# Photo-oxidation of freely suspended submicron films of poly(3-nonylthiophene)

**M. Sandberg***, **S. Tanaka** and **K. Kaeriyama**†
*National Institute of Materials and Chemical Research, Higashi 1-1, Tsukuba, Ibaraki 305, Japan*

*(Received 20 January 1993; revised 20 May 1993)*

A new technique for preparing freely suspended submicron films of poly(3-nonylthiophene) (PNT) has been developed. These films were characterized by both i.r. and u.v. spectroscopy, allowing us to qualitatively analyse the effects of photo-oxidation and how these effects change with the period of time after the end of the irradiation treatment. Before these spectroscopic measurements were made, PNT was compensated with hydrazine in order to remove any chemical impurities resulting from the polymerization catalyst. The i.r. experiments indicate that when PNT was irradiated by light of wavelength longer than 466 nm, electrons were transferred from the PNT to oxygen. Thus, the photo-oxidation process resulted in the formation of positive polarons on the polymer chains, plus superoxide anions. In the dark, electrons were transferred back to the polymer chains, which therefore returned to their neutral state. This mechanism was supported by e.s.r. experiments. Irradiation by light of wavelength shorter than 466 nm induced i.r. absorptions due to both polarons and sulfonyl groups, as well as conjugation-breaking reactions. When impurities were not removed, the formation of polarons and sulfonyl groups was observed even if wavelengths shorter than 466 nm were excluded. These impurities also accelerated the conjugation-breaking reactions.

**(Keywords: freely suspended films; poly(3-nonylthiophene); photo-oxidation)**

## INTRODUCTION

The science of conjugated polymers developed rapidly at the end of the 1970s as a consequence of the increased interest in electrically conducting polymers[1]. In the 1980s, applications were reported in rechargeable batteries and high-performance capacitors. More recently, the possession of interesting optical properties for a number of conjugated polymers, in particular non-linear optical responses and electroluminescence, have resulted in an avalanche of publications dealing with the physical aspects of the photoresponse of these types of materials[2]. In this connection, the photochemistry of such polymers is an important aspect to be considered. However, only a few very recent publications have addressed the solid-state photochemical properties of these materials[3,4].

In this paper, we have focused on the optical response of thin films of poly(3-nonylthiophene), considered from a polymer degradation point of view. The photo-oxidation of polymers takes place mainly on the surface. Moreover, the products formed initially after photo-oxidation are generally unstable, which means that the effects of photo-oxidation change with the lapse of time after irradiation. To facilitate characterization of the photo-oxidation process, we have put much effort into preparing thin films which were freely suspended on a metal wire frame. Using these submicron films, both photoinduced doping with superoxide anions and conjugation-breaking reactions were studied by difference i.r., u.v. and e.s.r. spectroscopic techniques.

While polypyrrole in its doped state is obtained by the oxidative coupling of pyrrole with iron(III) chloride as the catalyst/oxidant, poly(3-alkylthiophene) is undoped by the work-up procedure. However, poly(3-nonylthiophene) does indeed contain a small amount of impurities from the polymerization catalyst. In this present study, the effects of photo-oxidation on a film compensated with hydrazine were compared with those of an uncompensated film; impurities turned out to have an important effect in the characterization of the photochemical properties of the polymer films.

## EXPERIMENTAL

### *Materials*

PNT was prepared by an oxidative coupling polymerization reaction of 3-nonylthiophene, using iron(III) chloride as the oxidant/catalyst[5]. 3-Nonylthiophene (4 mmol) (Tokyo Kasei) in choloroform (5 ml) was added to $FeCl_3$ (2.6 g) suspended in chloroform (15 ml) at −15°C. Nitrogen was bubbled through the polymerization mixture, which was kept at a temperature of −15°C during the polymerization. After 3 h, the mixture was poured into 100 ml of cold methanol and then washed with this solvent. Residual iron(III) chloride and other impurities were extracted with methanol in a Soxhlet

---

* Present address: Yoshimura π-Electron Materials Project, c.o. Tosoh Corporation (Tsukuba Research Laboratory), Miyukigaoka 43, Tsukuba 305, Japan

† To whom correspondence should be addressed

0032-3861/94/030468-07

extractor. The polymer was then dissolved in chloroform, filtered, cast into a film, washed first with DMF and then methanol, and then dried and stored in the dark. Molecular weights were measured by size exclusion chromatography (s.e.c.) using chloroform as eluent ($M_w = 6.6 \times 10^4$ g mol$^{-1}$ (polystyrene standard); $M_w/M_n = 1.8$).

### *Freely suspended submicron films*

PNT was spin-coated from toluene solutions onto KBr tablets, which were polished, where necessary, with poly(ethylene glycol 300) just before use. Spin rates were kept low enough to enable an outer ring of polymer solution to be formed at the periphery of the KBr tablet, as a result of surface tension effects (*Figure 1a*). After the solvent was evaporated, the KBr tablet was found to be covered by a thin film, with a much thicker ring at its periphery. The KBr tablet was then carefully floated on the surface of water contained in a large beaker. After dissolution of the KBr, a frame of metal wires was inserted under the film (see *Figure 1b*) and then carefully lifted to support and suspend the film, as depicted in *Figure 1c*. The films were dried in the dark, and thicknesses were measured by comparing the u.v. and i.r. optical densities with those of thicker films that had been measured with a Talystep profilometer or a micrometer.

### *Preparation of samples for e.s.r. measurements*

1 mg of PNT dissolved in a few drops of chloroform was placed at the bottom of a quartz e.s.r. tube, which was fixed in a rotor so that the bottom of the tube dipped down slightly from the horizontal. A Teflon tube was fitted into a coaxially drilled hole in an e.s.r. tube cap. Rotation under reduced pressure produced films on the inside walls of the tubes with thicknesses which were estimated to be 0.2–0.4 μm.

### *Removal of spin-generating impurities from the polymerization reaction*

Thin film samples, either freely suspended films or films cast in e.s.r. tubes, were treated with 3 wt% solutions of hydrazine in water for at least 1 h and then washed several times with 95% ethanol. Since this process is often referred to as *compensation*, we refer to samples as being either *compensated* or *uncompensated* in the following discussion.

### *Measurements*

U.v. spectra were recorded on a Hitachi U-3400 spectrometer, while i.r. spectra were recorded on a Perkin-Elmer 1710 instrument. Eight scans were recorded for each spectrum. When a time for the acquisition of a spectrum is reported later in the text, this refers to the time-interval between the midpoint of the scanning period and the end of the irradiation period. Scanning times were ~20 s for each spectrum, and the resolution was 4 cm$^{-1}$. E.s.r. spectra were recorded on a JEOL JES-RE3X e.s.r. spectrometer at a sweep rate of 2.5 mT min$^{-1}$, a field modulation width of $1 \times 10^{-2}$ mT, and a time constant of 0.03 s.

### *Irradiations*

For broad-band irradiation, a high-pressure Hg lamp, giving an intensity of 250 mW cm$^{-2}$ after a water filter, was used as the light source. A Corning 3-70 filter (transmittance < 0.5% below 466 nm) was used if high-energy light was to be excluded. Using this cut-off filter, the light is mainly absorbed by the $\pi$–$\pi^*$ band of the polymer. For convenience, we refer to this light as being *filtered*, while light that was only filtered through water is referred to as being *unfiltered* light. If not otherwise stated, the films were exposed for a period of 60 s.

## RESULTS

### *Freely suspended submicron films*

A toluene solution of PNT, which was prepared by the oxidative coupling of 3-nonylthiophene, was spin-coated onto the surface of a KBr tablet. After the evaporation of toluene, a submicron film with a much thicker ring at its fringe was produced on the tablet. When the latter was placed on the surface of water, the film which remained after the dissolution of the KBr was lifted off with a metal wire frame. The thicker ring at the periphery was necessary in order to keep the tablet floating during the dissolution stage and provide the mechanical strength required for when the film was

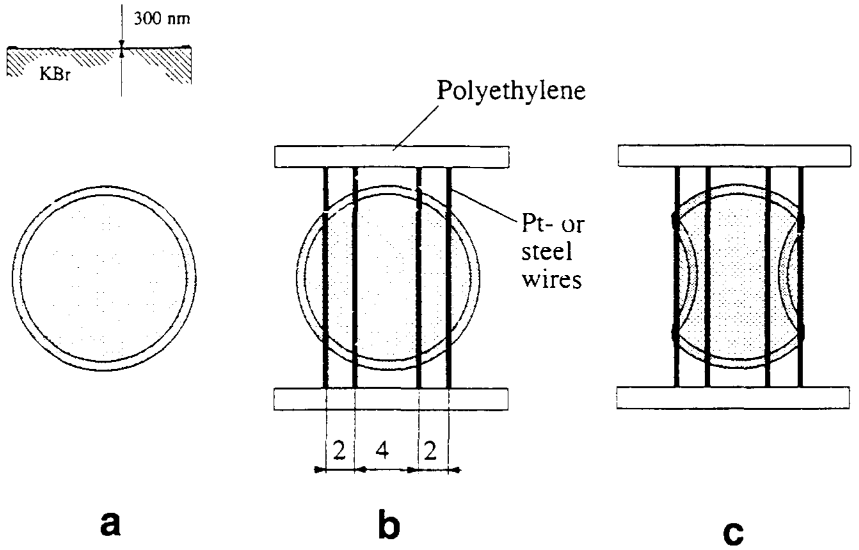


**Figure 1** A schematic representation of the procedure used in submicron film preparation: (a) a film of PNT after being spin-coated onto a KBr tablet; (b) a suspension frame positioned under the film; (c) the film suspended on the frame

lifted from the water surface. The outer supporting ring was unnecessary for a film with an overall thickness greater than 0.4 μm. Films with thicknesses as small as 0.2 μm were obtained by this method.

This type of film gave rise to interference patterns, as well as apparent absorption, when analysed by an interferometer. Such undesirable effects as interference were cancelled out by measuring difference spectra and thus these films were useful in degradation studies. Spectroscopic analysis could be carried out over the whole optical range, even for strongly absorbing films, due to the absence of any substrate. Since absorption spectroscopy could be used, these films could be analysed by i.r. spectroscopy immediately after irradiation, which was difficult to achieve with typical surface analysis techniques. Furthermore, the absence of substrate enabled further chemical treatment of the thin films to be carried out after their preparation, which was necessary for the removal of undesirable impurities resulting from the polymerization catalyst. These impurities were found to have a profound effect on the photo-oxidation behaviour of PNT. E.s.r. experiments showed that such impurities were easily removed from submicron films, but only with difficulty from thicker films.

### *Compensated samples*

*Effects of filtered light, i.r. and e.s.r. measurements.* The difference spectra in *Figure 2* show the effects of photo-oxidation on a film 0.3 μm thick of PNT previously treated with hydrazine. Three spectra were recorded, i.e. before irradiation, 30 s after, and 24 min after the end of the irradiation period. By subtraction of the spectrum obtained 30 s after irradiation from the spectrum obtained before irradiation, it can be seen that photo-oxidation results in i.r. modes at 1260, 1210, 1110, 1090 and 1030 cm$^{-1}$ (see *Figure 2a*). The effects induced by photo-oxidation gradually decreased with the lapse of time, and the spectrum returned to its original form after 24 min (see *Figure 2b*).

*Figure 3* shows the change in the e.s.r. spectrum of a PNT sample after irradiation in air. A signal was detected immediately after irradiation, and gradually disappeared as the spectrum returned to its original form.

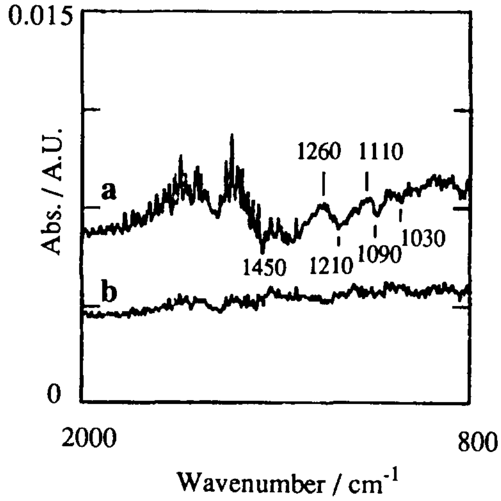


**Figure 2** I.r. difference spectra obtained for a PNT film after photo-oxidation with filtered light, using an irradiation time of 60 s: (a) 30 s and (b) 24 min after the end of the irradiation period

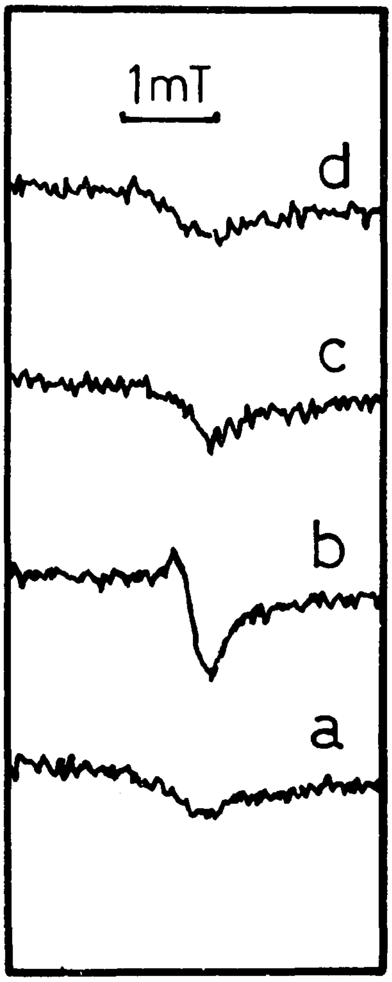


**Figure 3** The effect of irradiation in air by filtered light on the e.s.r. spectrum of a thin film of PNT, using an irradiation time of 30 s: (a) spectrum before irradiation; spectra obtained by sweeping through the centre of the spectrum (b) 20 s, (c) 5 min and (d) 15 min after the end of the irradiation period

The effects were different from those described above, when irradiation was carried out under a nitrogen atmosphere; no significant effects could be detected by i.r. spectroscopy in the latter case. The photoresponse of the e.s.r. spectrum of a sample treated in a nitrogen atmosphere was different from that observed after photo-oxidation, in that a residual spin was generated, although its intensity was lower than that of a sample irradiated in air (*Figure 4*). This photoinduced signal did not disappear with the lapse of time as did the signal generated by photo-oxidation.

Since the life-times of the effects of photo-oxidation observed by both i.r. and e.s.r. spectroscopy are of the same time-scale, it is reasonable to believe that the observed effects originate from the same phenomena. Moreoever, since the effects of irradiation depend on the presence of air, these effects can be assigned as being induced by photo-oxidation.

The i.r. spectra, together with the e.s.r. observations, indicate that the polymers became doped with superoxide anions upon irradiation, but 'undoped' spontaneously in the dark. This explanation is compatible with the results from a recent paper reporting that the formation of superoxide anions on photo-oxidation is responsible for the residual photoconductivity of poly(3-hexylthiophene) after irradiation[6].

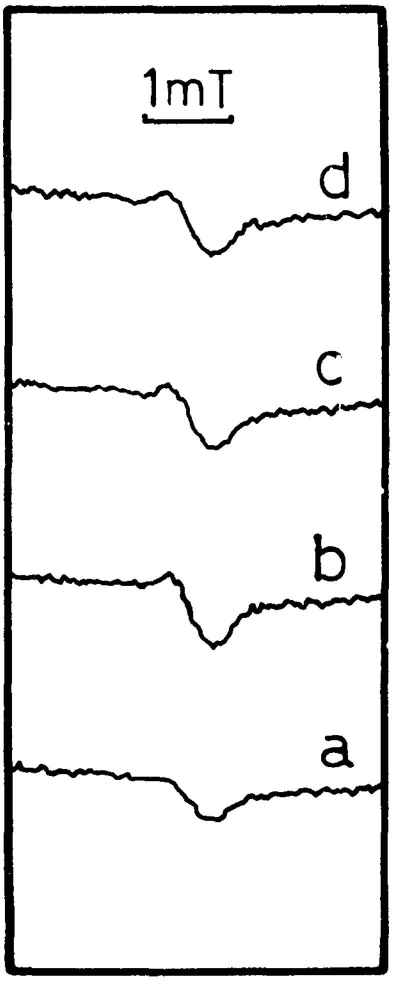


**Figure 4** The effect of irradiation on the e.s.r. spectrum of a thin PNT film, using filtered light in a nitrogen atmosphere with an irradiation time of 30 s: (a) spectrum before irradiation; spectra obtained by sweeping through the centre of the spectrum (b) 20 s, (c) 5 min and (d) 15 min after the end of the irradiation period

Consequently, the i.r. modes at 1260, 1210, 1110, 1090 and 1030 cm$^{-1}$ could be assigned as bands that are specific for positive polarons on the polymer chain. In the dark, electrons are transferred back to these polarons, and since the effect is reversible, the process can be regarded as a charge recombination of the photoexcitations through the oxygen. This recombination route of photo-induced polarons via oxygen can explain the long lifetime of these effects.

*Effects of unfiltered light.* *Figure 5* shows the effect of photo-oxidation for a sample that had been exposed to light of wavelength less than 466 nm. The photo-oxidation-induced absorptions remaining 30 s after the end of the irradiation period were mainly characterized by increased absorptions at approximately 1305 and 1150 cm$^{-1}$, with shoulders at 1330 and 1180 cm$^{-1}$, and decreased absorptions at approximately 1450, 1220, 1100 and 1020 cm$^{-1}$. To simplify the interpretation of the spectra, the effects were divided into a 'reversible' component and a component which still remained 48 min after irradiation. In the 'remaining' component (shown in *Figure 5b*), the shoulders at 1330 and 1180 cm$^{-1}$ appeared more clearly while the intensities of the other effects decreased, suggesting that sulfonyl groups were formed. The difference spectrum shown by *Figure 5c* is obtained by subtracting the spectrum obtained 48 min after irradiation from that obtained 30 s after irradiation, and thus shows the absorptions that disappeared during this period. The reversible component exhibited a pattern which was similar to that previously described as being characteristic of polarons, i.e. bands at 1020, 1100 and 1220 cm$^{-1}$, with strong bands centred at 1450 cm$^{-1}$.

### *Uncompensated samples*

*Effects of filtered light.* Although PNT was undoped after extraction with methanol, it still contained a small amount of impurities which gave an e.s.r. signal, possibly due to residual doping. The signal disappeared upon compensation with hydrazine. Poly(3-alkylthiophenes) are often characterized without any compensation treatment. Thus, the effects of these residual impurities on the photochemistry of PNT were studied in this work.

The difference spectra in *Figure 6* show the effects of photo-oxidation on the i.r. spectra of an uncompensated

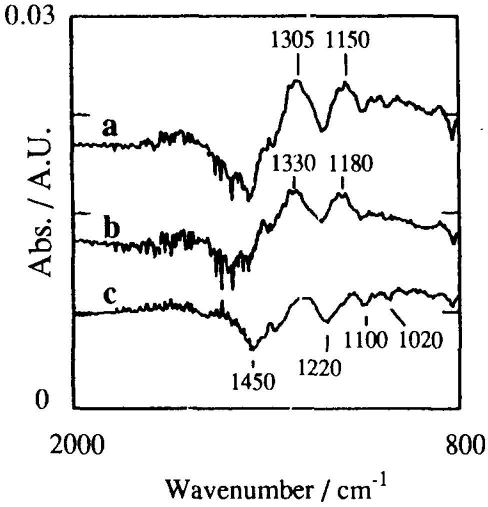


**Figure 5** I.r. difference spectra obtained for a PNT film after photo-oxidation, using unfiltered light and an irradiation time of 60 s: (a) 30 s and (b) 48 min after the end of the irradiation period. The spectrum (c) is obtained by subtracting spectrum (b) from spectrum (a)

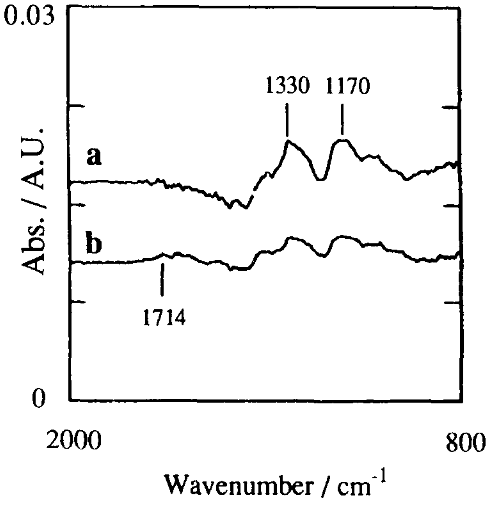


**Figure 6** I.r. difference spectra obtained for an uncompensated PNT film using filtered light and a photo-oxidation time of 60 s: (a) 30 s and (b) 24 min after the end of the irradiation period

sample. This sample exhibited qualitatively similar behaviour to that of a compensated sample which had been exposed to unfiltered light. The main peaks occurred at 1330 and 1170 $\mathrm{cm}^{-1}$ (*Figure 6a*) and still remained after 24 min, while the shoulder at 1350 $\mathrm{cm}^{-1}$ became more dominant in the post-irradiation period (*Figure 6b*).

*Effects of unfiltered light at high exposures.* Increasing the exposure time resulted in the appearance of absorptions in the carbonyl region, in addition to the photo-oxidation-induced bands discussed above (*Figure 7a*). Furthermore, it can be seen from *Figure 7b* that reduction of the sample by hydrazine after irradiation only removed the doping-induced bands and left the bands in the carbonyl region and the bands at 1330 and 1180 $\mathrm{cm}^{-1}$ intact.

The i.r. bands induced by photo-oxidation at short wavelengths resembled the bands induced by chemical or electrochemical doping of poly(thiophene) and its derivatives. Doping-induced bands were reported by Hotta *et al.*[7] to occur at 1030, 1120, 1200 and 1330 $\mathrm{cm}^{-1}$. It is therefore plausible to assign the shoulders at 1330 and 1170 $\mathrm{cm}^{-1}$ to bipolaron bands which have been formed by the spin combination of polarons. However, these bands did not disappear upon treatment with hydrazine, and therefore could not be due to polarons on the polymer chains. The results indicate that these bands are due to symmetric (1170 $\mathrm{cm}^{-1}$) and asymmetric (1330 $\mathrm{cm}^{-1}$) stretching vibrations of sulfonyl groups[8] formed upon photo-oxidation and that the reversible component contained bands resulting from the charged defects on the polymer chains.

*U.v. measurements. Figure 8* shows the effect of photo-oxidation on the electronic spectrum of the same sample as is shown in *Figure 6*. It can be seen that such treatment shifted the absorption maximum from 511 to 471 nm and reduced the optical density, indicating that conjugation-breaking reactions took place during photo-oxidation. It is reasonable to assume that these conjugation-breaking reactions could be accounted for by reactions of singlet oxygen via ene-reactions or cycloadditions.

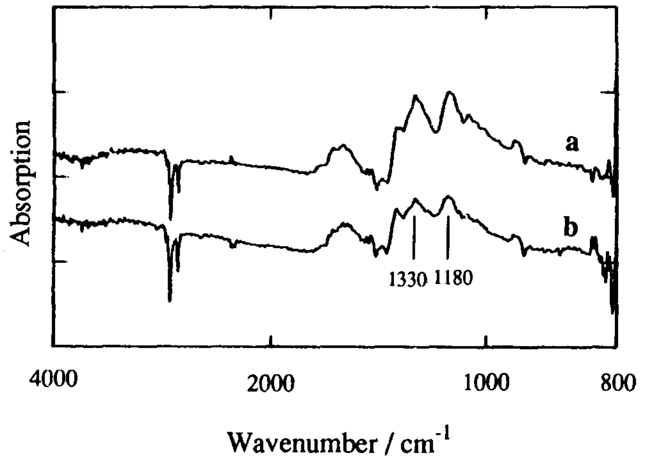


**Figure 7** I.r. difference spectra of a PNT sample showing the effects of compensation with hydrazine, using unfiltered light and a photo-oxidation time of 6 min: (a) before compensation and (b) the same sample after compensation

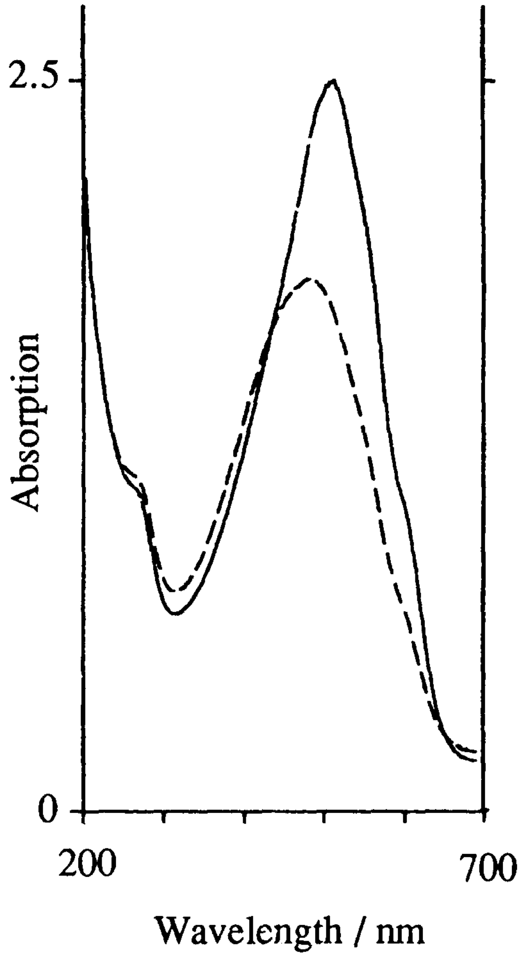


**Figure 8** Electronic spectra of the same sample as is shown in *Figure 6*, before (——) and after (– – –) irradiation

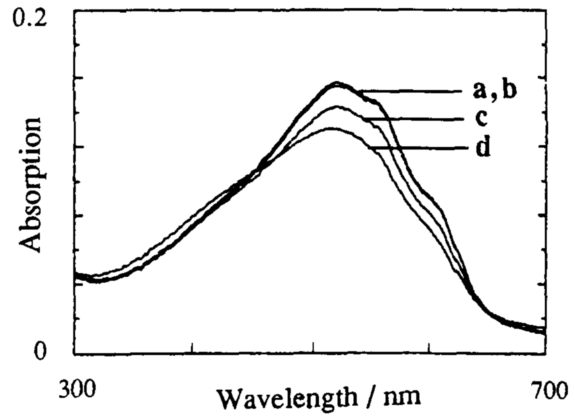


**Figure 9** The effect of compensation on the conjugation-breaking reactions: (a) a compensated film on quartz; (b) an uncompensated film on quartz; (c) film (a) after photo-oxidation; (d) film (b) after photo-oxidation. A photo-oxidation time of 4 min was used, and film thicknesses were ~0.03 μm

The effect of impurities resulting from the polymerization reaction on these conjugation-breaking reactions is shown in *Figure 9*. Although there was no appreciable difference between the spectra of compensated and uncompensated films (both grown on a quartz substrate), the conjugation-breaking reactions were clearly accelerated by impurities from the polymerization catalyst. However, an interruption of conjugation took place even when these impurities were removed by chemical compensation.

## DISCUSSION

Since we could not find any published methods for making submicron poly(3-alkylthiophene) films suitable for measurement by absorption spectroscopy over the entire i.r.–u.v. region, we developed a new method, which enabled us to prepare freely suspended submicron films of PNT, in spite of the relatively poor mechanical properties of this material. As this method is both simple and easily accessible, films made in this way may be useful not only for photodegradation studies but also for the measurement of physical properties, and in device fabrication.

Holdcroft[9] suggested a mechanism involving singlet oxygen for the photo-oxidation of poly(3-hexylthiophene) in solution, where the polymer itself acted as a sensitizer for the formation of singlet oxygen. This mechanism is supported by the ability of terthiophene to act as a singlet-oxygen sensitizer[10]. The reactions of singlet oxygen with low-molecular-weight thiophene derivatives are well documented, and generally these processes lead to the formation of carbonyl and sulfinyl groups via cycloadditions[11,12] and ene-reactions[9]. In these present investigations of solid films, however, we were unable to detect any typical signs of singlet-oxygen reactions with thiophene rings and no carbonyl or sulfinyl groups were detected, except in high-exposure experiments, in which case, carbonyl bands did appear. Instead, we observed reversible and irreversible effects that were due to electron transfer to oxygen and formation of sulfonyl groups (*Scheme 1*), respectively. Recently, Binh *et al.*[6] suggested that the formation of superoxide anions upon photo-oxidation of poly(3-hexylthiophene) was responsible for the residual photoconductivity that was detected after irradiation.

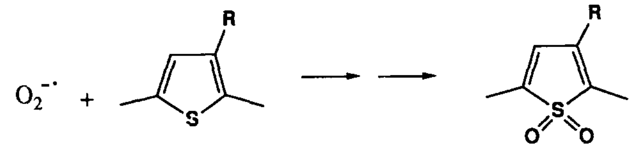
Photoexcitation of extended one-dimensional $\pi$-electron systems results in positive polarons, $P^+$, and negative polarons, $P^-$, or in other terms, radical cations and radical anions, with localized structural deformations to which the charges are associated. Electrons on the upper polaron levels of the negative polarons are transferred to oxygen to produce superoxide anions which then form ionic pairs with the positive polarons in order to maintain electrical neutrality. Thus the positive polarons have a relatively long relaxation time. In this sense, the photo-oxidation properties of PNT are similar to those of inorganic semiconductors such as $TiO_2$ and CdS[13–15]. In this context, it should be mentioned that photoinduced electron transfer from poly(3-hexylthiophene) to carbon dioxide has recently been reported by Kawai *et al.*[3,16].

The present results show clearly that impurities from the polymerization reaction have a profound effect on the photo-oxidation properties of PNT. Due to their low concentration, it was not possible to determine the exact nature of these impurities, but it is reasonable to presume that they consist of $FeCl_4^-$ ions or related complexes. Complexes containing iron(III) are known to be sensitive to light[17]. It has been previously reported that photoirradiation of PNT films doped with iron(III) chloride resulted in decomposition of the $FeCl_4^-$ ions and partial 'undoping' of the material[18]. It is therefore not surprising that the photoresponse of PNT depends strongly on the presence of impurities.

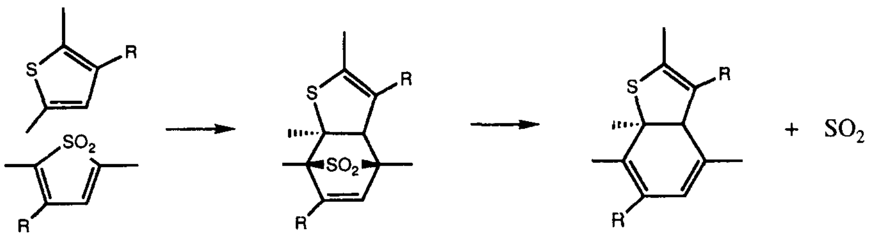
To our knowledge, this is the first report describing the i.r. spectral changes resulting from the oxidation of a compensated film of poly(3-alkylthiophene). It is therefore interesting to note the difference between the i.r. spectra associated with the polarons in this present work and those reported from experiments where charges were generated by chemical and electrochemical means or by photo-oxidation of uncompensated samples. The main difference is that oxidation of the compensated samples resulted in no absorption bands in the 1300–1330 $cm^{-1}$ region, where the strongest band for polythiophenes oxidized chemically or electrochemically usually appears[11,19,20].

Considering that even traces of singlet oxygen can initiate auto-oxidation of the aryl methylenes, which are very labile in poly(3-alkylthiophenes), the initial absence of any carbonyl groups is somewhat surprising. At the same time, the present results suggest that nucleophilic addition of superoxide anions to the sulfur atom is the main reaction pathway in the low-exposure photo-oxidation of PNT. In this context, it should be noted that thiophene-1,1-dioxide, formed by oxidation of the thiophene ring, is prone to undergo cycloaddition to neighbouring double bonds, followed by the extrusion of sulfur dioxide (as shown in *Scheme 2*)[21,22]. It is known that this type of oxidative decomposition of thiophenes can inhibit auto-oxidation of hydrocarbons[23]. Any signs of singlet-oxygen reactions which are normally amplified by auto-oxidation, could therefore be obscured by this inhibiting process, and routes via singlet oxygen can therefore not be ruled out by our observations.

Cycloaddition of thiophene-1,1-dioxide results in crosslinking of the polymer as well as a reduction in the conjugation length. This reaction can therefore account for the crosslinking of poly(3-hexylthiophene), even at very low levels of exposures[2]. At high exposures, photo-oxidation resulted in the formation of carbonyl



**Scheme 1**



**Scheme 2**

bands in the i.r. spectra. This could be a sign of singlet oxygen, but at this late stage in the photo-oxidation process, it is difficult to specify any particular mechanism.

## ACKNOWLEDGEMENT

One of the authors (MS) is grateful to the Science and Technology Agency for a fellowship.

## REFERENCES

1 'Handbook of Conducting Polymers' (Ed. T. A. Skotheim) Marcel Dekker, New York, 1986
2 Proceedings of the Conference on Optical Probes of Conjugated Polymers, Snowbird, UT, 1991 (Eds G. L. Baker and Z. V. Vardeny). Published in *Synth. Met.* 1992, **49**, **50**
3 Kawai, T., Kuwabara, T. and Yoshino, K. *J. Chem. Soc., Faraday Trans.* 1992, **88**, 2041
4 Abdon, M. S. A., Xie, Z. W., Leung, A. M. and Holdcroft, S. *Synth. Met.* 1992, **52**, 159
5 Sugimoto, R., Takeda, S., Gu, H. B. and Yoshino, K. *Chem. Express* 1986, **1**, 635
6 Binh, N. T., Gailberger, M. and Hässler, H. *Synth. Met.* 1992, **47**, 77
7 Hotta, S., Shimotsuma, W. and Taketani, M. *Synth. Met.* 1985, **10**, 85
8 Bellamy, L. J. 'The Infrared Spectra of Complex Molecules', 2nd Edn, Chapman and Hall, London, 1985, Vol. 2, Ch. 7, p. 222
9 Holdcroft, S. *Macromolecules* 1991, **24**, 4834
10 Evans, C. H. and Scaiano, J. C. *J. Am. Chem. Soc.* 1990, **112**, 2694
11 Skold, C. N. and Schlessinger, R. H. *Tetrahedron Lett.* 1970, 791
12 Wasserman, H. H. and Strehlow, W. *Tetrahedron Lett.* 1970, 795
13 Fox, M. A. *Acc. Chem. Res.* 1983, **16**, 314
14 Pienta, N. J. in 'Photoinduced Electron Transfer', Part C (Eds M. A. Fox and M. Chanon) Elsevier, Amsterdam, 1988, Ch. 4.7, p. 445
15 Noda, H., Oikawa, K. and Kamada, H. *Bull. Chem. Soc. Jpn* 1992, **65**, 2505
16 Kawai, T., Kuwabara, T. and Yoshino, K. *Jpn J. Appl. Phys.* 1992, **31**, L49
17 Balzani, V. and Carassiti, V. in 'The Photochemistry of Coordination Compounds' Academic Press, New York, 1970, Ch. 10, p. 183
18 Sandberg, M., Tanaka, S. and Kaeriyama, K. *Synth. Met.* 1993, **60**, 171
19 Christensen, P. A., Hamnett, A., Hillman, A. R., Swann, M. J. and Higgins, S. J. *J. Chem. Soc., Faraday Trans.* 1992, **88**, 595
20 Neugebauer, H., Nauer, G., Neckel, A., Tourillion, G., Garnier, F. and Lang, P. *J. Phys. Chem.* 1984, **88**, 652
21 Raasch, M. S. in 'Thiophene and its Derivatives', Part 1 (Ed. S. Gronowitz), Wiley, New York, 1985, Ch. 7, p. 579
22 Bailey, W. J. and Cummins, E. W. *J. Am. Chem. Soc.* 1954, **76**, 1940
23 van Tilborg, W. J. M. and Smael, P. *Rec. Trav. Chim. Pays-Bas* 1976, **95**, 132