

Doping Effects of Water-Soluble Poly(3-thiopheneacetic acid) (P3TAA) and its Gel

Byoung-Suhk Kim*

Department of Chemical Engineering, Sogang University, Seoul 121-742, Korea

Li Chen, Jian Ping Gong, and Yoshihito Osada

Division of Biological Sciences, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

Received February 9, 2000

Abstract : The doping behaviors of water-soluble poly(3-thiopheneacetic acid) (P3TAA) and its gel using I_2 and concentrated $HClO_4$ aqueous solutions were investigated by UV-Visible absorption spectrometer. Electrical conductivity of the doped polythiophene gel was also studied. I_2 -doping of water-soluble P3TAA gave rise to a new broad polaron peak at around 749 nm, which corresponds to localization of electron. It was found that doping ability of P3TAA gel was strikingly dependent on the concentration of $HClO_4$ solution.

Introduction

For most of the history of polymer technology one of the most valued properties of synthetic polymers has been their ability to act as excellent electrical insulators, both at high voltage and at high frequency. Recently, there has been interest for many years in the possibility of producing electrically conducting polymers. The attractions of polymers to the electrical/electronics industries include the ease and low cost of their preparation and fabrication, as compared to semiconductors and metals, especially in films and fibres, and their mechanical properties, particularly flexibility and impact resistance.¹

The growth in the intensive study of highly conducting polymers began in 1977 with the discovery of the change in the electrical conductivity of polyacetylene on doping with B_{12} , I_2 and AsF_5 .² Electrical conductivities of all these polymers can be increased through appropriate chemical or electrochemical oxidation (so called p-type doping) and sometimes through reduction (so called n-type doping). Among the many poly(heterocyclic)s, polythiophene (PT) and its derivatives have aroused

great interest. A large number of investigations were later carried out to solve many questions, such as structure-properties relationships, increasing of stability and processability.

Doping of π -conjugated polymers using a certain dopant is a method to turn the low electrically conductive polymers to semiconductive or conductive materials. Most of the I_2 -doping for conductive polymers has been performed in vapor or solution state. On the other hand, the study of electronic process in aqueous solution has been highly limited. That is, electron mobility has been observed in various simple liquids such as hydrocarbon and rare gas liquids, but their electronic band mechanism has not been clarified. In particular, the electron conduction in polymer aqueous solution has not been studied. In this paper, doping behaviors of water-soluble polythiophene and its gel using I_2 and concentrated $HClO_4$ solution as dopants in water were investigated by measuring the UV-Visible absorption spectra. Electrical conductivity of doped polythiophene gel was also studied.

Experimental

Materials. 3-Thiopheneacetic acid (3TAA) (Tokyo

*e-mail : kbsuhk@family.sogang.ac.kr

Kasei) and anhydrous FeCl_3 (Wako Pure) were all used as received. Adipoyl dihydrazide (ADH) (Wako Pure) as a cross-linking agent and N,N' -dicyclohexylcarbodiimide (DCC) (Tokyo Kasei) as a condensation agent were used as received. Perchloric acid solution (HClO_4 , 60 wt%) (Junsei) and I_2 (Junsei) as the dopants were used as received. Dimethylsulfoxide (DMSO) (Wako Pure) was dried over CaH_2 for 24 hr under N_2 and distilled under vacuum before use.

Preparation of Water-Soluble P3TAA and its Gel. The poly(3-thiopheneacetic acid) (P3TAA) was synthesized by chemical oxidative coupling in dry CHCl_3 using anhydrous FeCl_3 as a catalyst and a series of P3TAA gel with different cross-linking densities were prepared by condensation reaction of a 10 wt% solution of P3TAA polymer in the presence of a prescribed amount of ADH and DCC in DMSO at 25 °C for 2 days according to the method previously reported, respectively.^{3,5} The chemical structure of P3TAA is shown in Figure 1.

Characterizations. The structure of polymer was investigated by FT-IR (Japan Spectroscopic Co., MFT-2000) and $^1\text{H-NMR}$ (JEOL JNM-400, 400 MHz). The weight-average molecular weight (M_w) was estimated by gel-permeation chromatography with standard polystyrene as a reference using THF as an eluent at 40 °C.³

UV-Visible absorption spectra were obtained with a Hitachi UV-Visible spectrophotometer (Model U-3000) at various conditions. P3TAA aqueous solution was prepared with the buffer solution (pH = 7.0; using a phosphate buffer solution) containing 0.2 M KI and placed in an argon atmosphere before doping. Doping was carried out by mixing P3TAA solution with I_2 solution at 25 °C. Doping content was controlled by varying the amount of dopant. The concentration of polymer solution was 10^{-4} M. The measurement of absorption spectra was made using gel membranes (about 2 μm thick), being prepared by spincoater, with the degree of cross-linkage (DCL) of 5, 7, 10 mol%, respectively.⁴

Electrical conductivity of polythiophene gel was

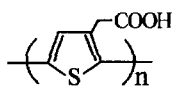


Figure 1. Chemical structure of P3TAA.

measured by ac two-terminal method using an LCZ meter at 20 °C. The frequency range was from 50 Hz to 100 kHz and the applied voltage was 1 V. Polythiophene gel was cut into 5×5×2 mm rectangular shape and was sandwiched between a pair of parallel-plate electrodes.^{6,7}

Results and Discussion

Doping of P3TAA in Water. Figure 2 shows UV-Visible absorption spectra of neutral (B) and doped (C) states of P3TAA solution. The absorption spectrum of polymer solution in its neutral (insulating) state shows a maximum absorption peak at about 440 nm, corresponding to a characteristic peak of conjugated polymer. In its oxidized (conducting) state a very broad spectrum appears at around 749 nm, which is contributed to polaron after doping and corresponding to localization of electron.¹² This change in the visible range of absorption spectrum corresponds to a change of the color of polymer solution from yellow (neutral state) to black (oxidized state).

Since I_2 -doped P3TAA solution is unstable in air, all of measurements were performed in argon atmosphere. In addition, when absorption intensity at 749 nm indicating the doped state was plotted by the amount of I_2 , absorption intensity increased dramatically at a concentration as low as 0.5×10^{-3} wt%, and almost became constant at 1.0×10^{-3} wt% (Figure 3). It suggests that I_2 -doping of P3TAA

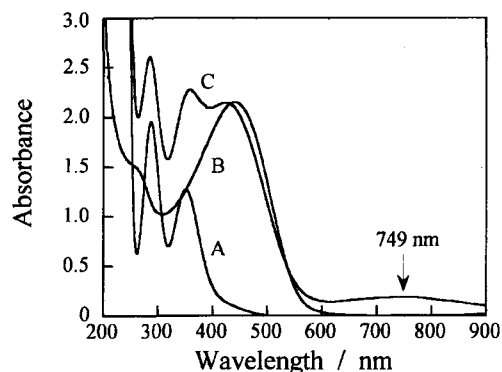


Figure 2. UV-Visible absorption spectra of (A) 2×10^{-3} wt% I_2 solution in the presence of 0.2 M KI, (B) 5×10^{-4} M P3TAA solution (pH=7.0; using a phosphate buffer solution), and (C) I_2 -doped P3TAA solution at 25 °C.

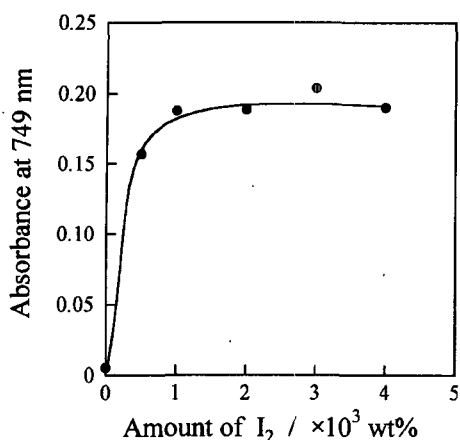


Figure 3. Dependence of absorption intensity of doped P3TAA solution at 25 °C on the concentration of I₂ as a dopant.

aqueous solution depends on the amount of dopant. The other doping experiments on polymer powders were also performed using the oxidant HClO₄ solution (60 wt%) or H₂SO₄ solution (98 wt%). We have found that doping ability was striking depending on the concentration of the HClO₄, H₂SO₄ solutions. Electrical properties of doped polymers should be further studied.

Electrical Properties of P3TAA Gel. Doping of P3TAA gel was carried out by immersing the gel membrane in various concentrations of HClO₄ solution under an argon atmosphere. When a water-swollen P3TAA gel was immersed in 60% HClO₄

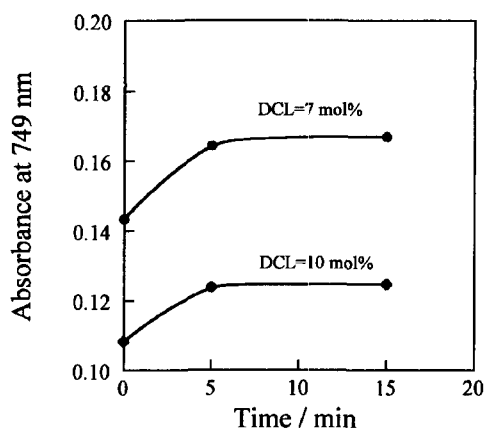


Figure 4. Time dependence of absorption intensity at 749 nm of HClO₄-doped P3TAA gel at 25 °C. ● : DCL = 7 mol%, ◆ : DCL = 10 mol%.

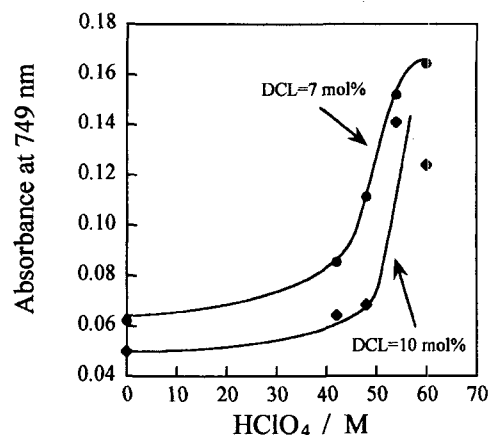


Figure 5. Dependence of absorption intensity at 749 nm of doped P3TAA gel at 25 °C on the HClO₄ concentration. ● : DCL = 7 mol%, ◆ : DCL = 10 mol%.

solution, the gel turned black (oxidized state) color. After 1 hour, absorption spectra was measured and a broad peak at around 749 nm, which is also contributed to polaron after doping and corresponding to localization of electron, was observed in addition to the maximum of absorption wavelength at around 405 nm. Figure 4 shows the change of absorption intensity at 749 nm with the time. It can be seen that absorption intensity increases with increase of time and reaches a constant value after only 5 min. The concentration dependence of HClO₄ solution on absorption intensity at 749 nm of doped gel was investigated and the result was shown in Figure 5. As shown in Figure 5, it was found that oxidation rate and maximum doping level depended strongly on the concentration of HClO₄ solution used as a dopant. Doping increases remarkably when HClO₄ concentration is higher than 40 wt%. It is also seen that the higher the DCL, the less the doping level.

Electrical conductivities of P3TAA gels doped with 60 wt% HClO₄ solution were also measured in order to investigate these doping effects further. For example, undoped wet and dry gels showed the electrical conductivities of 7×10^{-4} S cm⁻¹ and 7×10^{-8} Scm⁻¹, while the electrical conductivities of wet and dry gels doped with HClO₄ solution are found to be 2×10^2 Scm⁻¹ and 1×10^3 Scm⁻¹, respectively. Though the electrical conductivity of doped P3TAA gels is lower than that of electrochemically

doped poly(3-alkylthiophene),^{13,14} the obtained results clearly demonstrate that the increase in the conductivity of doped P3TAA gel, both in the dry and wet state, which means the successful doping of water-soluble P3TAA gel.

References

- (1) N. C. Billingham and P. D. Calvert, *Adv. Polym. Sci.*, **90**, 1 (1989).
- (2) C. K. Chiang, C. R. jr. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, and A. G. MacDiarmid, *Phys. Rev. Lett.*, **39**, 1098 (1977).
- (3) B. S. Kim, L. Chen, J. P. Gong, and Y. Osada, *Macromolecules*, **32**, 3974 (1999).
- (4) B. S. Kim and Y. Osada, *Korea Polymer J.*, **7**(6), 350 (1999).
- (5) L. Chen, B. S. Kim, J. P. Gong, and Y. Osada, *Macromolecules*, **33**, 1232 (2000).
- (6) J. P. Gong, N. Komatsu, T. Nitta, and Y. Osada *J. Phys. Chem.B*, **101**, 740 (1997).
- (7) T. Mitsumata, J. P. Gong, K. Ikeda, and Y. Osada *J. Phys. Chem.B*, **102**, 5246 (1998).
- (8) W. P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. Lett.*, **42**, 1698 (1979).
- (9) S. Kivelson, *Phys. Rev. Lett.*, **46**, 1344 (1981).
- (10) J. C. Scott, P. Pfluger, M. T. Krounbi, and G. B Street, *Phys. Rev. B*, **28**, 2140 (1983).
- (11) Y. H. Kim, S. Hotta, and A. J. Heeger, *Phys. Rev. B*, **36**, 7486 (1987).
- (12) Y. Cao, P. Smith, and A. J. Heeger, *Synth. Met.*, **32**, 263 (1989).
- (13) M. Leclerc, F. M. Diaz, and G. Wegner, *Makromol. Chem.*, 190, 3105 (1989).
- (14) H. Mao, B. Xu, and S. Holdcroft, *Macromolecules*, **26**, 1163 (1993).