Stability of a Conductive State of Poly(3-alkoxythiophene)s

Kouji Hatakeyama, Hitoshi Koizumi,* and Tsuneki Ichikawa

Division of Materials Chemistry, Graduate School of Engineering, Hokkaido University, Kita-ku, Sapporo 060-8628

Received July 8, 2008; E-mail: koizumih@eng.hokudai.ac.jp

Stability of a conductive state of iodine-doped poly(3-octyloxythiophene) (P3OOT) was compared with that of poly(3-octylthiophene) (P3OT). Temporal decay in the electric conductivity of P3OOT after the doping was much slower than that of P3OT. The cation of P3OOT was stable and an increase in the spin concentration was not observed. The results support the mechanism of dedoping of poly(3-alkylthiophene)s proposed by the authors [*J. Phys. Chem. B* **2005**, *109*, 15288]: the dedoping proceeds through deprotonation of the cation, which results in the formation of a stable polyenyl radical. The deprotonation of the cation of P3OOT occurs with difficulty since deprotonation gives an unstable radical. The conductive state of P3OOT is hence stable.

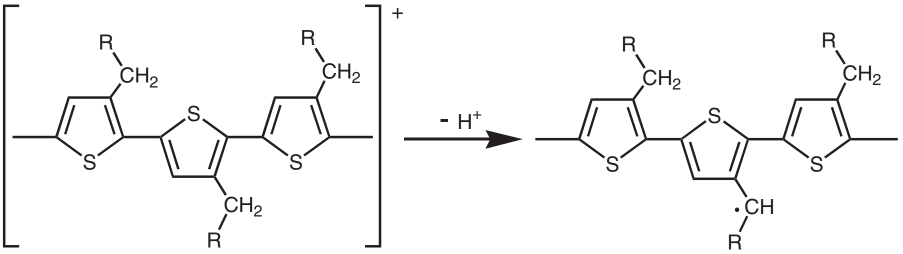
Conducting polymers have received considerable attention since they have the potential for many applications, such as organic transistors, light-emitting diodes, solar cells, sensors, actuators, batteries, and magnetic shielding materials.[1–3] Polythiophene (PT) and its derivatives are one of the most investigated conducting polymers for their environmental and thermal stability.[1] PT itself is an intractable solid since it is insoluble in solvents and infusible. Poly(3-alkylthiophene)s (P3AT) with side chains longer than butyl are soluble in some solvents[4] and fusible,[5] however their doped state are unstable. The conductivity of doped P3AT decays with time. This thermal dedoping is a serious problem for the applications of P3AT.

Many studies on the dedoping of P3AT have been carried out since mid-1980. The rate of dedoping depends on the dopants,[6–10] side chain length of P3ATs,[10,11] temperature,[9,10,12] and humidity of the surrounding gas.[12–14] However, the mechanism of the dedoping had not been clear. We have proposed a mechanism in a previous paper:[15] the dedoping proceeds through the deprotonation of the cation (polaron) of P3AT. The deprotonation from a carbon atom of alkyl chains nearest to a thienyl ring causes the formation of a polyenyl radical (Scheme 1). Since polyenyl radicals are relatively stable, the deprotonation will easily occur. The dedoping thereby takes place.

If our mechanism is correct, derivatives of polythiophene with side chains that have no hydrogen at atoms adjacent to the thienyl rings will not undergo dedoping. Poly(3-alkoxythiophene)s (P3AOT) are such polymers, which are reported to be soluble conducting polymers with a stable doped state.[16–18] Koeckelbergths et al. supposed that the stability of the doped state can be ascribed to the difference in oxidation potentials of P3AOT and P3AT.[17] However, the explanation seems to be doubtful since the doped state of regio-random P3AOT with a comparable oxidation potential to P3AT is also stable. Our mechanism of the dedoping of P3AT can explain the stability of a conductive state of P3AOT: since the deprotonation of the cation of P3AOT does not give a stable state, the dedoping does not occur. In this paper, we examine the stability of doped-poly(3-octyloxythiophene) (P3OOT) to confirm our mechanism of the dedoping of P3AT. Iodine was mainly used as a dopant. The conductive state of iodine-doped P3AT is one of the least-stable ones.[7] Differences between P3AT and P3AOT will be observed in a shorter time by doping.

Experimental

3-Octyloxythiophene was synthesized from 3-methoxythiophene and octanol with sodium hydrogensulfate ($NaHSO_4$) as a catalyst.[17] P3OOT was obtained by polymerization of the monomer with the GRIM (Grignard metathesis) method.[19] The monomer was dibrominated with *N*-bromosuccinimide (NBS) to afford 2,5-dibromo-3-octyloxythiophene, which was subsequently transformed into the Grignard derivative with methylmagnesium bromide and polymerized with a Kumada coupling reaction, catalyzed by 1,3-bis(diphenylphosphino)propane]nickel(II) dichloride [$NiCl_2$(dppp), dppp = 1,3-bis(diphenylphosphino)propane]. The weight-averaged molecular weight (M_w) and the



Scheme 1.

Published on the web February 13, 2009; doi:10.1246/bcsj.82.202

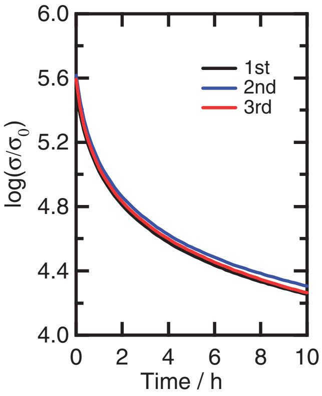


Figure 1. Temporal change in the conductivity of doped poly(3-octyloxythiophene). The sample was doped in an atmosphere of iodine vapor for 1 h, and kept under vacuum. The doping was repeated three times at one-day intervals: 1st (—), 2nd (—), and 3rd (—). σ_0 and σ are conductivities before and after the doping, respectively.

polydispersity (M_w/M_n) of the polymer determined by GPC against polystyrene standards were 9900 and 1.72, respectively.

Poly(3-octylthiophene) (P3OT) was purchased from Aldrich. This polymer has a 98.5% head-to-tail regiospecific structure. The values of M_w and M_w/M_n were 99000 and 2.01, respectively.

Iodine and nitrosonium tetrafluoroborate ($NOBF_4$) were purchased from Kanto Kagaku and Aldrich, respectively. They were used as received.

Films of P3OOT and 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 after exposure to iodine vapor and electrical conductivity was measured by two-probe method under vacuum.

Powder of P3OOT and P3OT was used for ESR measurements. The samples were sealed in high quality quartz tubes under vacuum after exposure to iodine vapor or after dipping the polymer powder into 0.1 M solution of $NOBF_4$ in acetonitrile.[7,20] ESR measurements were performed with an X-band ESR spectrometer (JEOL JES-TE200) at ambient temperature. The amount of the spin concentration was determined by double integration of ESR spectra using TEMPO as a reference. The microwave frequency was measured with a microwave counter (Advantest TR5212). Perylene cation in concentrated sulfuric acid was used as a standard for the determination of g factors.

Results and Discussion

Temporal change in electric conductivity of P3OOT is shown in Figure 1. The films were exposed to iodine vapor at ambient temperature for 1 h, and placed under vacuum. The conductivity of P3OOT decreased by one order over 10 h after the first doping. The conductivity of P3OT decreased by more than 4 orders over 10 h after the iodine doping.[15] The decrement of P3OOT is much less than that of P3OT. The doping was repeated three times at 1-day intervals. The conductivity of P3OOT recovered to the initial value by the 2nd and 3rd dopings. It is completely different from P3OT. The conductivity of P3OT does not recover by re-doping.[15] The repeated doping deteriorated the electronic properties of the P3OT film. In contrast, the temporal decay and re-doping of P3OOT is a reversible process.

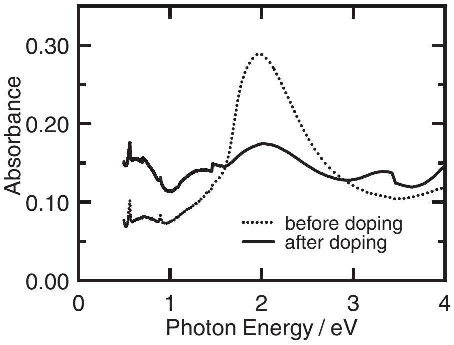


Figure 2. Photoabsorption spectra of poly(3-octyloxythiophene) before (· · ·) and after (—) doping. The sample film was doped in an atmosphere of iodine vapor for 1 h, and measured in an ambient atmosphere.

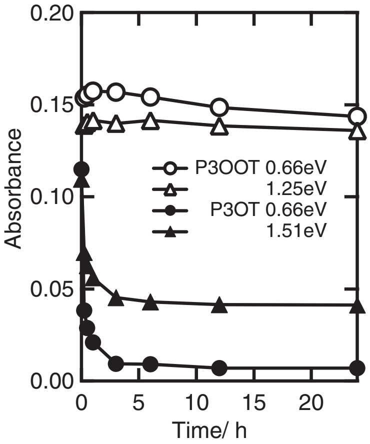


Figure 3. Temporal changes in the absorbances of doped poly(3-octyloxythiophene) (0.66 eV (○) and 1.25 eV (△)) and poly(3-octylthiophene) (0.66 eV (●) and 1.51 eV (▲)). The samples were doped in an atmosphere of iodine vapor for 1 h, and kept in an ambient atmosphere.

Photoabsorption spectra of a P3OOT film before and after doping are shown in Figure 2. The film was exposed to iodine vapor for 1 h and measured in an ambient atmosphere. The two peaks at about 0.7 and 1.3 eV after the doping are assigned to the cation (polaron) of P3OOT. The photoabsorption peaks of the cation of P3OT are at 0.7 and 1.5 eV.[15,21,22] Temporal changes in the absorbance of the cation of P3OOT and P3OT after the iodine doping are shown in Figure 3. The concentration of the cation of P3OOT was nearly constant, whereas that of P3OT rapidly decreased.[15] The cations are hence mobile charge carriers. The cation of P3OOT is more stable than that of P3OT.

The ESR spectrum of P3OOT after iodine doping is shown in Figure 4. The powder of P3OOT was exposed to iodine vapor for an hour and evacuated for 30 min. The spin concentration increased about three times during the doping.

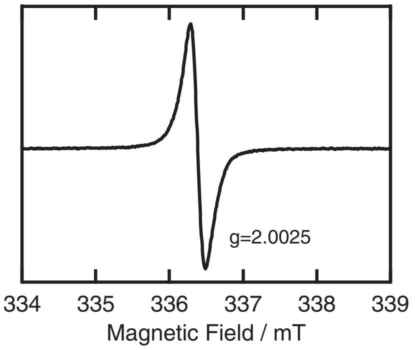


Figure 4. ESR spectrum of doped poly(3-octyloxythiophene). The sample was exposed to iodine vapor for 1 h, and evacuated for 30 min.

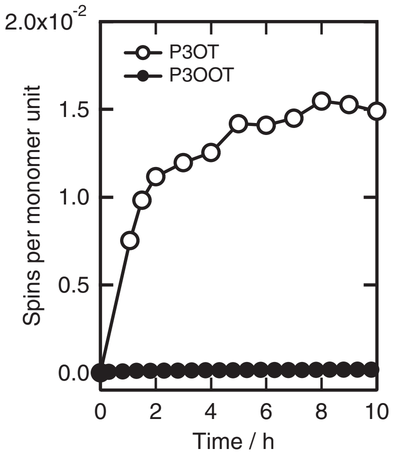


Figure 5. Temporal changes in the spin concentrations of doped poly(3-octyloxythiophene) (●) and poly(3-octylthiophene) (○). The samples were doped in an atmosphere of iodine vapor for 1 h, evacuated for 30 min, and sealed in quartz tubes.

The value of the *g* factor is 2.0025. The ESR spectrum of P3OT after the doping was also a singlet one with a *g* factor of 2.0019. The increments in the spin concentrations of P3OOT and P3OT after the doping are compared in Figure 5. The increase in the spin concentration of P3OOT is very small, which is less than 2×10^{-4} spins per monomer unit, whereas that of P3OT increased about 0.015 spins per monomer unit during 10 h.[15] Paramagnetic species are little generated in P3OOT, whereas a significant amount of radicals are generated in P3OT after the doping.

Similar difference in behaviors of spin concentrations of P3OOT and P3OT was also observed by $NOBF_4$ doping as shown in Figure 6. The spin concentration of P3OOT was nearly constant after the doping, whereas that of P3OT much increased. The increment over 10 h for $NOBF_4$-doped P3OT is 1/20 of that for iodine-doped P3OT. This difference will be ascribed to the stability of the doped states. Decay of $NOBF_4$-doped P3OT is slower than that of iodine-doped P3OT.[7] The spin concentration in Figure 5 is nearly saturated, while that in Figure 6 keeps increasing and is unsaturated.

The above results support our mechanism of dedoping of P3AT:[15] spinless pairs of polarons or bipolarons of P3AT cause deprotonation, and result in the formation of stable polyenyl radicals. The cation of P3OOT has no protons whose elimination gives a stable polyenyl radical. The deprotonation of the cation may result in the formation of unstable radicals (Scheme 2). The deprotonation and the formation of these radicals occur with difficulty. The doped state of P3OOT is hence stable.

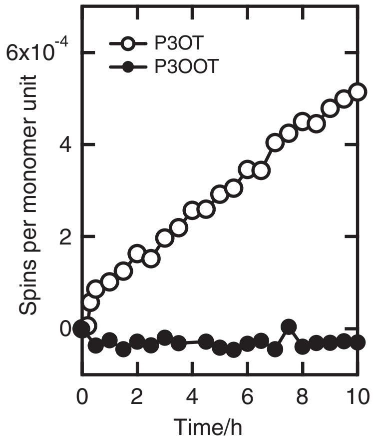
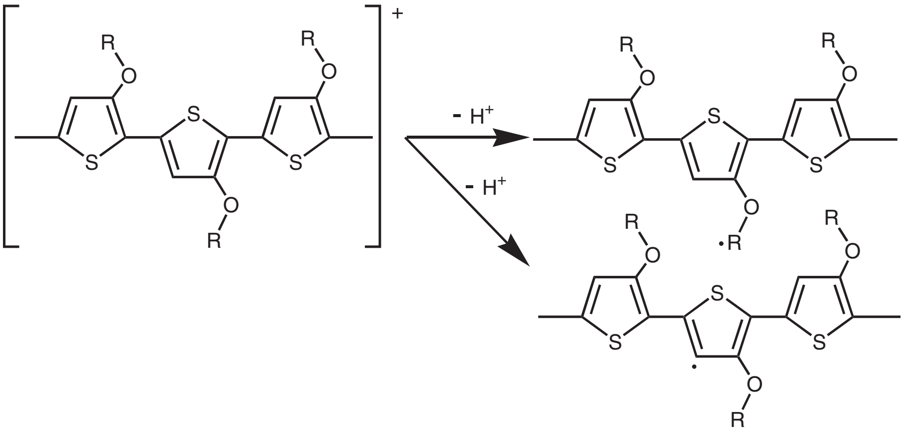


Figure 6. Temporal changes in the spin concentrations of doped poly(3-octyloxythiophene) (●) and poly(3-octylthiophene) (○). The samples were dipped in 0.1 M solution of $NOBF_4$ in acetonitrile for 0.5 h, evacuated for 30 min, and sealed in quartz tubes.

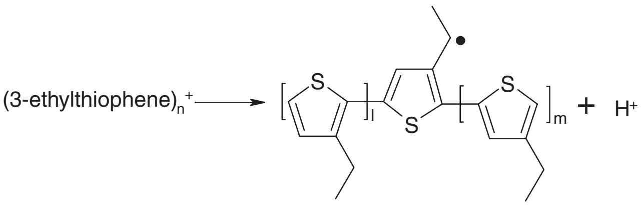
Alkoxy groups are electron-donating groups. They may stabilize the oxidized state. However, the difference in the stability of P3AT and P3AOT is not caused by this property. Regio-random P3AOT whose oxidation potential is comparable to that of P3OT also has a stable conductive state.[17,18] The oxygen atom of an alkoxy group reduces the binding energy of C–H bonds adjacent to the oxygen. The binding energy of $H–CH_2OCH_3$ is 389 kJ mol^{-1},[23] while the energy of $H–CH_2CH_3$ is 423.0 kJ mol^{-1}.[24] A conjugated double bond reduces the binding energy of C–H bonds more: the binding energy of $H–CH_2CH=CH_2$ is 364.8 kJ mol^{-1}.[23] The large reduction of the binding energy due to a conjugated double bond will promote the deprotonation reaction of P3AT.

The stability of a doped state of P3AT increases with increasing the radius of dopants. The order of doping stablity is $(CF_3SO_2)_2N^- \geq AuCl_4^- > CF_3SO_3^- > FeCl_4^- > BF_4^- \approx PF_6^- > I_3^-$.[7] This dependence might be caused by mobility of the dopants in P3AT. With increasing radius of dopants, it becomes difficult to change the orientation of the dopants to a conformation preferable for the proton transfer from polymer side chains to a counter ion.

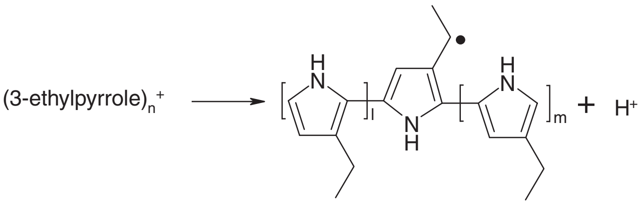
The doped state of poly(3-alkylpyrrole) (P3APy) is more stable than that of P3AT.[25] This difference is caused by the of heats of the deprotonation reactions. We have made preliminary molecular orbital calculations of the heats of deprotonation of model compounds (Schemes 3 and 4) by PM3 in the Hyper Chem. 6.03 program. The heats of the deprotonation reactions (absorbed energy) of 3-ethylthiophene oligomers are 841.9 ($n = 5$, $l = m = 2$), 821.8 ($n = 6$, $l = 2$, $m = 3$), and 822.2 ($n = 7$, $l = m = 3$) kJ mol^{-1}, while those of 3-ethylpyrrole oligomers are 939.7 ($n = 5$, $l = m = 2$), 939.2 ($n = 6$, $l = 2$, $m = 3$), and



Scheme 2.



Scheme 3.



Scheme 4.

944.3 ($n = 7$, $l = m = 3$) kJ mol^{-1}. The heats of the deprotonation reactions of the model compounds of P3AT are 97–122 kJ mol^{-1} lower than those of P3APy. The doped state of P3AT is less stable than that of P3APy because the deprotonation of P3AT is energetically more favorable than that of P3APy.

The deprotonation mechanism of dedoping of P3AT suggests that polythiophene derivatives with side chains whose atom nearest to the thienyl ring has no hydrogens, such as poly(3-phenylthiophene)s and poly(3-(1,1-dimethylalkyl)thiophene)s will also have a stable conductive state. Investigations of these polymers are in progress. It will be reported shortly.

Conclusion

Poly(3-alkoxythiophene)s have a stable conductive state because the deprotonation of their cation occurs with difficulty. Grafting of side chains whose atom nearest to the thienyl ring has no hydrogens will give soluble polythiophene derivatives with a stable conductive state.

This work was supported by THE SUHARA MEMORIAL FOUNDATION.

References

1 D. Fichou, *Handbook of Oligo- and Polythiophenes*, Wiley-VCH, Weinheim, **1999**.

2 T. A. Skotheim, J. R. Reynolds, *Conjugated Polymers: Processing and Applications*, CRC Press, Boca Raton, **2007**.

3 T. A. Skotheim, J. R. Reynolds, *Conjugated Polymers: Theory, Synthesis, Properties, and Characterization*, CRC Press, Boca Raton, **2007**.

4 R. L. Elsenbaumer, K. Y. Jen, R. Oboodi, *Synth. Met.* **1986**, *15*, 169.

5 K. Yoshino, S. Nakajima, M. Onoda, R. Sugimoto, *Synth. Met.* **1989**, *28*, 349.

6 M. Ahlskog, *Synth. Met.* **1995**, *72*, 197.

7 J.-L. Ciprelli, C. Clarisse, D. Delabouglise, *Synth. Met.* **1995**, *74*, 217.

8 K.-Y. Jen, G. G. Miller, R. L. Elsenbaumer, *J. Chem. Soc., Chem. Commun.* **1986**, 1346.

9 M. T. Loponen, T. Taka, J. Laakso, K. Väkiparta, K. Suuronen, P. Valkeinen, J.-E. Österholm, *Synth. Met.* **1991**, *41*, 479.

10 Y. Wang, M. F. Rubner, *Synth. Met.* **1990**, *39*, 153.

11 W. Chun-Guey, C. Mei-Jui, L. Yii-Chung, *J. Mater. Chem.* **1998**, *8*, 2657.

12 G. Gustafsson, O. Inganäs, J. O. Nilsson, *Synth. Met.* **1989**, *28*, 427.

13 Q. Pei, O. Inganäs, G. Gustafsson, M. Granström, *Synth. Met.* **1993**, *55–57*, 1221.

14 L. Szabo, G. Čík, J. Sitek, M. Seberíni, *Synth. Met.* **1997**, *88*, 79.

15 H. Koizumi, H. Dougauchi, T. Ichikawa, *J. Phys. Chem. B* **2005**, *109*, 15288.

16 G. Daoust, M. Leclerc, *Macromolecules* **1991**, *24*, 455.

17 G. Koeckelberghs, M. Vangheluwe, C. Samyn, A. Persoons, T. Verbiest, *Macromolecules* **2005**, *38*, 5554.

18 F. Tanaka, T. Kawai, S. Kojima, K. Yoshino, *Synth. Met.* **1999**, *102*, 1358.

19 R. S. Loewe, S. M. Khersonsky, R. D. McCullough, *Adv. Mater.* **1999**, *11*, 250.

20 S. Otsuka, H. Fukumoto, T. Yamamoto, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 536.

21 Y. Furukawa, *J. Phys. Chem.* **1996**, *100*, 15644.

22 A. J. Heeger, S. Kivelson, J. R. Schrieffer, W.-P. Su, *Rev. Mod. Phys.* **1988**, *60*, 781.

23 D. F. McMillen, D. M. Golden, *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

24 J. Berkowitz, G. B. Ellison, D. Gutman, *J. Phys. Chem.* **1994**, *98*, 2744.

25 H. Masuda, K. Kaeriyama, *J. Mater. Sci.* **1991**, *26*, 5637.