Values for polythiophenes prepared by chemical oxidation of α -silylated (pTh(n -Si)) and related non-silylated (pTh(n)) monomers

| n | ρ (pTh(n -Si)) (%) | ρ (pTh(n)) (%) |
|-----|----------------------------|-------------------------|
| 1 | 95 | 70 |
| 2 | 155 | 130 |
| 3 | 120 | 100 |
| 4 | 160 | 150 |

The ρ values measured for the different samples are given in Table 3. The values are higher in pTh(n -Si) than in pTh(n). These values are in good agreement with the ρ/R correlation shown in Fig. 3 (symbol ●).

In chemical oxidative polymerization also, the presence of silyl substituents on the monomer results in an increase of the conjugation length of the polymeric chain. The largest difference between the two series of polythiophenes synthesized from silylated and non-silylated monomers was observed for monothiophene pTh(1-Si) and pTh(1).

A detailed analysis of the Raman spectra of pTh(1-Si) and pTh(1) samples shows the following.

(a) In the $600\text{--}750$ cm^{-1} region, the intensity of the 682 cm^{-1} Raman line, related to a vibrational mode in a non-planar chain conformation, is significantly weaker for pTh(1-Si) than for pTh(1).

(b) The inter-ring stretching mode at 1222 cm^{-1} is better defined for pTh(1-Si) than for pTh(1). However, the contribution of the 1177 cm^{-1} mode, assigned to a structural defect, is also weaker for pTh(1-Si) than for pTh(1).

(c) There is a broadening of the 1458 cm^{-1} Raman line and an increase of the intensity of the 1500 cm^{-1} line in pTh(1) due to disorder.

The photoluminescence bands of all the samples display a profile consisting of a series of discrete peaks separated by an optic phonon frequency. The main zero-phonon line and the one-phonon line are observed at around 1.95 and 1.78 eV respectively (Fig. 8). In addition to the narrow and well-defined peaks (with an energy separation of 0.175 eV), extra peaks appear in the case of pTh(n -Si) samples for $n = 2, 3, 4$. Similar peaks are observed in crystalline compounds [5f]. Furthermore, X-ray examination of the samples showed that the polymer obtained from silyl monomers exhibited high crystallinity [5f].

5. A route to high molecular weight poly(alkylthiophene)

We also extended the use of silyl monomers to the preparation of soluble polymers containing 3-alkylthiophene units. Regioselective silylation was achieved in the case of a substituted thiophene ring. Selective attachment of a trimethylsilyl group at the 2-

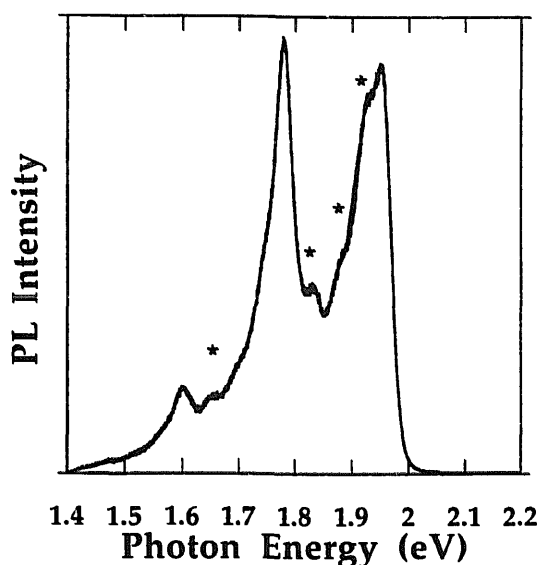
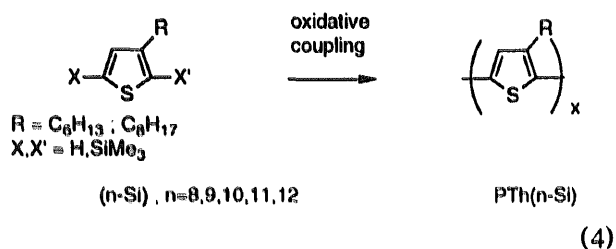


Fig. 8. Low temperature ($T = 10$ K) photoluminescence of pTh(3-Si) chemically prepared ($\lambda_{exc} = 5145$ Å), * = substructure peaks appearing in crystalline compounds.

or 5-position of 3-alkylthiophene was achieved in good yield, as shown in Scheme 3 [5c].

Poly(3-alkylthiophenes), which are easily prepared by oxidative polymerization of 3-alkylthiophene, have also been synthesized by oxidation of silylated 3-alkylthiophene (8-Si, 9-Si, 10-Si, 11-Si, 12-Si) [5c]:



The polymerization was performed under electrochemical conditions, using a Pt electrode dipping into an electrolytic solution, or under chemical conditions using FeCl_3 in chloroform. The poly(3-alkylthiophene) samples obtained were soluble in common solvents, allowing facile characterization. The molecular weights were estimated by use of GPC. In Table 4 the experimental values obtained after calibration of the GPC column using polystyrene standards are reported.

As shown in Table 4, high molecular weights were obtained by electropolymerization of α, α' -bis-silylated 3-alkylthiophenes. The electrogenerated polymers showed average molecular weights M_n respectively 64 and 14 times larger than those obtained by electropolymerization of the non-silylated monomers under similar conditions. At the same time, the polydispersity M_w/M_n was reduced by a factor of between 2 and 3.5. The use of α, α' -bis-silylated monomers in the chemical oxidative polymerization also led to polymers with a higher

average molecular weight and a lower polydispersity than those for polymers made from non-silylated precursors.

Polymerization of the monosilyl thiophenes (11-Si) and (12-Si) was also studied and gave a broader distribution of the molecular weights. Moreover, the GPC trace was unimodal and exhibited two peaks and shoulders. This may be indicative of a complex polymerisation reaction and may be attributed to competing desilylation of the monomer during the polymerization of (11-Si) and (12-Si). These monomers with hydrogen at the 5-position of the thiophene ring undergo coupling with loss of either the silyl group or protons. The increased acidity of the reaction medium causes a protodesilylation of the monomer, producing 3-alkyl thiophene. The poly(alkyl)thiophene formed may therefore arise from the reactions of both silylated and non-silylated thiophene. This was confirmed by analysis of the reaction mixture. The unreacted monomer that remained in the electrolytic solution after formation of the polymer film contained 20% non-silylated 3-alkylthiophene. Moreover, Me_3SiF was also isolated from the electrolytic mixture and characterized.

6. Mechanism

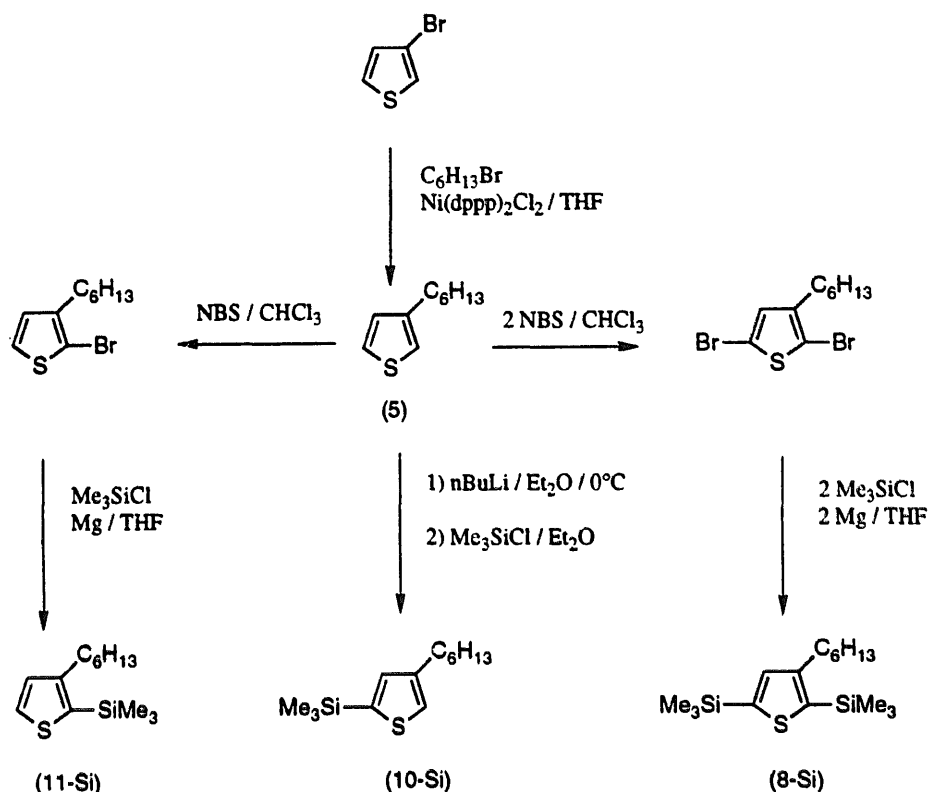
It was apparent that the presence of a silyl substituent substantially enhanced the ease of the oxidative coupling of thiophene. Two SiMe_3 substituents, in the 2- and 5-positions of the thiophene ring, are necessary. The role of the Me_3Si group may be interpreted in terms of increased stabilization of an intermediate β -silyl cationic species. The electropolymerization of thiophene has been suggested to occur via coupling of thiophene radical cations [13].

The coupling reaction of silyl thiophene is shown in Scheme 4.

(i) In the first step (Scheme 4(1)) the radical cation is generated by oxidation of the monomer. The C–Si bond which is oxidized at very high potential [14] ($V > 2.5$ V/SCE) is unaffected by the mild experimental conditions used ($V < 1.8$ V/SCE).

(ii) In the second step (Scheme 4(2)) a dicationic species arises from the coupling of two radical cations. The enhanced stability of the dicationic species is suggested to arise from a hyperconjugative interaction between the electron deficient π -molecular orbital of the thiophene ring and the filled σ -molecular orbital of the Si–C bond. Related stabilizations of carbocation β to a silyl substituent are known [2,12].

(iii) The next step (Scheme 4(3)) involves a re-aromatization of the bicationic species with cleavage of the C–Si bonds. The cleavage occurs by nucleophilic attack at silicon. Reaction with the large excess of supporting electrolyte, to give the thermodynamically stable Si–F bond, is likely to occur and this is supported



Scheme 3. Selective silylation of 3-alkylthiophenes.

by the identification of Me_3SiF in the reaction mixture. In the case of monosilyl thiophene, the coupling can occur in two ways: coupling of C–Si or C–H bonds. The coupling of a C–H bond would liberate a proton which may react with the monomer to give, upon protodesilylation, the non-silylated thiophene identified in the reaction mixture. Competitive electropolymerisations between silylated and non-silylated thiophene units

probably occur in the case of monomers (11-Si) and (12-Si).

7. Concluding remarks

In conclusion, the Me_3Si group has a major influence on the oxidative polymerisation. As shown by Raman and photoluminescence criteria, the presence of silyl

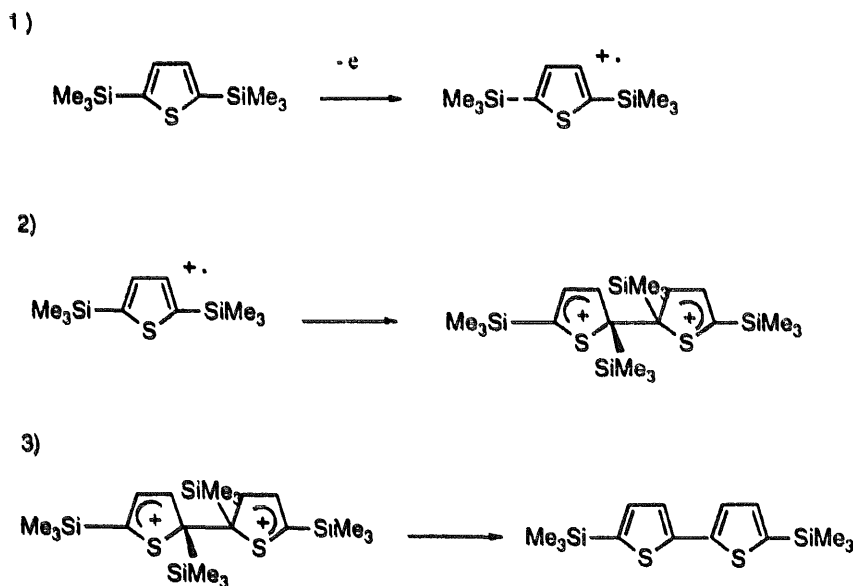
Scheme 4. Mechanism of oxidative polymerization of bis α,α' -silylated thiophenes.

Table 4

GPC data for poly(3-alkylthiophene) obtained by electrochemical (E) and chemical oxidation (C) of 3-alkylthiophenes and silylated 3-alkylthiophenes. D_{pn} is the average degree of polymerization

| Polymer | Oxidation (C,E) | $10^{-3} M_n$ | M_n/M_w | $10^{-2} D_{pn}^a$ |
|------------|-----------------|---------------|--------------|--------------------|
| pTh(5) | E | 21 | 4.5 | 1.2 |
| pTh(8-Si) | E | 1338 | 1.3 | 79.6 |
| pTh(6) | E | 39 | 2.6 | 2.3 |
| pTh(9-Si) | E | 839 | 1.2 | 42.8 |
| pTh(6) | C | 38.6 | 2.4 | 1.96 |
| pTh(9-Si) | C | 116.8 | 1.9 | 5.96 |
| pTh(10-Si) | E | 55 | ^a | 3.2 |
| pTh(11-Si) | E | 57 | ^a | 3.4 |

^a The GPC trace was not unimodal and showed a broad peak with two maxima or shoulders.

substituents on both the 2- and 5-positions of the thiophene ring raises the reactivity, and selective α - α' coupling of thiophene units leads to highly conjugated polymers with improved conjugation properties. In contrast, the use of β -silylated monomers leads to poorly conjugated polymers. The observed activation by the silyl substituents also allows the preparation of high molecular weight poly(3-alkyl) thiophene with low polymolecularity. The presence of Me_3Si groups on the 2- and 5-positions of the thiophene ring was shown to be necessary to ensure high molecular weight and low polydispersity

The use of silylated monomers seems promising for synthesis of conjugated polymers. Its extension to the synthesis of other unsaturated polymers may lead to various upgraded conjugated polymeric structures. The polymerization of silylthiophene units was also achieved in the solid state in the case of thienylene-bridged silsesquioxane. Its oxidative polymerization gives an organic-inorganic composite consisting of polythiophene chains and an interpenetrating silicate network [5b].

We are currently investigating the use of silylated monomers in the polymerization of various unsaturated monomers. An improved degree of polymerization and higher conjugation are obtained in the polymeric material [15].

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