Poly(isothianaphthene) from 2,5-bis(trialkylsilyl)isothianaphthenes: preparation and spectroscopic characterization

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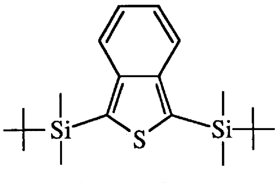
A new method for the preparation of poly(isothianaphthene) is proposed, namely electropolymerisation of bis(*tert*-butyldimethylsilyl)isothianaphthene (BTBDMS)ITN. The advantage offered by this method is based on the fact that (BTBDMS)ITN is a stable monomer at ambient conditions whereas unsubstituted isothianaphthene is unstable and must be prepared prior to the polymerisation. Poly(isothianaphthene) (PITN) prepared from (BTBDMS)ITN shows an average polymerisation degree of 20 and spectral and spectroelectrochemical characteristics similar to classical PITN. FT Raman spectroelectrochemical studies show that during oxidative doping PITN undergoes similar changes to poly(alkylthiophenes) and poly(alkoxythiophenes).

In modern molecular electronics significant research effort is directed towards the preparation of low band-gap conjugated polymers due to several possible industrial applications of such systems. Poly(isothianaphthene) (PITN) initially synthesized by Wudl *et al.*[1] exhibits the lowest band-gap of all polyconjugated systems studied to date. Both PITN and its C_6 ring substituted derivatives can be prepared by electrochemical oxidative polymerisation of isothianaphthene or its derivatives.[1–5] However the monomers used for these syntheses are rather unstable at ambient conditions and must be freshly prepared prior to the polymerisation. In order to avoid the inconveniences associated with electropolymerisation, chemical oxidation procedures have been suggested involving the oxidation of dihydroisothianaphthene with $FeCl_3$, O_2,[6] or *N*-chlorosuccinimide.[7]

PITN can also be prepared by dehydrogenation of the PITN precursor, namely poly(dihydroisothianapthene) (PDHITN) with such dehydrogenation agents as SO_2Cl_2,[8] or *tert*-butyl hypochlorite.[9] This last method is especially interesting because dehydrogenation of PDHITN in solution leads to a stable PITN solution. Thus films of PITN can be prepared on an appropriate substrate by casting. Here, we propose a new method for the preparation of PITN *via* electropolymerisation of disilyl derivatives of ITN. Silicon directed reactions have been widely used in organic chemistry with the goal of improving the selectivity of carbon–carbon bond formation.[10] Recently they have been applied to the preparation of polythiophene[11] and poly(3-alkylthiophene).[12] In order to prepare PITN we have used 2,5-bis(*tert*-butyldimethylsilyl)isothianaphthene (BTBDMS)ITN:



(BTBDMS)ITN

which, in contrast to isothianaphthene, is a stable monomer and can be stored for extended times in a bottle in laboratory conditions. In addition to the description of the electrochemical behaviour of PITN prepared from (BTBDMS)ITN we characterize the obtained polymer by UV–VIS–NIR, XPS and Raman spectroscopies.

Experimental

For the synthesis of the monomer 2,5(*tert*-butyldimethylsilyl)-isothianaphthene the procedure described by Okuda *et al.* was used.[13] Electropolymerisation was carried out in a reaction medium consisting of NBu_4BF_4 and (BTBDMS)ITN dissolved in nitrobenzene. The concentrations of the electrolytic salt and the monomer were 0.2 and 0.1 M respectively. The reaction was performed in a three-electrode electrochemical cell with a platinum counter electrode and Ag/AgCl wire as the reference electrode. Three types of working electrodes were used, platinum, gold and ITO, depending on the subsequent spectroscopic studies of the deposited polymer film. The polymerisation was performed at a constant potential of 1.4 V *vs.* Ag/AgCl.

In addition to the deposition of the polymer on the working electrode, the formation of soluble oligomers took place which was manifested by a change of the colour of the electrolyte solution in the vicinity of the working electrode. The deposition of a homogeneous film required electrolysis times exceeding 5 min.

The electropolymerised film was then reduced electrochemically at $E = -0.6$ V *vs.* Ag/AgCl to give the neutral polymer of a distinct blue colour. The electrode with the film deposited on it was then carefully rinsed with pure nitrobenzene and then with acetonitrile in order to remove all oligomeric species. All operation were carried out in a dry nitrogen atmosphere.

Cyclic voltammetry

Cyclic voltammograms were recorded in a monomer free 0.2 M NBu_4BF_4 solution in acetonitrile using a PAR 273 potentiostat/

galvanostat. The working electrode consisted of a layer of poly(isothianaphthene) deposited on a platinum foil. As in the electropolymerisation experiments a Pt counter electrode and an Ag/AgCl reference electrode were used.

UV–VIS–NIR spectroelectrochemistry

UV–VIS–NIR spectroelectrochemical studies were performed in the same electrolyte solutions as in the cyclic voltammetry studies, using the same counter and reference electrodes. Poly(isothianaphthene) was deposited on an indium tin oxide transparent electrode (ITO).

FT Raman spectroelectrochemistry

The Raman spectra were recorded with a near-IR excitation line (1064 nm) on a FT-Raman Bruker RFS spectrometer working in a back scattering geometry. For Raman studies the film of PITN was deposited on a Pt electrode. The same electrolyte, counter and reference electrodes as in cyclic voltammetry were used.

XPS studies

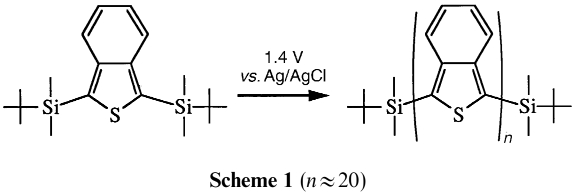
The XPS measurements were performed on a Leybold LH 12 analyser (CNRS Université de Nantes) using an Mg-Kα X-ray source in a UHV system. The pressure of the chamber was kept in the 10^{-9} mbar range during experiments. The polymer film were deposited on ITO substrates and no charging effect due the beam radiation was observed. The binding energy was referenced to the Au $4f_{7/2}$ line (84 eV) from a gold probe evaporation on the surface of the sample holder. The collected data were treated by a computer program with satellite background subtraction. Semi-quantitative determination of the composition of the analysed surface was performed from the obtained spectra taking account of the sensitivity of the elements present.

Results and Discussion

(BTBDMS)ITN readily polymerises electrochemically to give PITN. However, as has been stated before, the preparation of homogeneous films on the electrode requires higher concentrations of the silylated monomer as compared to unsubstituted isothianaphthene. In addition longer electrodeposition times are required. This may imply that in the case of (BTBTMS)ITN the electropolymerisation mechanism is significantly different than in the case of unsubstituted ITN. There is a low electropolymerisation yield and the presence of the oligomeric species in the vicinity of the electrode is only one of several electrooxidation products. Studies of the polymerisation mechanism are in progress.

Due to the presence of the leaving silyl groups in the monomer the polymerisation degree in the polymer can be conveniently determined by end group analysis, and more precisely from the analytically determined S/Si molar ratio. XPS studies of the poly(isothianaphthene) film deposited on the ITO electrode show that this ratio is close to 10 which gives an average polymerisation degree equal to 20. Thus the trialkylsilyl groups are efficiently eliminated during the electrochemical oxidation according to Scheme 1

It should be stressed that, in contrast to ITN, its silylated derivatives can be stored for extended times before their use for the polymerisation reaction. The polymerisation carried out after 2 months using the same batch of ITN gave identical polymer. In the neutral (*i.e.* reduced at $E=-0.6$ V) PITN film, XPS spectroscopy shows the presence of carbon, sulfur and a small amount of oxygen in addition to the already mentioned silicon. The C 1s peak is located at 284.7 eV with a skewed arc at the high energy side and a full width at half maximum of 2 eV. The S 2p line shows a peak at 163.5 eV with a widened base at low binding energy. These features are similar to those observed for polythiophene except that some carbon atoms are affected by the silyl end groups.[14]



Scheme 1 ($n \approx 20$)

Cyclic voltammograms of PITN prepared from (BTBDMS)ITN are shown in Fig. 1. We restricted ourselves to oxidative (p-type) doping although there are literature reports of p- and n-type doping of PITN.[15,16]

Oxidative doping of PITN synthesized from the disilyl derivative of ITN gives rise to two broad strongly overlapping oxidation peaks (due to anion doping) and two reduction peaks associated with undoping. The shape of the current–voltage curves is essentially the same as that reported by Higgins *et al.*[17] for poly(benzo[*c*]thiophene) cycled in NBu_4X–acetonitrile electrolyte.

In the case of PITN the shape of the current–voltage curve depends on the history of the sample and, more precisely, on whether the scan range has been extended to n-doping prior to p-doping. In such case a pre-peak is observed.[15] Onada *et al.*[16] have ascribed the existence of these additional peak to the difficulty in the removal of all negative charge upon oxidation of previously n-doped polymer. The release of this residual charge gives rise to this additional 'pre-oxidation peak'. We do not observe this peak, in agreement with other authors,[16,17] in the experiments where PITN was not previously n-doped.

It should be stressed here than our PITN has a very good cycling stability. In addition the oxidative doping of our PITN seems to be more reversible than that reported in ref. 18. UV–VIS–NIR spectra registered for increasing electrode potentials are shown in Fig. 2. In the reduced polymer ($E=-400$ mV) the dominant peak ascribed to the π–π^* transition in the conjugated backbone shows a maximum at 690–700 nm, *i.e.* it is blue shifted by *ca.* 50 nm as compared to the PITN spectrum reported in ref. 15, and by *ca.* 90–100 nm in comparison to the spectra recorded in refs. 9 and 16. Since the position of the π–π^* transition band can be taken as a measure of conjugation we conclude that PITN obtained from (BTBDMS)ITN is less conjugated. This effect may be associated with the influence of the silyl end groups taking into

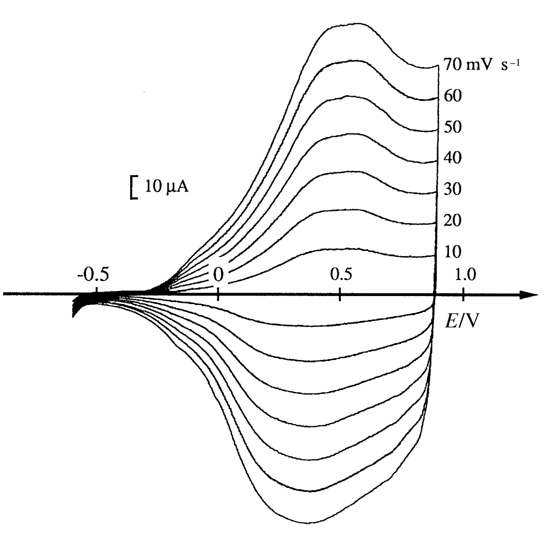


Fig. 1 Cyclic voltammograms of PITN recorded in 0.1 mol dm^{-3} NBu_4BF_4 solution in acetonitrile

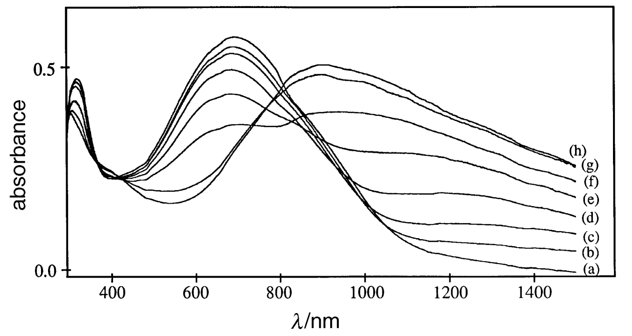


Fig. 2 *In situ* UV–VIS absorbance curves of PITN recorded for selected electrode potentials (*vs.* Ag/AgCl): (a) −400; (b) 200; (c) 300; (d) 400; (e) 500; (f) 600; (g) 900; (h) 1000 mV

account that the polymerisation degree in our polymer is rather low (average polymerisation degree of *ca.* 20).

In conjugated polymers oxidative doping is usually manifested by bleaching of the π–π* transition peak with simultaneous growth of a peak (peaks) in the near-IR part of the spectrum. Qualitatively the same behaviour is observed for the PITN studied in this research. However UV–VIS–NIR spectroelectrochemistry gives evidence of two distinctly different doping stages. Up to potentials $E=0.6$ V, which is in the vicinity of the maximum of the oxidative doping peak, two isosbestic points are observed at 365 and 430 nm. This means that only two optically different phases are present in the system. At $E=0.6$ V the polymer is only partially doped as judged from a rather high absorbance at 690–700 nm. Complete doping manifested by total bleaching of the π–π* peak requires electrode polarization at potentials exceeding 0.9 V. In the second oxidation step no isosbestic points are observed. It seems therefore plausible that during the first oxidation step polarons (radical cations) are formed which then recombine to bipolarons (dications) at higher potentials. Such a transformation clearly explains the existence of the isosbestic points at the beginning of the oxidation and their absence at the end of the oxidative doping.

This conclusion is also supported by the ellipsometric and FTIR results of Christiansen *et al.*[19] who also claimed two-step oxidative doping of PITN. However additional verification by joint cyclic voltammetry and EPR studies is required; such studies are in progress. We have also undertaken Raman spectroelectrochemical studies of PITN. In general Raman studies of polyconjugated systems are complicated by resonance effects which result in a strong dependence of the Raman line intensities (and sometimes their shape and positions) on the excitation wavelength energy. In addition the resonance conditions are altered significantly in the course of the doping reaction due to the doping induced changes in the electronic spectra of conjugated polymers.

We have selected the near-IR excitation line ($\lambda_{ex}=1064$ nm) mainly because its position is very close to the maximum of the doping induced electronic transition. In addition at this wavelength we are also within the π–π* transition peak of the neutral form of PITN and a small but not negligible absorbance is registered at 1064 nm for this compound.

FT Raman spectra registered for increasing electrode potentials are shown in Fig. 3. The Raman spectrum of neutral ($E=-0.3$ V) PITN prepared from the disilyl derivative is different from that reported by Hoogmartens *et al.*[18] In fact, the spectrum published in ref. 18 is essentially identical to our spectrum of slightly doped PITN, *i.e.* that recorded at $E=0.3$ V. Taking into account that $\lambda_{ex}=1064$ nm almost matches the maximum of the electronic absorption in the doped polymer, strong resonant enhancement of vibrations characteristic of the doped structure is expected. It is therefore highly probable that the features of the doped polymer may appear even if minute amounts of dopant are present. A recently published PITN spectrum[20] is very similar to that reported here; however, it contains one additional peak between the modes at 1301 and 1166 cm^{-1} which is absent in our spectrum. Careful spectroscopic analysis of PITN and model compounds by Raman[21] and NMR[21,22] spectroscopies seems to indicate that in the neutral state this polymer adopts the quinonoid sequence of bonds. Such a conclusion is also supported by theoretical calculations.[23]

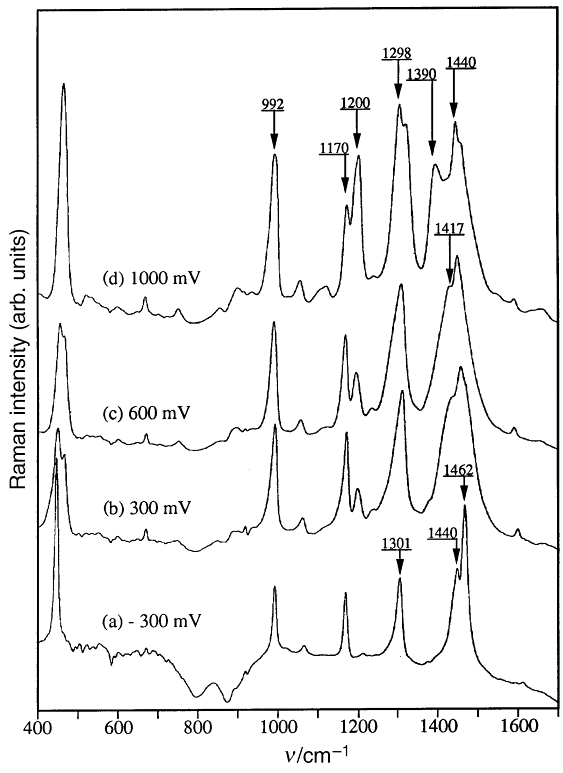


Fig. 3 Raman spectra with $\lambda_{ex}=1064$ nm of PITN recorded during the oxidative process (potentials *vs.* Ag/AgCl): (a) −300; (b) 300; (c) 600; (d) 1000 mV

However, as has been pointed out by Kiebooms,[24] the energy difference between the quinonoid and aromatic states is very small (2.4 kcal mol^{-1}, 1 cal = 4.184 J) so the structure of the neutral polymer may be influenced by the nature of the end groups in the monomer used for the synthesis. Since (BTBDMS)ITN monomer should favour the aromatic sequence of bonds in the resulting polymer it is highly probable that in PITN prepared from the disilyl derivative the aromatic structure is adopted in the neutral state; thus the doping should lead to the quinonoid structure. This hypothesis is based on the close similarity of the Raman spectroelectrochemical behaviour of PITN and regioregular poly(3-alkylthiophenes)[25] and poly(dialkoxybithiophenes).[26] In the last two cases oxidative doping causes the transformation of the aromatic structure into the quinonoid one.

As probed by Raman spectroscopy, doping induced spectral changes start at potentials $E>0$ V *vs.* Ag/AgCl. However between 0.1 and 0.6 V the spectra are essentially the same showing the features of the doped sample. The main changes occurring upon doping can be characterized as follows. (i) The band at 1462 cm^{-1} in neutral PITN ascribed to C_α—C_β stretchings shifts to lower wavenumber (1417 cm^{-1}) and decreases in intensity with respect to other bands. Identical behaviour has been observed for poly(3-alkylthiophenes)[23] and poly(alkoxythiophenes).[24] (ii) The band at 1440 cm^{-1} in the neutral PITN ascribed to the vibrations of the benzene ring condensed with the thiophene ring is essentially unaffected by the doping. (iii) A band at 1195 cm^{-1} appears which can be interpreted as originating from the $C_\alpha-C_{\alpha'}$ inter-ring vibrations of the quinonoid structure.

At $E > 0.6$ V further spectral changes occur which support the hypothesis of the quinonoid structure formation upon doping. In particular the peak at 1301 cm^{-1} in the neutral polymer and ascribed to $C_\beta-C_{\beta'}$ stretching broadens and shifts to slightly higher wavenumber whereas the peak due to $C_\alpha-C_\beta$ stretchings continues to shift towards lower wavelengths (from 1462 cm^{-1} in the neutral polymer to 1400 cm^{-1} for the quinonoid $C_\alpha-C_{\alpha'}$ sequence of bonds). The inter-ring stretching peak continues to grow.

It should be stressed once more that these changes are qualitatively the same as those observed for poly(3-alkylthiophenes)[25] and poly(alkoxythiophenes).[26] The comparison with poly(3,3′-dibutoxy-2,2′-bithiophene) should be instructive. For both polymers the near-IR excitation line ($\lambda_{ex} = 1064$ nm) is located in the vicinity of the doping induced absorption maximum and both polymers undergo very similar changes in the Raman spectra upon electrochemical doping.

Conclusions

We have demonstrated that electropolymerisation of bis(*tert*-butyldimethyl)silylisothianaphthene (BTBDMS)ITN leads to poly(isothianaphthene) with an average polymerisation degree of 20. The obtained polymer shows spectral features similar but not identical to poly(isothianaphthene) prepared by classical methods. The main advantage of the procedure proposed here relies on the fact that (BTBDMS)ITN is a stable monomer and can be stored for extended times whereas isothianaphthene must be synthesized prior to the electropolymerisation.

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