Cathode- and Anode-Active Poly(nitroxylstyrene)s for Rechargeable Batteries: p- and n-Type Redox Switching via Substituent Effects

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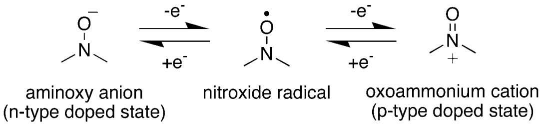
ABSTRACT: Three polystyrenes bearing redox-active nitroxide radical(s) in each repeating unit, poly[4-(*N*-*tert*-butyl-*N*-oxylamino)styrene] (**1**), poly[3,5-di(*N*-*tert*-butyl-*N*-oxylamino)styrene] (**2**), and poly[4-(*N*-*tert*-butyl-*N*-oxylamino)-3-trifluoromethylstyrene] (**3**), were synthesized via free radical polymerization of protected precursor styrenic derivatives and subsequent chemical oxidation. The radicals in these polymers were robust at ambient conditions, and the polymers possessed radical densities of 2.97×10^{21}, 4.27×10^{21}, and 1.82×10^{21} unpaired electrons/g for **1**−**3**, respectively, resulting in an electrode-active material with a high charge/discharge capacity. Particularly, the dinitroxide functional polymer **2** possessed the highest radical density. Cyclic voltammetry of the poly(nitroxylstyrene) **1** revealed a reversible redox at 0.74 V vs Ag/AgCl, which was assigned to the oxidation of the nitroxide radical to form the oxoammonium cation (p-type doped state). On the other hand, the poly(nitroxylstyrene) *ortho*-substituted with the electron-withdrawing trifluoromethyl group **3** showed a reversible redox at −0.76 V, ascribed to the n-type redox pair between the nitroxide radical and the aminoxy anion. Thus, the nitroxide radical polymer could be switched from p-type material suitable for a cathode to n-type material (anode-active) via altering the electron-withdrawing character of the substituents on the poly(nitroxylstyrene). This is the first report of an n-type radical polymer and the first report of using substituent effects to switch the redox behavior of the polymer. This versatile switching ability enables these polymers to function as components of metal-free electrodes in rechargeable batteries.

Introduction

Redox-active organic polymers have been widely used as antioxidants and photostabilizers for commodity plastics as well as oxidizing agents for organic synthesis due to their rapid and reversible oxidation and reduction processes.[1−9] Accompanied with the electron transfer in the redox processes, ionic mass transport also results in potential applications in sensors, actuators, and drug delivery systems.[10−15] Among the unique features of these polymers, charge storage within the redox-active organic polymer based on its reversible redox reaction is one of the most promising capabilities, leading to new electrode-active materials for application in rechargeable batteries.[8,9] Organic-based, electrode-active materials inherently possess several advantages: lightweight, tunable redox property, mechanical flexibility, and processing compatibility. Since the discovery of doped polyacetylene, intrinsically conducting polymers (polyacetylene, polyaniline, polypyrrole, and polythiophene) and redox-active compounds bearing disulfide derivatives have been proposed and investigated as potential alternatives to inorganic-based electrode-active materials.[16−19] However, these previously studied organic-based battery materials suffer from limitations in terms of the low degree of doping, slow electrochemical processes, and fluctuating voltage. Thus, there are almost no reports on organic-derived electrode-active materials in practical use.

Prompted by the remarkable development of portable electronic devices, high energy and power densities are required for rechargeable batteries such as the lithium ion battery.[20,21] While metal- or metal oxide-based materials such as $LiCoO_2$, $LiMnO_2$, and V_2O_5 are widely exploited as electrode-active materials, they are problematic due to the toxicity of heavy metals and the limitation of natural metal resources. Alternately, organic-derived electrode-active materials are environmentally benign and produced from readily available resources.

Scheme 1. Redox Couples of a Nitroxide Derivative



Recently, we have explored the use of organic radical species,[22−26] particularly pendent nitroxide functional radical polymers, as cathode-active, charge-storage materials for secondary Li ion batteries.[27−31] Earlier work on radical polymers in our laboratories focused on poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA).[24,25] This polymer contains 2,2,6,6-tetramethylpiperidinyl-*N*-oxy (TEMPO), which is chemically robust as well as rapidly, reversibly, and nearly stoichiometrically oxidized to the corresponding oxoammonium cation or p-type doped state via chemical or electrochemical oxidation (Scheme 1).[32,33] We have described the characteristics of organic radical polymer batteries composed of the nitroxide radical polymer cathode as follows:[27] (1) high charge/discharge capacity (ca. 100 mA h/g), ascribed to the stoichiometric redox of the nitroxide radical or the quantitative doping of the polymer, in contrast to the limited doping level of π-conjugated conducting polymers, (2) high charging and discharging rate performance resulting from the rapid electron-transfer processes of the nitroxide radical,[34] and (3) long cycle-life, often exceeding 1000 cycles, derived from the chemical stability of the nitroxide radical and from the amorphous electrode structure. On the basis of these characteristics, our radical polymer battery has attracted much attention as a high power density and environmental-benign secondary battery for a next-generation energy-storage device.

One of the current challenges for developing organic radical batteries is the enhancement of the charge capacity or energy

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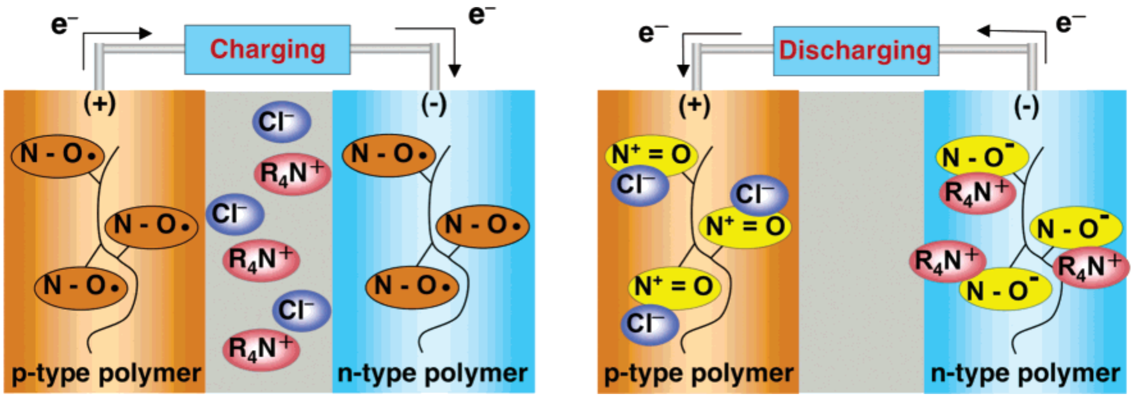


Figure 1. Schematic diagram of an all-organic-based radical battery.

density. For example, the theoretical charge capacity of PTMA as the cathode-active material is 111 mA h/g, which is about two-thirds of the charge capacity of metal oxide-based cathode materials (150−170 mAh/g) in conventional Li ion batteries.[20] To address this issue, we present, for the first time, poly[4-(*N*-*tert*-butyl-*N*-oxylamino)styrene] (**1**) and poly[3,5-di(*N*-*tert*-butyl-*N*-oxylamino)styrene] (**2**) as p-type cathode-active nitroxide radical polymers with a compact molecular structure and a low molecular weight per active nitroxide site which results in a high charge capacity. We have selected the polystyrene backbone as the carrier of the radical moiety due to the ease of modification to introduce the radical moiety on the phenyl ring. Furthermore, the poly(nitroxylstyrene)s possess selective solubility in common organic solvents such as THF and chloroform and remain insoluble in typical electrolytes containing propylene carbonate. In comparison to PTMA, the theoretical capacities of **1** and **2** are 141 and 194 mA h/g, respectively, which corresponds to a 26% and 74% enhancement over that of PTMA. Poly(nitroxylstyrene) **2** bearing two nitroxide groups on the monomer unit holds the highest capacity among the previously synthesized and proposed radical polymers.[27−29]

Another challenge for organic radical batteries is the development of an n-type redox polymer. An n-type radical polymer would serve as an anode-active material, promising an all-organic battery. Such an all-organic battery comprising both p-type and n-type polymers bearing nitroxide groups is illustrated in Figure 1. During the charging process, the p-type nitroxide radical polymer in the cathode is oxidized to the oxoammonium cation form and the n-type polymer in the anode is reduced to the aminoxy anion form. During the discharging process, the nitroxide radicals are regenerated through the reduction of the oxoammonium cation and via oxidation of the aminoxy anion in the cathode and anode, respectively. However, there has been no previous report on such an n-type radical polymer due to the chemical instability of the reduced, aminoxy anion form. In this paper, we focus on the dependence of the radical redox potentials on substituents electronic effects and envision the tunability of nitroxide radical polymers from p-type to n-type behavior. We report here, for the first time, the synthesis of an n-type nitroxide radical polymer **3**, which possesses an electron-withdrawing trifluoromethyl (CF_3) group.

Along with the aforementioned molecular design of electrode-active radical polymers, this paper describes the synthesis of three poly(nitroxylstyrene)s and the mechanism of p- and n-type redox activity of the polymers using their monomeric analogues **4**. Future directions in designing and constructing radical polymer-based batteries are also discussed.

Experimental Section

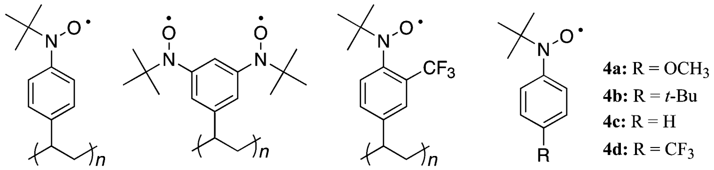
Materials. 4-(*N*-*tert*-Butyl-*N*-oxylamino)anisole (**4a**),[35,36] 4-(*N*-*tert*-butyl-*N*-oxylamino)-*tert*-butylbenzene (**4b**),[35,36] 4-(*N*-*tert*-butyl-*N*-oxylamino)benzene (**4c**),[35,36] 4-[*N*-*tert*-butyl-*N*-(*tert*-butyldimethylsilyloxy)amino]bromobenzene (**5**),[37,38] 3,5-bis[*N*-*tert*-butyl-*N*-(*tert*-butyldimethylsilyloxy)amino]bromobenzene (**8**),[39] and 5-bromo-2-iodobenzotrifluoride (**12**)[40] were prepared according to the literature.

4-[(*N*-*tert*-Butyl-*N*-*tert*-butyldimethylsilyloxy)amino]styrene (6). To a toluene solution (76 mL) of 4-[*N*-*tert*-butyl-*N*-(*tert*-butyldimethylsilyloxy)amino]bromobenzene (**5**) (5.0 g, 14.0 mmol) were added tetrakis(triphenylphosphine)palladium(0) (464 mg, 145 μmol), 2,6-di-*tert*-butyl-4-methylphenol (16 mg), and tri-*n*-butyl(vinyl)tin (5.4 g, 6.7 mmol), and the mixture was stirred at 100 °C for 15 h. The reaction mixture was extracted with ether, washed with water, and dried over anhydrous sodium sulfate. The crude product was purified by flash column chromatography with hexane as an eluent to afford a colorless oil (2.9 g, yield 68%). ^{1}H NMR ($CDCl_3$, 500 MHz; ppm): δ 7.27 (d, $J = 8.5$ Hz, 2H, Ph), 7.18 (d, $J = 7.6$ Hz, 2H, Ph), 6.68 (dd, $J = 18$, 11 Hz, 1H, vinyl), 5.68 (d, $J = 18$ Hz, 1H, vinyl), 5.17 (d, $J = 11$ Hz, 1H, vinyl), 1.09 (s, 9H, *N*-*t*-Bu), 0.90 (s, 9H, *t*-Bu), −0.13 (br, 6H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, 125 MHz; ppm): δ 150.9, 136.6, 133.9, 125.19, 125.12, 112.5, 61.0, 26.15, 26.13, 17.9, −4.7. Mass (FAB): *m*/*z* 305 [M$^+$], 305.5 (calcd). Anal. Calcd for $C_{18}H_{31}NOSi$: C, 70.8; H, 10.2; N, 4.6. Found: C, 70.8; H, 10.5; N, 4.6.

3,5-Di[(*N*-*tert*-butyl-*N*-*tert*-butyldimethlsilyloxy)amino]styrene (9). The styrenic monomer **9** was synthesized in the similar manner as **6**. Yield 75%. ^{1}H NMR ($CDCl_3$, 500 MHz; ppm): δ 7.11 (bs, 2H, Ph), 6.97 (bs, 1H, Ph), 6.65 (dd, $J = 18$, 11 Hz, 1H, vinyl), 5.66 (d, $J = 18$ Hz, 1H, vinyl), 5.17 (d, $J = 11$ Hz, 1H, vinyl) 1.08 (s, 18H, *N*-*t*-Bu), 0.90 (s, 18H, *t*-Bu), −0.10 (br, 12H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, 125 MHz; ppm): δ 150.5, 137.5, 135.6, 122.2, 119.8, 112.9, 61.1, 26.3, 26.2, 17.9, −4.5. Mass (FAB): *m*/*z* 506 [M$^+$], 506.9 (calcd). Anal. Calcd for $C_{28}H_{54}N_2O_2Si_2$: C, 66.3; H, 10.7; N, 5.5. Found: C, 66.2; H, 10.8; N, 5.4.

5-Bromo-2-[(*N*-*tert*-butyl-*N*-*tert*-butyldimethylsilyloxy)amino]-benzotrifluoride (13). A pentane solution (1.60 M, 43 mL) of *n*-butyllithium (69 mmol) was slowly added to 5-bromo-2-iodobenezotrifluoride **12** (22 g, 63 mmol) in 112 mL of ether at −78 °C. After being warmed at room temperature, 2-methyl-2-nitrosopropane (6.6 g, 76 mmol, 1.21 equiv) in 70 mL of ether was added at −78 °C and stirred for 12 h at room temperature. The solution was first washed with aqueous ammonium chloride and then with water. The ether layer was dried over anhydrous sodium sulfate. After evaporation, the crude product was protected with silyl group without purification. The crude product (20 g, 63 mmol), *tert*-butyldimethylsilyl chloride (24 g, 158 mmol, 2.5 equiv), and imidazole (11 g, 158 mmol, 2.5 equiv) were dissolved in 62 mL of DMF and stirred for 12 h at 60 °C. The reaction mixture was extracted with ether and then washed with water. The ether layer was dried over anhydrous sodium sulfate. After evaporation, the crude product was purified by column chromatography on silica

Chart 1



4a: R = OCH_3
4b: R = *t*-Bu
4c: R = H
4d: R = CF_3

	1	**2**	**3**
radical density (unpaired electron/g)	3.16×10^{21}	4.36×10^{21}	2.33×10^{21}
theoretical capacity (mAh/g)	141	194	103

gel (hexane) to afford a colorless oil (1.4 g, yield 5.2%). ^{1}H NMR ($CDCl_3$, 500 MHz; ppm): δ 7.68 (d, $J = 9.1$ Hz, 1H, Ph), 7.67 (s, 1H, Ph), 7.58 (d, $J = 8.9$ Hz, 1H, Ph), 1.09 (s, 9H, *N*-*t*-Bu), 0.89 (s, 9H, *t*-Bu), 0.20 (s, 3H, $SiCH_3$), −0.42 (s, 3H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, 125 MHz; ppm): δ 149.0, 134.3, 129.6 (q, 5 Hz), 129.55, 127.9 (q, 30 Hz), 123.1 (q, 274 Hz), 119.1, 62.3, 26.0, 25.7, 18.0, −5.1, −5.2. Mass (FAB): *m*/*z* 425 [(M − 1)$^+$], 427 [(M + 1)$^+$], 426.4 (calcd). Anal. Calcd for $C_{17}H_{27}BrF_3NOSi$: C, 47.9; H, 6.4; N, 3.3. Found: C, 48.3; H, 6.3; N, 3.1.

4-[(*N*-*tert*-Butyl-*N*-*tert*-butyldimethylsilyloxy)amino]-3-trifluoromethylstyrene (14). The styrene monomer **14** was synthesized in a similar manner as **6**. Yield 31%. ^{1}H NMR ($CDCl_3$, 600 MHz; ppm): δ 7.74 (d, $J = 9.1$ Hz, 1H, Ph), 7.53 (s, 1H, Ph), 7.52 (d, $J = 8.9$ Hz, 1H, Ph), 6.69 (dd, $J = 18$, 11 Hz, 1H, vinyl), 5.77 (d, $J = 18$ Hz, 1H, vinyl), 5.31 (d, $J = 11$ Hz, 1H, vinyl) 1.10 (s, 9H, *N*-*t*-Bu), 0.89 (s, 9H, *t*-Bu), 0.20 (s, 3H, $SiCH_3$), −0.43 (s, 3H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, 150 MHz; ppm): δ 149.4, 135.5, 129.8 (q, 5 Hz), 128.6, 128.1, 126.6 (q, 29 Hz), 124.8 (q, 5 Hz), 124.2 (q, 273 Hz), 115.2, 62.5, 26.2, 25.9, 18.2, −4.95, −4.98. Mass (FAB): *m*/*z* 373 [M$^+$], 373.5 (calcd). Anal. Calcd for $C_{19}H_{30}F_3NOSi$: C, 61.1; H, 8.1; N, 3.8. Found: C, 61.4; H, 8.3; N, 3.9.

Poly[4-{(*N*-*tert*-butyl-*N*-*tert*-butyldimethylsilyloxy)amino}-styrene] (7). To a benzene solution (1.0 mL) of the monomer **6** (1.1 g) was added azobis(isobutyronitrile) (AIBN, 2.8 mg), and the mixture was stirred for 15 h at 75 °C. The solution was poured into methanol, and the precipitate was purified by reprecipitation from THF to methanol to yield the corresponding polymer as a white powder. Yield 81%; $M_n = 21\,400$, $M_w/M_n = 1.58$. ^{1}H NMR ($CDCl_3$, 500 MHz; ppm): δ 6.84 (br, 2H, Ph), 6.26 (br, 2H, Ph), 1.78 (br, 1H, C*H*CH_2), 1.29 (br, 2H, CHC*H*$_2$), 1.02 (s, 9H, *N*-*t*-Bu), 0.88 (s, 9H, *t*-Bu), −0.14 (br, 6H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, 125 MHz; ppm): δ 148.2, 141.0, 126.4, 124.4, 60.5, 45.0, 39.7, 26.2 ($-C(CH_3)_3$, 2C), 17.9, −4.6. Anal. Calcd for $C_{18}H_{31}NOSi$: C, 70.8; H, 10.2; N, 4.6. Found: C, 70.7; H, 10.2; N, 4.5.

Poly[3,5-di{(*N*-*tert*-butyl-*N*-*tert*-butyldimethylsilyloxy)amino}-styrene] (10). Radical polymerization of **9** was carried out as well as that of **6**. Yield 35%; $M_n = 2100$, $M_w/M_n = 1.2$. Anionic polymerization of **9** was performed as follows: The monomer **9** (0.48 g) was degassed and dissolved in the freshly distilled THF (1.0 mL) under argon. A heptane solution (0.97 M, 48 μL) of dibutylmagnesium (48 μmol) was added to the solution and stirred for 0.5 h at room temperature. A cyclohexane solution (0.97 M, 100 μL) of *sec*-butyllithium (96 μmol) was added to the mixture at −78 °C, and the solution was stirred for 3 h. The color of reaction mixture turned reddish. The polymerization was terminated by adding methanol to the solution and poured into methanol. The polymer was purified by reprecipitation from THF into methanol to yield a white powder. Yield 47%; $M_n = 2500$, $M_w/M_n = 1.1$. ^{1}H NMR ($CDCl_3$, 500 MHz; ppm): δ 6.89 (br, 3H), 2.45−1.60 (br, 3H), 1.05, 0.90 (br, 36H), 0.10, −0.19 (br, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz; ppm): δ 149.7, 141.7, 127.0, 125.0, 60.9, 48.6−42.9, 40.2, 29.6, 26.5, 18.3, −4.35. Anal. Calcd for $C_{28}H_{54}N_2O_2Si_2$: C, 66.3; H, 10.7; N, 5.5. Found: C, 66.6; H, 10.4; N, 5.6.

Poly[3,5-di{(*N*-*tert*-butyl-*N*-*tert*-butyldimethylsilyloxy)amino}-styrene-*co*-acrylonitrile] (11). To a toluene solution (1.0 mL) of the monomer **9** (0.62 g), distilled acrylonitrile (80 μL) and AIBN (10 mg) were added and degassed for several times. The mixture was stirred for 3 h at 100 °C. The solution was poured into methanol, and the polymer was purified by reprecipitation from THF into methanol to yield the corresponding polymer as a white powder. Yield 76%; $M_n = 23\,600$, $M_w/M_n = 1.54$. ^{1}H NMR($CDCl_3$, 500 MHz, ppm): $\delta = 6.94$ (bs, 2H, Ph), 6.51 (bs, 1H, Ph), 2.56 (s, 0.3H, C*H*CN), 1.3 (b, 3H, C*H*$_2$C*H*), 1.02 (s, 18H, *N*-*t*-Bu), 0.87 (s, 18H, *t*-Bu), 0.05 (s, 6H, Si−CH_3), −0.33 (b, 6H, Si−CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): $\delta = 151.5$, 124.6, 121.8, 121.0, 61.5, 41.3, 26.6, 23.9, 18.3, 14.6, 0.41, −3.84. IR (cm^{-1}): 2957, 2929 (ν Ph−H), 2857 (ν methyl C−H), 2238 (ν C≡N), 1443 (ν C=C), 1359 (ν *t*-Bu C−H), 1247 (ν Si−CH_3). Anal. Found: C, 65.9; H, 10.4; N, 6.8%.

Poly[4-{(*N*-*tert*-butyl-*N*-*tert*-butyldimethylsilyloxy)amino}-3-trifluoromethylstyrene] (15). The monomer **14** was polymerized in a similar manner as monomer **6**. Yield 62%; $M_n = 35\,900$, $M_w/M_n = 1.35$. ^{1}H NMR ($CDCl_3$, 500 MHz; ppm): δ 7.49 (br, 1H, Ph), 6.70 (br, 2H, Ph), 1.90 (br, 1H, C*H*CH_2), 1.37 (br, 2H, CHC*H*$_2$), 1.10 (s, 9H, *N*-*t*-Bu), 0.86 (s, 9H, *t*-Bu), 0.15 (s, 3H, $SiCH_3$), −0.50 (s, 3H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, 125 MHz; ppm): δ 148.0, 141.7, 127.9, 126.2, 124.8, 122.6, 120.5, 62.0, 40.0, 29.7, 25.9, 25.7, 17.9, −5.31. IR (cm^{-1}): 2957, 2930 (ν Ph−H), 2858 (ν methyl C−H), 1472 (ν C=C), 1360 (ν *t*-Bu C−H), 1250 (ν Si−CH_3). Anal. Calcd for $C_{19}H_{30}F_3NOSi$: C, 61.1; H, 8.1; N, 3.8. Found: C, 61.3; H, 8.2; N, 3.7.

Poly[4-(*N*-*tert*-butyl-*N*-oxylamino)styrene] (1). To a THF solution (60 mL) of the precursor polymer **7** (140 mg) was added tetrabutylammonium fluoride (0.34 g), and the mixture was stirred for 3 h at room temperature. Then, silver oxide (0.3 g) was added to the solution, and the mixture was vigorously stirred for 12 h at room temperature. The oxidizing agent was removed by filtration, and the filtrate was poured into methanol to yield the radical polymer **1** as an orange powder. Yield: 54%. IR (cm^{-1}): 2971, 2930 (ν Ph−H), 2857 (ν methyl C−H), 1360 (ν *t*-Bu C−H). Anal. Calcd for $C_{12}H_{16}NO$: C, 75.8; H, 8.5; N, 7.4. Found: C, 75.5; H, 8.6; N, 7.2.

Poly[3,5-di(*N*-*tert*-butyl-*N*-oxylamino)styrene] (2a). Yield 68%. IR (cm^{-1}): 2964 (ν Ph−H), 1362 (ν *t*-Bu C−H); Anal. Calcd for $C_{16}H_{24}N_2O_2$: C, 69.5; H, 8.8; N, 10.1. Found: C, 69.8; H, 8.6; N, 10.2.

Poly[3,5-di(*N*-*tert*-butyl-*N*-oxylamino)styrene-*co*-acrylonitrile] (2b). Yield 75%. IR (cm^{-1}): 2962 (ν Ph−H), 2236 (ν C≡N), 1362 (ν *t*-Bu C−H). Anal. Found: C, 75.5; H, 8.6; N, 7.2.

Poly[4-(*N*-*tert*-butyl-*N*-oxylamino)-3-trifluoromethylstyrene] (3). Yield 53%. IR (cm^{-1}): 2964 (ν Ph−H), 1362 (ν *t*-Bu C−H); Anal. Calcd for $C_{13}H_{15}F_3NO$: C, 60.5; H, 5.9; N, 5.4. Found: C, 60.8; H, 6.1; N, 5.5.

4-(*N*-*tert*-Butyl-*N*-oxylamino)benzotrifluoride (4d). A hexane solution (1.44 M, 69.0 mL) of *tert*-butyllithium (99.5 mmol) was added to 4-bromobenzotrifluoride (10.5 g, 46.5 mmol) in 154 mL of ether at −78 °C under an argon atmosphere. The solution was stirred for 1 h at −78 °C and 0.5 h at room temperature, and then the mixture was cooled again to −78 °C. 2-Methyl-2-nitrosopropane (5.03 g, 57.7 mmol) was dissolved in 35 mL of ether and added to the reaction mixture. The solution was stirred for 1.5 h at −78 °C, and further stirring was continued for 12 h at room temperature. The solution was first washed with aqueous ammonium chloride and then with water. The ether layer was dried over anhydrous sodium sulfate. After evaporation, the crude product was purified by column chromatography on silica gel (hexane/ether 4/1), followed by recrystallization from hexane to yield the corresponding hydroxylamine as a colorless crystal (4.55 g, yield 42%); sublimation point: 64 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): $\delta = 7.55$ (d, 2H, $J = 8.5$ Hz, Ph), 7.48 (d, 2H, $J = 8.5$ Hz, Ph), 6.17 (s, 1H, N$-$OH), 1.14 (s, 9H, *N*-*t*-Bu). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm): $\delta = 152.8$, 127.0 (q, $J = 33.1$ Hz), 124.7 (q, $J = 4.1$ Hz), 124.4, 124.3 (q, $J = 272$ Hz), 61.1, 26.3. Mass: *m*/*z* 233 (found), 233.2 (calcd). IR (cm^{-1}): 3223 (ν O$-$H), 2978 (ν Ph$-$H), 1363 (ν *t*-Bu C$-$H). Anal. Calcd for $C_{11}H_{13}F_3NO$: C, 56.7; H, 6.1; N, 6.0%. Found: C, 56.6; H, 6.0; N, 6.2%.

The obtained hydroxylamine (65.0 mg) was dissolved in benzene (27.9 mL), and potassium carbonate (385 mg) and silver oxide (646 mg) were added to the solution. The reaction mixture was vigorously stirred for 30 h at room temperature. The oxidizing agent and the base were removed using filtration, and the final radical solution was characterized using ESR spectroscopy. The solution was freeze-dried to yield the radical derivative **4d** as an orange powder (yield 46%). Mass: *m*/*z* 232 (found), 232.2 (calcd). IR (cm^{-1}): 2984 (ν Ph$-$H), 1371 (ν *t*-Bu C$-$H). Anal. Calcd for $C_{11}H_{12}F_3NO$: C, 56.9; H, 5.6; N, 6.0%. Found: C, 57.1; H, 5.5; N, 6.2%.

SQUID Measurements. Magnetization and magnetic susceptibility of the powder polymer sample were measured using a Quantum Design MPMS-7 SQUID (superconducting quantum interference device) magnetometer. The magnetic susceptibility was measured from 10 to 300 K under a 1.0 T field. The radical concentration was analyzed by the slope of the Curie plots and the saturated magnetization.

Electrochemical Measurements. Cyclic voltammetry was performed using a normal potentiostat system (BAS Inc. ALS660B) with a conventional three-electrode cell under a dry argon atmosphere. A platinum disk, coiled platinum wire, and Ag/AgCl were used as the working, auxiliary, and reference electrode, respectively. The cyclic voltammogram was measured in a dichloromethane solution in the presence of 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte. The formal potential of the ferrocene/ferrocenium redox couple was 0.45 V vs the Ag/AgCl reference electrode.

Electrolytic ESR and UV/vis Spectroscopy. 0.5 mM **1** or **3** in the dichloromethane solution containing 0.1 M tetrabutylammonium perchlorate was oxidized with a platinum wire or a platinum gauze (100 mesh) electrode at a given potential using a potentiostat NPOT-2501 (Nikko Keisoku Co.). The UV/vis spectra were recorded with a JASCO V-570 UV/vis/NIR spectrophotometer.

Chemical Characterization. ^{1}H NMR, ^{13}C NMR, and mass spectra were recorded using a JEOL Lambda 500 or a Bruker AVANCE 600 spectrometer and a JMS-SX102A or Shimazu GCMS-QP5050 spectrometer. Gel permeation chromatography was performed with a chloroform or THF eluent using a Tosoh HLC-8220 instrument, and the molecular weight and polydispersity were calibrated with polystyrene standards. ESR spectra were taken using a JEOL JES-TE200 ESR spectrometer with a 100 kHz field modulation.

Results and Discussion

Switching of p- and n-Type Redox Activity in Nitroxylbenzene Model Compounds. To investigate effect of the electron-donating and -withdrawing substitutent groups on the redox properties of the nitroxide radical polymers, a series of (*N*-*tert*-butyl-*N*-oxylamino)benzene model compounds *para*-substituted with methoxy, *tert*-butyl, hydrogen, and trifluoromethyl groups **4a−d** were characterized by ESR spectroscopy and cyclic voltammetry (CV). ESR spectra of the **4a−d** benzene solutions gave a strong absorption at $g = 2.0055$ with triplet hyperfine structure ascribed to an oxygen-centered radical conjugated with the nuclear spin of nitrogen atom (^{14}N, $I = 1$). The unpaired electron density on the N$-$O bond was estimated from the hyperfine coupling constant (a_N) using the McConnell equation:[41] The hyperfine coupling constant (a_N) of the nitrogen atom decreased with the electron-withdrawing ability of the substitutent group, which suggested the decrease of the unpaired electron density on the N$-$O group (Table 1). It is presumed that the electron-withdrawing effect of *para*-substituent tuned the SOMO (single occupied molecular orbital) energy level of nitroxide radical, which is closely related to the redox potential.

Table 1. ESR Hyperfine Constants (a_N), Redox Potentials ($E°$),[b] and Electron-Transfer Rate Constants (k_0)[e] of the 4-Substituted Nitroxylbenzenes 4a−d

radical	a_N (mT)[a]	$E°$ (V)	ΔE (mV)	k_0 (cm s^{-1})[e]
4a	1.28	0.56[c]	59[c]	0.17
4b	1.23	0.75[c]	62[c]	0.11
4c	1.21	0.83[c]	68[c]	0.042
4d	1.17	−0.92[d]	267[d]	0.0012

[a] Estimated with the ESR absorption. [b] Estimated from cyclic voltammetry. [c] Reversible redox on the anodic side. [d] Reversible redox on the cathodic side. [e] Determined by the Nicholson method.[42]

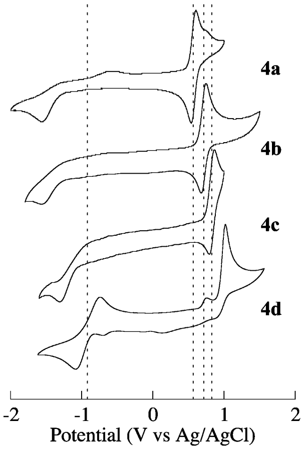
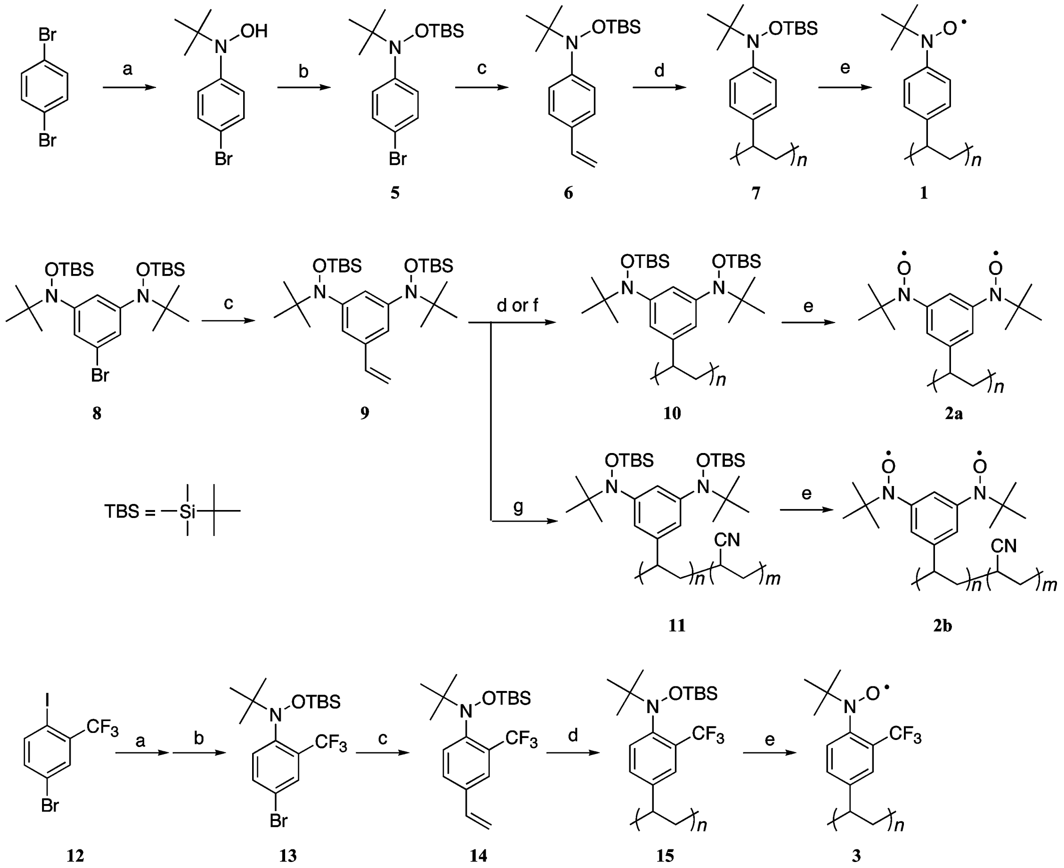


Figure 2. Cyclic voltammograms of the nitroxylbenzene derivatives **4a−d** in 1.0 mM acetonitrile solution with 0.1 M $(C_4H_9)_4N^+BF_4^-$; scan rate = 100 mV/s, $E°(Fc/Fc^+) = 0.45$ V vs Ag/AgCl.

Cyclic voltammograms of the nitroxylbenzene derivatives **4a−d** are depicted in Figure 2. The nitroxylbenzene *para*-substituted with methoxy **4a**, *tert*-butyl **4b**, and hydrogen **4c** substituents displayed the reversible redox potentials (formal redox potential $E°$) at 0.56, 0.75, and 0.83 V vs Ag/AgCl, respectively, which was assigned to the oxidation of the nitroxide radical to the corresponding oxoammonium cation or the p-type doping of the material. The p-type redox reversibility could be ascribed to the stabilization of the oxoammonium cation with electron-donating substituents. The redox potentials ($E°$) for the p-type doping of **4a−c** shifted cathodically with the electron-donating contribution of the methoxy or *tert*-butyl substituents to the nitroxide radical moiety. This corresponded to changes in the SOMO energy level which was tuned by the *para*-substituent electronic effect. On the cathodic side, **4a−c** exhibited an irreversible redox behavior, which suggested that the electron-donating substituents destabilized the formed aminoxy anion and that the n-doped state was chemically unstable for **4a−c**.

On the other hand, the nitroxylbenzene *para*-substituted with the electron-withdrawing trifluoromethyl group **4d** exhibited a clear reversible redox at −0.92 V vs Ag/AgCl, which corresponded to the reduction of the nitroxide radical to the corresponding aminoxy anion or n-type doping of material. The n-type redox wave was observed for more than 1000 cycles, indicating a very long cycle-life. This remarkable stability of the n-type redox was assumed to result from the stability of the corresponding aminoxy anion containing the strong electron-withdrawing trifluoromethyl group.

Scheme 2. Synthesis of the Poly(nitroxylstyrene)s 1−3[a]



[a] Reagents and conditions: (a) *t*-C_4H_9Li, 2-methyl-2-nitrosopropane, ether; (b) TBDMS-Cl, imidazole, DMF; (c) tributyl(vinyl)tin, $Pd(PPh_3)_4$, 2,6-di(*tert*-butyl)-4-methylphenol, toluene; (d) AIBN, benzene; (e) $(C_4H_9)_4N^+F^-$, Ag_2O, THF; (f) *s*-C_4H_9Li, THF; (g) acrylonitrile, AIBN, benzene.

The peak separation width ($E_{pa} - E_{pc}$, E_{pa}: anodic peak potential; E_{pc}: cathodic peak potential) for the p-type redox waves of **4a**−**c** was ~60 mV at scan rates of 100 mV/s, which was close to the theoretical value (59 mV) of a Nernstian or reversible electron-transfer system.[42] The electron-transfer rate constant k_0 for **4a**−**c** was estimated using the Nicholson method to be ca. 10^{-1} cm s^{-1}, which places the nitroxide radical in the category of a rapid electron-transfer system.[34] On the other hand, the peak separation in the n-type redox of **4d** was wider (ca. 270 mV), and the n-type doping was classified as a quasi-reversible electron-transfer reaction with $k_0 = 10^{-3}$ cm s^{-1}. Despite the slower n-type doping process of the nitroxide moiety, the electron-transfer rate constants k_0 for the redox of **4a**−**d** were several orders of magnitude larger than those for redox reactions of organic electrode-active materials, such as the reaction of a disulfide to form thiols with $k_0 = 10^{-11}$ cm s^{-1}.[18,19] The remarkably fast redox reactions of the nitroxide polymers could lead to a high power rate performance in the battery composed of the nitroxide electrode.

The electrochemical results described above demonstrate that the nitroxide radical provides both p- and n-type redox activity suitable for creating cathode- and anode-active materials, respectively. Furthermore, we demonstrate that the redox potential or the battery voltage may be tuned via the substituent electronic effects and molecular design of the nitroxide radicals.

Synthesis of Poly(nitroxylstyrene)s 1−3. The styrenic monomers bearing nitroxide precursor(s), **6** and **9**, were synthesized in three steps from the corresponding aromatic bromides. The di- or tribromobenzene was lithiated, and the following reaction with 2-methyl-2-nitrosopropane gave the corresponding hydroxylamines. After the protection of the hydroxylamino moiety with the *tert*-butyldimethylsilyl group, Stille coupling with tributyl(vinyl)tin using palladium(0) catalyst yielded the corresponding styrenic monomers. Conventional radical polymerization of **6** yielded the precursor polymer **7** (e.g., $M_n = 2 \times 10^4$), and the one-pot deprotection with tetrabutylammonium fluoride and oxidation with silver oxide afforded the corresponding radical polymer **1** as an orange powder. The obtained radical polymer **1** exhibited selective solubility in common organic solvents such as THF, chloroform, and toluene, and insolubility in propylene carbonate, a common electrolyte solvent. Polymer **1** was insoluble, but slightly swollen, in the electrolyte solution such as propylene carbonate and diethyl carbonate. The radical densities of **1** were estimated at 2.95×10^{21} unpaired electrons/g (0.93 radicals per monomer unit) and 2.97×10^{21} unpaired electrons/g (0.94 radicals per monomer unit) from the intensity of the ESR (electron spin resonance) signal and from SQUID (superconducting quantum interference device) measurement, respectively, and the values estimated by the two methods agreed well with each other. The radical generation via oxidation of the corresponding hydroxylamine was quantitative and advantageous, in comparison with that via the oxidation of the secondary amine. The unpaired electron concentration of **1** was the highest among the previously synthesized and reported radical polymers[27−31] and stable under ambient conditions (half-life >1 month). The polymer **1** was thermally stable ($T_{d10\%} = 230$ °C), and the radical moiety was also durable until this temperature. The glass transition temperature (T_g) was 110 °C.

Radical polymerization of the styrenic monomer bearing two protected nitroxide groups **9** resulted in an oligomeric product ($M_n = 2100$). The molecular weight of **10**, which was polym-

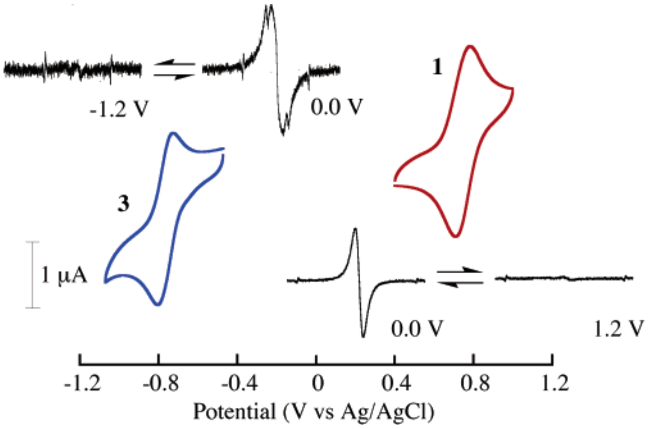


Figure 3. Cyclic voltammograms of the radical polymers **1** and **3** at 1.0 mM concentration in CH_2Cl_2 solution with 0.1 M $(n\text{-}C_4H_9)_4N^+BF_4^-$. Scan rate = 100 mV/s. Inset: electrolytic in-situ ESR spectra of **1** under applied potentials of 0.0 and 1.2 V vs Ag/AgCl and **3** under the applied potentials of 0.0 and −1.2 V.

erized via the anionic polymerization with *sec*-butyllithium as the initiator, also remained low (M_n = 2500). The ^{1}H NMR and APCI-mass spectra of **10** indicated that the absence of side reactions such as deprotection of the silyl group during the polymerization. With the hypothesis that steric hindrance of the propagating chain end was hindering polymerization, acrylonitrile was selected as a comonomer in consideration of both the compact molecular structure and the tendency toward alternating polymerization with styrenic monomers based on the $Q-e$ value. Radical copolymerization of **9** with 1 equiv of acrylonitrile afforded the corresponding copolymer **11** with a higher molecular weight (e.g., $M_n = 2.4 \times 10^4$). ^{1}H NMR spectroscopy revealed a mole fraction of 0.70 of monomer **9** in the copolymer **11**, whereas elemental analysis produced a value of 0.75. One-pot deprotection and oxidation of **10** afforded the corresponding radical polymer. The radical density of **2a** was 4.27×10^{21} unpaired electrons/g (1.96 radicals per monomer unit), nearly 1.5 and 1.8 times those of **1** and PTMA, respectively. The copolymer **2b** exhibited 3.14×10^{21} unpaired electrons/g, which was consistent with the radical residue content calculated from the copolymer composition.

The styrenic monomer bearing the trifluoromethyl electron-withdrawing group, **14**, was synthesized from 5-bromo-2-iodobenzotrifluoride (**12**) by selective lithiation at the iodine substituent,[41] followed by protection of the hydroxyamine group and subsequent Stille coupling with tributyl(vinyl) tin. Radical polymerization of **14** yielded a protected nitroxide functional polymer with a high molecular weight (e.g., $M_n = 3.6 \times 10^4$). Deprotection and oxidation of **14** afforded the corresponding radical polymer **3** as an orange powder. The obtained polymer **3** possessed solubility in common organic solvents, and its radical density was 1.82×10^{21} unpaired electrons/g (0.78 radicals per monomer unit). The nitroxide residues of **3** were stable and maintained their initial radical density under ambient atmospheric conditions (half-life >1 month).

Electrochemical Properties of Radical Polymers. Cyclic voltammograms of poly(nitroxylstyrene)s **1** and **3** are shown in Figure 3. Poly(nitroxylstyrene) **1** produced a reversible redox wave at 0.74 V vs Ag/AgCl on the anodic side (exceeding 100 cycles) in a similar fashion to the model compounds **4a**−**c**. Electrolytic in-situ ESR spectroscopy revealed the complete disappearance of the strong ESR signal of **1** attributed to the nitroxide radical at g = 2.0056 upon application of a 1.2 V potential. The ESR signal was regenerated upon returning the potential to 0 V (Figure 3, inset). This reversible redox couple was attributed to the oxidation of the nitroxide radical to the oxoammonium cation or p-type doping of poly(nitroxylstyrene) **1**. Electrolytic in-situ UV/vis spectroscopy also supported the hypothesis of a reversible redox reaction. The UV/vis absorption (λ_{max} = 295, 304 nm) decreased under the applied potential at 1.0 V, and a new absorption appeared at 319 nm, producing an isosbestic point at 308 nm (Figure 4a). Cyclic voltammetry of **2** revealed an oxidation peak on the anodic side at 1.0 V, which proved to be irreversible. This instability of the redox process of **2** could be ascribed to the lack of a stabilizing *para*-substitutent (2,6-positions of **2**) on the nitroxide radicals.

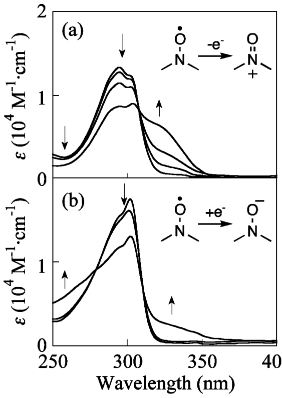


Figure 4. Electrolytic UV/vis spectra of (a) **1** at potentials of 0.4, 0.6, 0.8, and 1.0 V and (b) **3** at potentials of −0.4, −0.7, −1.0 V, in 0.5 mM CH_2Cl_2 solution with 0.1 M $(n\text{-}C_4H_9)_4N^+ClO_4^-$.

The poly(nitroxylstyrene) *ortho*-substituted with the trifluoromethyl group **3** produced a reversible redox wave ($E°$ = −0.76 V) on the cathodic side (Figure 3), consistent with the model compound **4d**, corresponding to the n-type doping process. This n-type doping process was also characterized using electrolytic ESR and UV/vis spectroscopy. The ESR signal for **3** disappeared under an applied potential of −1.2 V and then regenerated at 0 V (Figure 3, inset). The UV/vis absorption (λ_{max} = 294, 303 nm) also decreased under an applied potential of −1.0 V, and a new absorption appeared at 327 nm with isosbestic points at 281 and 308 nm. Polymer **3** is the first n-type redox polymer developed from nitroxide radical polymers applicable as an anode-active material.

These results support our molecular design approach for tuning the electrochemical properties of redox-active polymers: Substituent electronic effects enabled control of the redox potential of the radical through changes in the radical electron density. The stabilization of the oxidized or reduced form of the nitroxide radical using substituent group effects could thus switch the redox type of the radical polymer, from p- to n-type doped polymers. Such p- and n-type redox-active polymers possess potential applications as cathode- and anode-active materials leading to an all-organic battery. A completely organic cell comprising both p-type **1**/carbon composite cathode and n-type **3**/carbon composite anode can be fabricated using an ethylene carbonate and diethyl carbonate solution of 1.0 M lithium hexafluorophosphate as an electrolyte. The cell performance will be reported in a future publication.

Conclusions

Three poly(nitroxylstyrene)s containing robust and redox-active nitroxide radicals with higher radical densities, poly[4-(*N*-*tert*-butyl-*N*-oxylamino)styrene] (**1**), poly[3,5-di(*N*-*tert*-butyl-*N*-oxylamino)styrene] (**2**), and poly[4-(*N*-*tert*-butyl-*N*-oxylamino)-3-trifluoromethylstyrene] (**3**) were synthesized. Cyclic voltammetry, in-situ electrolytic ESR, and UV/vis spectroscopy revealed that the reversible p-type redox of poly(nitroxylstyrene) **1**, attributed to the oxoammonium cation formation and n-type redox of poly(nitroxylstyrene) *ortho*-substituted with trifluoromethyl group **3** corresponding to the aminoxy anion formation, was tuned by the electronic effects of substituent groups. p- and n-type redox switching with chemical modification also promises potential applications of these polymers as cathode- and anode-active materials in all-organic batteries.

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