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## LETTER TO THE EDITOR

# The absorption spectrum and a cyclic voltammogram of $C_{60}$ -doped poly(3-alkylthiophene)

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**Abstract.** The absorption spectrum and a cyclic voltammogram for poly(3-hexylthiophene) changed upon  $C_{60}$  doping but those for poly(3-octadecylthiophene) did not. This suggests that  $C_{60}$  is an effective dopant for poly(3-hexylthiophene) in the ground state but not for poly(3-octadecylthiophene). The threshold of cyclic voltammetry has shifted to a higher potential in  $C_{60}$ -doped poly(3-hexylthiophene). This is explained by the lowering of the valence band top due to the electron transfer from poly(3-hexylthiophene) to  $C_{60}$ . The shift depends on alkyl chain length and decreases with alkyl chain length in accordance with the results of photoemission spectroscopy.

Recently,  $C_{60}$ , also known as Buckminsterfullerene, has attracted great attention as the third form of carbon which exhibits novel properties such as superconductivity [1] and ferromagnetism [2] upon doping with alkali metals and TDAE, respectively. In these studies, fullerenes have been considered to be hosts for dopants, in many cases donors. That is, in all cases, various dopants were doped into fullerenes.

In contrast, however, we have found that  $C_{60}$  can be doped into conducting polymers such as poly(3-alkylthiophene) whose main chains are composed of highly extended conjugated electron systems [3–5].

Two types of characteristic were found in  $C_{60}$ -doped conducting polymers depending on their molecular structures. (1) Remarkable change of absorption spectrum, quenching of photoluminescence, slight enhancement of conductivity and change of ESR spectrum were observed in poly(3-hexylthiophene) [3,4]. These doping effects were relatively weak compared with those of conventional strong dopants such as iodine,  $BF_4^-$  and  $ClO_4^-$ . (2) Small changes to the absorption spectrum, conductivity and ESR, quenching of photoluminescence and a remarkable enhancement of photoconductivity were observed in conducting polymers such as poly(3-octadecylthiophene), suggesting that  $C_{60}$  is not an effective dopant for this polymer [5]. These different doping effects for poly(3-alkylthiophene) with different alkyl chain length were tentatively explained by the difference of the top of valence band of poly(3-alkylthiophene)s relative to the LUMO of  $C_{60}$ .

In this letter, the absorption spectrum and a cyclic voltammogram of poly(3-alkylthiophene) are studied and the electron transfer from poly(3-alkylthiophene) as a function of alkyl chain length is discussed.

Poly(3-alkylthiophene) was prepared from 3-alkylthiophene monomer utilizing  $\text{FeCl}_3$  as a catalyst. The detailed polymerization method and procedure have already been reported in our previous paper [6].

$\text{C}_{60}$  prepared by an arc discharge from graphite and washed with toluene (provided by Science Laboratories Co Ltd) was used in this experiment.

Both poly(3-alkylthiophene) and  $\text{C}_{60}$  of appropriate ratio were dissolved in the common solvent, toluene. A thin film was then prepared by casting the solution on a conducting ITO (indium tin oxide) coated quartz plate.

Absorption spectrum measurements were carried out utilizing a Hitachi 330 spectrophotometer.

Electrochemical measurements were carried out by the standard technique. An HB-105 Hokuto Denko Ltd arbitrary function generator and an HA-105 Hokuto Denko Ltd potentiostat were used in the system. Li counter and reference electrodes in propylene carbonate containing  $\text{LiBF}_4$  of  $0.1 \text{ mol l}^{-1}$  were also employed.

Figure 1 indicates absorption spectra of poly(3-hexylthiophene) at various  $\text{C}_{60}$  doping concentrations. As shown in this figure, the absorption of the interband transition of poly(3-hexylthiophene) decreased in intensity and the peak wavelength shifted to shorter wavelength upon  $\text{C}_{60}$  doping. This suggests that  $\text{C}_{60}$  is an effective dopant for poly(3-hexylthiophene) in the ground state. Absorption peaks at about 260 nm and 330 nm due to  $\text{C}_{60}$  appeared for higher concentrations of  $\text{C}_{60}$ .

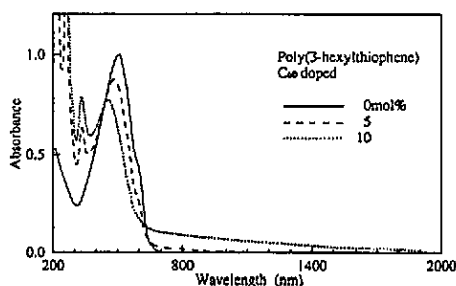


Figure 1. Absorption spectra of poly(3-hexylthiophene) as a function of  $\text{C}_{60}$  concentration.

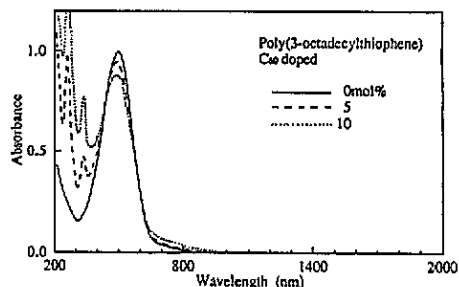


Figure 2. Absorption spectra of poly(3-octadecylthiophene) as a function of  $\text{C}_{60}$  concentration.

In contrast to the system of poly(3-hexylthiophene)- $\text{C}_{60}$ , the absorption spectrum of poly(3-octadecylthiophene) was scarcely influenced upon  $\text{C}_{60}$  doping as shown in figure 2. The absorption peaks due to  $\text{C}_{60}$  also appeared for higher concentrations of  $\text{C}_{60}$ . However, the interband absorption of poly(3-octadecylthiophene) was not suppressed markedly and the peak wavelength did not shift upon  $\text{C}_{60}$  doping. This result indicates that  $\text{C}_{60}$  is not an effective dopant for poly(3-octadecylthiophene) in the ground state.

These facts have been interpreted by assuming electron transfer from poly(3-hexylthiophene) to  $\text{C}_{60}$  but not from poly(3-octadecylthiophene) to  $\text{C}_{60}$ , taking the difference of the top of the valence band of poly(3-alkylthiophene) into consideration [5].

Figure 3 shows cyclic voltammograms of undoped and  $\text{C}_{60}$ -doped poly(3-hexylthiophene). As shown in this figure, the threshold of cyclic voltammetry shifted to a higher potential upon  $\text{C}_{60}$  doping.

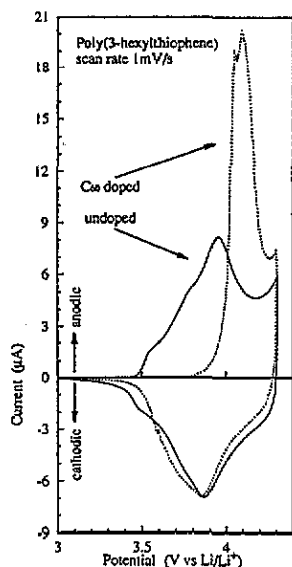


Figure 3. Cyclic voltammogram of non-doped and  $C_{60}$ -doped poly(3-hexylthiophene).

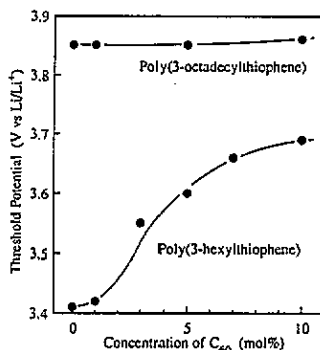


Figure 4. Dependence of threshold potentials of cyclic voltammograms of poly(3-hexylthiophene) and poly(3-octadecylthiophene) on the concentration of  $C_{60}$ .

This change is more clearly shown in figure 4, which indicates the dependence of the threshold potential of cyclic voltammetry in poly(3-hexylthiophene) and poly(3-octadecylthiophene) on the concentration of  $C_{60}$ . That is, the threshold potential of poly(3-hexylthiophene) became higher with increasing  $C_{60}$  concentration. On the other hand, in the system of poly(3-octadecylthiophene)- $C_{60}$ , the cyclic voltammogram was not influenced upon  $C_{60}$  doping.

These results clearly indicate that in the system of poly(3-hexylthiophene)- $C_{60}$ , charge transfer occurs in the ground state but does not occur in the system of poly(3-octadecylthiophene)- $C_{60}$  in the ground state because the threshold potential of cyclic voltammetry reflects the valence band top of the conducting polymer [7]. That is, the electron in the valence band of poly(3-hexylthiophene) was transferred to the LUMO of  $C_{60}$ . Then the top of the valence band of poly(3-hexylthiophene) may be consequently lowered in energy with increasing  $C_{60}$  concentration. In poly(3-hexylthiophene), the lowering of the valence band top upon  $C_{60}$  doping was observed in the cyclic voltammogram in contrast to poly(3-octadecylthiophene), in which the lowering of the valence band top was not observed due to the difficulty of the electron transfer. These results are supported by the change of absorption spectrum of  $C_{60}$ -doped poly(3-alkylthiophene) as shown in figures 1 and 2.

Figure 5 indicates the dependence of the threshold potential shift of the cyclic voltammogram of  $C_{60}$ -doped poly(3-alkylthiophene) on alkyl side chain length. As evident in this figure, the threshold potential shift decreases with alkyl chain length. This indicates that the top of the valence band of poly(3-alkylthiophene) becomes lower in energy with alkyl chain length in accordance with the results of photoemission spectroscopy [8]. That is, the charge transfer to  $C_{60}$  may be favourable in poly(3-alkylthiophene) with a shorter alkyl side chain because the valence band top is

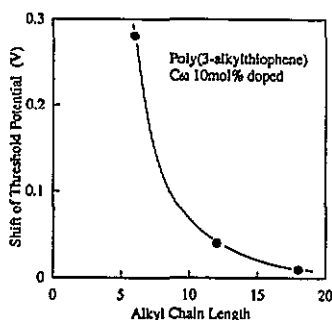


Figure 5. Dependence of threshold potential shift of cyclic voltammogram of  $C_{60}$  10 mol% doped poly(3-alkylthiophene) on alkyl side chain length.

higher in energy for a shorter alkyl chain. This is consistent with the observed cyclic voltammograms.

In conclusion, the threshold of the cyclic voltammogram of poly(3-alkylthiophene), for which  $C_{60}$  was an effective dopant in the ground state, was shifted to a higher potential upon  $C_{60}$  doping. This threshold potential shift was more remarkable in poly(3-alkylthiophene) of shorter alkyl side chain, in which the valence band top was higher in energy. The lowering of the valence band top is due to the charge transfer from poly(3-hexylthiophene) to  $C_{60}$  in the ground state, resulting in the effective doping of  $C_{60}$  and a remarkable change in absorption spectrum. That is,  $C_{60}$  is an effective dopant for conducting polymers with the valence band top high in energy.

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