Carrier Mobilities in a Regioregular Poly(3-octylthiophene) Film at Various Oxidation Stages

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Apparent mobilities of positive charge carriers in a regioregular poly(3-octylthiophene) film in varying oxidation states were successfully evaluated by using electrochemical techniques. Electrochemical ClO_4^- doping caused a decrease of the mobility by about one order of magnitude until the doping level reached about 2%. Further electrochemical doping resulted in the drastic increase of the mobilities up to 0.5 cm^2 V^{-1} s^{-1} at a maximum doping level of 23%.

Highly stacked films of π-conjugated oligomers and polymers such as sexithiophene, pentacene, antradithiophene and regioregular poly(3-alkylthiophene) give high filed-effect mobilities of 10^{-2} - 1 cm^2 V^{-1} s^{-1} in their neutral states.[1] These values are much greater than the mobilities (μ) of 10^{-6} - 10^{-4} cm^2 V^{-1} s^{-1} for amorphous films of π-conjugated polymers in their neutral or lightly doped states.[2,3] Apparent mobilities of positive charge carriers in amorphous films of polythiophene (PT), poly(3-methylthiophene) (PMT) and polyacetylene (PA) are found to increase by electrochemical or chemical dopings.[2,3] For example, the μ for the PMT film increased monotonously from 2 x 10^{-5} cm^2 V^{-1} s^{-1} to 0.1 cm^2 V^{-1} s^{-1} by electrochemical ClO_4^- doping.[2] To our best knowledge, however, μ values for highly stacked films have not been reported in their variously doped states, because the FET technique or traditional time-of-flight technique is not applicable to these doped films exhibiting relatively high conductivities.

In this work, μ values of charge carriers in a regioregular poly(3-octylthiophene) (POT) film at various oxidation stages are evaluated by use of a recently developed electrochemical technique, a combination of in-situ conductivity and potential-step chronocoulometry.[2] The POT is known to give a well-defined highly stacked film.[4] In-situ ESR measurements are also performed in order to characterize charge carriers in the POT film.

$AgClO_4$ and POT were used as received. Other chemicals were purified before use. Thin films of POT were prepared by spin coating with chloroform as a solvent. Conductivities (σ) and doping levels (y) were in-situ measured by two-probe method and potential-step chronocoulometry, respectively.[2] Here, the y value is defined as the number of charges per thiophene ring. Apparent μ values for the POT film at various doping levels were calculated by the relation $\mu = \sigma/ne$, where n denotes the density of charge carriers obtained from a doping level, a film thickness and a molecular weight of a repeat unit of the POT film. In-situ ESR measurements were performed as described elsewhere.[5] The intensities and magnetic fields of the ESR spectra of the POT films were calibrated by the simultaneously measured ESR spectra of Mn^{2+} in MgO as an external standard. All the measurements were performed at room temperature under N_2 atmosphere.

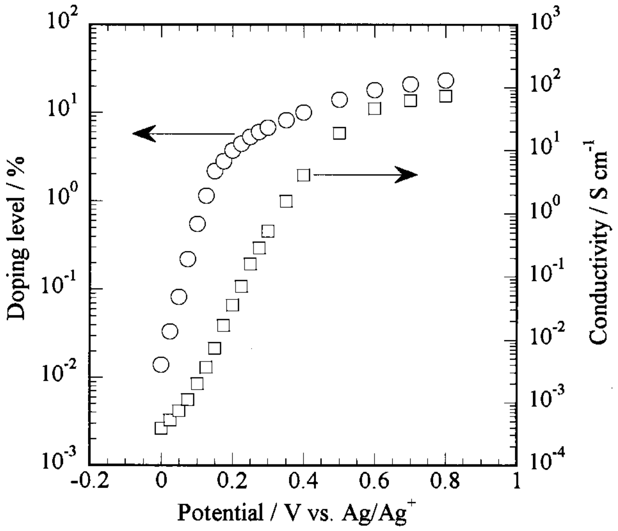

Figure 1. Conductivities (□) and doping levels (○) of the POT film as a function of potential.

The σ and y values for the POT film were measured several times and were found to be quite reproducible. As shown in Figure 1, the σ value increases with potential by about five orders of magnitude from 3.8 x 10^{-4} S cm^{-1} at 0 V to 74 S cm^{-1} at 0.8 V. The y value is 0.014% at 0 V, increases with the increase in potential and reaches 23% at 0.8 V.

Figure 2 depicts the resulting μ plot for the POT film as a function of y. The μ value at the lowest y of 0.014% attainable

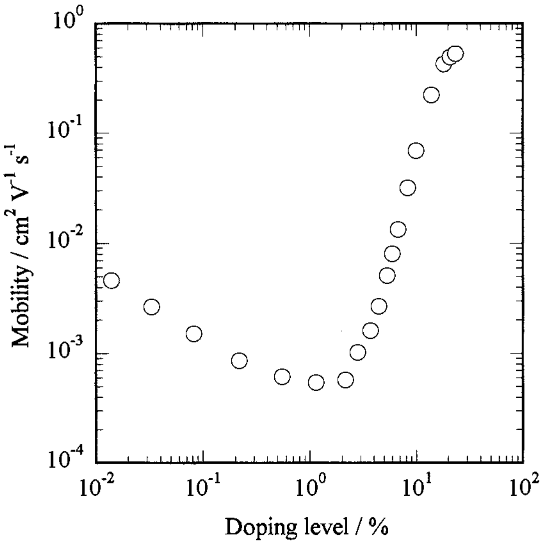

Figure 2. Apparent mobilities of charge carriers in the POT film at different doping levels.

in the present experiment is 0.5 x 10^{-2} cm^2 V^{-1} s^{-1} which is close to the field-effect mobilities (0.01-0.045 cm^2 V^{-1} s^{-1}) for undoped regioregular poly(3-hexylthiophene) films.[1c] Interestingly, the μ value decreases with the increase in y and reaches a minimum of 5.4 x 10^{-4} cm^2 V^{-1} s^{-1} at y = 1.1%. Further electrochemical doping induced a drastic increase of μ over about three orders of magnitude, reaching 0.53 cm^2 V^{-1} s^{-1} at y = 23%. The observed variation of μ with y is in contrast to those reported for common conducting polymers such as PT, PMT and PA, where the μ values increased monotonously with the increase of y.[2,3]

Figure 3 depicts a double logarithmic plot of relative number of spins (N_s) versus y for the POT film, where N_s was obtained by double integration of ESR spectra. The N_s increases with the increase of y up to about 2%. However, the slope of the log-log plot is smaller than unity, suggesting that spinless species as well as polarons are generated in this doping range y = 0.014% - 2%. The plot levels off at y values beyond 2%, showing that the spinless species are predominantly formed in the high doping range. Peak-to-peak linewidths (ΔH_{pp}) of the ESR spectra for the POT film were almost constant at 3 Gauss until the y reached about 2%. Further doping caused a remarkable broadening of the ESR spectra and the ΔH_{pp} reached 14.3 Gauss at y = 23%.

The spinless species seem to be bipolarons or cation radical π-dimers. The latter diamagnetic species are found to be formed by dimerization of cation radicals (polarons) on separate oligothiophene chains.[6] Recently, we have successfully evaluated μ values of polarons and bipolarons in the PMT and PT films.[2] The μ values of polarons are of the order 10^{-5} cm^2 V^{-1} s^{-1} while those of bipolarons are much greater than the μ values of polarons. The drastic increase of apparent μ values with the increase of y was explained by increased molar fractions of bipolarons.[2] We have also found that the μ value of π-dimers in a poly[(ethoxypropyl-silanylene)quinque(2,5-thienylene)] film is extremely small compared with the one of polarons in this polymer film.[7] On these bases, we presume that the diamagnetic species in the POT at y values up to ca. 2% are immobile π-dimers instead of mobile bipolarons. In fact, π-dimers may be favored over bipolarons in the highly stacked POT film. Obviously, the stacked nature of the polymer film arises from the regioregularity of the POT polymer. The decrease of apparent μ values with the increase of y is explained by the increase of molar fractions of immobile π-dimers. On the other hand, the jump up of the μ value in the POT film at y = 2 - 23% can be accounted for in terms of the formation of bipolarons, followed by the evolution of the metal-like conduction. The evolution of the metallic conduction is consistent with the sharp rise of ΔH_{pp} at y values exceeding ca. 2%.[5]

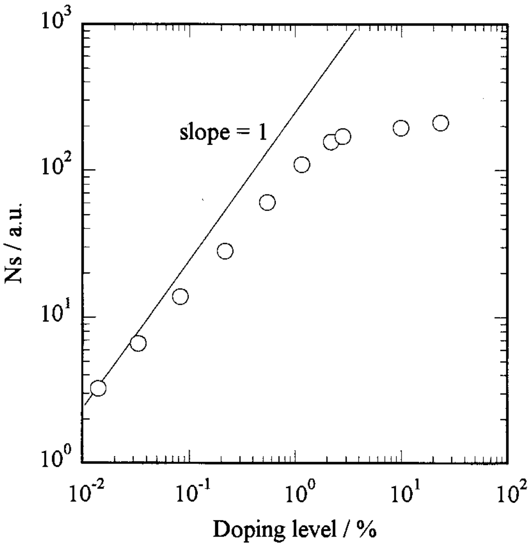

Figure 3. N_S in the POT film as a function of doping level.

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