CHEMISTRY LETTERS, pp. 927-930, 1989.

Electrochemical Polymerization of N-Trimethylsilylpyrrole and Characterization of the Resulting Conducting Polymer

Mitsutoshi OKANO,* Atsuko TODA, and Kunio MOCHIDA
Department of Chemistry, Gakushuin University,
1-5-1 Mejiro, Toshima-ku, Tokyo 171

A new conducting polymer was synthesized by electrochemical polymerization of N-trimethylsilylpyrrole. The polymer had good film producibility. The as grown film, which was in the doped state, showed conductivity of 5×10^{1} S cm^{-1}. The film showed three colors depending on the doping level, blue in the doped state, yellow in the undoped state, and reddish color in between.

Organic conducting polymers are important materials for secondary batteries[1] and electrochromic display devices.[2] The authors had attempted to obtain a new polymer which has new and/or better properties by means of modifying polypyrrole structure because polypyrrole is one of the few polymers which have good stability and film producibility. Though syntheses of poly(N-alkylpyrrole)s and poly(p-substituted N-phenylpyrrole)s have been reported, their properties were mostly similar to those of polypyrrole.[3,4] In this paper, the authors report synthesis of poly(N-trimethylsilylpyrrole) and its characteristics. Introduction of silicon into the polymer structure may cause change in the polymer properties because it is well known that introduction of silicon into a molecular structure often causes drastic changes in the properties of the molecule. It is said that the empty d orbital of silicon often play an important role there.

N-Trimethylsilylpyrrole (See Fig. 1) was synthesized by the reaction of pyrrole and hexamethyldisilazane according to the method of Fessenden et al.[5] The reaction product was identified by IR, NMR, and mass spectroscopy. IR spectrum of the compound was identical with that in the literature. Electrochemical study was performed in a three electrode system using an acetonitrile solution of 0.1 mol dm^{-3} N-trimethylsilylpyrrole ($Py\text{-}SiMe_3$) and 0.1 mol dm^{-3} tetrabutylammonium perchrolate (TBAP) as the electrolyte solution. A platinum wire or a tin dioxide transparent electrode was used for the working electrode. The reference electrode and the counter electrode were a silver wire and a platinum wire, respectively. Conductivity of the resultant polymer film was measured by the four point probe method.

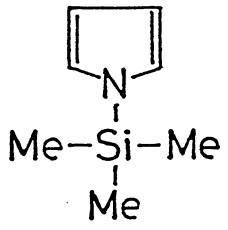

Fig. 1. Structure of the N-trimethylsilylpyrrole.

$Py\text{-}SiMe_3$ was not stable in acetonitrile which contained about 1% of water. It was concluded by the study using gas chromatography that $Py\text{-}SiMe_3$ decomposed into pyrrole and hexamethyldisiloxane as

the result of its reaction with water in the solution. However, Py-$SiMe_3$ was proved to be stable in acetonitrile which was dried with CaH_2. Therefore, thus prepared acetonitrile was used in further experiments. TBAP was dried in vacuum over P_2O_5.

Current-potential relationship for the oxidation of Py-$SiMe_3$ is shown in Fig. 2. The electrolyte solution contained 0.1 mol dm^{-3} of Py-$SiMe_3$ and 0.1 mol dm^{-3} of TBAP in acetonitrile. Anodic current was observed in the potentials more positive than +1.05 V vs. Ag, which is 200 mV positive than that for the oxidation of pyrrole. Therefore, it is clear in the experiment that what was oxidized on the electrode was Py-$SiMe_3$ itself but not pyrrole, which may be produced in the solution by the decomposition of Py-$SiMe_3$. The 200 mV positive shift is large compared with the reported value of 20 mV for N-n-butylpyrrole.[3] Probably, the bulkiness of trimethylsilyl group is a reason for the large shift. Continuous oxidation at +1.10 V vs. Ag gave a polymer film on the electrode. Water in the electrolyte solution must be carefully excluded because hydrolysis product pyrrole is oxidized at potentials more positive than +0.85 V vs. Ag, which is less positive value than that for Py-$SiMe_3$. The oxidation and polymerization of pyrrole is preferred when both pyrrole and Py-$SiMe_3$ are present in the solution.

As seen in Fig. 3, the resulting poly(Py-$SiMe_3$) showed the oxidation-reduction current response. The anodic peak potential was +1.05 V vs. Ag and the cathodic peak potential was +0.70 V vs. Ag, while those for polypyrrole were +1.14 and +0.05 V vs. Ag in the same conditions. These large shifts of more than 600 mV denys polypyrrole to be the resultant polymer, but they indicate the polymer to be poly(Py-$SiMe_3$). The oxidation-reduction current slightly decreased upon repeated cycling but the peak potentials did not show any significant shift to the negative direction. Therefore, the trimethylsilyl group on the polypyrrole structure must be stable under the experimental conditions. The poly(Py-$SiMe_3$) also showed change in color while the oxidation-reduction process of the polymer. Therefore, it was concluded that poly(Py-$SiMe_3$) undergoes the doping-undoping

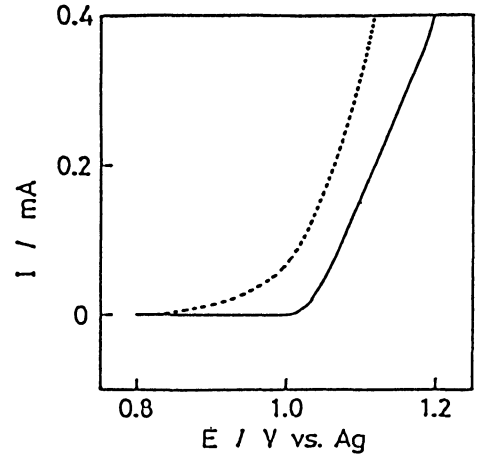

Fig. 2. Current-potential relationship for oxidation of pyrrole (dotted line) and that for oxidation of Py-$SiMe_3$ (solid line).

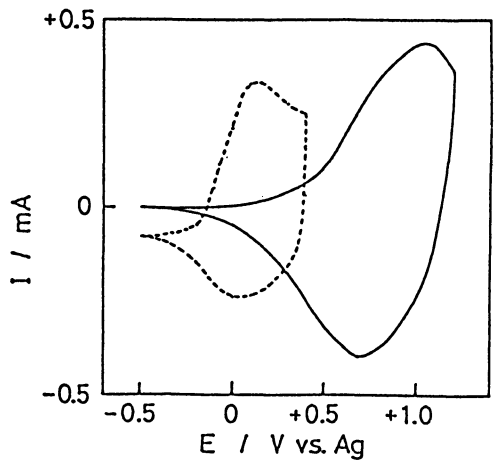

Fig. 3. Cyclic voltammogram for polypyrrole (dotted line) and that for poly(Py-$SiMe_3$) (solid line).

process. This fact was confirmed by the result of conductivity measurement which is described below. The polymer was blue in the doped state, yellow in the undoped state, and reddish color in between. The reddish color has never reported for polypyrrole and poly(N-alkylpyrrole)s.

Chemical polymerization of Py-$SiMe_3$ was also seen in the following way. Py-$SiMe_3$ was added into an acetonitrile solution of $FeCl_3$. The resulting solution turned to reddish color which is a characteristic of the slightly doped poly(Py-$SiMe_3$). In case of pyrrole, the solution became dark blue.

Electron spectrum for Py-$SiMe_3$ was measured in acetonitrile. The absorption maximum was 232.5 nm, which was located at 23.7 nm longer wavelength compared with pyrrole. Considering the absorption maximum for pyrrole (209 nm) and that for thiophene (231 nm), together with that for polypyrrole (393 nm) and that for polythiophene (480 nm), the absorption maxima for poly(Py-$SiMe_3$) was expected to be 486 nm. However, it was not seen at 486 nm but at 350 nm as described below.

Potential dependence of the absorption spectrum for poly(Py-$SiMe_3$) is shown in Fig. 4. The spectra were measured as the film on the transparent tin dioxide electrode in the electrolyte solution under argon atmosphere. The film was blue at +0.7 V, reddish color at +0.2 V, and yellow at -0.2 V vs. Ag. Three absorption peaks around 800, 500, and 350 nm, respectively were observed. Compared with those for polypyrrole film, no new peaks were found. In case of polypyrrole, these three peaks shifted largely to the shorter wavelength as the doping level increases. A suitable explanation was given in literature.[6] However, in case of poly(Py-$SiMe_3$), the peaks around 800 nm and 350 nm did not shift significantly. The absorption around 500 nm did not decrease as lowering the doping level though that for polypyrrole largely decreased. Probably, this somewhat persisting absorption around 500 nm is the reason for the reddish color in the slightly doped poly(Py-$SiMe_3$). Exact reproduction of the absorption spectra at certain potentials in course of a potential cycling was failed because it takes a few hours waiting for the film to take the stable state at each potential. Decomposition, maybe caused by the reaction of the polymer with the remaining oxygen and water in the electrolyte solution, took place and such measurement was not possible. However, quick cycling of the electrode potential gave swift change in the color of the film and the three distinct color were seen repeatedly.

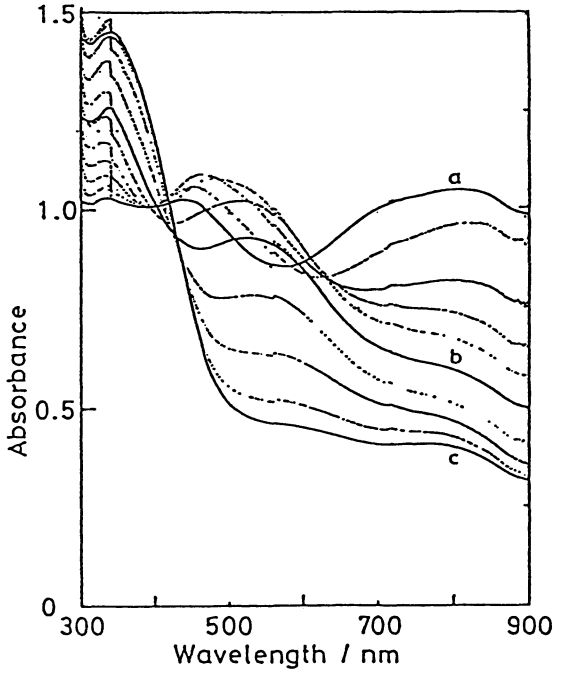

Fig. 4. Absorption spectra of poly(Py-$SiMe_3$) at 0.7 V vs. Ag (a), at 0.2 V vs. Ag (b), and at -0.2 V vs. Ag (c).

By means of constant current electrolysis using p-toluenesulfonic acid as the supporting electrolyte, flexible

free standing films were obtained. In order to measure the conductivity, polymer films were removed from the substrate tin-dioxide electrode. Conductivity was measured in air at room temperature. The value was 50 S cm^{-1} for the as grown doped film and 5 x 10^{-4} S cm^{-1} for the electrochemically undoped film. The conductivity was also measured in vacuum at various temperatures between -100 °C and +100 °C. Arrhenius plots for the electrical conductivity were made. As seen in Fig. 5, mainly two regions were observed in the figure. The activation energies were ca. 1 x 10^{-2} eV below -20 °C and ca. -3 x 10^{-2} eV above -20 °C. The plots must be carefully examined because of the problem in the sample polymer film as described below.

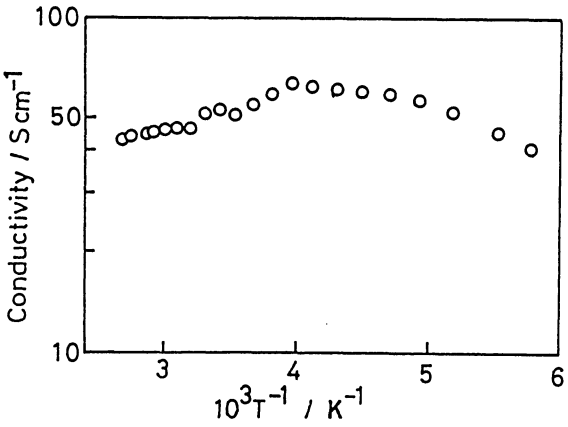

Fig. 5. Arrehenius plots for the electrical conductivities of poly-(Py-$SiMe_3$).

Silicon content in the electrochemically polymerized poly(Py-$SiMe_3$) was determined by X-ray photoelectron spectroscopy. The ratio of Si to N was ca. 1 to 3. The value is explained as follows. The poly(Py-$SiMe_3$) consisted of Py-$SiMe_3$ units only shortly after polymerization. The polymer, however, slowly reacted with moisture in air and a part of Py-$SiMe_3$ units changed to pyrrole and hexamethyldisiloxane. In order to measure X-ray photoelectron spectroscopy, the film was evacuated and the hexamethyldisiloxane was removed from the film. The authors believe that the analyzed polymer sample was constructed with pyrrole units and Py-$SiMe_3$ units.

The authors thank Mr. Toshiyuki Oosawa and Mr. Takatoshi Kimura of Ricoh Research Center for the kind help in the analyses of polymer films.

References

1) P. J. Nigrey, D. MacInnes, Jr., D. P. Nairns, A. G. MacDiarmid, and A. J. Heeger, J. Electrochem. Soc., 128, 1651(1981).
2) E. M. Genies, G. Bidan, and A. F. Diaz, J. Electroanal. Chem., 149, 101(1983).
3) A. F. Diaz, J. Castillo, K. K. Kanazawa, and J. A. Logan, J. Electrochem. Soc., 133, 233(1982).
4) A. Diaz, M. C. Rock, J. Electrochem. Soc., 131, 1802(1984).
5) R. Fessenden and D. F. Crowe, J. Org. Chem., 25, 598(1960).
6) J. L. Bredas and G. B. Street, Acc. Chem. Res., 18, 309(1985).

(Received January 31, 1989)