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# Dual Dopable Poly(phenylacetylene) with Nitronyl Nitroxide Pendants for Reversible Ambipolar Charging and Discharging

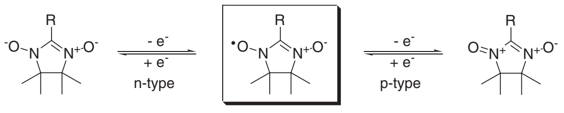
Kenichi Oyaizu, Takashi Sukegawa, and Hiroyuki Nishide*
*Department of Applied Chemistry, Waseda University, Tokyo 169-8555*

(Received November 22, 2010; CL-100977; E-mail: nishide@waseda.jp)

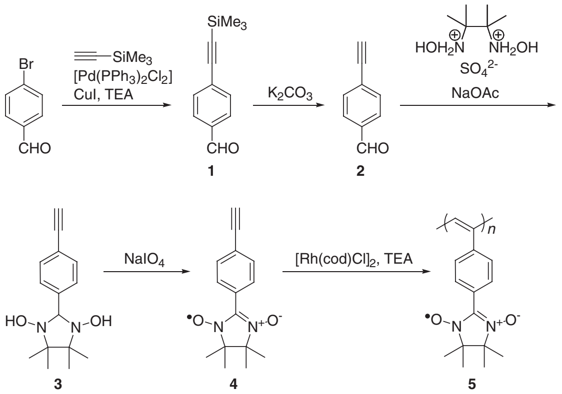
An electrode-attached layer of poly(phenylacetylene) bearing a pendant nitronyl nitroxide group per repeating unit, obtained by the Rh-catalyzed polymerization of 2-(4-ethynylphenyl)-4,4,5,5-tetramethylimidazoline-l-oxyl 3-oxide, underwent oxidation and reduction at 0.80 and −0.84 V vs. Ag/AgCl, respectively. The magnetically determined unpaired electron density of 92% was coulometrically reproduced, which supported the presumption that the radical survived during the course of the polymerization to allow both positive and negative charging of the pristine neutral polymer substantially per repeating unit. Galvanostatic Coulomb titration revealed the charge storage capability of the polymer, which demonstrated usefulness as organic electrode-active material with unprecedented ambipolar chargeability.

Recent progress in the chemistry of charge transport by nonconjugated polymers with ultimate density of redox sites[1] has demonstrated that these polymers are promising as electroactive materials for various electronic devices such as rechargeable batteries,[2] hybrid capacitors,[3] solar cells,[4] electrochromic cells,[5] sensors,[6] and memory devices.[7] We have focused on various aliphatic polymers bearing organic robust radicals as pendant groups per repeating unit. The so-called "radical polymers" are characterized by reversible charging/discharging behaviors at a typical mass specific capacity of 111 mA h g$^{-1}$ for 2,2,6,6-tetramethylpiperidin-*N*-oxyl (TEMPO)-substituted polymethacrylate (PTMA), with an excellent rate capability allowing full charging and discharging within a few seconds.[8] Such performance has led to the development of the "radical battery" as a new class of thin, flexible, light, and yet high-power storage device.[9]

The radical polymers have typically been examined as cathode-active materials, because many of them exhibit redox potentials near 0.8 V vs. Ag/AgCl[10] where the electrically neutral radicals undergo positive (i.e., p-type) charging into cations. Radical batteries with a configuration of (−)Li|electrolyte|PTMA(+) produce an emf of 3.6 V based on the gap between the redox potentials.[8] One could expect that the battery configuration would be much more simplified by employing a nitronyl nitroxide pendant which undergoes both p- and n-type (i.e., negative) charging reversibly (Scheme 1), because of its potential capability of playing a dual role as cathode- and anode-active material.[11] However, such challenges have been impeded by the difficulties in preparing vinyl polymers with pendant nitronyl nitroxide groups, which undergo side reactions with the propagating end. Similar difficulties have also been encountered in the polymerization of galvinoxyl-substituted styrene and appear to be inherent in radical monomers with n-type charging capability. Indeed, galvinoxyl-substituted polystyrene has only been prepared by the polymerization of hydrogalvinoxyl precursor, followed by a polymer-analogous reaction to generate the radical.[12] Development of a straightforward method to polymerize n-type radical monomers has been an important subject of research.[13]



**Scheme 1.** Reversible 1e$^-$ redox reaction of nitronyl nitroxides.



**Scheme 2.** Synthesis of **5**.

Iwamura et al. reported the synthesis of conjugated poly(phenylacetylene) carrying nitronyl nitroxide pendants by the Rh-catalyzed coordination polymerization of 2-(4-ethynylphenyl)-4,4,5,5-tetramethylimidazoline-l-oxyl 3-oxide, with a view to obtain a magnetic polymer.[14] However, the expected ferromagnetic coupling among the radical centers through the conjugated chain was not operative, due to the limited spin delocalization into the conformationally twisted skeleton. We anticipated that such structural features, regarded as negative for the spin coupling, should turn out to be positive for the blocking of the redox coupling.[15] Here we revisit the polymer, focusing on the unprecedented ambipolar chargeability, which is accomplished by the redox isolation of the radical pendants from the conjugated system.

Polymer **5** was synthesized according to a previous method,[14] with slight modifications as follows (Scheme 2). Sonogashira coupling of ethynyltrimethylsilane with 4-bromobenzaldehyde followed by desilylation and annulation with 2,3-bis(hydroxyamino)-2,3-dimethylbutane produced 2-(4-ethynylphenyl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (**3**), which was carefully oxidized with sodium periodate at 0 °C to give a deep blue crystalline **4** with an unpaired electron density of 100% based on a SQUID magnetization experiment. The monomer **4** in THF (0.3 M) was polymerized using 1% chloro(1,5-cyclooctadiene)rhodium(I) dimer as the catalyst and 25% triethylamine. After vigorous stirring at room temperature for 25 min, **5** was obtained as a deep bluish and powdery solid in a reasonable yield (78%), which was almost insoluble but swellable in electrolyte solutions.

While **4** gave a five-line ESR signal centered at $g = 2.0068$ (Figure 1a), a featureless spectrum was obtained for the soluble

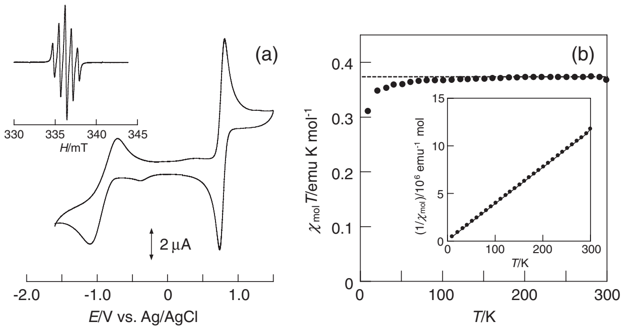


**Figure 1.** (a) ESR spectrum and cyclic voltammogram ($0.1\,V\,s^{-1}$) obtained for 1 mM $CH_2Cl_2$ and $CH_3CN$ solutions of **4**, respectively. The electrolyte was tetrabutylammonium perchlorate (0.1 M). (b) Plots of $\chi_{mol}T$ vs. $T$ and $1/\chi_{mol}$ vs. $T$ with Curie–Weiss fitting for **5** (19.6 mg) obtained by SQUID measurements, where $\chi_{mol}$ was based on mol of the radical. Dotted line represents the theoretical value of $\chi_{mol}T$ for $S = 1/2$.

part of **5** due to the spin-exchange interaction between the locally populated unpaired electrons. The unpaired electron density in **5** was determined from the $1/\chi_{mol}$ vs. $T$ plots (Figure 1b), based on the Curie–Weiss rule according to $1/\chi_{para} = T/C - \theta/C$ where $C$ is a Curie constant defined as $N_e g^2 \mu_B{}^2 S(S+1)/(3k_B)$. The slope of the $1/\chi_{mol}$ vs. $T$ plots gave an unpaired electron density of $N_e = 2.14 \times 10^{21}$ spin/g, which corresponded to 92% of the existing nitronyl nitroxide units in **5**. The paramagnetic ($S = 1/2$) nature of **5** at room temperature also allowed determination of the unpaired electron density by integrating the ESR signal using **4** as a standard, which agreed with that from the SQUID measurement and was comparable with that of the Iwamura polymer (95%).[12]

Cyclic voltammogram for **4** showed two reversible responses at 0.80 and −0.86 V vs. Ag/AgCl (Figure 1a), which were ascribed to the p- and n-type reactions, respectively (Scheme 1). The redox response remained intact after continuous potential cycling for more than 100 times, which demonstrated the robustness of the radical, the cation, and the anion. Similar ambipolar charging was observed for a carbon nanocomposite electrode of **5** prepared on a current collector (Figure 2). Galvanostatic coulometry revealed the plateau voltages for both p- and n-type charging, which agreed with their redox potentials. An intriguing aspect is the unprecedented ambipolar ultimate doping of the polymer with a capacity of $96\,mA\,h\,g^{-1}$. The charging capacity of 92% with respect to the redox site, obtained by the integration of the cyclic voltammogram, coincided with the unpaired electron density, which demonstrated that the radical survived during the Rh-catalyzed polymerization. It may be noted that the charging behavior of **5** is reminiscent of the p- and n-doping of polyacetylene.[16] However, the charging at the redox-isolated pendant nitronyl nitroxide was characterized by the higher reversibility and charge population than those for the doping of polyacetylene. Indeed, the conjugated polyene chain in **5** was not operative for the redox reaction or the electric conduction, which was indicated by the lack of these properties for poly(phenylacetylene)s with similar conformational constraints.

A capacity of ca. 30% with respect to the theoretical capacity obtained for the galvanostatic experiments (Figure 2) suggested some limitation of electroneutralization during charging. Tuning the swelling properties of the composite electrode to facilitate the diffusion of electrolyte counterion for charge compensation, while maintaining the redox cyclability, is the topics of our continuous research.

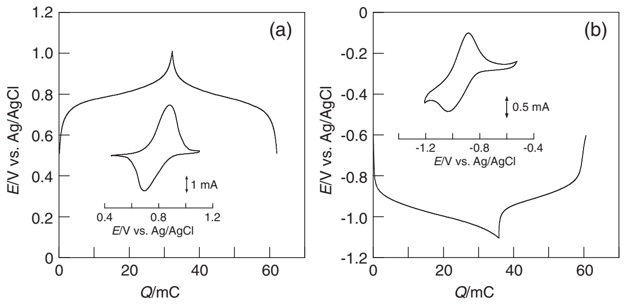


**Figure 2.** (a) Cyclic voltammograms ($5\,mV\,s^{-1}$) and charging/discharging curves for the p-type reaction of the carbon nanocomposite electrode of **5** (0.59 mg) with a composition of **5**/VGCF/PVdF (1/8/1 in w/w/w), where VGCF was a vapor-grown carbon fiber and PVdF was poly(vinylidene fluoride). The electrolyte conditions were as in Figure 1. (b) Repeat of (a) for the n-type reaction of **5** (0.32 mg) in the presence of tetrabutylammonium hydroxide (0.1 M).

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