Supplementary Information

Photo-Crosslinked Nitroxide Polymer Cathode Leading to an Organic-Based Paper Battery

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Experimental

2,3-Bis(2',2',6',6'-tetramethylpiperidinyl-*N*-oxyl-4'-oxycarbonyl)-5-norbornene 2. The norbornene monomer **2** was synthesized by modifying the previously reported procedure.[1] To 300 ml of a dry benzene solution of *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (3.41 g) were added 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-*N*-oxy (6.63 g), *N,N*-dimethylaminopyridine (1.07 g) and triethylamine (4 ml), and the mixture was stirred for 12 h at 80°C under nitrogen and then cooled to room temperature. 2-Chloro-1-methylpyridinium iodide (6.63 g) was added to the reaction mixture, which was vigorously stirred for 12 h at room temperature. The precipitate (the residue of 2-chloro-1-methylpyridinium iodide) was removed by filtration, and triethylamine was removed in vacuo. The crude product was extracted with chloroform, washed with an aqueous solution of ammonium chloride, and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo, and the residue was purified using a silica gel column with an ethyl acetate/chloroform/hexane (1/6/3) eluent. Two diastereomers, the *endo-, endo-* and *endo-, exo*-derivatives, were isolated as orange crystals by recrystallization from hexane/chloroform in the yield of 33 and 12%, respectively.

Each structure was characterized by the 2D-NMR spectra by chemically reducing them with phenylhydrazine; *endo-, endo*-derivative: mp. 164 ° C, ^{1}H-NMR (CDCl$_3$, 600 MHz, ppm, reduced with phenylhydrazine): δ = 6.26 (bs, 2H, olefinic =CH), 5.01 (m, 2H, piperidine methine), 3.22 (bs, 2H, *endo*-methine), 3.14 (bs, 2H, bridgehead CH), 1.93 (m, 4H, piperidine CH$_2$), 1.65 (m, 4H, piperidine CH$_2$), 1.47 (m, 1H, bridge carbon CH$_2$), 1.31 (m, 1H, bridge carbon CH$_2$), 1.27 (s, 12H, TEMPO CH$_3$), 1.21 (d, 12H, TEMPO CH$_3$); ^{13}C-NMR (CDCl$_3$, 150 MHz, ppm): δ = 175.9, 138.7, 70.2, 64.5, 52.5, 52.1, 50.3, 47.4, 35.4, 24.3; IR (cm^{-1}): 2974 (ν_{C-H}), 1740 ($\nu_{C=O}$), 1178, 1159 (ν_{C-O}); Mass: *m/z* 490 (found), 490.6 (calcd); Found: C, 66.0; H, 8.8; N, 5.7%. Calcd for $C_{27}H_{42}N_2O_4$: C, 66.1; H, 8.6; N, 5.7%; Rf 0.65 (ethyl acetate/hexane = 1/1); *endo-, exo*-derivative: mp. 191 ° C, ^{1}H-NMR(CDCl$_3$, 600 MHz, ppm, reduced with phenylhydrazine): δ = 6.29 (dd, 1H, olefinic =CH), 6.07 (dd, 1H, olefinic =CH), 5.08 (m, 1H, piperidine methine), 5.01 (m, 1H, piperidine methine), 3.33 (t, 1H, *endo*-methine), 3.25 (bs, 1H, bridgehead CH), 3.10 (bs, 1H, bridgehead CH), 2.63 (dd, 1H, *exo*-methine), 1.93

(b, 4H, piperidine CH_2), 1.68 (b, 4H, piperidine CH_2), 1.60 (d, 1H, bridge carbon CH_2), 1.45 (dd, 1H, bridge carbon CH_2), 1.28 (bs, 12H, TEMPO CH_3), 1.24 (s, 6H, TEMPO CH_3), 1.22 (s, 6H, TEMPO CH_3); ^{13}C-NMR ($CDCl_3$, 150 MHz, ppm): δ = 177.8, 176.7, 141.5, 138.8, 70.7, 70.5, 64.5, 64.2, 51.9, 51.6, 51.3, 51.2, 49.5, 47.3, 35.1, 24.5; Mass: *m/z* 490 (found), 490.6 (calcd); Rf 0.70 (ethyl acetate/hexane = 1/1).

Ring-opening metathesis polymerization of 2. To a 1.0 ml toluene solution of the monomer **2** (100 mg) was added the Grubbs second generation catalyst (Aldrich, 2.3 mg), and the mixture was stirred for 12 h at 40°C under an argon atmosphere. The polymerization mixture was poured into hexane, and the precipitated polymer powder was purified by reprecipitation from chloroform into diethyl ether to afford the pale orange powder of **1a** (yield 93%). M_n = 13,100, M_w/M_n = 1.2; ^{1}H-NMR($CDCl_3$, 600 MHz, ppm, reduced with phenylhydrazine): δ = 5.46 (bs, 2H, olefinic =CH), 4.93 (s, 2H, piperidine methine), 3.15 (bs, 2H, cyclopentane mechine), 2.80 (bs, 2H, cyclopentane methine), 1.83 (s, 4H, piperidine CH_2), 1.72 (bs, 1H, cyclopentane CH_2), 1.40 (bs, 4H, piperidine CH_2), 1.25 (bs, 1H, cyclopentane CH_2), 1.07 (bs, 24H, TEMPO CH_3); ^{13}C-NMR ($CDCl_3$, 150 MHz, ppm): δ = 170.5, 131.2, 66.1, 57.9, 50.5, 43.8, 32.4, 20.8, 20.0; IR (cm^{-1}): 2974 (ν_{C-H}), 1732 ($\nu_{C=O}$), 1174 (ν_{C-O}). The bifunctional monomer **3**, 1,4-di(norborn-2-en-5-yl)benzene, was synthesized via palladium coupling of norbornadiene and 1,4-diiodobenzene based on a previous report.[2,3] To a 1.0 ml toluene solution of the monomer **2** (100 mg) and 1,4-di(norborn-2-en-5-yl)benzene (1.5 mg) was added the Grubbs 2 nd catalyst (2.3 mg), and the mixture was stirred for 15 h at 40°C under an argon atmosphere. The polymerization mixture was poured into diethyl ether, and Soxhlet extraction with acetonitrile to remove the soluble parts and afford a pale orange powder of **1b** (Yield 89%). IR (cm^{-1}): 2975 (ν_{C-H}), 1732 ($\nu_{C=O}$), 1175 (ν_{C-O}). The composition of the crosslinked copolymer of **2** and **3** was determined by the elemental analysis and the SQUID measurement. The composition almost agreed with the feed ratio (Table 1).

Table 1. Ring-opening metathesis copolymerization[a)]

Entry	Solvent	Yield (%)	Feed ratio **2/3**	Composition of the polymer[b)] **2/3**	Solubility in CH_3CN
1	CH_2Cl_2	87	0.97/0.03	0.90/0.10	Soluble
2	CH_2Cl_2	75	0.92/0.08	0.84/0.16	Soluble
3	CH_2Cl_2	70	0.83/0.17	0.68/0.10	Insoluble
4	toluene	89	0.96/0.04	0.90/0.10	Insoluble

a) [**2**+**3**] = 0.2 M, [Grubbs 2nd cat.] = 1.0 mol%, temp. = 40°C, 15 h.

b) determined by elemental analysis.

Photocrosslinking. To an ethyl lactate solution of the radical polymer **1a** (25 mg, 4 wt%) was added a toluene/ethyl lactate (1/1) solution of 2,6-bis(*p*-azidobenzal)-4-*t*-amylcyclohexanone (BAC-TA, Toyo Gosei Co., Ltd.) **3** and the mixed solution was spin-coated on a ITO glass substrate using a spin coater (Mikasa spin coater 1H-D3) at 2000, 4000 and 6000 rpm. After UV irradiation (Ushio Inc. USH-250D, 40 mJ/cm^2), the substrate was washed with chloroform to remove soluble species. The film thickness was estimated using a contact stylus profiler (KLA Tencor P-15) to be 83, 66, and 50 nm. Photocrosslinking of **1a** on an ITO/polyethylene telephtalate film (Toyobo Co., Ltd., ITO film 300R) was carried out as well, and washed with acetonitrile to remove any soluble part of the polymer **1a**.

The radical polymer **1a**/carbon fiber composite electrode *via* photocrosslinking was prepared as follows: An ethyl lactate/toluene solution of the radical polymer **1a** (30 mg) and bisazide **3** (3 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 a solvent. The resulting black clay was spread onto an aluminum plate and dried in vacuo. The photocrosslinking was carried out by UV irradiation (5 J/cm^2).

The crosslinked copolymer **1c**/carbon composite electrode was prepared as follows: the crosslinked copolymer **1c** (30 mg) and 60 mg of a graphite fiber were mixed with 10 mg of a binder polymer in the presence of a solvent. The resulting black clay was spread onto a aluminum plate and dried in vacuo. A SEM image of **1c**/carbon composite electrode is shown in Fig. 5.

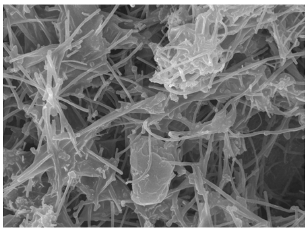

Figure 5. A SEM image of the **1c**/carbon nanofiber composite electrode.

Characterization of the radical concentration. The radical concentration 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 2,2,6,6-tetramethylpiperidinyl-*N*-oxy (TEMPO) solution. The spin 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.

Electrochemical measurements. The electrochemical measurements were performed using a conventional cell under an atmosphere of dry argon. A normal potentiostat system (BAS Inc. ALS660B) was used for the cyclic voltammetry, chronopotentiometry and other electrochemical methods. 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 Performance. A coin cell was fabricated by stacking the polymer/carbon composite cathode with a separator film and lithium metal as the anode. Ethylene carbonate/diethyl carbonate (1/1) solution of LiPF6 (1 M) was used as the electrolyte. The cyclability performance of the fabricated cell was tested by repeated charge-discharge galvanostatic cycles at different current densities. The cutoff potentials were 3.0 - 4.0 V vs. Li/Li+.

General. The 1H- and 13C NMR spectra were recorded using a JEOL Lambda 500 or Bruker AVANCE 600 spectrometer, and mass spectra were recorded on a JMS-SX102A or Shimazu GCMS-QP5050 spectrometer. Gel permeation chromatography was performed with chloroform or THF using 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. Scanning electron microscopy (SEM, Hitachi S2500CX) was used for observing the polymer/carbon fiber composite electrode.

References

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