

Mechanism of Dedoping Processes of Conducting Poly(3-alkylthiophenes)

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To clarify the mechanism of thermal dedoping processes of conducting poly(3-alkylthiophenes), temporal changes in electric conductivity, photoabsorption, and electron spin resonance of iodine-doped poly(3-octylthiophene) were examined. A decrease in the electric conductivity was accompanied by a decrease in the photoabsorption of the polymer cation and an increase in the spin concentration: the cation is a spinless charge carrier and it was converted to an immobile paramagnetic species. The conversion proceeds through deprotonation of the cation, which results in the formation of a polyenyl radical.

Introduction

Conducting polymers have the potential for many applications in electronics, such as light-emitting diodes, organic transistors, solar cells, sensors, batteries, photoresists, and magnetic shielding materials.¹ Polythiophene (PT) and its derivatives are one of the most investigated conducting polymers for their environmental and thermal stability.² PT itself is an intractable solid, which is insoluble in solvents and infusible. Introduction of alkyl side chains at the 3-positions of the thienyl rings makes the polymers processable.^{3–6} However, the side chain substitution causes thermal instability of the doped polymers. Thermal dedoping is a serious problem for the applications of poly(3-alkylthiophenes) (PATs).

Many studies have been carried out on the dedoping processes of PATs. The rate of dedoping depends on the dopants,^{7–11} side chain length of PATs,^{8,12} temperature,^{8,9,13} and humidity of the surrounding gas.^{14–16} The stability of the doped polymers is increased by cross-linking of the polymers.^{17,18} However, the mechanism of the dedoping processes is still ambiguous. It is not clear why the grafting of side alkyl chains causes the instability of the doped states.

Several authors explained that the instability is caused by interactions due to steric hindrance of the long flexible side chains.^{8,14,15,18} The interactions cause the polymer backbone to take on a less planar conformation at elevated temperatures thereby increasing its oxidation potential. Such an increase may reverse the oxidation process and may regenerate the original neutral polymer. Since the oxidation potential at room temperature is low enough to be doped with the dopant, this mechanism suggests that redoping should occur upon cooling to room temperature after the dedoping at elevated temperatures. However, as far as we know, the redoping has not been reported.

Loponen et al. proposed other mechanisms of the dedoping.⁹ They proposed two mechanisms based on the observation of releases of HCl from FeCl₃-doped PATs and HI from I₂-doped PATs during the dedoping. One is that the charge transfer is reversed, producing a neutral polymer and a neutral radical. The radical captures a hydrogen from the polymer creating a defect

and HCl or HI. The other mechanism is that a proton is released from the polymer. The proton reacts with the dopant ion producing HCl or HI. These mechanisms suggest the dedoping results in the formation of polymer radicals. However, they have not tried to detect the radicals, and have not explained the difference in the stability of PT and PATs.

Wu et al. proposed a mechanism for the dedoping. They explained that the dedoping proceeds through reduction by water.¹² The reduction by water is probable, since the rate of dedoping is increased by exposure to water vapor.^{14–16} However, the dedoping occurs even under dry nitrogen^{9,19} or in the vacuum.¹⁸ Other mechanisms should be considered in these cases. In addition, water is a reducing agent even for PT.^{19,20} We cannot explain the difference in the stability of PT and PATs by this mechanism alone.

In this paper, we examine the dedoping process of iodine-doped poly(3-octylthiophene) (P3OT). We compare the electric conductivity, the spectra of photoabsorption, and electron spin resonance (ESR) of the polymer during the dedoping. The purposes of the present paper are to obtain insight into the mechanism of the dedoping of PATs and to clarify why doped PATs are unstable.

Experimental Section

Poly(3-octylthiophene) (P3OT), which has a 98.5% head-to-tail regiospecific structure, was obtained from Aldrich. Iodine obtained from Kanto Chemicals was used as a dopant. Films of P3OT were prepared by spin coating from a solution of tetrahydrofuran on quartz plates. The thickness of the films was approximately 100 nm. The polymer films were dried overnight at 80 °C under vacuum. Photoabsorption measurements of the films were performed with a Shimadzu UV-3101PC spectrophotometer in an ambient atmosphere after exposure of the films to the dopant. Au electrodes were evaporated on the films for electrical conductivity measurements. The distance between the electrodes was 5 mm. The films were put in a vacuum chamber and electrical conductivity was measured by a two-probe method in an atmosphere of dopant or under vacuum. Powder of P3OT was used for ESR measurements. The sample was sealed in high-quality quartz tubes under vacuum after exposure to iodine vapor or sealed with the dopant. ESR measurements were performed with an X-band ESR spectrometer (JEOL JES-

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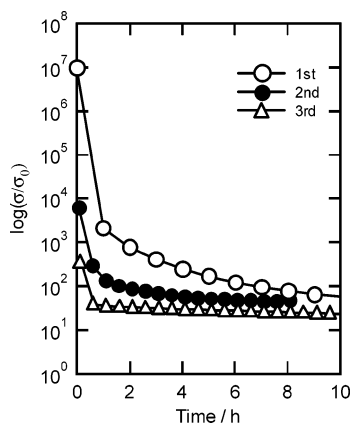


Figure 1. Temporal change in the conductivity of doped poly(3-octylthiophene). The sample was doped in an atmosphere of iodine vapor for an hour, and kept under vacuum. The doping was repeated three times at 1-day intervals: first (○), second (●), and third (△). σ_0 and σ are conductivities before and after the doping, respectively.

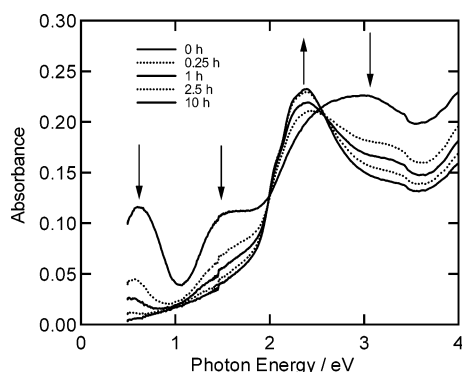


Figure 2. Temporal change in the photoabsorption spectra of doped poly(3-octylthiophene). The sample was doped in an atmosphere of iodine vapor for an hour and kept in an ambient atmosphere.

TE200) at ambient temperature. The amount of spin concentration was determined by double integration of ESR spectra with TEMPO as a reference. The concentrations of iodine atom in the doped polymers were determined by fluorescent X-ray analysis with a JEOL JSX-3220Z element analyzer.

Results and Discussion

Dedoping of Poly(3-octylthiophene). Figure 1 shows a temporal change in electric conductivity of a P3OT film. The film was exposed to iodine vapor for an hour, and placed in the vacuum. The conductivity decreased more than four orders during 10 h after the first doping. The doping was repeated three times at 1-day intervals. The repeated doping deteriorated the electronic property of the polymer film. This result indicates that the dedoping process is not simply the reverse of the doping.

The temporal change in the electric conductivity was accompanied by a change in photoabsorption spectra of the film. Figure 2 shows the temporal change in photoabsorption spectra of an iodine-doped P3OT film. The spectra were measured after exposure to iodine vapor for an hour and placed in an ambient atmosphere. The two peaks at about 0.7 and 1.5 eV just after the doping are due to the cation of P3OT.^{21,22} The peaks decreased with time, whereas a peak at 2.3 eV increased. The cation is hence the charge carrier in the film, and the species corresponding to the peak at 2.3 eV are the immobile ones.

Formation of Paramagnetic Species during the Dedoping. Undoped P3OT powder contains paramagnetic species. A singlet ESR spectrum with the peaks-to-peak line width of 0.3 mT was

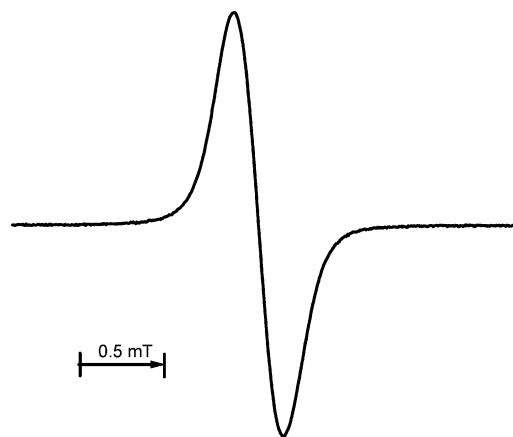


Figure 3. ESR spectrum of undoped poly(3-octylthiophene).

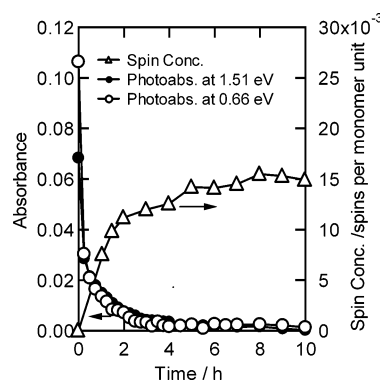


Figure 4. Comparison of temporal changes in the spin concentration (△) and the absorbances (1.51 (●), 0.66 eV (○)) of doped poly(3-octylthiophene). The samples were doped in an atmosphere of iodine vapor for an hour, and kept under vacuum for the ESR measurement and in an ambient atmosphere for the measurement of photoabsorption.

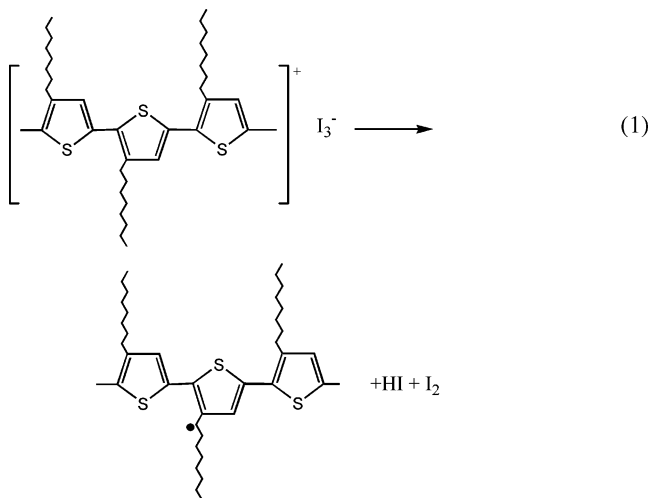
observed as shown in Figure 3. The powder was exposed to iodine vapor for an hour and then the sample tube was evacuated. The shape of the ESR spectrum was almost unchanged during the exposure and after the evacuation. The spin concentration was constant during the iodine doping, whereas it increased after the evacuation. Figure 4 compares the increment in the spin concentration and the absorbances of the cation during the dedoping. The decrease in the concentration of the cation accompanied the increase in the spin concentration. The cation is hence a spinless species, which can be assigned as a bipolaron²¹ or a pair of two polarons in a polymer chain,^{22–24} and becomes a paramagnetic species during the dedoping.

The increment in the spin concentration during the dedoping is about 0.02 spins per monomer unit. On the other hand, the concentration of iodine atom was constant during the period at 0.054 atoms per monomer unit. The concentration ratio between the paramagnetic species and the iodine atom is hence about 1:3. If the iodine dopant is present as the I_3^- ion,²⁵ the initial concentration of the cation is nearly the same as that of the increment in the spin concentration. Most of the cation was converted to the paramagnetic species.

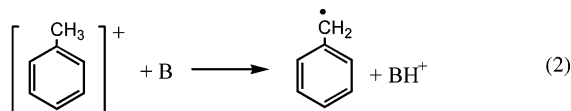
Mechanism of Dedoping of Poly(3-alkylthiophenes). The photoabsorption spectrum of the paramagnetic species resembles the one for the undoped P3OT. It indicates that the paramagnetic species is a neutral radical. The singlet ESR spectrum can be assigned as a polyenyl radical. The delocalization of the electron associated with a long chain of conjugated unsaturation is

expected to produce a singlet ESR spectrum.^{26,27} The cation of P3OT is hence converted to a polyenyl radical during the dedoping.

The polyenyl radical will be generated through the following deprotonation reaction from the cation of P3OT:

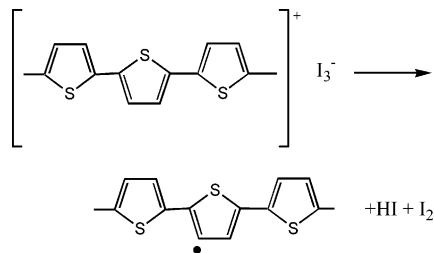


The deprotonation from the carbon atom in the alkyl chain nearest to the thienyl ring causes the formation of the polyenyl radical. The unpaired electron is delocalized over the conjugated double bonds of the thienyl rings and the radical will be very stable. Cation radicals of alkylaromatics may undergo proton transfer from α -carbon and become neutral radicals:^{28–30}



where B is a proton acceptor. Similar reactions will occur for the cation radical of P3OT. Lopenen et al. observed the HI release from iodine-doped PATs.⁹ This observation also supports the above mechanism.

The deprotonation from PT causes the formation of a vinyl-type radical:



This radical is a σ -radical, whose unpaired electron occupies an sp^2 hybrid orbital.^{31,32} It is less stable than the polyenyl radical, and hence the deprotonation from PT is difficult. This

difference will cause the difference in the stabilities of doped PT and PATs.

Conclusions

The dedoping of PATs proceeds through the deprotonation from the cation of the polymers. The doped PATs are easily dedoped because the dedoping causes the formation of a stable polyenyl radical. On the other hand, the dedoping of PT is difficult because the deprotonation of the doped PT causes the formation of an unstable vinyl-type radical.

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