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Nitroxide-Substituted Polyether as a New Material for Batteries

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Summary: Nitroxide-substituted polyether was synthesized as a cathode-active material for a secondary battery. Anionic ring-opening polymerization of a TEMPO-bearing glycidyl ether was carried out under bulk conditions to yield the corresponding polymer with the molecular weight of $>10^4$. The obtained polymer was insoluble, but slightly swollen in the electrolyte solution (ethylene carbonate/propylene carbonate). The test cell fabricated with a carbon composite cathode of this radical polymer displayed a plateau voltage at 3.5 V vs. Li/Li^+. The cell performance was maintained even with a higher amount of the radical polymer loaded in the composite electrode, which could be ascribed to the flexible and rubbery polyether backbone and its higher compatibility with the electrolyte solution.

Keywords: anionic ring-opening polymerization; electrode-active material; nitroxide; polyether; radical polymer

Introduction

An organic radical molecule bearing one unpaired electron had been classified as an unstable and intractable material; however, some organic radicals can be chemically modified into stable compounds through sterically protected structures and/or resonance structures around the radical center.[1,2] A typical example is nitroxide radicals, such as 2,2,6,6-tetramethylpiperidinyl-*N*-oxy (TEMPO), which are stable under ambient conditions and widely used as a spin-label and a spin-trap.[3] The nitroxide radical has redox couples attributable to the oxidation to the corresponding oxoammonium cation (p-type doping) and the reduction to the corresponding aminoxy anion (n-type doping) (Scheme 1). Based on these redox couples, nitroxide polymers have been extensively studied in the 1970s as redox reagents or redox resins, which catalyze the oxidative and/or reductive reactions of organic compounds.[4,5] For example, poly(acrylic acid)-combined TEMPOs were synthesized and studied as a catalytic reagent for the oxidation of alcohols into aldehydes and ketones.[6] The organic radical-based or metal-free redox reagents have been recently reexamined from the perspective of green or environmentally compatible chemical reaction processes.[7]

However, there has been no report, except for our work, in which the nitroxide polymers have been utilized as the electrode-active or charge-storage component for a secondary battery.[8,9] For example, poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA) has a robust TEMPO radical moiety, and displays a reversible redox behavior attributable to the p-type doping. Figure 1 shows the charging and discharging mechanism of a prototype organic radical-based lithium-ion battery in which the p-type nitroxide radical polymer forms a cathode operated in conjunction with a carbon anode. During the charging process, the p-type radical polymer in the cathode is oxidized to the oxoammonium form. During the discharging process, the nitroxide radical is regenerated by reduction of the oxoammonium. The organic radical battery composed of the radical polymer electrode

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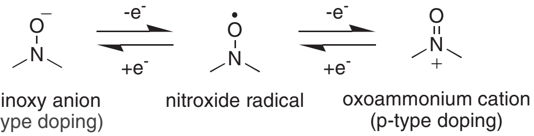
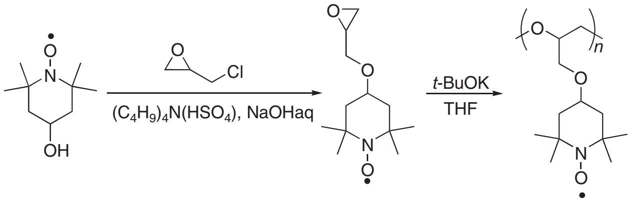


Scheme 1.
Redox couples of a nitroxide derivative.

has several advantages: (1) high capacity (ca. 100 mAh/g), ascribed to the quantitative doping, compared with the limited doping of the π-conjugated conductive polymer electrode, (2) high-power rate performance, derived from the rapid electron-transfer process of the nitroxide radical moiety,[10] and (3) long cycle life (more than 1000 cycles) ascribed to the chemical stability of the nitroxide radical moiety and to the amorphous electrode structure. However, PTMA lacks any molding ability during battery fabrication. We selected in this study, a polyether backbone to provide a good compatibility with a current collector and an electrolyte solution. The polyether backbone also involves a flexibility of the main chain, expecting an enhancement of the high power rate performance. We report in this paper, the synthesis of a TEMPO-substituted polyether **1** and its electrochemical property. The test cell was fabricated with a higher loaded radical polymer in the composite cathode, of which the battery performance is also demonstrated.



2 **1**

Scheme 2.
Synthesis of TEMPO-substituted polyether **1**.

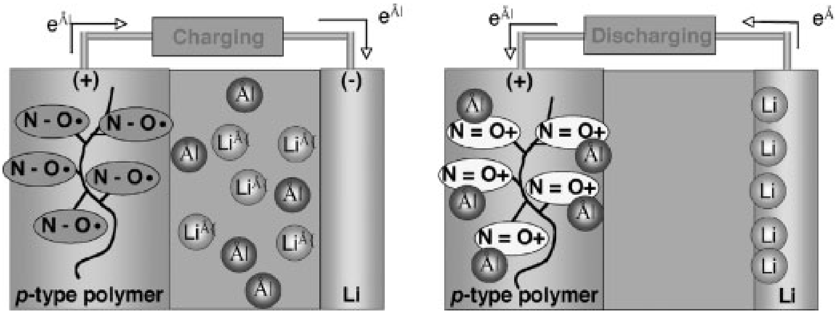


Figure 1.
The prototype organic radical battery composed of a nitroxide radical polymer cathode.

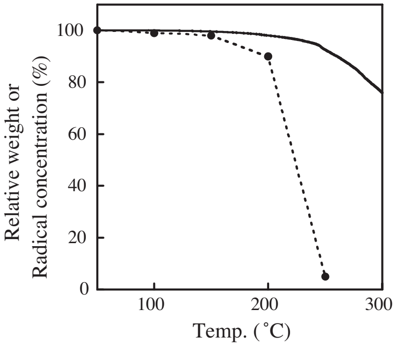


Figure 2.
Thermal gravimetric analysis of polymer **1** (solid line) and the radical concentration of the polymer **1**.

Experimental

Preparation of 4-Glycidyloxy-2,2,6,6-Tetramethylpiperidine-1-oxyl (2)

To 4 ml of a sodium hydroxide aqueous solution(50 wt%) were added epichlorohydrin (2.5 ml) and tetrabutylammonium hydrosulfate (0.84 g), and the mixture was then vigorously stirred, cooling with a water bath. 4-Hydroxy-2,2,6,6-tetramethylpiperidin-*N*-oxy (1.03 g) was added into the mixture, and vigorously stirred for 12 h at room temperature. The mixture was added into ice water and the crude product was extracted with ether, washed with water, and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo, and the residue was purified using a silica gel column with hexane/ether (1/1) eluent. The TEMPO-radical containing epoxy monomer **2**, 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl, was isolated as a red solid (Yield 84%).

The radical containing monomer **2** was chemically reduced with phenylhydrazine, and characterized by the NMR spectroscopy. ^{1}H-NMR(CDCl$_3$, 500 MHz, ppm): $\delta = 3.70$ (dd, 1H, $J = 11.3$, 3.0 Hz, OCH$_2$), 3.64 (m, 1H, piperidine CH), 3.40 (dd, 1H, $J = 11.3$, 5.8 Hz, OCH$_2$), 3.11 (m, 1H, epoxide CH), 2.77 (t, 1H, $J = 4.6$ Hz, epoxide CH$_2$), 2.58 (dd, 1H, $J = 5.2$, 2.7 Hz, epoxide CH$_2$), 1.92 (m, 2H, piperidine CH$_2$), 1.44 (q, 2H, $J = 12.2$ Hz, piperidine CH$_2$), 1.19 (s, 6H, CH$_3$), 1.14 (s, 6H, CH$_3$); ^{13}C-NMR (CDCl$_3$, 125 MHz, ppm): $\delta = 71.1$, 68.9, 58.9, 50.9, 44.5, 44.3, 32.0, 20.5; Mass: *m/z* 228 (found), 228.3 (calcd). IR (cm^{-1}): 1243 (ν epoxide 8 μ), 901 (ν epoxide 11 μ), 852 (ν epoxide 12 μ); Found: C, 62.9; H, 9.5; N, 6.2%. Calcd for $C_{12}H_{22}NO_3$: C, 63.1; H, 9.7; N, 6.1%

Anionic Ring-Opening Polymerization of the Epoxy Monomer 2

To the epoxy monomer **2** (100 mg) was added potassium *t*-butoxide (5 mol%) under an argon atmosphere. The mixture was stirred for 24 h at 60 °C. The polymerization mixture was dissolved in chloroform and poured into hexane. The precipitate was dissolved in chloroform and reprecipitated into hexane to yield an orange powder (Yield 66%).

The obtained polymer **1** was chemically reduced with phenylhydrazine, and characterized by the NMR spectroscopy. ^{1}H-NMR (DMSO-d_6, 500 MHz, ppm): $\delta = 4.00$ (b, 1H, OCH$_2$), 3.75 (m, 1H, piperidine CH), 3.61 (b, 3H, polyether CH and CH$_2$), 1.94 (bs, 2H, piperidine CH$_2$), 1.33 (bs, 2H, piperidine CH$_2$), 1.18 (s, 6H, CH$_3$), 1.14 (s, 6H, CH$_3$); ^{13}C-NMR(DMSO-d_6, 125 MHz, ppm): $\delta = 79.2$, 70.6, 69.5, 67.8, 57.8, 44.6, 32.4, 20.7; IR (cm^{-1}): 1040 ($\nu_{C\text{–}O\text{–}C}$); Found: C, 62.8; H, 9.5; N, 6.2%. Calcd for $C_{12}H_{22}NO_3$: C, 63.1; H, 9.7; N, 6.1%

Coodinated Anionic Ring-Opening Polymerization of the Epoxy Monomer 2

Diethyl zinc in a 1.0 M hexane solution (2.0 ml) was reacted with 36 μl of pure water under an argon atmosphere to prepare the initiator as a yellow solution. The initiator (10 mol%) was added into the epoxy monomer **2** under an argon atmosphere. The reaction mixture was stirred for 24 h at room temperature, and then poured into hexane. The precipitate was purified by Soxhlet extraction to yield an orange solid (Yield 73%). The obtained polymer was insoluble in common organic solvents.

Characterization of the Radical Polymer

The polymer **1** was characterized by the *g*-value (2.0065) of the ESR signal to contain the TEMPO moiety. The radical concentration or the concentration of the unpaired electron of each sample was determined on the basis of the assumption of being paramagnetic at room temperature by integration of the ESR signal standardized with that of the TEMPO solution. The radical concentration was also analyzed by the slope of the Curie plots and the saturated magnetization in the SQUID measurement. These radical concentration values estimated by the two methods almost agreed with each other.

Electrode Preparation and Electrochemical Measurement

The polymer **1** (30 mg) was mixed with 60 mg of a graphite fiber (vapor grown carbon fiber: VGCF, Showa Denko Co.) and 10 mg of a binder powder (polyvinylidenefluoride resin: KF polymer, Kureha Chemical Co.) in the presence of *N*-methyl-2-pyrrolidone (NMP). The mixture was pasted on aluminum foil and dried overnight in vacuo at 80 °C. The composite electrodes with a series of **1**-loading ratios (**1**/carbon/binder = 1/8/1, 2/7/1, 3/6/1) were also prepared.

The electrochemical measurements were performed using a conventional cell under a dry argon atmosphere. A normal potentiostat system (BAS Inc. ALS660B) was used for the cyclic voltammetry, chronopotentiometry and other electrochemical measurements. A platinum disk, coiled platinum wire, and Ag/AgCl were used as the working, auxiliary, and reference electrode, respectively. Cyclic voltammogram of the polymer/carbon composite electrode was measured in an acetonitrile solution in the presence of 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. The formal potential of the ferrocene/ferrocenium redox couple was 0.45 V vs. Ag/AgCl reference electrode.

Cell Fabrication and Battery Performance

A coin cell was fabricated by stacking the polymer/carbon composite cathode with a separator film (cell guard #2400, Hohsen Corp.) and lithium metal as the anode under an argon atmosphere. An ethylene carbonate/diethyl carbonate (1/1) solution of lithium hexafluorophosphate (1 M) was used as the electrolyte. The cycle performance of the fabricated cell was tested by repeated charge-discharge galvanostatic cycles at different current densities. The cut-off potentials were 3.0 and 4.0 V vs. Li/Li^+.

Other Measurements

The ^1H- and ^{13}C NMR spectra were recorded using a JEOL Lambda 500 or Bruker AVANCE 600 spectrometer, and the mass spectra were recorded by a JMS-SX102A or Shimazu GCMS-QP5050 spectrometer. Gel permeation chromatography was performed with chloroform or THF using a Tosoh HLC-8220 instrument. The ESR spectra were taken using a JEOL JES-TE200 ESR spectrometer with a 100 kHz field modulation. The magnetization and magnetic susceptibility of the powder polymer sample were measured by a Quantum Design MPMS-7SQUID (superconducting quantum interference device) magnetometer. The magnetic susceptibility was measured from 10 to 300 K in a 1.0 T field. The thermal analyses were performed by a Seiko DSC220C and TG/DTA 220 thermal analyzer at the heating rate of 10 °C/min under nitrogen.

Results and Discussion

The TEMPO-substituted epoxy monomer, 4-(glycidyloxy)-2,2,6,6-tetramethylpiperidine-oxyl **2**, was synthesized from 4- hydroxy-2,2,6,6-tetramethylpiperidin-*N*-oxy and epichlorohydrin in the presence of a phase transfer agent. This reaction proceeded with a higher yield than the previous report.[11] The TEMPO radical moiety of the monomer was chemically reduced to the corresponding hydroxylamine with phenylhydrazine, and characterized by ^1H- and ^{13}C-NMR spectroscopies.

The anionic ring-opening polymerization of the monomer **2** using potassium *t*-butoxide as an initiator in THF yielded the corresponding polymer. The polymer with a higher molecular weight ($M_n = 3.2 \times 10^4$) was obtained for the polymerization under bulk conditions (without solvent). The radical concentration per monomer residue in the polymer **1** was estimated to be ca. 90%. The polymer **1** was also chemically reduced with phenylhydrazine and characterized by the NMR spectrum, supporting the fact that the polymerization of **2** proceeded without any side reactions. The obtained polymer **1** was insoluble in any common solvents, but slightly swollen in chloroform, THF, and the electrolyte solution (ethylene carbonate/diethyl carbonate solution (1/1) containing 1.0 M $LiPF_6$). The radical concentration of the polymer **1** obtained by the coordinated anionic ring-opening polymerization using $ZnEt_2/H_2O$ was not quantitative, indicating the side reactions on the TEMPO moieties.

The thermal analyses data of **1** and PTMA are summarized in Table 2. Both polymers were thermally decomposed at 260 °C. The radical moieties on these polymers were very stable even at high temperature and almost stable up to this thermal decomposition temperature (the latter was monitored with the radical concentration of the polymers). The radical concentration of **1** remained unchanged for 3 months under ambient conditions. The glass transition temperature (T_g) for change to a rubbery state was 18 °C and 71 °C for **1** and PTMA, respectively. The low T_g value of **1** could be ascribed to the flexible polyether backbone of **1**, and suggested a good molding ability and higher compatibility of **1** with the carbon, the current collector, and also with the electrolyte solution.

Table 2.
Glass transition temperature (T_g) and thermal 10%-decomposition temperature T_d (10%) of **1** and PTMA.

Polymer	T_g/°C	T_d (10%)/°C
1	18	260
PTMA	71	263

The radical polymer **1** itself does not show sufficient electric conductivity; therefore, **1** is mixed with graphite fibers to give a composite electrode. Cyclic voltammograms of the **1**/carbon composite electrode displayed a reversible redox wave at 0.78 V vs. Ag/AgCl in an acetonitrile solution (Figure 3), which was ascribed to the oxoammonium cation formation or the p-type doping of the TEMPO radical moiety of the polymer **1**. Electrolytic ESR spectroscopy supported the ESR-silent oxoammonium formation under the applied potential at 1.1 V and regeneration of the nitroxide radical at 0.6 V. A symmetric redox wave with a narrow peak-to-peak separation ($\Delta E = 90$ mV) indicated fast electrode reaction kinetics for the p-type doping of the nitroxide radical.

The test cell was fabricated by stacking the polymer **1**/carbon composite cathode with a separator film and lithium metal as an anode. The charge-discharge curves for the fabricated cell display a plateau voltage at 3.54 V vs. Li/Li^+ (Figure 4), corresponding to the redox potential of the polymer **1** (0.78 V vs. Ag/AgCl, Figure 3): This revealed that **1** served as a cathode-active

Table 1.
Anionic ring opening polymerization of the epoxy monomer **2**$^{a)}$.

Entry	Solvent	Monomer concn/M	$M_n/10^3$	M_w/M_n	Yield/%	Radical concn/mol%
1	THF	0.5	2.5	1.2	25	88
2	THF	1.0	3.2	1.3	43	91
3	THF	2.0	3.6	1.4	57	90
4	–	Bulk	32.0	1.8	88	84
5$^{b)}$	–	Bulk	10.9	1.5	73	62

$^{a)}$ time: 24 h, initiator: potassium *t*-butoxide (5 mol%).
$^{b)}$ initiator: $ZnEt_2/H_2O$ (10 mol%).

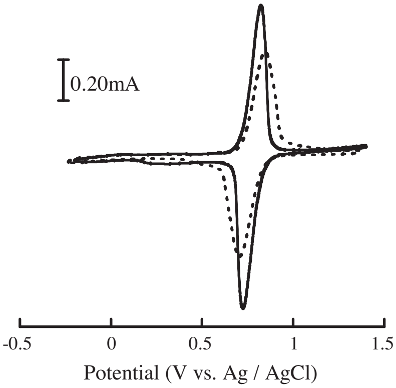


Figure 3.
Cyclic voltammogram of **1**/carbon composite electrode (solid line) and the PTMA/carbon composite electrode (dashed line) in CH_3CN with 0.1 M $(C_4H_9)_4NClO_4$. A platinum wire and Ag/AgCl were used as the counter and reference electrodes, respectively. Scan rate = 5 mV/s.

material. The cycle performance during charging and discharging at the cut-off voltages of 3.0 and 4.0 V, respectively, displayed no significant deterioration in the capacity up to 1000 cycles. This surprisingly stable cyclability could be ascribed to the simple one-electron transfer of the nitroxide radical, the flexible backbone sufficiently swollen with the electrolyte solution, and the amorphous electrode structure. When the amount of the radical polymer (**1** and PTMA) loaded in the composite electrode was 10–20%, the cell performance displayed no significant difference between **1** and PTMA. However, as the loaded amount of the polymer in the electrode increases up to 30 wt%, the discharge capacity for the PTMA/carbon composite electrode decreased. The discharge capacity for the **1**/carbon composite electrode maintained unchanged even at high current density (10 C rate), suggesting the high compatibility of the radical polymer **1** with the current collector and the electrolyte solution.

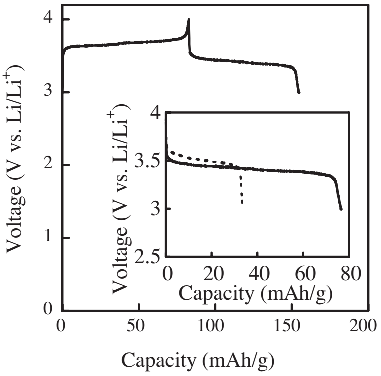


Figure 4.
Charge/discharge curves of the test cell fabricated with the polymer **1**/carbon cathode and Li anode in ethylene carbonate/diethyl carbonate with 1.0 M $LiPF_6$. Current density = 10 C rate; The 1 C is defined as the current density at which the charging or discharging of the cell takes 1 h. Inset: discharge curves for **1**/carbon composite cathode (solid line) and PTMA/carbon composite cathode (dashed line), in which a 30 wt% radical polymer was loaded.

Conclusion

The anionic ring-opening polymerization of the TEMPO-substituted glycidyl ether **2** yielded the corresponding radical polymer which was insoluble, but swollen with the electrolyte solution. The fabricated cell composed of this polymer cathode displayed a plateau voltage at 3.54 V and stable charging and discharging curves. The cell performance was maintained even with a higher amount of **1** loaded in the composite electrode, which could be ascribed to the flexible polyether backbone and its higher compatibility with the electrolyte solution. We reported in this paper that the flexible backbone structure played an important role as a matrix for electron transfer. The electron transfer process in the polymer film with various backbone structures; e.g., polyether, polyacrylate, polyisocyanate, and polynorbornene, will be discussed later. The molecular design of the main chain such as a branched or network structure will be the next target to enhance the compatibility and processability of the polymer.

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