© 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 1716—1719 (1990) [Vol. 63, No. 6

Electrochemical Polymerization of *N*-Trimethylsilylpyrrole and Other Substituted Pyrroles Which Contain Si or Ge Atom(s) in Their Monomer Structures

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(Received January 20, 1990)

N-Trimethylsilylpyrrole and three new compounds; *N*-trimethylgermylpyrrole, *N*-chloromethyldimethylsilylpyrrole, and *N*-pentamethyldisilanylpyrrole, were synthesized. These four monomers were electrochemically polymerized and four new organic conducting polymers were obtained. Resulting polymers had good film producibility and conductivity as high as that for polypyrrole. They showed three distinguishable colors at different potentials: blue in the doped state, yellow in the undoped state, and reddish color in between.

Organic conducting polymers have been studied by many workers and application to polymer batteries,[1] electrochromic device,[2] electronic devices,[3] and etc.,[4] was widely investigated. On the other hand, many new organic conducting polymers were synthesized in order to obtain polymers with film producibility, stability in air,[5] and higher conductivity.[6] Though a lot of fruitful results were obtained from the pursuit of new polymers, polypyrrole is still the only one polymer which has both good film producibility and stability in air. (Lately, good poly-aniline films were obtained.[7]) These facts made the authors to synthesize substituted pyrroles and to look for better and/or new properties. While syntheses of many substituted polypyrroles were already reported in literature,[8–17] the authors intended to synthesize a quite different series of monomers; silicon or germanium containing monomers because it is well known that introduction of silicon and/or germanium atom(s) into a molecular structure often causes drastic change in the properties of the molecule. It is said that electropositivity and/or the empty d orbital of silicon and germanium play important roles there.

The authors reported the preliminary results for the electrochemical polymerization of *N*-trimethylsilylpyrrole and characteristics of the resulting polymer.[18] The polymer showed three colors at different electrode potentials, while polypyrrole shows two colors. Here, the authors report the results for *N*-trimethylsilylpyrrole and other substituted pyrroles which contain Si or Ge atom in their monomer structures and their polymers, in order to know if the above characteristics are common to the polymers of this kind.

Experimental

Synthesis of Monomers. *N*-Trimethylsilylpyrrole (Py-SiMe$_3$) was synthesized by the reaction of pyrrole and hexamethyldisilazane according to the method of Fessenden et al.[19] *N*-Trimethylgermylpyrrole (Py-GeMe$_3$), *N*-chloromethyldimethylsilylpyrrole (Py-SiMe$_2$CH$_2$Cl), and *N*-pentamethyldisilanylpyrrole (Py-Si$_2$Me$_5$) were synthesized by the reaction of chlorides with 1-potassiopyrrole (Scheme 1), where E stands for Si and Ge.

$$\text{1-potassiopyrrole} + \text{Cl-ER}_3 \dashrightarrow \text{Py-ER}_3 + \text{KCl}$$

Scheme 1.

The reaction products were distilled under reduced pressure under argon atmosphere and the isolated compounds were identified by IR, NMR, mass spectroscopy, and CHN analysis. Py-SiMe$_2$CH$_2$Cl was further purified by gas chromatography using a PEG column. It was concluded by the study using gas chromatography that each monomer decomposed upon reaction with water and gave pyrrole and siloxane (or germoxane).

Py-GeMe$_3$: bp 90.5 °C (44 mmHg; 1 mmHg≈133.322 Pa), n_D^{22}=1.4894, Anal. Calcd for C$_7$H$_{13}$NGe: C, 45.75; H, 7.13; N, 7.62%. Found: C, 45.40; H, 7.27; N, 7.38%. ^{1}H NMR (CDCl$_3$) δ=0.65 (s, 9H), 6.30 (d, d, 2H), 6.70 (d, d, 2H), MS (M$^+$) 185.

Py-SiMe$_2$CH$_2$Cl: bp 101 °C (30 mmHg), $n_D^{19.5}$=1.4897, Anal. Calcd for C$_7$H$_{12}$ClNSi: C, 48.40; H, 6.96; N, 8.06%. Found: C, 48.19; H, 7.07; N, 7.83%. ^{1}H NMR (CDCl$_3$) δ=0.60 (s, 6H), 3.00 (s, 2H), 6.43 (d, d, 2H), 6.92 (d, d, 2H) MS (M$^+$) 173.

Py-Si$_2$Me$_5$: bp 100 °C (30 mmHg), $n_D^{19.5}$=1.4582, Anal. Calcd for C$_9$H$_{19}$NSi$_2$: C, 54.75; H, 9.70; N, 7.09%. Found: C, 51.34; H, 10.20; N, 6.84%. ^{1}H NMR (CDCl$_3$) δ=0.11 (s, 9H), 0.88 (s, 6H), 6.31 (d, d, 2H), 6.72 (d, d, 2H) MS (M$^+$) 197.

Electrochemical Measurements. Measurements were carried out in a three-electrode system using platinum wires for the working and the counter electrodes and a silver wire for the reference electrode. In spectroelectrochemical measurements, tin dioxide transparent electrodes were used as the working electrodes, and the electrochemical cell, which had windows on both sides, was placed in the UV-Vis spectrometer. A typical electrolyte composition was 0.1 mol dm^{-3} substituted pyrrole, 0.1 mol dm^{-3} tetrabutylammonium perchlorate (TBAP) in CH$_3$CN. TBAP was dried in vacuum over P$_2$O$_5$ at about 80 °C. Acetonitrile was refluxed with CaH$_2$ for 6 hr, distilled, and stocked under Ar atmosphere. A potentiostat and a potential sweeper were used to control the potential of the working electrode against the reference electrode.

Results and Discussion

Oxidation Potentials. Onset potentials of monomer oxidation were measured in the presence of ferrocene in solutions containing 0.1 mol dm^{-3} substituted pyrrole and 0.1 mol dm^{-3} TBAP in acetonitrile. The addition of the small amount of ferrocene to the

Table 1. Onset Oxidation Potentials (Emonomer) for Monomers, and Anodic Peak Potentials (E_{pa}) and Cathodic Peak Potentials (E_{pc}) for the Resulting Polymers

X	Emonomer /V vs. Fc/Fc$^+$	E_{pa} /V vs. Fc/Fc$^+$	E_{pc} /V vs. Fc/Fc$^+$
H	$+0.47 \pm 0.01$	-0.42 ± 0.10	-0.55 ± 0.08
Me	$+0.50 \pm 0.01$	$+0.05 \pm 0.09$	-0.09 ± 0.01
$SiMe_3$	$+0.53 \pm 0.01$	-0.23 ± 0.05	-0.31 ± 0.01
$GeMe_3$	$+0.57 \pm 0.01$	-0.22 ± 0.02	-0.28 ± 0.04
$SiMe_2CH_2Cl$	$+0.60 \pm 0.01$	-0.31 ± 0.05	-0.45 ± 0.15
Si_2Me_5	$(+0.60)$	(-0.30)	(-0.40)

electrolyte solution did not cause any significant change in the voltammogram. Thus measured potentials are listed in Table 1. They are expressed in volts relative to the reversible peaks of ferrocene (Fc) and (Fc$^+$). All four Si and Ge containing monomers showed their oxidation potentials, which were more positive than that for unsubstituted pyrrole. These positive potential shifts indicate that those oxidized on the electrode were the substituted pyrroles but not unsubstituted pyrroles, which may be produced in the electrolyte solution by the reaction of the substituted pyrroles with trace amount of water. Addition of small amount of water into the electrolyte solution affected the onset potentials to move toward that of pyrrole. Good reproducibility of the oxidation potentials, however, shows that the measured potentials are those of pure substituted pyrroles but not the mixture of substituted and unsubstituted pyrroles.

It is known that effects of substituent groups on the oxidation potentials are caused by their polar, steric, and mesomeric effects.[20] This behavior can be described by the Hammett-Taft equation

$$E = \rho_\pi \sigma + S$$

where $\rho_\pi \sigma$ describes the polar-mesomeric parameters, and S accounts for the steric factor. Positive shift of 30 mV for *N*-methylpyrrole is attributable to the steric effect of the electrode reaction because the ionization potential of *N*-methylpyrrole, 7.95, is smaller than that for pyrrole, 8.21.[21] If the well known linear relationship between the ionization potentials and the oxidation potentials.[22] is considered, the oxidation potential of *N*-methylpyrrole should be more negative than that for pyrrole in the absence of the steric effect. The same goes for the Si and Ge containing pyrroles. The positive shifts are attributable to the steric effects because the trimethylsilyl and trimethylgermyl groups are usually known as weak electron donating groups.[23] Py-$SiMe_2CH_2Cl$ is an exception because it has an electron withdrawing group, -CH_2Cl in the substituting group and the electron donating/withdrawing characteristic of the whole -$SiMe_2CH_2Cl$ is unknown.

Continuous oxidation of the monomers gave polymer films on the electrodes. The continuous oxidation on a film indicates that the resulting polymer is conductive. Water in the electrolyte solution must be carefully excluded because hydrolysis product pyrrole is oxidized at potentials more positive than +0.47 V vs. Fc/Fc$^+$, which is less positive value than those for the Si and Ge substituted pyrroles. The oxidation and polymerization of pyrrole is preferred when both pyrrole and the substituted pyrrole are present in the solution.

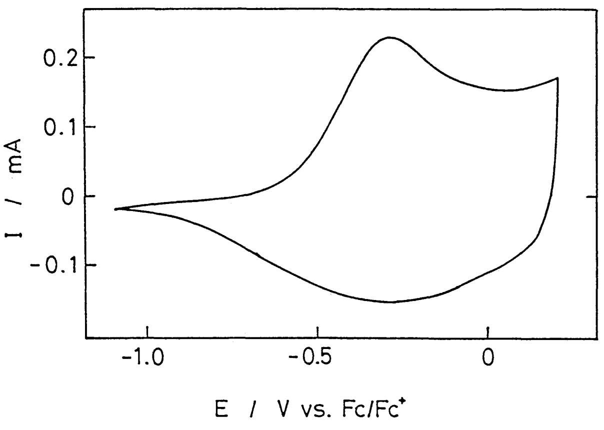

Fig. 1. Cyclic voltammogram for the poly(Py-$SiMe_3$) measured in the electrolyte solution for polymetrization directly after the polymerization.

Oxidation-Reduction Response of the Resulting Polymers. In Fig. 1, a cyclic voltammogram of the resulting poly(Py-$SiMe_3$) is shown. The anodic and cathodic currents were observed accompanying color changes of the polymer upon cycling of the electrode potential. Therefore, it is concluded that the doping and undoping reactions, which are incorporation and release of electrolyte anions, respectively, were taking place because the same kind of behavior is seen for polypyrrole and understood as such. This is further confirmed by the fact obtained from conductivity measurement of the film (shown below) that the oxidized film had higher conductivity and the reduced film had lower conductivity, which are typical characteristics of the doped and undoped polymers of this kind.

The oxidation peak potentials (E_{pa}) and the reduction peak potentials (E_{pc}) are listed in Table 1. Potentials were determined against Ag reference electrode and the potential of Ag reference electrode was determined against Fc/Fc$^+$. Potentials calculated from the above data are listed in Table 1, because reliable peaks for Fc/Fc$^+$ were not obtained during the oxidation-reduction cycles of the polymers and the direct determination of potentials for the polymers were not possible.

The oxidation and reduction currents slightly decreased upon repeated potential cycling but peak potentials did not show any significant shifts to the negative direction. Therefore, the substituent groups on the polypyrrole structure must be stable under the experimental conditions. The each Si or Ge containing polymer showed three distinct colors depending upon the doping level, blue in the oxidized state, yellow in the reduced state, and reddish color in between, while polypyrrole shows only two colors blue in the oxidized and yellow in the reduced states.

Chemical Polymerization. Chemical polymerization of the pyrroles were performed by adding the pyrrole into an acetonitrile solution of $FeCl_3$. The resulting solution turned to reddish color in case of the four substituted pyrroles but it turned to dark blue in case of pyrrole and *N*-methylpyrrole. The reddish color is the characteristic of the slightly doped substituted pyrroles.

Conductivity and Element Analysis. In order to measure conductivity of polymer films, free standing films were prepared by constant current electrolysis using *p*-toluenesulfonic acid as the supporting electrolyte. The polymer films were removed from the substrate tin dioxide electrodes and conductivity was measured in air at room temperature by the four point probe method. The values were ca. 5 to 50 $S\,cm^{-1}$ for the doped films and ca. 10^{-4} $S\,cm^{-1}$ for the reduced films. These values were similar to those for polypyrrole measured under the same conditions.

The conductivity of poly(Py-$SiMe_3$) was also measured in vacuum at various temperature between −100 and +100 °C. Arrhenius plots for the electrical conductivity were made. As seen in Fig. 2, mainly two regions were observed in the figure. Repeated cycling of temperature gave mostly the same figure. The activation energies were roughly 1×10^{-2} eV below −20 °C and -3×10^{-2} eV above −20 °C. The plots must be carefully examined because of the problem in the sample polymer film as pointed out in Ref. 18.

Potential Dependence of Absorption Spectra of the Polymers. As already described above, the four polymers showed three different colors depending on the electrode potential. Absorption spectra at various electrode potentials for poly(Py-$SiMe_2CH_2Cl$) are shown in Fig. 3 because the polymer showed the clearest reddish color among four. 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 +0.9 V, reddish color at +0.3 V, and yellow at −0.1 V vs. Ag. The small peak between 500 nm and 600 nm in spectrum c is not an additional peak, but it is attributable to the residual dopants, because the peak in spectrum b gradually shifted there as the electrode potential lowered. Three absorption peaks around 800, 500, and 350 nm, respectively were observed. Compared with those for polypyrrole film, no new peaks were found. Therefore, absorption peaks can be readily compared between the polymers. In the reduced state, polypyrrole has an absorption maximum at 392 nm. This absorption is believed to be the interband transition[24,25] For poly(Py-$SiMe_2CH_2Cl$), the corresponding peak was seen at 350 nm. Values for the other polymers are listed in Table 2. In case of polypyrrole, those three peaks between 300 nm and 950 nm shifted largely to the shorter wavelength as the

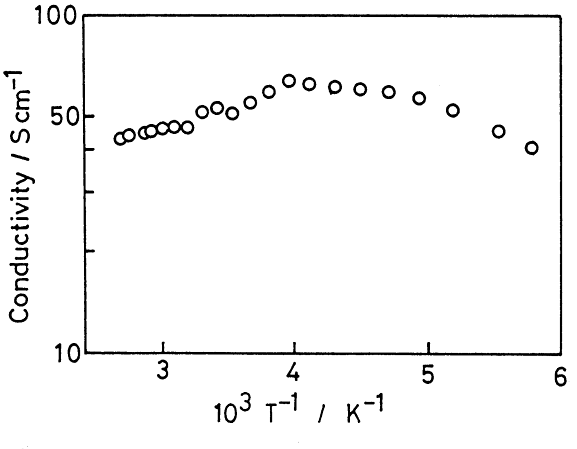

Fig. 2. Arrehenius plots for the electrical conductivities of poly(Py-$SiMe_3$) measured in vacuum.

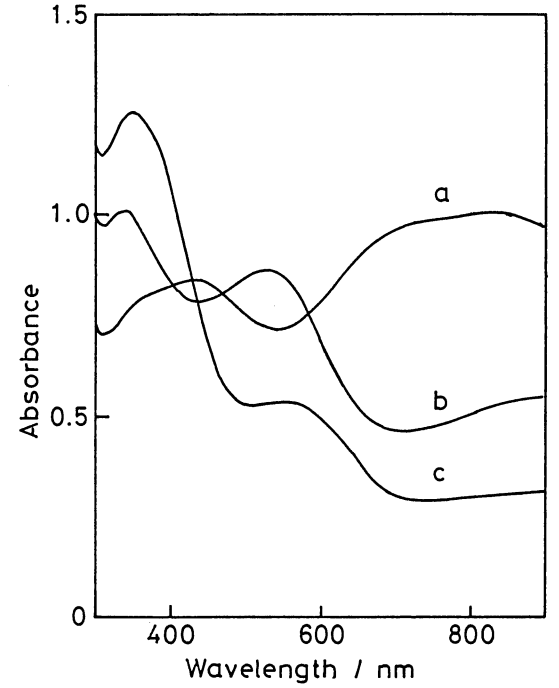

Fig. 3. Absorption spectra of poly(Py-$SiMe_2CH_2Cl$) at +0.9 V vs. Ag (a), at +0.3 V vs. Ag (b), and at −0.1 V vs. Ag (c).

Table 2. Absorption Maxima for the Monomers and Those for the Polymers

Monomer	Monomer max/nm	Polymer max/nm
Pyrrole	209	392
Thiophene	230	480
Py-$SiMe_3$	233	350
Py-$GeMe_3$	274	—
Py-$SiMe_2CH_2Cl$	220	350
Py-Me	216	340

doping level increased. A suitable explanation was given in literature.[24,25] However, in case of poly(Py-$SiMe_2CH_2Cl$), the peak at 350 nm did not shift significantly. The absorption around 500 nm persisted there as lowering the doping level, while that for polypyrrole swiftly decreased. Probably, this somewhat persisting absorption around 500 nm is the reason for the reddish color in the slightly doped state of poly(Py-$SiMe_2CH_2Cl$) and three other polymers. Cycling of the electrode potential gave swift change in the color of the film and the three distinct colors were seen repeatedly. However, after ca. 20 cycles, the color change gradually became less distinct. Probably, the polymer reacted with the residual water in the electrolyte solution.

Conclusion

It was found that the electrochromic characteristics, to show the three distinct colors, are the common characteristics of the polymers of this series. It was also shown that in the pursuit of multi-color electrochromic materials, new materials or new special techniques are not necessarily required, but modification of well known polymers can be enough.

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

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