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## A photo-electron emission study of polythiophene derivatives

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**Abstract.** The difference between the energy of the top of the valence band in polythiophene and those in poly(3-alkylthiophene)s has been evaluated by photo-electron spectroscopy in air. The top of the valence band becomes higher in energy on gradually increasing alkyl chain length. This indicates that an acceptor dopant is relatively stable in poly(3-alkylthiophene)s with longer alkyl chain lengths, as observed. In doped polythiophene and poly(3-methylthiophene), the difference in the threshold energy of photo-electron emission is explained tentatively by electron emission from the polaron and bi-polaron levels formed by the dopant.

### 1. Introduction

Recently, conducting polymers with a highly extended  $\pi$ -electron system in their polymer main chain have attracted much attention from both fundamental (Su *et al* 1979, Scott *et al* 1983) and practical viewpoints (Chen *et al* 1980, Nigrey *et al* 1981, Yoshino *et al* 1983), because various new concepts such as the soliton, polaron and bi-polaron have been introduced and also many types of applications utilising these conducting polymers have been proposed. In particular, heterocyclic polymers such as polythiophene and polypyrrole have been most extensively studied because high-quality stable films can be prepared relatively easily by either an electrochemical (Diaz *et al* 1979, Kaneto *et al* 1982, Ohsawa *et al* 1984) or a chemical method (Yoshino *et al* 1984). These polymers were considered to be non-soluble in solvents and non-fusible even when heated above their decomposition temperatures, thus restricting the practical use of conducting polymers. Recently, however, polythiophene derivatives substituted with long alkyl chains at the 3 position of a thiophene ring [poly(3-alkylthiophene)] such as poly(3-methylthiophene), poly(3-hexylthiophene) and poly(3-dodecylthiophene), have been found to be soluble in some solvents (Sato *et al* 1986, Elsenbaumer *et al* 1986) and even fusible at a relatively low temperature (Yoshino *et al* 1987a, b).

On the contrary, dopant in poly(3-methylthiophene) is known to be relatively stable compared with that in polythiophene in which the dopant is automatically removed by air. However, details of the origin of this difference in the stability of dopant have not

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been completely clarified. In the acceptor-doped state, electrons are considered to be transferred from the valence band to the acceptor and polaronic levels are created. The stabilities of acceptor dopants are expected to be dependent on the electronic energy state of the polymer (especially the top of the valence band), the electronegativity of the dopant and the size of the dopant. Therefore, it is very interesting to investigate the energy of the top of valence band in poly(3-alkylthiophene)s with various alkyl chain lengths and stabilities of dopants in it. However, those details have not been fully understood until now.

The photo-electron spectroscopy technique is one of the most effective methods for investigating the electronic energy scheme. Recently, a new technique has been developed by which photo-electron emission can be monitored even in air (Kirihara and Uda 1981). In a recent paper, we reported an experimental study on electron emission in polythiophene and poly(3-methylthiophene) using this new method (Yoshino *et al* 1988).

In this paper, we study the photo-electron emission spectra of doped and undoped poly(3-alkylthiophene)s and also of poly(3,4-dialkylthiophene)s using this new method.

## 2. Experimental details

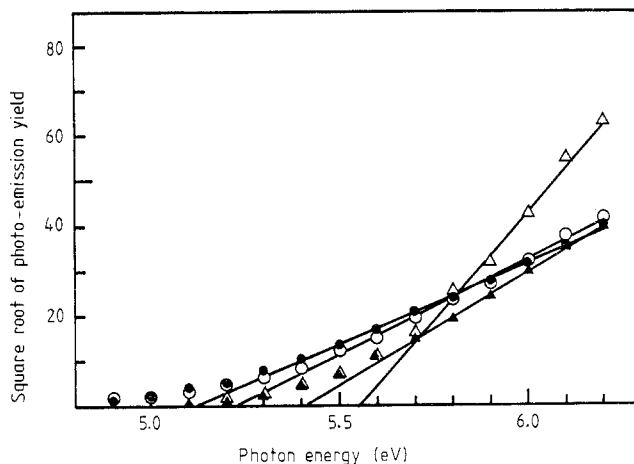
Poly(3-alkylthiophene)s and poly(3,4-dialkylthiophene)s can be prepared by both electrochemical and chemical methods. However, in this paper, the samples were prepared by the electrochemical polymerisation technique from thiophene, 3-alkylthiophene and 3,4-dialkylthiophene monomers, respectively, in about 0.5 mol% of  $\text{LiBF}_4$  per litre of benzonitrile supporting electrolyte. 3-alkylthiophene and 3,4-dialkylthiophene monomers were prepared by the Grignard reaction utilising 3-bromothiophene and 3,4-dibromothiophene as the starting materials. Details of the polymerisation procedure have already been reported in our previous paper (Yoshino *et al* 1984). The removal of the dopant from polythiophene, poly(3-alkylthiophene) and poly(3,4-dialkylthiophene) films was carried out as follows:

- (i) electrochemical reduction;
- (ii) compensation of residual anions by washing with aqueous ammonia;
- (iii) washing with methanol, ethanol and acetone;
- (iv) heat treatment at 200 °C for 20 h under vacuum.

The photo-electron emission signal in air was measured utilising a low-energy photo-electron spectroscopy instrument (Rikenkeiki Co. Ltd model A-AC-1M) in which monochromated ultraviolet light in the energy range 3.5–6.2 eV irradiated the sample in air. The photo-electrons emitted from the sample were monitored with a low-energy electron counter operatable in air.

## 3. Results and discussion

Figure 1 shows the photo-electron emission spectra in undoped polythiophene and poly(3-alkylthiophene)s with various alkyl chain lengths. In this figure the square root of the yield was plotted as a function of photon energy. By extrapolating a line fitted to the data point at the higher-energy part, the threshold energy for the electron emission was evaluated. Although the reason why such a plot gives a linear relationship has not

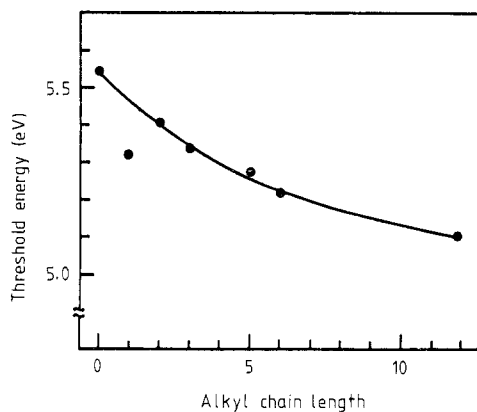


**Figure 1.** Photo-electron emission spectra of undoped polythiophene and poly(3-alkylthiophene)s;  $\triangle$ , polythiophene, 5.55 eV;  $\blacktriangle$ , poly(3-ethylthiophene), 5.41 eV;  $\circ$ , poly(3-hexylthiophene), 5.22 eV;  $\bullet$ , poly(3-dodecylthiophene), 5.11 eV. (The units of the ordinate are  $(\text{counts s}^{-1})^{1/2}$ .)

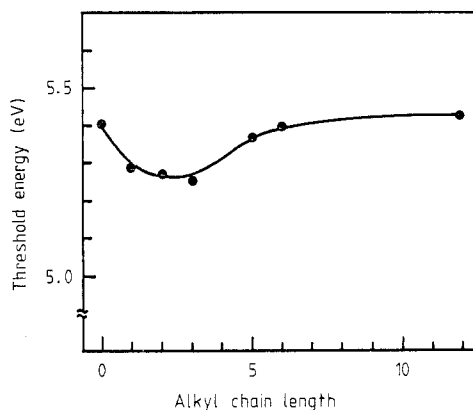
been clarified, this plot has been utilised in most studies and the evaluated emission threshold has been considered to be reasonable. Therefore, we also made this square-root plot.

It is clear from this result that the threshold energy of photo-electron emission is smaller in poly(3-alkylthiophene)s with relatively long alkyl chain lengths such as poly(3-dodecylthiophene). The small tail of the photo-electron emission yield below threshold is considered to originate in the surface levels, localised levels, etc.

Figure 2 shows the alkyl chain length dependence of the threshold energy of photo-electron emission in poly(3-alkylthiophene)s evaluated by this method. The photo-electron emission signal in this experiment is influenced slightly by the ambient con-



**Figure 2.** Alkyl chain length dependence of the threshold energy of photo-electron emission for undoped polythiophene and poly(3-alkylthiophene)s evaluated from figure 1.



**Figure 3.** Alkyl chain length dependence of the threshold energy of photo-electron emission for the  $\text{BF}_4^-$ -doped polythiophene and poly(3-alkylthiophene)s.

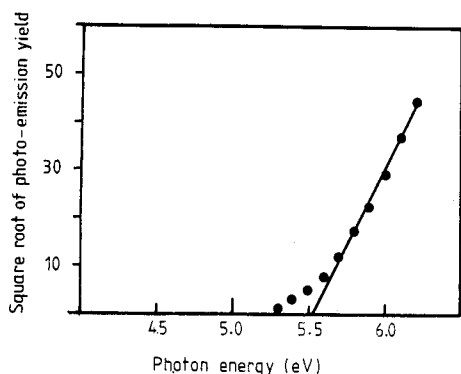
ditions such as humidity, temperature, etc, because of the measurement in air. However, it is clearly indicated that the threshold energy of photo-electron emission in poly(3-alkylthiophene)s becomes smaller on gradually increasing the alkyl chain length. This indicates that the top of the valence band of poly(3-alkylthiophene)s with longer alkyl chain lengths is located at a higher-energy state. For example, the threshold energy of photo-electron emission in poly(3-dodecylthiophene) is smaller than that of polythiophene by about 0.4 eV. This indicates that the top of the valence band of poly(3-dodecylthiophene) is located at a higher-energy state than that of polythiophene by about 0.4 eV. The difference in the tops of the valence bands corresponds to the difference in the ionisation potentials. This result satisfactorily explains the stability of a dopant in poly(3-alkylthiophene)s compared with polythiophene. In poly(3-alkylthiophene)s with smaller ionisation energies and higher energies of the top of the valence bands, electrons tend to be transferred to the acceptor dopant. This results in a relatively strong charge transfer interaction. On the contrary, in polythiophene, electrons transferred to a dopant tend to be relatively easily back-transferred to the polymer chain. This is due to the higher ionisation energy, and the smaller energy difference between the top of the valence band and the energy state of the dopant. For the electrochemically doped state, the coupling of doped anions with positive polarons formed by removing electrons from the valence band seems to be stronger in the material in which the top of the valence band is located at a higher energy, because the removal of electrons from valence bands becomes much easier.

The relatively small ionisation potentials of poly(3-alkylthiophene)s should be due to the donating characteristic of the alkyl group which elevates the top of the valence band with respect to energy. This may also be partly related to the expected enhancement of one-dimensionality in poly(3-alkylthiophene)s with longer alkyl chains in which a smaller inter-polymer chain interaction on account of the longer inter-chain distance is expected owing to the hindrance effect of the bulky alkyl group.

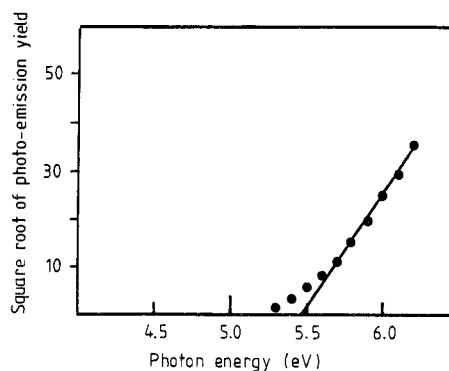
Figure 3 shows the alkyl chain length dependence of the threshold energy of the photo-electron emission spectra of  $\text{BF}_4^-$ -doped poly(3-alkylthiophene)s. For polythiophene and poly(3-alkylthiophene)s with shorter alkyl chain lengths such as poly(3-methylthiophene) and poly(3-ethylthiophene), the threshold energy is slightly lower than or almost the same as those in figure 2. Specifically, if electron emission in the doped sample originates only from the valence band, the threshold energy must be increased contrary to observations, because the Fermi energy seems to be lowered by the charge transfer from the valence band.

The results could be explained as follows. When polythiophene and their derivatives are acceptor doped, Moraes *et al* (1984) have reported that polarons do not exist as a stable species. They are converted automatically to bi-polarons, because bi-polarons are considered to be a stable species energetically. On the contrary, we reported that both polarons and bi-polarons coexist even at a relatively high doping level from the observed optical spectral change, electron spin resonance (ESR) and photo-induced ESR measurements (Vareny *et al* 1986, Kaneto and Yoshino 1987). In these experiments, dopants in polythiophene and poly(3-alkylthiophene)s with shorter alkyl chain lengths may have their degree of doping slightly reduced because of the measurement being in air. In such a case, the existence of polaron states should be favoured. The polaron state is higher in energy than the original top of the valence band. Therefore the threshold energy for electron emission from the polaron state should become smaller.

The present result seems to support our interpretation of polaron formation, because the threshold of electron emission was slightly lowered in energy.



**Figure 4.** Photo-electron emission spectrum of undoped poly(3,4-dimethylthiophene) (5.53 eV). (The units of the ordinate are  $(\text{counts s}^{-1})^{1/2}$ .)



**Figure 5.** Photo-electron emission spectrum of  $\text{BF}_4^-$ -doped poly(3,4-dimethylthiophene) (5.47 eV). (The units of the ordinate are as for figure 4.)

At this stage, however, another possibility of explaining electron emission with a lower threshold energy cannot be completely excluded. For example, band bending at the surface of a doped sample may play a role and explain the observed results. Even in the doped state, the thin surface layer may be undoped in air. In such a case, the difference between the Fermi energies of the surface and bulk regions can create band bending at the surface. This may result in a lowered threshold energy of photo-electron emission as is the case for inorganic semiconductors. However, it is not clear whether band bending is indeed occurring in this sample at this stage of the experiment or not.

In contrast, the threshold energy of photo-electron emission in doped poly(3-alkylthiophene)s with longer alkyl chain lengths such as poly(3-dodecylthiophene) clearly becomes larger compared with that of the undoped sample shown in figure 2. This corresponds to a lower energy of the top of valence band in the doped sample compared with that in the undoped sample. In doped poly(3-alkylthiophene)s with longer alkyl chain lengths, the bi-polaron state may be formed owing to the stability of dopants even in air. In this case, electron emission from the empty bi-polaron level is not probable. Therefore the shift of the threshold energy to a lower energy should not be observed using this bi-polaron model. On the contrary, the top of the valence band is located at a lower energy than the original state, because electrons are taken away from the valence band.

Figure 4 shows the photo-electron emission spectrum for undoped poly(3,4-dimethylthiophene). In this figure, the threshold energy is evaluated as about 5.5 eV. This indicates that the top of valence band of poly(3,4-dimethylthiophene) is in almost the same position as that of polythiophene. The band gap of poly(3,4-dimethylthiophene) obtained from the absorption spectra was about 3.1 eV, being larger than that (2.1 eV) of polythiophene. This large band gap of poly(3,4-dimethylthiophene) coincides with the value reported by Bureau *et al* (1985). The blue shift of the absorption edge and the larger band gap of poly(3,4-dimethylthiophene) than that of polythiophene could originate in the torsion of neighbouring thiophene rings at the bonding due to the large steric hindrance between alkyl chains and S atoms and also between the two alkyl chains, resulting effectively in a shorter conjugation length. Accordingly, the bottom of the conduction band of poly(3,4-dimethylthiophene) is expected to be located higher than that of polythiophene by about 1.0 eV.

Figure 5 shows the photo-electron emission spectrum of  $\text{BF}_4^-$ -doped poly(3,4-dimethylthiophene). It is clear from this figure that the threshold energy of photo-electron emission for doped poly(3,4-dimethylthiophene) is lower than that for undoped poly(3,4-dimethylthiophene). This may be also explained by electron emission from the polaron state.

#### 4. Summary and conclusion

The present experimental study can be summarised as follows.

(i) The energy of the top of the valence band for polythiophene and poly(3-alkylthiophene)s was evaluated from photo-electron emission spectra in air.

(ii) The threshold energy of photo-electron emission for poly(3-alkylthiophene)s becomes smaller on gradually increasing the alkyl chain length. This indicates that the dopant is relatively stable in poly(3-alkylthiophene)s with longer alkyl chain lengths.

(iii) For doped polythiophene and poly(3-alkylthiophene)s with shorter alkyl chain lengths, the energies of photo-electron emission were found to be slightly lower than or almost the same as those of undoped samples. This is explained tentatively by electron emission from the polaron level.

(iv) In contrast to this, for doped poly(3-alkylthiophene)s with longer alkyl chain lengths, the energy of photo-electron emission was found to be higher than that for undoped samples. This is explained by the bi-polaron formation and the lowering of the top of the valence band in energy compared with that of the undoped sample.

(v) For undoped poly(3,4-dimethylthiophene), the top of the valence band is evaluated to be almost the same as that of polythiophene. Therefore the larger band gap (3.1 eV) of poly(3,4-dimethylthiophene) suggests that the bottom of conduction band is at a higher energy.

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