Synthesis and Characterization of Radical-Bearing Polyethers as an Electrode-Active Material for Organic Secondary Batteries

Kenichi Oyaizu, Takeo Suga, Kentaro Yoshimura, and Hiroyuki Nishide*

Department of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan

Received November 20, 2007; Revised Manuscript Received June 21, 2008

ABSTRACT: In search of polymer backbones to bind organic radical pendant groups as redox centers for high-density charge storage application, polyether was employed as a flexible chain with a low glass transition temperature and affinity to electrolyte solutions. Cyclic ethers bearing nitroxide radicals were synthesized and polymerized via ring-opening polymerization utilizing various initiators. Polyethers bearing robust radical substituents such as 2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl and 2,2,5,5-tetramethyl-2,5-dihydro-1*H*-pyrrol-1-oxyl-3-yl groups with high density, i.e., per repeating unit with small equivalent weights, were prepared by the anionic polymerization of the corresponding epoxides. Cyclic voltammetry of the radical polyethers, obtained for polymer/carbon composites confined at an aluminum current collector, revealed large redox capacities comparable to the formula weight-based theoretical values, which was ascribed to the efficient swelling and yet insoluble properties of the polyethers in electrolyte solutions by virtue of their high molecular weights and adhesive properties to be held on electrode surfaces. The redox capacity also indicated that the ionophoric polyether matrix accommodated electrolyte anions to compensate positive charges produced by the oxidation of the neutral radicals at the polymer/electrode interface, allowing charge propagation deep into the polymer layer by a site-hopping mechanism. Test cells fabricated with the polymer/carbon composite as the cathode and a Li anode, sandwiching an electrolyte layer, performed as a secondary battery at output voltages near 3.6 V without substantial degradation even after 100 charging−discharging cycles.

Introduction

Theredox chemistry of polymers containing organic robust radical groups per repeating unit has been stimulated by our recent approach to the "radical battery",[1] which is characterized by an excellent rate performance and capability of fabricating purely organic, flexible, paper-like, and transparent rechargeable energy-storage devices.[2] While the radical polymers constituted an important and extensively studied group of functional materials, such as organic ferromagnets,[3] metal-free redox mediators for synthetic applications,[4] and electron and hole transport materials for organic devices,[5] the idea of using them as electrode-active materials for batteries had never been proposed prior to our recent investigation.[6] Indeed, electrochemically active polymers typically examined for batteries are conducting polymers, such as polyacetylene, polyaniline, polypyrrole, polythiophene, and polyphenylene.[7] Sulfur compounds and redox polymerization electrodes have also been reported as electroactive materials.[7a] However, the low doping levels in conducting polymers result in small theoretical capacity. Moreover, the charging/discharging processes have often been impeded by their inherent slow kinetics for the electrode reactions. Another group of molecules investigated for charge storage is a series of redox polymers with nonconjugated backbones and redox centers localized in pendant groups such as tetrathiafulvalene,[8] ferrocene,[9] and carbazole.[10] In this case, the redox centers, not the polymer backbone, govern the electrochemical behaviors. Conductivity arises when these centers exchange electrons, by way of hopping between the redox sites isolated in the polymer. However, the lack of long-term stability, due to the dissolution of polymer layers into electrolyte solutions and the concurrent decomposition during repeated redox reactions, has impeded extensive studies to use them as active materials for batteries.

Taking advantages of the rapid and electrochemically reversible 1e$^-$ redox properties, we have demonstrated that organic radicals, such as 2,2,6,6-tetramethylpiperidin-1-oxy (TEMPO), are potentially useful as the redox centers for charge-storage materials.[11] Our principal finding is that the radical polymer layers attached to electrode surfaces, when they are swollen in electrolyte solutions, exhibit substantial redox capacity, which indicates that the mass-transfer process for electrolyte ions is accomplished to compensate charges produced by the electrode reaction. Poly(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl methacrylate) (PTMA) has been the most typically employed as the cathode-active materials.[12] However, the charging/discharging capacity of the fabricated radical battery was comparable to the formula weight-based theoretical capacity only in the form of composite carbon electrodes, with relatively high composition of the carbon fiber up to 80 wt %. To maximize the redox capacity of the composite electrode by increasing the loaded amount of the radical polymers while retaining their redox activity is an important subject of the current research.

We anticipated that the redox capability might be enhanced with a flexible polyether backbone to allow propagation of charges deep into the polymer layer from the polymer/electrode interface. One could also expect that the adhesive polyether layers should stay on electrodes without dissolution into electrolyte solutions and that the ionophoric ether linkages would help electrolyte anions diffuse easily into the polymer layer,[13] accompanied by the oxidation of the neutral radical pendants to the oxoammonium cations. In this paper, we report the synthesis and polymerization behaviors of a series of epoxides and oxetanes bearing nitroxide radicals and the first attempt to employ the radical polyethers as electrode-active materials in batteries. The improved charging/discharging capacity of the fabricated test cell provided insights into the nature of the charge storage within the layers of the redox polyethers.

Experimental Section

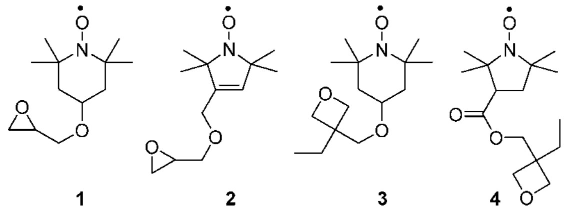
Materials. All solvents were purified by distillation prior to use. A vapor grown carbon fiber (VGCF) was obtained from Showa Denko Co. A binder powder, poly(vinylidene fluoride) (PVdF) resin (KF polymer), was purchased from Kureha Chemical Co. Tetrabu-

---

* Corresponding author: Tel +81-3-3200-2669; Fax +81-3-3209-5522; E-mail: nishide@waseda.jp.

10.1021/ma702576z CCC: $40.75

Chart 1. Cyclic Ethers Containing Nitroxide Radical Groups



1 2 3 4

tylammonium perchlorate (TBAClO$_4$) was obtained from Tokyo Kasei Co. and purified by recrystallization. An electrochemical grade solution of 1 M lithium hexafluorophosphate (LiPF$_6$) in ethylene carbonate/diethyl carbonate (1/1 in v/v) was obtained from Kishida Kagaku Co. All other regents were obtained from Kanto Chemical Co. or Tokyo Kasei Co. and were used without further purification.

Preparation of Cyclic Ether Monomers Containing Nitroxide Radicals. An epoxide **1** (Chart 1) was preprared by the S$_N$2 reaction of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxy (TEMPOL) with epichlorohydrin using a phase-transfer catalyst to avoid decomposition of the epoxide group under the strongly basic conditions. 3-Hydroxymethyl-2,2,5,5-tetramethyl-2,5-dihydro-1*H*-pyrrol-1-oxy was employed in place of TEMPOL to prepare **2**. An oxetane **3** was prepared by the condensation of TEMPOL and methanesulfonic acid 3-ethyloxetan-3-ylmethyl ester. 2,2,5,5-Tetramethylpyrrolidin-1-oxy (PROXYL) having a 3-carboxyl group was reacted with 3-ethyl-3-hydroxymethyloxetane to give **4**. The paramagnetic products were characterized by NMR spectroscopy after conversion to the corresponding diamagnetic *N*-hydroxypiperidine, *N*-hydroxy-2,5-dihydropyrrole, and *N*-hydroxypyrrolidine derivatives, using phenylhydrazine as a reducing agent.

2,2,6,6-Teramethyl-4-oxiranylmethoxypiperidin-1-oxy (1). The monomer **1** was prepared according to the previously reported method,[6b,14] with slight modifications using a phase-transfer agent as follows. To an aqueous solution of 50 wt % NaOH (4 mL) placed in a glass round-bottom flask were added epichlorohydrin (2.5 mL) and tetrabutylammonium hydrosulfate (0.84 g). The resulting mixture was stirred at room temperature by magnetic stirring. TEMPOL (1.03 g) was added to the mixture, which was kept stirring for a further 12 h. Then the mixture was added into ice water. The crude product was extracted with diethyl ether, which was washed with water and dried over anhydrous magnesium sulfate. After removing the solvent under vacuum, the residue was purified by silica gel column chromatography with a hexane/diethyl ether (1/1 in v/v) eluent and dried under vacuum at slightly reduced temperatures around 10 °C to give 2,2,6,6-teramethyl-4-oxiranylmethoxypiperidin-1-oxy or glycidyl 2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl ether (**1**) as a red powder. Yield: 84%. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm, after reduction with phenylhydrazine): δ 3.71(dd, $J = 3.0$ Hz, 1H), 3.64 (m, 1H), 3.40 (dd, $J = 5.8$ Hz, 1H), 3.11 (m, 1H), 2.77 (t, $J = 4.6$ Hz, 1H), 2.59 (dd, $J = 2.7$ Hz, 1H), 1.92 (m, 2H), 1.45 (q, $J = 12.2$ Hz, 2H), 1.19 (s, 6H), 1.14 (s, 6H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm, after reduction with phenylhydrazine): δ 71.1, 68.8, 58.9, 50.9, 44.5, 44.3, 32.0, 20.5. MS (*m*/*z*): Calcd for M$^+$ 228.3. Found: 228. IR (KBr, cm^{-1}): 1243 (ν, epoxide 8μ), 901 (ν, epoxide 11μ), 852 (ν, epoxide 12μ). Anal. Calcd for C$_{12}$H$_{22}$NO$_3$: C, 63.1; H, 9.7; N, 6.1%. Found: C, 62.9; H, 9.5; N. 6.2%. The monomer **1** melted at room temperature, which allowed the bulk polymerization (vide infra).

2,2,5,5-Tetramethyl-3-oxiranylmethoxymethyl-2,5-dihydro-1*H*-pyrrol-1-oxy (2). The monomer **2** was prepared in the same manner as **1** except TEMPOL was replaced by 3-hydroxymethyl-2,2,5,5-tetramethyl-2,5-dihydropyrrol-1-oxy. Yield: 80%. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm, after reduction with phenylhydrazine): δ 5.53 (s, 1H), 4.03 (s, 2H), 3.73 (dd, 1H), 3.39 (dd, 1H), 3.17 (m, 1H), 2.79 (m, 1H), 2.61 (m, 1H), 1.26 (s, 6H), 1.24 (s, 6H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm, after reduction with phenylhydrazine): δ 140.2, 130.7, 70.3, 69.5, 67.3, 67.1, 50.2, 43.7, 25.4, 24.2. MS (*m*/*z*): Calcd for M$^+$ 226.1. Found: 226. IR (KBr, cm^{-1}): 1253 (ν, epoxide 8μ), 903 (ν, epoxide 11μ), 842 (ν, epoxide 12μ).

4-(3-Ethyloxetan-3-ylmethoxy)-2,2,6,6-tetramethylpiperidin-1-oxy (3). To 3-ethyl-3-hydroxymethyloxetane (0.39 g) was added triethylamine (0.57 mL) and toluene (4.3 mL). After cooling the mixture to 0 °C under nitrogen, methanesulfonyl chloride (0.43 g) was slowly added. The resulting mixture was vigorously stirred at room temperature for 3 h. Removal of the solvent by rotary evaporation followed by purification by silica gel column chromatography gave methanesulfonic acid 3-ethyloxetan-3-ylmethyl ester (0.48 g). Yield: 85%. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 4.45 (q, 4H), 4.38 (s, 2H), 3.07 (s, 3H), 1.81 (q, 2H), 0.94 (t, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm): δ 77.2, 70.9, 42.9, 37.4, 26.2, 7.99. MS (*m*/*z*): Calcd for M$^+$ 194.1. Found: 193. To a solution of TEMPOL (0.86 g) in DMF (10 mL) was added NaH (0.25 g) under nitrogen. The resulting mixture was stirred at 50 °C for 1 h. Then, the sulfonic acid ester (0.97 g) was added to the mixture, which was kept stirring at 90 °C for 2 h. After cooling the mixture to room temperature, the solvent was removed by rotary evaporation. The crude product was extracted with diethyl ether and purified by silica gel column chromatography using diethyl ether/hexane (1/1 in v/v) as an eluent to give **3** (1.24 g). Yield: 92%. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm, after reduction with phenylhydrazine): δ 4.40 (s, 4H), 3.58 (m, 1H), 3.56 (s, 2H), 1.94 (d, 2H), 1.73 (q, 2H), 1.51 (d, 2H), 1.24 (s, 6H), 1.18 (s, 6H), 0.88 (t, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm, after reduction with phenylhydrazine): δ 78.6, 71.0, 70.9, 44.4, 43.4, 31.5, 26.7, 15.6, 8.21. MS (*m*/*z*): Calcd for M$^+$ 270.2. Found: 270.

2,2,5,5-Tetramethylpyrrolidin-1-oxyl-3-carboxylic Acid 3-Ethyloxetane-3-ylmethyl Ester (4). To a solution of 3-carboxy-2,2,5,5-tetramethylpyrrolidin-1-oxy (3.1 g) and 3-ethyl-3-hydroxymethyloxetane (1.94 g) in CH$_2$Cl$_2$ (94 mL) was added 2-chloro-1-methylpyridinium iodide (5.0 g), 4-(dimethylamino)pyridine (0.84 g), and triethylamine (5.0 g). The resulting solution was stirred for 12 h. Extraction of the crude product with CH$_2$Cl$_2$ followed by purification by silica gel column chromatography using ethyl acetate/hexane (1/1 in v/v) gave **4** as an orange liquid (3.65 g). Yield: 77%. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm, after reduction with phenylhydrazine): δ 4.46 (s, 2H), 4.42 (s, 2H), 4.24 (s, 2H), 2.82 (m, 1H), 2.16 (m, 1H), 1.80 (m, 1H), 1.77 (q, 2H), 1.35 (s, 3H), 1.25 (s, 3H), 1.19 (s, 3H), 1.06 (s, 3H), 0.91 (t, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm, after reduction with phenylhydrazine): δ 172.6, 77.9, 77.8, 66.5, 66.0, 49.0, 42.4, 37.6, 27.7, 27.1, 26.8, 26.4, 19.5, 8.02. MS (*m*/*z*): Calcd for M$^+$ 284.4. Found: 284. IR (KBr, cm^{-1}): 1737 ($\nu_{C=O}$), 983 (ν_{C-O}).

Anionic Ring-Opening Polymerization of 1. To a solution of the monomer **1** (0.23 g, 1 mmol) in THF (1 mL) was added 5 mol % potassium *tert*-butoxide (*t*-BuOK) under argon. The mixture was stirred at 60 °C for 24 h. The resulting viscous mixture was dissolved in CHCl$_3$ and slowly poured into diethyl ether. The precipitate was collected by filtration, dissolved again in CHCl$_3$, and purified by reprecipitation from diethyl ether and dried under vacuum at room temperature to yield **5** as an orange powder. Yield: 43 wt % (entry 2 in Table 1). ^{1}H NMR (DMSO-*d*$_6$, 500 MHz, ppm, after reduction with phenylhydrazine): δ 4.00 (b, 1H), 3.75 (m, 1H), 3.61 (b, 3H), 1.94 (b, 2H), 1.33 (b, 2H), 1.18 (s, 6H), 1.14 (s, 6H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz, ppm, after reduction with phenylhydrazine): δ 79.2, 70.6, 69.5, 67.8, 57.8, 44.6, 32.4, 20.7. IR (KBr, cm^{-1}): 1040 (ν_{C-O-C}). Anal. Calcd for C$_{12}$H$_{22}$NO$_3$: C, 63.1; H, 9.7; N, 6.1%. Found: C, 62.8; H, 9.5; N. 6.2%. Bulk polymerization of **1** (i.e., in the absence of the solvent) with *t*-BuOK resulted in gelation after 1 h. Washing the product thoroughly with CHCl$_3$ and THF and drying for a sufficiently long time under vacuum at room temperature afforded the polymer **5** with a higher molecular weight based on GPC in a higher yield (entry 5 in Table 1). Determination of the molecular weight by end-group analysis using ^{1}H NMR was unsuccessful, as a result of peak broadening due probably to the presence of a substantial amount of a head-to-head structure in the polyether chain.

Anionic Coordinated Ring-Opening Polymerization of 1. A 1 M hexane solution of diethylzinc (2.0 mL) was cooled to

Table 1. Ring-Opening Polymerization of Nitroxide-Substituted Cyclic Ethers

entry	monomer	initiator[a]	solvent	monomer conc (M)	*T* (°C)	time (h)	yield (wt %)	M_n[b] ($\times 10^4$)	M_w/M_n
1	**1**	*t*-BuOK	THF	1.0	60	12	22	0.31	1.3
2	**1**	*t*-BuOK	THF	1.0	60	24	43	0.32	1.3
3	**1**	*t*-BuOK	THF	2.0	60	12	35	0.3	1.3
4	**1**	*t*-BuOK	THF	2.0	60	24	57	0.36	1.4
5	**1**	*t*-BuOK		bulk	60	24	88	3.2[c]	1.7
6	**1**	$ZnEt_2/H_2O$		bulk	r.t.	24	62	2.5	2.1
7	**2**	*t*-BuOK		bulk	60	24	84	0.54	1.3
8	**2**	$ZnEt_2/H_2O$		bulk	r.t.	24	62	40[c]	1.7
9	**3** or **4**	*t*-BuOK		bulk	60	24	0		
10	**3** or **4**	BF_3Et_2O	$CHCl_3$	1.0	r.t.	24	0		
11	**3** or **4**	$AlEt_3/H_2O$/acac		bulk	60	36	0		
12	**3** or **4**	$AlEt_3/H_2O$		bulk	r.t.	36	0		

[a] 5 mol %. [b] Molecular weights were determined by GPC with polystyrene standards. The elution curves were obtained using a UV detector set at 254 nm and/or a refractive index detector using $CHCl_3$ as an eluent. [c] Soluble part in $CHCl_3$ (ca. 60−70 wt % of the product).

−78 °C, to which was added H_2O (36 μL) under argon. The mixture was slowly heated to room temperature and stirred for 1.5 h to give the yellow solution of the $ZnEt_2/H_2O$ initiator. To the monomer **1** was added the initiator (10 mol %) under strictly anaerobic conditions. The reaction mixture was stirred at room temperature for 24 h. The resulting mixture was slowly poured into diethyl ether. The precipitate was collected by filtration, purified by Soxhlet extraction, and dried under vacuum to yield **5** as an orange powder. Yield: 62 wt % (entry 6 in Table 1). The obtained polymer was insoluble in common organic solvents.

Anionic Coordinated Ring-Opening Polymerization of 2. The monomer **2** was polymerized with the $ZnEt_2/H_2O$ initiator in the same manner as **1**. The corresponding high-molecular-weight polymer **6** was obtained as an orange solid. Yield: 62 wt % (entry 8 in Table 1). ^{1}H NMR (DMSO-*d*$_6$, 500 MHz, ppm): δ 5.54 (s, 1H), 3.99 (s, 3H), 3.46 (s, 4H), 1.16 (s, 12H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz, ppm): δ 141.4, 130.4, 78.3, 70.0, 69.5, 68.4, 66.2, 25.8, 24.6. IR (KBr, cm^{-1}): 1040 (ν_{C-O-C}).

Polymerization Conditions Examined for 3 and 4. The oxetanes **3** and **4** were examined as monomers for the ring-opening polymerization under bulk conditions with 5 mol % initiators for anionic (*t*-BuOK), cationic ($AlEt_3/H_2O$), and anionic coordinated ($AlEt_3/H_2O$/acac) polymerization and under solution conditions (1 M in $CHCl_3$) with a cationic initiator (BF_3Et_2O) (entries 9−12 in Table 1). See Results and Discussion for details.

Determination of the Radical Content. The radical polymer **5** was characterized by the *g* value (2.0065) of the ESR signal, which was in agreement with that of TEMPO. The radical concentrations were determined, assuming that the polymers were paramagnetic at room temperature, by comparing the integrated ESR intensity with that of the solution of TEMPO as the standard. The radical concentration was also determined by means of SQUID measurements using the Curie plots and the values for saturated magnetization (Figure S1). The two independently determined values agreed well with each other.

Electrode Preparation. The polymer **5** (30 mg) was mixed with VGCF (60 mg) and PVdF (10 mg) in NMP. The mixture was pasted on the aluminum foil and dried under vacuum at 80 °C for 12 h to give the composite electrode with a composition of **5**/VGCF/PVdF = 3/6/1 (w/w/w). The composite electrodes with a series of the loading amounts of the radical polymers (1/8/1 to 3/6/1) were prepared for **5** and **6**.

Electrochemical Measurements. Electrochemical analyses were carried out in a conventional cell under argon. The auxiliary electrode was a coiled platinum wire. The reference electrode was a commercial Ag/AgCl immersed in a solution of 0.1 M $TBAClO_4$ in CH_3CN. The formal potential of the ferrocene/ferrocenium couple was 0.45 V vs this Ag/AgCl electrode. An ALS 660B electrochemical analyzer was employed to obtain the voltammograms.

Fabrication and Characterization of Test Cells. A coin cell was fabricated by sandwiching the electrolyte layer of 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (1/1 in v/v) with the polymer/carbon composite cathode and the Li anode, using the separator film (cell guard #2400 from Hohsen Co.) under strictly anaerobic conditions. The cyclic performance of the fabricated cell was examined by repeated charging−discharging galvanostatic cycles at different current densities. The charging−discharging experiments were typically performed at a current density of 10 C, where 1 C represents the current density required for charging or discharging of the cell at 1 h.

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA500 or Bruker AVANCE 600 spectrometer with chemical shifts downfield from tetramethylsilane as the internal standard. Infrared spectra were obtained using a Jasco FT-IR 410 spectrometer with potassium bromide pellets. Molecular weight measurements were done by gel permeation chromatography using a TOSOH HLC8220 instrument with $CHCl_3$ or THF as the eluent. Calibration was done with polystyrene standards. Elemental analyses were performed using a Perkin-Elmer PE-2400 II and a Metrohm 645 multi-DOSIMAT. Two parallel analyses were performed for each sample. Mass spectra were obtained using a JMS-SX102A or Shimadzu GCMS-QP5050 spectrometer. ESR spectra were recorded using a JEOL JES-TE200 spectrometer with a 100 kHz field modulation frequency and a 0.1 mT width. The magnetization and the magnetic susceptibility of the powdery polymer samples were measured by a Quantum Design MPMS-7 SQUID magnetometer. The magnetic susceptibility was measured from 1.95 to 270 K in a 0.5 T field. Thermal analyses were performed by a Seiko DSC220C and TG/DTA 220 thermal analyzer under nitrogen.

Results and Discussion

Synthesis. Epichlorohydrin readily reacts with phenols to produce glycidyl ethers. However, the reaction with alcohols requires strongly basic conditions, which gives rise to the concurrent ring-opening of the epoxide unit.[14] To avoid the side reaction, the monomers **1** and **2** were prepared by employing tetrabutylammonium hydrosulfate as the phase transfer catalyst. A significant increase in the product yield was achieved compared to the previously reported low yields (ca. 70%) for the coupling reaction.[14] The TEMPO and PROXYL groups were conveniently bound to the less reactive oxetane unit through the ether (**3**) and the ester (**4**) linkages, respectively. Reduction of the paramagnetic nitroxides with phenylhydrazine to the corresponding diamagnetic hydroxylamines proceeded to completion, which demonstrated the utility of the reaction to characterize the radical polymers by NMR spectroscopy.

The anionic ring-opening polymerization of the monomer **1** using *t*-BuOK as an initiator in THF proceeded slowly, which required 24 h to yield the polymer **5** in moderate yields[14] (entries 1−4 in Table 1). The corresponding polymer **6** was similarly obtained from **2**. The products were soluble in $CHCl_3$ and THF but partially insoluble in CH_3CN. Unpaired electron density of the polymers, determined by SQUID and ESR measurements, revealed the presence of the radicals substantially per repeating unit. However, the solubility of the products in organic solvents was undesirable for use as electrode-active materials that should be positioned on the surface of the electrodes in batteries.

Even more difficulties were found for the polymerization of the radical-substituted oxetanes **3** and **4**. A number of oxetanes, less susceptible to ring-opening polymerization than the epoxide analogues due to the smaller ring-distortion energies, required heating up to 180 °C for the anionic ring-opening polymerization.[15] However, such conditions were incompatible with the monomers **3** and **4** because of the thermal decomposition of the radical groups at elevated temperatures. Indeed, functionalized polyethers from oxetanes bearing reactive pendant groups have been obtained by a cationic mechanism, typically using a BF_3 etherate as the initiator.[16] Attempts to polymerize **3** or **4** with the Lewis acidic BF_3 or other cationic initiators were unsuccessful, resulting from the undesired oxidation of the radical pendants. Initiators reported for anionic coordinated ring-opening polymerization, such as aluminum complexes,[17] were not effective for the polymerization of **3** and **4** (entry 11), which reacted with the radical groups to undergo decomposition.

Reasoning that polymerization of oxetanes might be limited by the radical substituents, we turned to focus on the polymerization of the epoxides **1** and **2** to obtain higher-molecular-weight products. We found that the polymerization of **1** under bulk conditions yielded the polymer **5** in a much higher yield (entry 5). The product was partially soluble in $CHCl_3$ and insoluble in other organic solvents but swollen in THF and the electrolyte solution employed for the electrochemical measurements. The swelling but insoluble property of the polymer, desirable for electrode fabrication, was likely to be ascribed to the high molecular weight up to 3×10^4, which was suggested from the GPC analysis for the chloroform-soluble fraction of the product. Magnetic measurements revealed that most of the unpaired electrons were persisted during the polymerization, which amounted to 0.82 spins per repeating unit. NMR spectra obtained after conversion to the corresponding hydroxylamine revealed the absence of noticeable defects in the polymer. The structure-defined and high-molecular-weight radical polyether **5** was thus obtained for the first time.

On the other hand, anionic coordinated ring-opening polymerization of **1** initiated with the $ZnEt_2/H_2O$ catalyst under the bulk conditions resulted in the decrease in the radical concentration down to 0.62 spins per repeating unit, although a high-molecular-weight product was ontained (entry 6). The anionic coordinated process was rather suitable for the polymerization of **2** (entry 8), which yielded the corresponding polymer **6** with a molecular weight of more than 4×10^5 and an unpaired electron density of 1.0 spin/repeating unit (i.e., 2.66×10^{21} spin/g) (Figure S1). The radical contents in the products are indicative of the even more robust nature of the 2,2,5,5-tetramethyl-2,5-dihydro-1*H*-pyrrol-1-oxy group than the TEMPO group. The product **6** was observed to swell but insoluble in organic solvents, probably due to the higher molecular weight, which was indeed quite favorable for battery applications to impede self-discharge accompanied by the dissolution into electrolyte solutions.

Thermal analysis revealed that the decomposition of **5** was initiated at temperatures higher than 150 °C and became significant around 200 °C (Figure 1a), and yet 90 wt % of the polymer remained up to 260 °C. The thermal stability against 10% weight loss was comparable to that of PTMA which showed the temperature for 10% weight loss at $T_{d10\%} = 263$ °C.[6a] The slow decomposition initiated near 120 °C is characteristic of the polyether backbone and could be ascribed to the hydrogen abstraction adjacent to the polyether oxygen atom by the nitroxide radical. The radical groups on the polyether backbone were stable at least at temperatures below 100 °C without substantial decomposition until the thermolysis was initiated, which was confirmed by monitoring the radical concentration after the thermal treatment at 100 °C. The radical polyethers were characterized by their low glass transition temperatures, as typically shown for **5** ($T_g = 18$ °C) in Figure 1b. The increased flexibility, compared with PTMA ($T_g = 71$ °C), suggested a good molding capability and higher compatibility of the radical polyethers with the current collector and the electrolyte solution in batteries. Indeed, **5** showed the lowest T_g among the radical polymers with various backbones reported so far, such as poly(meth)acrylates,[6a] polystyrenes,[1] and polynorbornenes.[2a] However, characterization of the glass transition from mechanical properties was impeded by the difficulty in preparing a free-standing film by a solution-casting method. The radical concentrations of **5** and **6** were persistent for more than 3 months under ambient conditions, which demonstrated the robust nature of the pendant nitroxide groups.

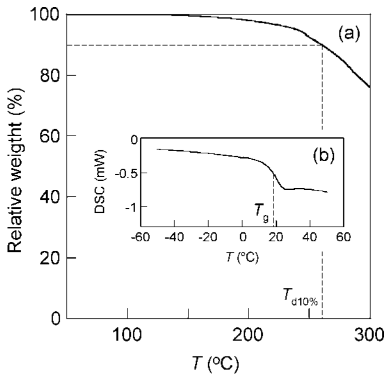


Figure 1. TG (a) and DSC (b) thermograms for **5**. The temperature was elevated at a rate of 10 °C/min.

The absence of substantial electric conductivity for **5** and **6** led us to examine their electrochemical analysis as a composite layer with a graphite fiber (VGCF) and a binder (PVdF). The polymer was coated on the surface of the carbon fiber by sufficient grinding of the mixture in NMP, which was supported by a SEM observation (Figure S2). The composite layer was placed on the surface of an electrode or a current collector by a solution-based wet process and immersed into the electrolyte solution for electrochemical measurements. The electrolytes were conventional tetrabutylammonium and lithium salts, dissolved in organic solvents such as CH_3CN and ethylene carbonate/diethyl carbonate. Cyclic voltammogram obtained for a carbon-rich composite layer, typically recorded for **5** with a composition of **5**/VGCF/PVdF = 1/8/1 (w/w/w), revealed an electrochemically reversible redox wave at $(E_{pa} + E_{pc})/2 = 0.71$ V vs Ag/AgCl, where E_{pa} and E_{pc} were the oxidation and the reduction peak potentials, respectively. The redox potential was in good agreement with that of TEMPO.[11b] The redox capacity determined by the integration of the voltammogram was more than 80% of the formula weight-based theoretical capacity (117 mAh/g), indicating that almost all of the TEMPO groups in the composite layer underwent the redox reaction according to

$$\rangle N{-}O^{\bullet} \rightleftharpoons \rangle N^{+}{=}O + e^{-} \tag{1}$$

where $\rangle N{-}O^{\bullet}$ and $\rangle N^{+}{=}O$ represent the nitroxide radical and the oxoammonium cation, respectively. Additional support for reaction 1 was provided by electrolytic in situ ESR spectroscopy, which revealed the disappearance of the ESR signal of the paramagnetic nitroxide radical accompanied by the electrolytic oxidation near 0.7 V. The symmetric voltammogram in Figure 2, characterized by a small peak-to-peak separation ($\Delta E_p = E_{pa} - E_{pc} = 0.038$ V) and the absence of the diffusion tail, indicated the fast electrode kinetics for the redox reaction of the TEMPO groups. Similar electrochemical behaviors were also observed for the **6**/carbon composite layer on the electrode at $(E_{pa} + E_{pc})/2 = 0.82$ V vs Ag/AgCl, which was ascribed to the reversible

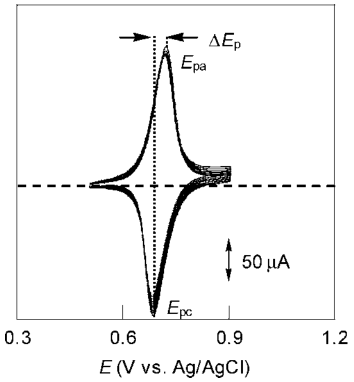


Figure 2. Cyclic voltammogram for the **5**/carbon composite layer (**5**/VGCF/PVdF = 1/8/1 in w/w/w) on an aluminum foil (current collector) immersed in CH_3CN containing 0.1 M $TBAClO_4$. The electrode potential was scanned at a rate of 5 mV/s for 10 cycles. A platinum wire and Ag/AgCl were used as the auxiliary and reference electrode, respectively.

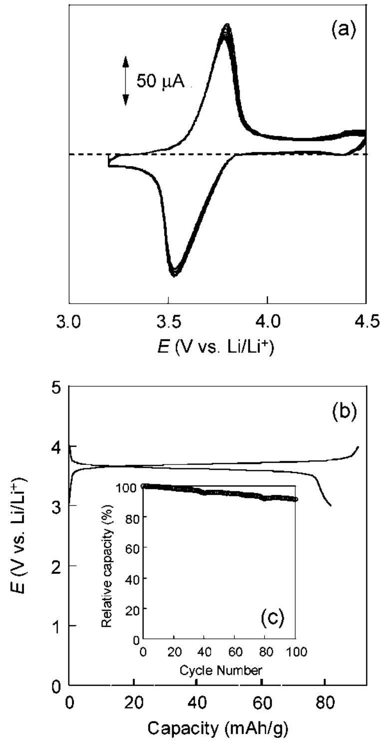


Figure 3. (a) Cyclic voltammogram for a coin cell fabricated with the **6**/carbon composite cathode (**6**/VGCF/PVdF = 1/8/1 (w/w/w) prepared on an aluminum foil) and the Li anode sandwiching an electrolye layer (ethylene carbonate/diethyl carbonate = 1/1 in v/v containing 1 M $LiPF_6$). The two electrodes were separated with a separator film. The electrode potential was scanned at a rate of 1 mV/s versus the Li anode. (b) Charging/discharging curves for the coin cell at a current density of 10 C. (c) Cycle performance of the cell.

$1e^-$ oxidation of the pendant 2,2,5,5-tetramethyl-2,5-dihydro-1*H*-pyrrol-1-oxyl-3-yl group in the polymer according to reaction 1.

A test cell was fabricated by sandwiching an electrolyte layer with the polymer/carbon composite layer and a Li foil using a separator film (see Experimental Section for details). Cyclic voltammetry recorded for the polymer/carbon cathode in the cell, with the electrode potential scanned versus the Li anode, showed a reversible response as typically shown for the **6**/carbon composite electrode in Figure 3a. The redox potential of $(E_{pa} + E_{pc})/2 = 3.66$ V roughly corresponded to the potential gap between those for **6** and $Li^{0/+}$. The charging/discharging curves obtained for the fabricated cell at a constant current of 0.1 mA were characterized by the presence of a plateau voltage near 3.63 V (Figure 3b), which was equal to the redox potential of **6** versus Li/Li^+ (Figure 3a). The charging process corresponded to the oxidation of the nitroxide radical according to reaction 1 at the cathode and the reduction of Li^+ to metallic Li at the anode. The cycle performance during the repeated charging−discharging process recorded with cutoff voltages at 3.0 and 4.0 V was free from significant deterioration in the charge-storage capacity even after 100 cycles (Figure 3c). The test cell prepared similarly with the **5**/carbon composite cathode showed a plateau voltage near 3.52 V and a good cycle performance for more than 500 charging−discharging cycles.

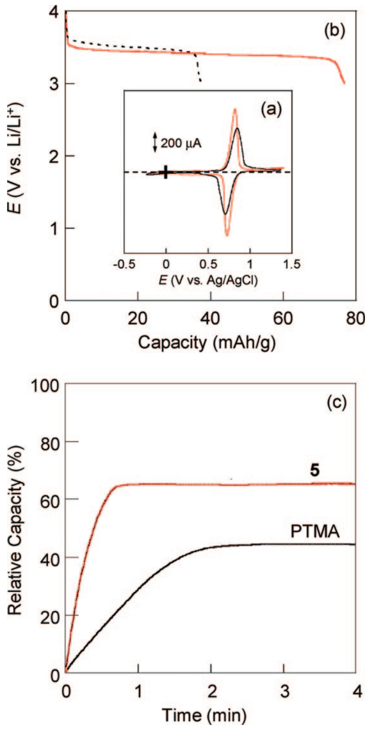
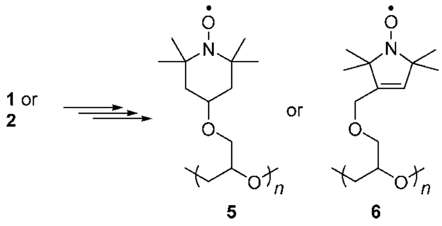


Figure 4. (a) Cyclic voltammograms for **5**/carbon (red curve) and PTMA/carbon (black curve) composite layers prepared on the aluminum current collector with a same composition of polymer/VGCF/PVdF at 3/6/1 (w/w/w). The electrolyte solution contained 0.1 M $TBAClO_4$ in CH_3CN. Potential scan rate = 1 mV/s. A platinum wire and Ag/AgCl were used as the auxiliary and reference electrode, respectively. (b) Discharging curves for the test cell fabricated with the **5**/carbon (red curve) and the PTMA/carbon (black curve) composite layers on the aluminum foil as the cathode. Current density = 10 C. Other configuration of the cell was as those in Figure 3. (c) Chronocoulometric response for the discharging process of the **5**/carbon (red curve) and the PTMA/carbon (black curve) composite electrodes set at a constant potential of 0.2 V vs Ag/AgCl. Relative capacity was defined as the amount of charges versus the theoretical capacity. The electrolyte conditions and the electrode configuration were as those in (a).

A striking feature of the radical polyethers is the capability of increasing the composition of the polymers in the carbon composite while maintaining their redox activity, which leads to the substantial increase in the charge-storage density of the composite layer. Figure 4 demonstrates the advantage of using **5** over PTMA in terms of redox capacity for a composite layer with an increased composition of the polymer up to 30 wt %. The redox capacity for PTMA in the composite layer, determined by the integration of the cyclic voltammmogram (Figure 4a) and coulometric titration experiments carried out in the electrolyte solution of CH_3CN, was only 40% of the theoretical capacity, while 60% of the theoretical capacity was accomplished for **5** under the same conditions. The larger substantial capacity for **5** was reflected in the charging/

Scheme 1. Polymerization of Cyclic Ethers Carrying Nitroxide Radical Groups



discharging capacity of the test cell fabricated with the polymer-rich composite cathode. The discharging curve of the test cell using **5** amounted to ca. 70% of the theoretical capacity, while only 35% of the capacity was obtained for the cell with the PTMA/carbon cathode (Figure 4b). Chronocoulometric responses obtained for the composite layer after charging, maintained at a constant potential to allow discharging, also revealed a higher relative capacity of 65% for **5** than that for PTMA (40%), which provided additional support for the higher redox activity of **5** in the composite layer (Figure 4c).

One could anticipate that the redox process of the polymer membrane is accompanied by an injection and a rejection of solvated counterions that compensate the charges produced by the redox reaction. Preliminary electrochemical quartz-crystal microbalance experiments suggested that the amount of ions incorporated into the polymer membrane was in agreement with the redox capacity determined by coulometric measurements. The flexible and ionophoric polyether backbone, allowing rapid electrode reaction of the radicals and the efficient charge propagation within the polymer membrane, led to an efficient charging−discharging characteristics, allowing large discharging currents without substantial loss of output voltages.

Our efforts have been directed toward further increasing the theoretical redox capacity of the radical polymer. For this purpose, radical polymers with even smaller formula weights per repeating unit and thus a higher radical density, in addition to the compatibility to electrolyte solutions, are designed for an efficient charge propagation process within the polymer layer by a site-hopping mechanism. Further characterization of the polyether backbone by thermomechanical analysis is underway, searching for polymerization conditions to yield much higher molecular-weight products. Optimization of the radical center and the polymer backbone, as well as the battery structure for the organic materials, are the topics of our continuous research.

Conclusion

The anionic ring-opening polymerization of epoxides carrying nitroxide groups under bulk conditions yielded the corresponding radical polyethers, which were insoluble and yet swollen in electrolyte solutions by virture of their high molecular weights. The radical polyethers proved to be a new class of redox polymers, which were characterized by the high-density charge storage capability. The ionophoric polyether backbone with a low glass transition temperature allowed efficient swelling in conventional electrolyte solutions which enabled efficient charge propagation and storage within the polymer layer. The use of radical polymers as electroactive materials led to the fabrication of organic-based rechargeable devices, with an excellent charging−discharging properties. In particular, the cycle performance of the fabricated device persisted for hundreds to thousands cycles without degradation, which revealed the repeatability of the redox process of the nitroxide centers in the polymers.

Acknowledgment. This work was partially supported by Grants-in-Aid for Scientific Research (Nos. 19105003, 19655043, and 19022035), the Global COE Program from MEXT, Japan, and the NEDO Project on "Radical Battery for Ubiquitous Power". We thank Dr. Shigeyuki Iwasa and Dr. Kentaro Nakahara of NEC Co. for technical discussions.

Supporting Information Available: Curie and χT vs T plots for the radical polymer **6** (entry 8), the SEM image of the **5**/carbon composite layer with a composition of **5**/VGCF/PVdF = 1/8/1 in w/w/w, and a typical GPC elution curve for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Nishide, H.; Oyaizu, K. *Science* **2008**, *319*, 737–738. (b) Nishide, H.; Suga, T. *Electrochem. Soc. Interface* **2005**, *14*, 32–36.

(2) (a) Suga, T.; Konishi, H.; Nishide, H. *Chem. Commun.* **2007**, 1730–1732. (b) Suga, T.; Pu, Y.-J.; Kasatori, S.; Nishide, H. *Macromolecules* **2007**, *40*, 3167–3173.

(3) (a) Murata, H.; Miyajima, D.; Nishide, H. *Macromolecules* **2006**, *39*, 6331–6335. (b) Fukuzaki, E.; Nishide, H. *J. Am. Chem. Soc.* **2006**, *128*, 996–1001. (c) Fukuzaki, E.; Nishide, H. *Org. Lett.* **2006**, *8*, 1835–1838. (d) Kaneko, T.; Makino, T.; Miyaji, H.; Teraguchi, M.; Aoki, T.; Miyasaka, M.; Nishide, H. *J. Am. Chem. Soc.* **2003**, *125*, 3554–3557. (e) Nishide, H.; Ozawa, T.; Miyasaka, H.; Tsuchida, E. *J. Am. Chem. Soc.* **2001**, *123*, 5942–5946.

(4) (a) Knoop, C. A.; Studer, A. *J. Am. Chem. Soc.* **2003**, *125*, 16327–16333. (b) Georges, M. K.; Lukkarila, J. L.; Szkurhan, A. R. *Macromolecules* **2004**, *37*, 1297–1303. (c) Dijksman, A.; Marino-Gonzalez, A.; Mairata i Payeras, A.; Arends, I. W. C. E.; Sheldon, R. A. *J. Am. Chem. Soc.* **2001**, *123*, 6826–6833. (d) Cameron, N. R.; Reid, A. J. *Macromolecules* **2002**, *35*, 9890–9895. (e) Huang, W.; Chiarelli, R.; Charleux, B.; Rassat, A.; Vairon, J.-P. *Macromolecules* **2002**, *35*, 2305–2317.

(5) (a) Yonekuta, Y.; Susuki, K.; Oyaizu, K.; Honda, K.; Nishide, H. *J. Am. Chem. Soc.* **2007**, *129*, 14128–14129. (b) Pu, Y.-J.; Soma, M.; Kido, J.; Nishide, H. *Chem. Mater.* **2001**, *13*, 3817–3819.

(6) (a) Nishide, H.; Iwasa, S.; Pu, Y.-J.; Suga, T.; Nakahara, K.; Satoh, M. *Electrochim. Acta* **2004**, *50*, 827–831. (b) Suga, T.; Yoshimura, K.; Nishide, H. *Macromol. Symp.* **2006**, *245−246*, 416–422. (c) Nakahara, K.; Iwasa, S.; Satoh, M.; Morioka, Y.; Iriyama, J.; Suguro, M.; Hasegawa, E. *Chem. Phys. Lett.* **2002**, *359*, 351–354. (d) Qu, J.; Katsumata, T.; Satoh, M.; Wada, J.; Igarashi, J.; Mizoguchi, K.; Masuda, T. *Chem.−Eur. J.* **2007**, *13*, 7965–7973. (e) Katsumata, T.; Satoh, M.; Wada, J.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Makromol. Rapid Commun.* **2006**, *27*, 1206–1211. (f) Takahashi, Y.; Oyaizu, K.; Honda, K.; Nishide, H. *J. Photopolym. Sci. Technol.* **2007**, *20*, 29–34.

(7) (a) Novák, P.; Müller, K.; Santhanam, K. S. V.; Haas, O. *Chem. Rev.* **1997**, *97*, 207–281. (b) Coppo, P.; Turner, M. L. *J. Mater. Chem.* **2005**, *15*, 1123–1133. (c) Roncali, J.; Blanchard, P.; Frère, P. *J. Mater. Chem.* **2005**, *15*, 1589–1610. (d) Roncali, J. *J. Mater. Chem.* **1997**, *7*, 2307–2321. (e) Roncali, J. *Chem. Rev.* **1997**, *97*, 173–205. (f) Oyaizu, K.; Iwasaki, T.; Tsukahara, Y.; Tsuchida, E. *Macromolecules* **2004**, *37*, 1257–1270. (g) Oyaizu, K.; Mikami, T.; Tsuchida, E. *Macromolecules* **2004**, *37*, 2325–2327.

(8) Kaufman, F. B.; Schroeder, A. H.; Engler, E. M.; Kramer, S. R.; Chambers, J. Q. *J. Am. Chem. Soc.* **1980**, *102*, 483–488.

(9) (a) Iwakura, C.; Kawai, T.; Nojima, M.; Yoneyama, H. *J. Electrochem. Soc.* **1987**, *134*, 791–795. (b) Hunter, T. B.; Tyler, P. S.; Smyrl, W. H.; White, H. S. *J. Electrochem. Soc.* **1987**, *134*, 2198–2204.

(10) (a) Compton, R. G.; Davis, F. J.; Grant, S. C. *J. Appl. Electrochem.* **1986**, *16*, 239–249. (b) Skompska, M.; Peter, L. M. *J. Electroanal. Chem.* **1995**, *383*, 43–52.

(11) (a) Suga, T.; Pu, Y.-J.; Oyaizu, K.; Nishide, H. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 2203–2204. (b) Yonekuta, Y.; Oyaizu, K.; Nishide, H. *Chem. Lett.* **2007**, *36*, 866–867. (c) Nakahara, K.; Iwasa, S.; Iriyama, J.; Morioka, Y.; Suguro, M.; Satoh, M.; Cairns, E. J. *Electrochim. Acta* **2006**, *52*, 921–927.

(12) (a) Bugnon, L.; Morton, C. J. H.; Novak, P.; Vetter, J.; Nesvadba, P. *Chem. Mater.* **2007**, *19*, 2910–2914. (b) Kim, J.-K.; Cheruvally, G.; Choi, J. W.; Ahn, J.-H.; Choi, D. S.; Song, C. E. *J. Electrochem. Soc.* **2007**, *154*, A839−A843. (c) Nakahara, K.; Iriyama, J.; Iwasa, S.; Suguro, M.; Satoh, M.; Cairns, E. J. *J. Power Sources* **2007**, *163*, 1110–1113. (d) Nakahara, K.; Iriyama, J.; Iwasa, S.; Suguro, M.; Satoh, M.; Cairns, E. J. *J. Power Sources* **2007**, *165*, 398–402. (e) Nakahara, K.; Iriyama, J.; Iwasa, S.; Suguro, M.; Satoh, M.; Cairns, E. J. *J. Power Sources* **2007**, *165*, 870–873.

(13) Yoshizawa, M.; Ohno, H. *Chem. Lett.* **1999**, 889–890.

(14) Endo, T.; Takuma, K.; Takata, T.; Hirose, C. *Macromolecules* **1993**, *26*, 3227–3229.

(15) (a) Kudo, H.; Nishikubo, T. *J. Polym. Sci., Polym. Chem. Ed.* **2007**, *45*, 709–726. (b) Morita, A.; Kudo, H.; Nishikubo, T. *J. Polym. Sci., Polym. Chem. Ed.* **2004**, *42*, 3739–3750.

(16) (a) Makal, U.; Uilk, J.; Kurt, P.; Cooke, R. S.; Wynne, K. J. *Polymer* **2005**, *46*, 2522–2530. (b) Bulut, U.; Crivello, J. V. *J. Polym. Sci., Polym. Chem. Ed.* **2005**, *43*, 3205–3220. (c) Nagai, D.; Nishida, M.; Ochiai, B.; Miyazaki, K.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **2006**, *44*, 3233–3241. (d) Bouchékif, H.; Philbin, M. I.; Colclough, E.; Amass, A. J. *Chem. Commun.* **2005**, 3870–3872. (e) Lin, Y.; Zeng-Guo, F.; Yu-Mei, Z.; Feng, W.; Shi, C.; Guo-Qing, W. *J. Polym. Sci., Polym. Chem. Ed.* **2006**, *44*, 3650–3665. (f) Biedroń, T.; Bednarek, M.; Kubisa, P. *Macromol. Rapid Commun.* **2004**, *25*, 878–881. (g) Xu, Y.; Gao, C.; Kong, H.; Yan, D.; Jin, Y. Z.; Watts, P. C. P. *Macromolecules* **2004**, *37*, 8846–8853. (h) Lin, Y.; Peng, G.; Feng, W.; Ying, B.; Zeng-Guo, F. *Polymer* **2007**, *48*, 1550–1556.

(17) Kanoh, S.; Takemura, A.; Fukuda, K.; Chinwanitcharoen, C.; Motoi, M. *J. Polym. Sci., Polym. Chem. Ed.* **2004**, *42*, 4570–4579.

MA702576Z