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Synthesis, Characterization, and Charge/Discharge Properties of Polynorbornenes Carrying 2,2,6,6-Tetramethylpiperidine-1-oxy Radicals at High Density

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ABSTRACT: TEMPO-containing norbornene monomers **1**−**8** (TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxy) were synthesized and polymerized via ring-opening metathesis using a ruthenium−carbene catalyst. The TEMPO moiety did not inhibit the polymerization, and the monomers gave corresponding polymers in good to high yields. Poly(**2**) and poly(**3**) were soluble in common solvents and possessed high molecular weight, while other polymers were insoluble. The resulting polymers were thermally stable up to ca. 240 °C according to TGA measurements in air. In the case of poly(**1**)−poly(**3**), the charge/discharge capacities of the polymer-based cells were largely dependent on the spatial arrangement of the two TEMPO moieties on each repeating unit. Quite interestingly, the capacity of the poly(**2**)-based cell reached its theoretical value (109 A h/kg), and a large capacity (>90 A h/kg) was retained even at high current densities up to 6 A/g, indicating the possibility of very fast charging (within 1 min). The cells utilizing the present polymers as cathode-active materials demonstrated excellent cycle life; e.g., the discharge capacities of poly(**2**) and poly(**3**) showed no more than 10% decrement even after 400 cycles.

Introduction

The olefin metathesis reaction has emerged as a powerful technique for the redistribution of carbon−carbon double bonds, thus offering a variety of excellent methodologies for the synthesis of organic molecules and novel polymers. In the field of polymer synthesis, ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) polycondensation are frequently employed to synthesize a wide range of functionalized polymers.[1] In particular, the recent development of ruthenium-based olefin metathesis catalysts has enabled the polymerization of various cycloolefin monomers possessing ether, ester, amide, alcohol, and carboxylic acid moieties owing to their excellent tolerance toward polar functional groups and the use of polar and protic solvents as well.[2] Polynorbornene and its derivatives can be easily obtained by ROMP of norbornene monomers by making use of metathesis catalysts.

Nitroxy radical-containing polymers can be synthesized in two ways: one is the oxidation of amine or hydroxyamine moieties of precursor polymers after the polymerization of monomers possessing these groups, while the other is the direct polymerization of nitroxy radical-containing monomers. As far as the former strategy is concerned, it can make use of not only the ionic and transition metal-catalyzed polymerization but radical polymerization as well; however, it is difficult to achieve quantitative incorporation of free radical moieties into the polymer chain as the formation of free radical is based on the subsequent polymer reaction. On the other hand, although radical polymerization cannot be exploited in the polymerization of radical-containing monomers, the resultant polymers should possess free radicals quantitatively. To date, there have been a few reports concerning the investigation of nitroxy radical-containing polymers, which include poly[4-(*N*-*tert*-butyl-*N*-oxylamino)styrene],[3] poly(methyl methacrylate) labeled with 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO),[4] and TEMPO-containing polyethers.[5] The former two polymers have been synthesized through the polymer reaction, and the latter one has been obtained by direct polymerization of the corresponding monomer. Although the use of transition metal catalysts for the polymerization of radical-containing acetylenic monomers is rare,[6] Rh catalysts have successfully been exploited for the polymerization of monosubstituted acetylenes carrying free radical moieties,[6e] whereas W and Mo catalysts which are well-known as metathesis polymerization catalysts are incapable even to effect the polymerization of phenylacetylene in the presence of a stable free radical compound, presumably due to their deactivation by the free radical moieties. It has been reported that the ruthenium−carbene complexes are immune to TEMPO and related free radical moieties[6b−d] and thus can be envisaged as suitable ROMP catalysts for the synthesis of polynorbornenes possessing TEMPO moieties at a high density.

Nitroxy radicals such as TEMPO are well-known stable organic radicals finding a variety of applications including spin-labels in the study of conformation and structural mobility of biological systems,[7] radical scavengers,[8] and oxidizing agents.[9] Polymers carrying stable organic radicals have also been intensively investigated with respect to electron spin resonance[10] and molecular motion[11] and frequently employed as functional materials such as polymeric stabilizers,[12] oxidants of alcohols,[6d,13] and spin- and charge-storage materials.[14]

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Scheme 1. Polymerization

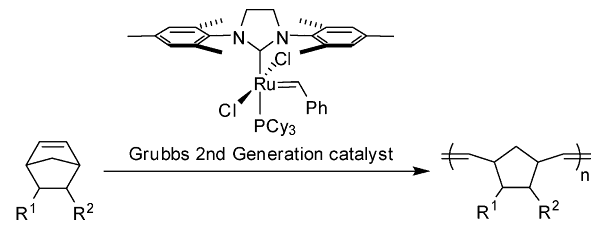
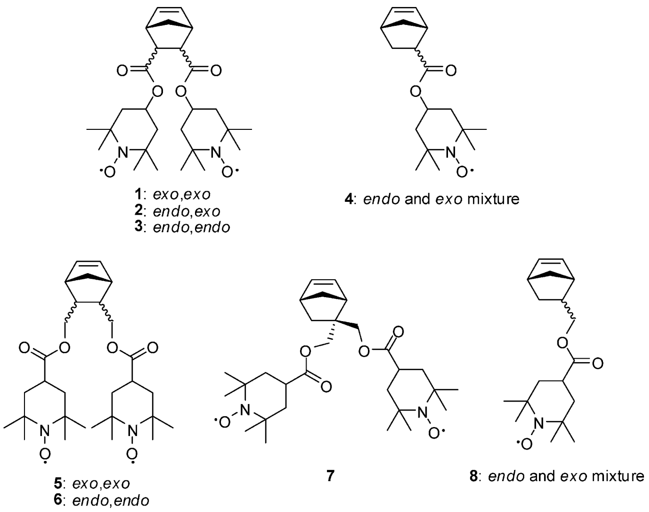


Chart 1. Structures of Monomers 1−8



The charge-storage materials based on polyradicals such as TEMPO- and PROXY-carrying (PROXY = 2,2,5,5-tetramethylpyrroline-1-oxy) polymers can be applied as cathode-active materials in organic radical batteries, which exhibit unique characteristics of high power density and quick charge/discharge ability, unlike the lithium ion batteries, and thus expected to serve as novel functional materials. Nakahara et al. have reported the synthesis of poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate) (PTMA), and the batteries using PTMA as a cathode material have displayed an average discharge voltage of 3.5 V and a discharge capacity of 77 A h/kg, which corresponds to 70% of its theoretical value.[15] We have preliminarily reported the synthesis and charge/discharge properties of a few TEMPO-containing polyacetylene and polynorbornene derivatives, among which the discharge capacity of poly(NB-2,3-*endo,exo*-(COO-4-TEMPO)$_2$) (NB = norbornene) attains the theoretical value (109 A h/kg).[6c] Moreover, the PROXY-containing polyacetylenes and polynorbornenes[6b] and TEMPO-containing polyacetylenes[6f] have also been investigated, and some of these polymers displayed high capacity (up to 117 A h/kg) and quick discharge properties.

The present paper deals with the synthesis of various TEMPO-carrying polynorbornenes by direct polymerization of the corresponding monomers (Scheme 1) with a ruthenium-based metathesis catalyst. Furthermore, the fundamental properties of the resulting polymers and their performance as cathode-active materials in organic radical batteries have been delineated in detail.

Results and Discussion

Monomer Synthesis. Norbornene monomers **1**−**8** (Chart 1) were synthesized by the condensation of anhydride, carboxylic acid, or hydroxy group of norbornene derivatives with hydroxy or carboxylic acid functionality of the TEMPO derivatives (Scheme 2). The attempted synthesis of norbornene-*endo,endo*-dicarboxylic acid di-TEMPO ester monomer **3** using 5-norbornene-*endo*-2,3-dicarboxylic anhydride provided a mixture of two isomers, although there had been no such description in the literature.[6d] Since it was impossible to measure the highly resolved ^{1}H and ^{13}C NMR spectra of the isomers due to the presence of free radicals, they were converted into the corresponding hydroxy compounds in order to measure their NMR spectra. One hydroxy compound showed single peaks based on the carbonyl and olefinic carbons in the ^{13}C NMR spectrum, from which the *endo* orientation for both ester groups can reasonably be concluded; i.e., it was identified as **3′**. The other exhibited two carbonyl carbon signals and two olefinic carbon signals in the ^{13}C NMR spectrum (see the Experimental Section), thus providing the evidence that one of the ester groups is oriented in *endo* and the other in *exo* configuration. Therefore, this compound is identified to be **2′**. Further evidence was obtained by the single-crystal X-ray diffraction analysis. Monomer **2** could afford needlelike crystals, which were too thin to carry out the X-ray crystallographic analysis, while a slow evaporation of a hexane/CHCl$_3$ solution of **3** yielded a single-crystal suitable for X-ray analysis. The crystal data of **3** (Table S1 in Supporting Information) manifested that both the ester groups are oriented in the *endo* configuration. An alternative route for the synthesis of monomer **2** is the condensation of 5-norbornene-2,3-*exo,endo*-dicarboxylic acid with 2 equiv of 4-hydroxy-TEMPO, which is preferable from the viewpoint of high yield (87%) and no necessity for the isolation of isomers, although the starting compound is somewhat expensive. NMR measurements were also employed to identify monomers **5**−**7**. The structures of monomers **1**−**8** were further confirmed by IR spectra and elemental analysis.

Polymer Synthesis. Table 1 summarizes the conditions and the results of ROMP of the norbornene monomers **1**−**8** using the Grubbs second-generation catalyst. Norbornenedicarboxylic acid ester **1** gave the polymer in a high yield (98%), which was insoluble in organic solvents after isolation by precipitation, although the reaction solution was homogeneous during polymerization (run 1 in Table 1). On the other hand, the polymerization of norbornenedicarboxylic acid esters **2** and **3** yielded organosoluble polymers with fairly high molecular weights in 59% and quantitative yields, respectively (runs 2 and 3 in Table 1). Although the polymerization solutions of **4**−**8** were homogeneous at the start (polymerization conditions: in CH$_2$Cl$_2$, 45 min, 30 °C, $[M]_0 = 0.50$ M, $[Ru] = 5.0$ mM), the solution viscosity continued to increase with the passage of time and finally led to the formation of transparent gels. These gels were insoluble in common organic solvents such as toluene, acetone, THF, CH$_2$Cl$_2$, and CHCl$_3$, probably due to very high molecular weight or cross-linking of the polymers. Despite being insoluble, poly(**1**) and poly(**4**)−poly(**8**) could be used as cathode-active materials for a rechargeable battery.

Characterization of the Polymers. Though no evident information was obtained by IR and NMR spectroscopies, it is likely that poly(**1**)−poly(**8**) were formed by ROMP of the norbornene moiety. IR spectra of all the polymers showed strong absorption maxima at 1364 cm^{-1} assignable to the stretching vibration of N−O$^\bullet$ bonds, indicating the incorporation of TEMPO moiety into the polymers. Poly(**2**) and poly(**3**) were soluble in relatively nonpolar organic solvents including toluene, CHCl$_3$, CH$_2$Cl$_2$ and THF, while the rest of the polymers were insoluble in any of the common organic solvents. Figure 1 illustrates the TGA thermograms of poly(**1**)−poly(**8**), whose onset temperatures of weight loss were in the range of 220−240 °C (under air), thus possessing moderate thermal stability. The decomposition of all the TEMPO-containing polymers

Scheme 2. Monomer Synthesis

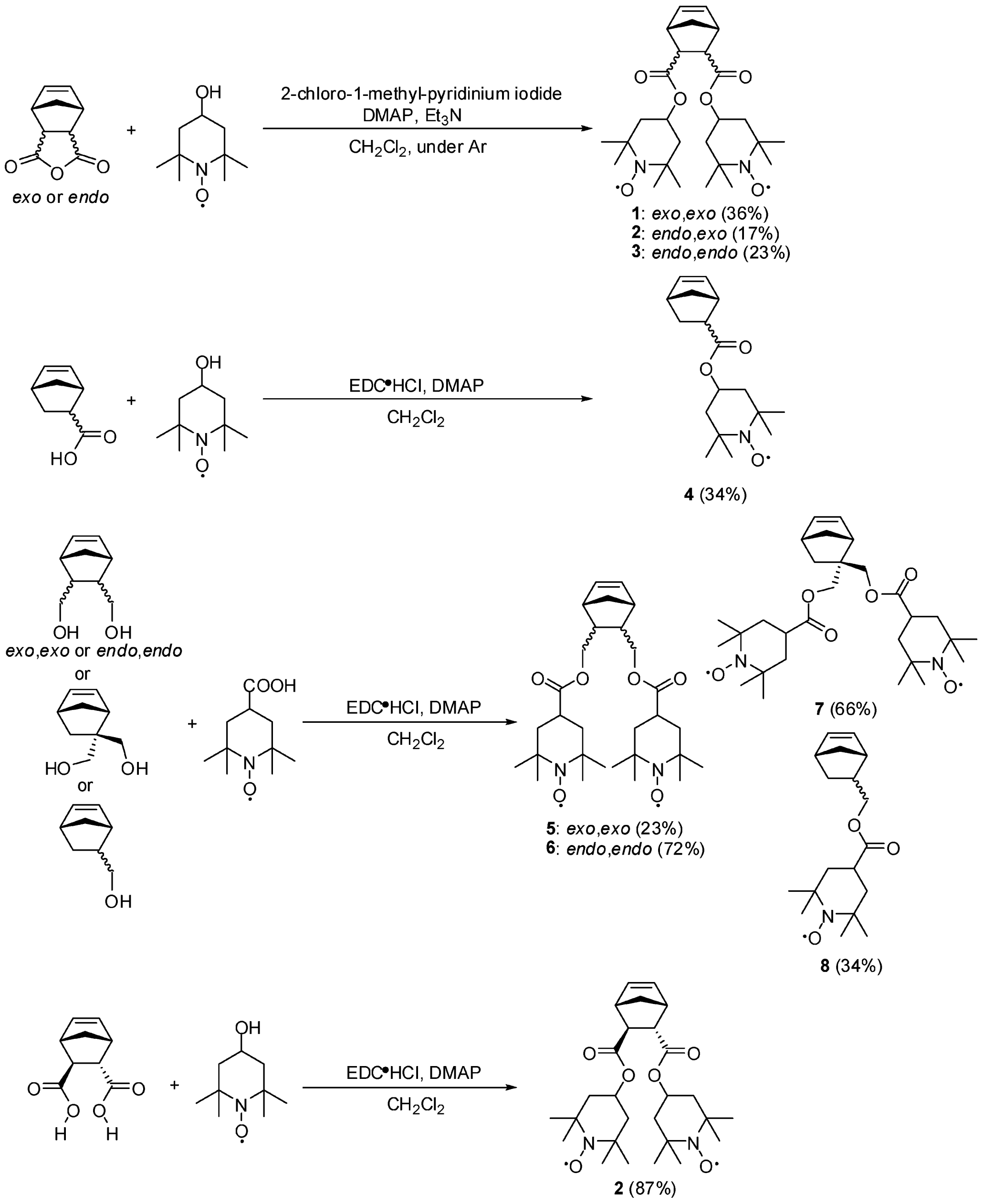


Table 1. Polymerization of TEMPO-Containing Norbornenes 1−8 with the Grubbs Second-Generation Catalyst

		polymer[c]		
run	monomer	yield, %	M_n[d]	M_w/M_n[d]
1[a]	**1**	98	*e*	*e*
2[b]	**2**	59	185 000	1.92
3[a]	**3**	100	137 000	2.31
4[a]	**4**	100	*f*	*f*
5[a]	**5**	88	*f*	*f*
6[a]	**6**	72	*f*	*f*
7[a]	**7**	92	*f*	*f*
8[a]	**8**	96	*f*	*f*

[a] In CH_2Cl_2, 45 min, 30 °C; $[M]_0 = 0.50$ M, [Ru] = 5.0 mM. [b] In CH_2Cl_2, 30 min, 30 °C; $[M]_0 = 1.0$ M, [Ru] = 10 mM. [c] MeOH-insoluble part. [d] Determined by GPC (THF, polystyrene calibration). [e] Although the polymerization system was homogeneous, the isolated polymer was insoluble in any common organic solvents. [f] Insoluble in any solvents.

followed basically the same fashion, suggesting that the ester linkage is cleaved at first followed by the degradation of the main chain.

The ultraviolet−visible (UV−vis) spectra of poly(**2**) and poly(**3**) and the corresponding monomers (**2** and **3**) are shown in Figure 2. All the monomers and polymers displayed weak absorptions around 450 nm, originating from the free radical electrons located in the nonbonding singly occupied molecular orbitals (SOMOs). The spectral features of monomers and polymers were hardly different from each other in terms of the absorption wavelength (λ_{max}) and molar absorptivity (ϵ), hence ruling out any possibility of the disappearance of the radical moieties in the course of polymerization. All the polymers possessed orange-red color similar to those of the monomers.

Table 2 summarizes the ESR data of poly(**1**)−poly(**3**). The ESR spectra of all the polymers exhibited a sharp single peak based on the TEMPO moiety at $g = 2.0064{-}2.0073$, which is close to $g = 2.0055$ of the TEMPOL (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxy) crystal but slightly higher probably due to the effect of the polymer backbone. Precise determination of the spin concentrations of poly(**1**)−poly(**3**) was carried out, and all of the TEMPO-containing polynorbornenes were found

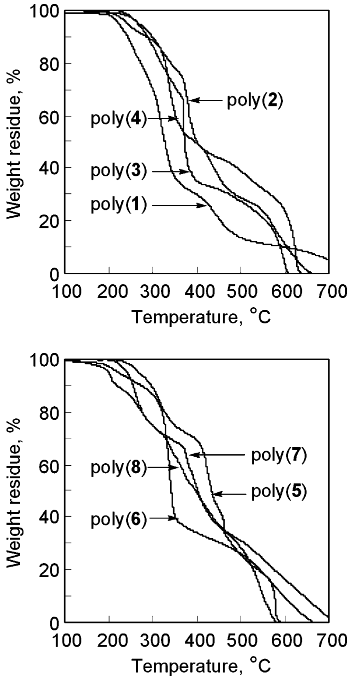


Figure 1. TGA curves of TEMPO-containing polynorbornenes poly(**1**)−poly(**8**) (measured in air; heating rate 10 °C/min).

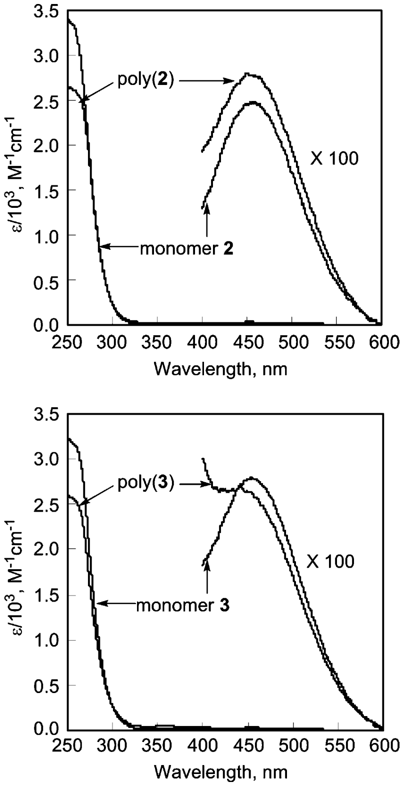


Figure 2. UV−vis spectra of poly(**2**) and poly(**3**) (measured in $CHCl_3$, $c = (1.0-1.4) \times 10^{-3}$ M).

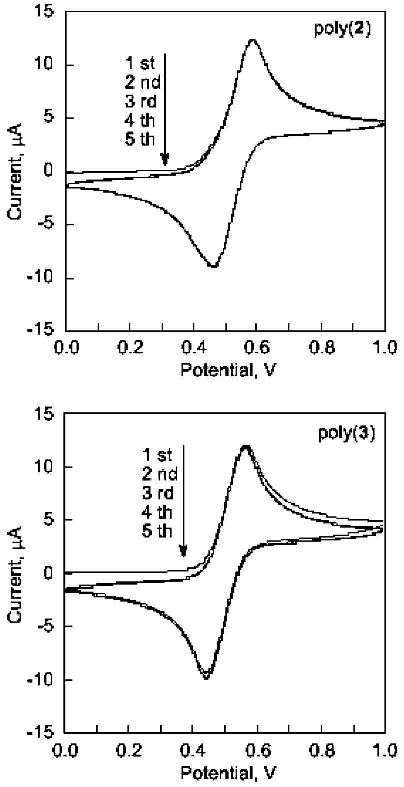


Figure 3. Cyclic voltammograms of poly(**2**) and poly(**3**) (1.0 mM) measured in CH_2Cl_2 solution in the presence of TBAP (tetrabutylammonium perchlorate) (0.10 M) with consecutive scans at 0.1 V/s.

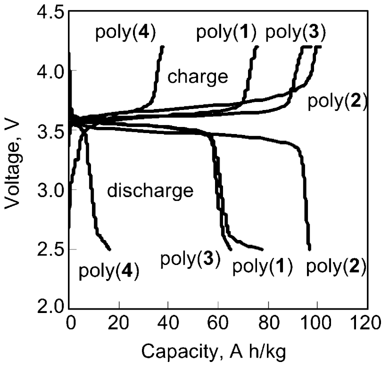


Figure 4. Charge/discharge curves of poly(**1**)−poly(**4**) at a current density of 0.088 mA/cm² (0.034−0.081 A/g) in a cell voltage range of 2.5−4.2 V.

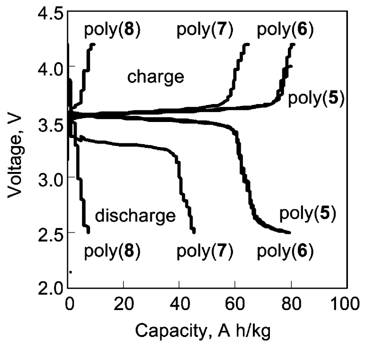


Figure 5. Charge/discharge curves of poly(**5**)−poly(**8**) at a current density of 0.088 mA/cm² (0.084−0.12 A/g) in a cell voltage range of 2.5−4.2 V.

to possess free radical moieties in approximately quantitative amounts, i.e., nearly two per repeating unit in poly(**1**) and poly(**2**) and slightly less than two in poly(**3**). Both the Curie−Weiss temperature Θ and the frequency dependence of ESR line width are consistent with the 1-D magnetic interaction between TEMPO radicals attached to the polymer backbone. The Θ of the polymers with the 1-D chain of TEMPO radicals should be lower than that of the TEMPOL crystal (7 K) in which the 3-D magnetic interaction dominates the Θ value. The ESR line widths in the 1-D electronic systems should depend on the ESR frequency,[16] as demonstrated in Table 2.

Table 2. Magnetic Properties of Poly(1)−Poly(3)

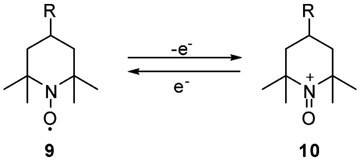
polymer	no. of spins per monomer unit	Curie−Weiss temperature Θ (K)	ESR *g*-factor	ESR line width (G)	
				∼50 MHz	∼9400 MHz
poly(**1**)	2.0 ± 0.1	1.8	2.0073	17.9	10.7
poly(**2**)	1.9 ± 0.1	1.5	2.0064	16.0	10.1
poly(**3**)	1.8 ± 0.1	1.5	2.0066	17.0	9.9

Table 3. Capacity Data of the Poly(1)−Poly(8)

polymer	*m*/*e*[a]	theor capacity, A h/kg[b]	obsd capacity, A h/kg[c]	obsd capacity/ theor capacity, %
poly(**1**)	245.3	109.3	77.5	70.9
poly(**2**)	245.3	109.3	109.3	100
poly(**3**)	245.3	109.3	65.2	59.7
poly(**4**)	292.4	91.7	16.4	17.9
poly(**5**)	259.4	103.3	79.2	76.7
poly(**6**)	259.4	103.3	78.3	75.8
poly(**7**)	259.4	103.3	45.4	43.9
poly(**8**)	306.4	87.5	7.2	8.2

[a] The polymer mass required per exchangeable unit. [b] Theoretical capacity (A h/kg), namely, specific charge calculated according to ref 21. [c] Observed capacity (A h/kg): initial discharge capacity at a current density of 0.088 mA/cm^2 (0.034−0.12 A/g) and a cutoff at 2.5 V.

Scheme 3. Reversible Oxidation of TEMPO Moiety



The cyclic voltammograms (CV) of poly(**2**) and poly(**3**), displaying reversible oxidation and reduction based on the TEMPO radical, are depicted in Figure 3. The difference in the redox potentials for both poly(**2**) and poly(**3**) at a sweep rate of 0.01 V/s is 0.123 V, which is smaller than those of other electroactive organic materials such as PTMA (ca. 0.146 V).[15c] This indicates that the electron-transfer rate constants of poly(**2**) and poly(**3**) are larger than that of PTMA and therefore that the redox reactions of the present polymers are faster than that of PTMA.[17] The CV spectra of the two samples did not undergo any change during five cycles, thus displaying stable redox behavior and the absence of side reactions.

Charge/Discharge Properties. The charge/discharge curves of the cells fabricated with poly(**1**)−poly(**8**) were measured at a constant current density of 0.088 mA/cm^2 (0.034−0.12 A/g), in a cell voltage range of 2.5−4.2 V. Figures 4 and 5 show clear voltage plateaus in both charge and discharge curves with all the cells, advocating the applicability of the TEMPO-containing polynorbornenes as cathode-active materials for a rechargeable battery. The plateau voltages of the charge/discharge processes are in the range of 3.4−3.8 V starting from ∼3.6 V vs Li/Li$^+$, which corresponds to the redox potential of the TEMPO radical. It is reasonable to assume that the charge process at the cathode is oxidation of TEMPO moieties (**9**) in the polymers to oxoammonium salt (**10**), and the discharge process is the reverse reaction, namely, reduction of the salt (Scheme 3). Taking into account the fact that each TEMPO moiety furnishes a single electron in this redox process, the theoretical capacities of the cells fabricated with poly(**1**)−poly(**8**) were estimated to be 87.5−109.3 A h/kg (Table 3); meanwhile, the actual initial discharge capacities of the cells evaluated from the values at 3 V in Figures 4 and 5 were found to be 7.2−109.3 A h/kg at a current density of 0.088 mA/cm^2 (0.034−0.12 A/g).

It is noteworthy that poly(**1**)−poly(**3**) exhibited considerably different charge/discharge performance from one another, although their monomers differ only in the configuration of the substituents. Quite interestingly, the average of the three charge capacity measurements (96, 120, and 112 A h/kg) for poly(**2**)-based cell attained the theoretical value (109 A h/kg), while those for poly(**1**) and poly(**3**) remained 77.5 and 65.2 A h/kg, respectively. X-ray crystallographic data of **3** as shown in Table S1 (in Supporting Information) have suggested a distance of 10 Å between the two radical moieties, oriented in the *endo*,*endo* fashion, in one repeating unit of poly(**3**) which should be the same for poly(**1**) having the *exo*,*exo*-orientation of substituents, whereas a comparatively large distance is expected between the TEMPO moieties of poly(**2**) because of their *endo*,*exo*-orientation. Although poly(**1**)−poly(**3**) are isomers and all of them possess free radicals quantitatively, quite different tendencies observed in their charge/discharge capacities signify the importance of configuration or three-dimensional arrangement of TEMPO moieties along the polymer backbone. Whether a polymer is soluble in nonpolar solvents or not usually does not largely affect the charge/discharge capacity. The appearance of a polymer sample may have influence, and if the sample is too hard to pulverize, the capacity may become lower than expected; however, it is not the case with poly(**1**)−poly(**3**). Thus, we think that the configurational difference is the main reason for the difference in capacity.

The theoretical capacities of the cells based on poly(**1**)−poly(**3**), possessing lesser methylene groups and thus higher radical concentrations per repeating unit, should be higher than those for poly(**5**)−poly(**7**), but experimental facts were not quite in accordance with the expected ones, suggesting the presence of multiple factors affecting the actual capacity of the polymer-based cells. The observed discharge capacities of poly(**4**) and poly(**8**) having one nitroxy radical in the monomer unit were even lower than expected as compared to those having two radical moieties per repeat unit, which might result from the increased crystallinity, regular structure, and/or large particle size due to the smaller number of substituents.

Figure 6 depicts the charge/discharge curves of poly(**2**) observed at different current densities. A slight decrement in the charge/discharge capacity was witnessed with increasing current density, which is attributable to the polarization of TEMPO. The poly(**2**)-based cell, however, displayed excellent charge/discharge characteristics even at extremely large current densities; e.g., the capacity estimated at a current density of

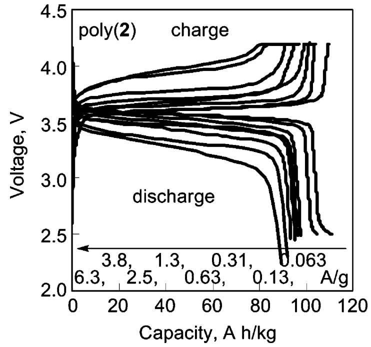


Figure 6. Charge/discharge curves of poly(**2**) at different current densities in a cell voltage range of 2.5−4.2 V.

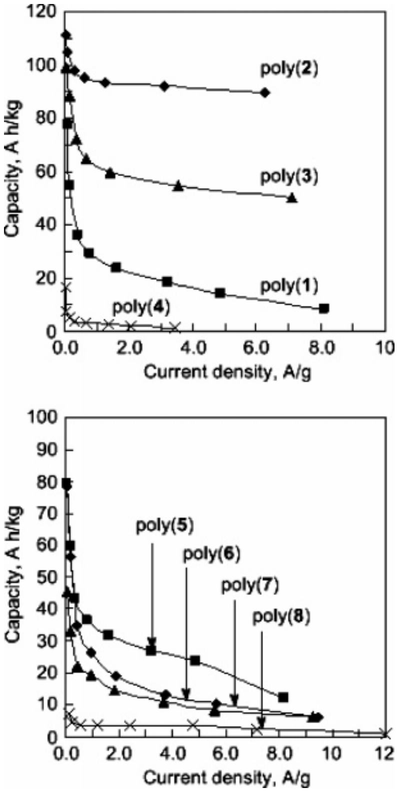


Figure 7. Dependence of capacity on current density in poly(**1**)−poly(**8**) in a cell voltage range of 2.5−4.2 V.

6.3 A/g (8.8 mA/cm^2) was ca. 90 A h/kg, which corresponds to 83% of the discharge capacity at 0.063 A/g (0.088 mA/cm^2) current density, evaluated at the same voltage (2.5 V).

The relationship between the capacity and current density of poly(**1**)−poly(**8**) is illustrated in Figure 7. An increase in current density led to a significant decrease in the charge capacities of poly(**1**)- and poly(**4**)−poly(**8**)-based cells, especially in the range of low current densities. On the contrary, the large capacities of poly(**2**) and poly(**3**) were retained even though the current density was increased up to more than 6 A/g (8.8 mA/cm^2), hence indicating the capability of being charged and discharged at a much faster rate (90 A h/kg/6.3 A/g = 0.014 h = 51 s) than the rest of the polymers. Few secondary batteries have been known which are characterized by such a high capacity and a high charge speed. Therefore, it can be said that especially poly(**2**) is a promising organic radical battery material.

Figure 8 delineates the cycle performance of the poly(**1**)−poly(**8**)/Li batteries, in which charge and discharge were repeated at a current density of 0.088 mA/cm^2 (0.034−0.12 A/g), under the application of cell voltage of 2.5−4.2 V. All the cells fabricated with the polymers under study as the cathode material possessed long cycle life; i.e., the discharge capacities hardly deteriorated after 100 cycles and especially with poly(**2**) and poly(**3**) decreased by no more than 10% of the initial values even after 500 and 400 cycles, respectively. The capacity of poly(**5**) clearly increased with increasing cycle number, which is probably due to the increase in the area of contact between the electrode and the electrolyte, resulting from the swelling of the polymer upon repeated charge and discharge. The cycle life of poly(**2**) was better than those of the corresponding PROXY-containing polymer[6b] and TEMPO-carrying polyacetylenes[6f] and comparable to that of the reported PTMA system.[15a]

The extraordinary characteristics of high charge capacity, excellent charge/discharge performance, and long cycle life of poly(**2**) are expected to signify its capability as a power source in a wide range of potential applications.

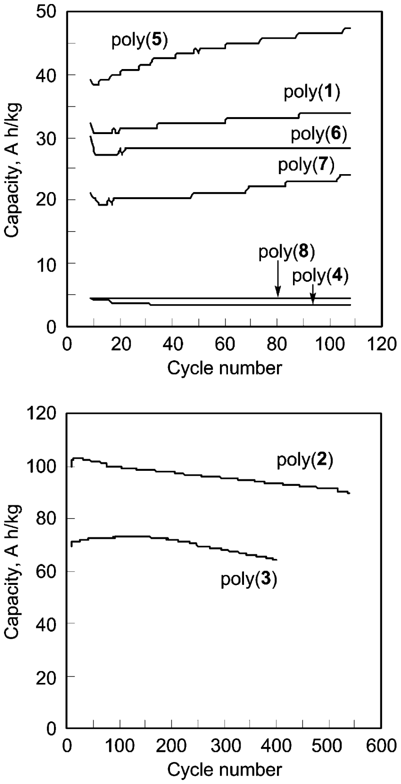


Figure 8. Dependence of capacity on cycle number in poly(**1**)−poly(**8**). Charge and discharge were repeated at a current density of 0.088 mA/cm^2 (0.034−0.12 A/g) in a cell voltage range of 2.5−4.2 V.

Conclusions

In the present study, a group of TEMPO-containing norbornene monomers **1**−**8** were synthesized and polymerized with a ruthenium-based metathesis catalyst. Monomers **2** and **3** gave polymers with number-average molecular weights of 185 000 and 137 000 in 59 and 100% yield, respectively, while monomers **1** and **4**−**8** gave insoluble polymers in 72−100% yield. All of the polymers were observed to be thermally stable up to ca. 240 °C under air. The ESR spectra of poly(**1**)−poly(**3**) exhibited a sharp single peak with *g*-factors typical of nitroxy radicals (around 2.0065), and the number of spins per repeating unit was almost quantitative. The most interesting feature of the present research is the very high charge capacity displayed by the poly(**2**)-based cell (109 A h/kg) which attained the theoretical value, and a large capacity (up to 90 A h/kg) was retained even at a high current density of ca. 6 A/g. The cell fabricated with poly(**2**) as a cathode material demonstrated a promising cycle life and the deterioration of charge capacity was hardly observed even after 500 cycles. Thus, poly(**1**)−poly(**8**), especially poly(**2**), are expected to find applications as charge-storage materials in organic radical batteries.

Experimental Section

Measurements. IR and UV−vis spectra were measured on a JASCO FT/IR-4100 and JASCO V-550 spectrophotometers, respectively. Cyclic voltammograms (CV) were recorded with an HCH Instruments ALS600A-n electrochemical analyzer. Melting points (mp) were determined with a Yanaco micro melting point apparatus, and elemental analyses were conducted at the Kyoto University Elemental Analysis Center. The number- and weight-average molecular weights (M_n and M_w) of polymers were determined by gel permeation chromatography (GPC) on a JASCO

Gulliver system (PU-980, CO-965, RI-930, and UV-1570) equipped with polystyrene gel columns (Shodex columns KF-805L × 3), using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min, calibrated with polystyrene standards at 40 °C. ESR spectra were recorded with a JEOL JES-FR30 X-band (9.48 GHz) spectrometer. A frequency counter (Anritsu, MF76A) and an NMR field meter (Echo Electronics, EFM-2000AX) were used for the determination of *g*-factor. The precise number of free radicals was estimated with a Quantum Design MPMS susceptometer and a home-built low-frequency ESR−NMR apparatus operated around 50 MHz.[18]

Crystallographic Study. A single crystal of **3** obtained by recrystallization from hexane/$CHCl_3$ solution was subjected to X-ray crystallographic analysis, and the measurement was made on a Rigaku RAPID-F imaging plate area detector with graphite-monochromated Mo Kα radiation. The structure was elucidated by a direct method using SIR92[19] and expanded by Fourier techniques (DIRDIF99).[20]

Materials. The solvents used for polymerization were distilled according to the standard procedure before use. The Grubbs second-generation catalyst was purchased from Materia, Inc., and used as received. 4-Carboxy-TEMPO (TCI), 4-hydroxy-TEMPO (TCI), 5-norbornene-*endo*,*exo*-2,3-dicarboxylic acid (Aldrich), 5-norbornene-*exo*-2,3-dicarboxylic anhydride (Aldrich), 5-norbornene-*endo*-2,3-dicarboxylic anhydride (Aldrich), 5-norbornene-*exo*,*exo*-2,3-dimethanol (Aldrich), 5-norbornene-*endo*,*endo*-2,3-dimethanol (Aldrich), 5-norbornene-2,2-dimethanol (Aldrich), *N*-(3-(dimethylamino)propyl)-*N′*-ethylcarbodiimide hydrochloride (EDC·HCl; Eiweiss Chemical Corp.), and 4-(dimethylamino)pyridine (DMAP; Wako) were purchased and used without further purification.

Monomer Synthesis. 5-Norbornene-*exo*,*exo*-2,3-dicarboxylic acid bis[4-(2,2,6,6-tetramethylpiperidine-1-oxy)] ester (**1**) was synthesized from 5-norbornene-*exo*-2,3-dicarboxylic anhydride and 4-hydroxy-TEMPO according to the literature method.[6d] The crude product was purified by flash column chromatography (eluent: ethyl acetate/hexane = 1/4). Yield 36%, pale red solid, mp 148.5−149.5 °C. IR (KBr, cm^{-1}): 2976, 2938, 1720 ($\nu_{C=O}$), 1464, 1364, 1316, 1266, 1242, 1176 (ν_{C-O}), 1111, 1012, 989, 900, 702. Anal. Calcd for $C_{27}H_{42}N_2O_6$: C, 66.10; H, 8.63; N, 5.71. Found: C, 65.97; H, 8.40; N, 5.64.

5-Norbornene-*exo*,*endo*-2,3-dicarboxylic acid bis[4-(2,2,6,6-tetramethylpiperidine-1-oxy)] ester (**2**) was synthesized as follows: 5-Norbornene-*exo*,*endo*-2,3-dicarboxylic acid (1.31 g, 4.00 mmol) was added to a solution of EDC·HCl (3.03 g, 8.80 mmol) and DMAP (1.08 g, 8.80 mmol) in CH_2Cl_2 (80 mL) at room temperature. 4-Hydroxy-TEMPO (1.52 g, 8.80 mmol) was added to the solution, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was washed with water (100 mL) three times, and the organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed to afford a crude product. It was purified by flash column chromatography (eluent: ethyl acetate/hexane = 1/2). Yield 1.70 g (87%), pale red solid, mp 183.0−184.0 °C. IR (KBr, cm^{-1}): 2977, 2939, 1739 ($\nu_{C=O}$), 1464, 1345, 1250, 1191 (ν_{C-O}), 1158, 1076, 1048, 905, 731. Anal. Calcd for $C_{27}H_{42}N_2O_6$: C, 66.10; H, 8.63; N, 5.71. Found: C, 66.11; H, 8.64; N, 5.66.

5-Norbornene-*endo*,*endo*-2,3-dicarboxylic acid bis[4-(2,2,6,6-tetramethylpiperidine-1-oxy)] ester (**3**) was synthesized from 5-norbornene-*endo*-2,3-dicarboxylic anhydride and 4-hydroxy-TEMPO according to the literature method.[6d] The crude product was a mixture of about same amounts of isomers **2** and **3**. These isomers were separated by flash column chromatography (eluent: ethyl acetate/hexane = 1/2). Yield of **3** 23%, pale red solid, mp 157.0−158.0 °C. IR (KBr, cm^{-1}): 2976, 2938, 2872, 1720 ($\nu_{C=O}$), 1463, 1364, 1317, 1266, 1175 (ν_{C-O}), 1111, 1009, 989, 962, 713. Anal. Calcd for $C_{27}H_{42}N_2O_6$: C, 66.10; H, 8.63; N, 5.71. Found: C, 66.09; H, 8.75; N, 5.62.

5-Norbornene-2-carboxylic acid 4-(2,2,6,6-tetramethylpiperidine-1-oxy)] ester (**4**) was synthesized as follows: 5-Norbornene-2-carboxylic acid (415 mg, 3.00 mmol) was added to a solution of EDC·HCl (864 mg, 3.30 mmol) and 4-(dimethylamino)pyridine (403 mg, 3.30 mmol) in CH_2Cl_2 (50 mL) at room temperature. 4-Hydroxy-TEMPO (517 mg, 3.00 mmol) was added to the solution, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was washed with water (50 mL) three times, and the organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed to afford a crude product. It was purified by flash column chromatography (eluent: ethyl acetate/hexane = 1/4). Yield 34%, pale red solid, mp 89.0−90.0 °C. IR (KBr, cm^{-1}): 3063, 2973, 2943, 2870, 1725 ($\nu_{C=O}$), 1465, 1337, 1271, 1174 (ν_{C-O}), 1112, 1021, 900, 839, 711. Anal. Calcd for $C_{17}H_{26}NO_3$: C, 69.83; H, 8.96; N, 4.79. Found: C, 69.78; H, 8.90; N, 4.79.

5-Norbornene-*exo*,*exo*-2,3-dimethyl bis(2,2,6,6-tetramethylpiperidine-1-oxy 4-carboxylate) (**5**) was synthesized form 5-norbornene-*exo*,*exo*-2,3-dimethanol and 2 equiv of 4-carboxy-TEMPO by following the same procedure as for/in a manner similar to **4**. Yield 23%, pale red solid, mp 148.5−149.5 °C. IR (KBr, cm^{-1}): 2970, 2938, 1726 ($\nu_{C=O}$), 1457, 1311, 1243, 1158 (ν_{C-O}), 1011, 970, 698. Anal. Calcd for $C_{29}H_{46}N_2O_6$: C, 67.15; H, 8.94; N, 5.40. Found: C, 67.11; H, 8.94; N, 5.12.

5-Norbornene-*endo*,*endo*-2,3-dimethyl bis(2,2,6,6-tetramethylpiperidine-1-oxy 4-carboxylate) (**6**) was synthesized from 5-norbornene-*endo*,*endo*-2,3-dimethanol and 2 equiv of 4-carboxy-TEMPO in a manner similar to **4**. Yield 72%, pale red solid, mp 156.5−157.5 °C. IR (KBr, cm^{-1}): 3052, 2974, 2945, 1735 ($\nu_{C=O}$), 1457, 1323, 1292, 1192, 1163 (ν_{C-O}), 972, 747. Anal. Calcd for $C_{29}H_{46}N_2O_6$: C, 67.15; H, 8.94; N, 5.40. Found: C, 66.96; H, 8.77; N, 5.34.

5-Norbornene-2,2-dimethyl bis(2,2,6,6-tetramethylpiperidine-1-oxy 4-carboxylate) (**7**) was synthesized from 5-norbornene-2,2-dimethanol and 2 equiv of 4-carboxy-TEMPO in a manner similar to **4**. Yield 66%, pale red solid, mp 152.0−153.0 °C. IR (KBr, cm^{-1}): 3070, 2972, 2874, 1718 ($\nu_{C=O}$), 1467, 1365, 1254, 1167 (ν_{C-O}), 1013, 725, 712. Anal. Calcd for $C_{29}H_{46}N_2O_6$: C, 67.15; H, 8.94; N, 5.40. Found: C, 67.18; H, 8.87; N, 5.27.

5-Norbornene-2-methyl (2,2,6,6-tetramethylpiperidine-1-oxy 4-carboxylate) (**8**) was synthesized from 5-norbornene-2-methanol and 4-carboxy-TEMPO in a manner similar to **4**. Yield 34%, pale red solid, mp 93.4−94.5 °C. IR (KBr, cm^{-1}): 3069, 2975, 2875, 1726 ($\nu_{C=O}$), 1469, 1367, 1254, 1150 (ν_{C-O}), 1013, 899, 710. Anal. Calcd for $C_{17}H_{26}NO_3$: C, 69.83; H, 8.96; N, 4.79. Found: C, 69.75; H, 8.99; N, 4.70.

Norbornene-2,3-*exo*,*exo*-dicarboxylic acid bis[4-(2,2,6,6-tetramethylpiperidine 1-hydroxy)] ester (**1′**) was synthesized by hydrogenation of **1** according to the literature method.[6d] Yield 100%, white solid, mp 58.5−58.9 °C. ^1H NMR ($CDCl_3$): δ 6.20 (2H, =CH−), 5.16−4.92 (2H, −OCH⟨), 4.06 (2H, −OH), 3.06 (2H, =CH−C*H*−), 2.54 (2H, ⟩CHCOO), 2.01−1.78 (2H, =CH−CHC*H*₂CH⟨), 1.74−1.42 (8H, −OCHC*H*₂C−), 1.20 (24H, ⟩C(CH_3)₂). ^{13}C NMR ($CDCl_3$): δ 171.7, 136.7, 65.6, 57.8, 46.1, 46.0, 44.5, 42.7, 30.8, 19.0. IR (KBr, cm^{-1}): 3445 (ν_{O-H}), 2974, 2937, 2873, 1728 ($\nu_{C=O}$), 1469, 1372, 1315, 1242 (ν_{C-O}), 1196, 1162, 1097, 1041, 1014, 955, 728, 600. HRMS (FAB): $[M + H]^+$, found 493.3276. $C_{27}H_{45}N_2O_6$ requires 493.3278.

Norbornene-2,3-*endo*,*exo*-dicarboxylic acid bis[4-(2,2,6,6-tetramethylpiperidine-1-hydroxy)] ester (**2′**) was synthesized from **2** in a manner similar to **1′**. Yield 80%, white solid, mp 149.5−151.0 °C. ^1H NMR ($CDCl_3$): δ 6.29 (1H, =CH−), 6.07 (1H, =CH−), 5.19−4.94 (2H, −OCH⟨), 4.40 (2H, −OH), 3.32 (1H, ⟩CHCOO), 3.24 (1H, ⟩CH−COO), 3.09 (1H, =CH−C*H*−), 2.63 (1H, =CH−C*H*−), 2.09−1.78 (2H, =CH−CHC*H*₂CH⟨), 1.78−1.42 (8H, −OCHC*H*₂C−),1.20 (24H, ⟩C(CH_3)₂). ^{13}C NMR ($CDCl_3$): δ 173.7, 172.5, 137.3, 134.7, 66.9, 66.7, 58.7, 47.8, 47.5, 47.1, 46.9, 45.4, 43.5, 31.8, 31.7, 20.1. IR (KBr, cm^{-1}): 3500 (ν_{O-H}), 2976, 2943, 1727 ($\nu_{C=O}$), 1467, 1362, 1315, 1267 (ν_{C-O}), 1177, 1011, 962, 712. HRMS (FAB): $[M + H]^+$, found 493.3270. $C_{27}H_{45}N_2O_6$ requires 493.3278.

Norbornene-2,3-*endo*,*endo*-dicarboxylic acid bis[4-(2,2,6,6-tetramethylpiperidine-1-hydroxy)] ester (**3′**) was synthesized from **3** in a manner similar to **1′**. Yield 90%, white solid, mp 165.5−167.0 °C. ^1H NMR ($CDCl_3$): δ 6.05 (2H, =CH−), 5.10−4.90 (2H,

−OCH⟨), 4.22 (2H, −OH), 3.22 (2H, ⟩CHCOO), 3.14 (2H, =CH−CH−), 2.00−1.78 (2H, =CH−CHC*H*$_2$CH⟨), 1.65−1.40 (8H, $-\mathrm{CH_2C(CH_3)_2}-$), 1.16 (24H, ⟩$\mathrm{C(CH_3)_2}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 170.8, 133.6, 65.5, 57.9, 47.5, 47.0, 45.2, 42.7, 31.1, 19.0. IR (KBr, cm^{-1}): 3503 ($\nu_{\mathrm{O-H}}$), 2976, 2941, 1739 ($\nu_{\mathrm{C=O}}$), 1468, 1362, 1342, 1254 ($\nu_{\mathrm{C-O}}$), 1193, 1076, 963, 726. HRMS (FAB): $[\mathrm{M+H}]^+$, found 493.3277. $\mathrm{C_{27}H_{45}N_2O_6}$ requires 493.3278.

5-Norbornene-*exo*,*exo*-2,3-dimethylbis(2,2,6,6-tetramethylpiperidine-1-hydroxy 4-carboxylate) (**5′**) was synthesized from **5** in a manner similar to **1′**. Yield 100%, white solid, mp 115.0−116.0 °C. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 6.20 (2H, =CH−), 4.52−3.42 (5H, $-\mathrm{OCH_2}-$, −OH), 2.89−2.50 (4H, =CH−C*H*−, −OCOCH⟨), 2.12−1.84 (2H, $-\mathrm{OCH_2}$C*H*⟨), 1.84−1.55 (8H, −C*H*$_2$$\mathrm{C(CH_3)_2}$−), 1.55−1.29 (2H, =CH−CHC*H*$_2$CH⟨)), 1.16 (24H, ⟩$\mathrm{C(CH_3)_2}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 171.0, 133.2, 61.3, 54.3, 40.5, 38.5, 37.4, 35.5, 30.7, 28.3, 15.2. IR (KBr, cm^{-1}): 3390 ($\nu_{\mathrm{O-H}}$), 2975, 2936, 2897, 1733 ($\nu_{\mathrm{C=O}}$), 1457, 1362, 1329, 1307, 1244 ($\nu_{\mathrm{C-O}}$), 1193, 1164, 1047, 1013, 962, 708. HRMS (CI): $[\mathrm{M+H}]^+$, found 520.3519. $\mathrm{C_{29}H_{49}N_2O_6}$ requires 521.3591.

5-Norbornene-*endo*,*endo*-2,3-dimethylbis(2,2,6,6-tetramethylpiperidine-1-hydroxy 4-carboxylate) (**6′**) was synthesized from **6** in a manner similar to **1′**. Yield 100%, white solid, mp 120.0−121.0 °C. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 6.18 (2H, =CH−), 4.32−3.45 (5H, $-\mathrm{OCH_2}-$, −OH), 2.92 (2H, =CH−C*H*⟨), 2.77−2.60 (2H, −OCOCH-⟨), 2.60−2.41 (2H, $-\mathrm{OCH_2}$C*H*⟨), 1.96−1.58 (8H, −C*H*$_2$$\mathrm{C(CH_3)_2}$−), 1.58−1.30 (2H, =CH−CHC*H*$_2$CH⟨), 1.30−0.99 (24H, ⟩$\mathrm{C(CH_3)_2}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 173.1, 133.5, 62.5, 56.3, 46.9, 43.3, 39.6, 38.5, 32.9, 30.3, 17.3. IR (KBr, cm^{-1}): 3496 ($\nu_{\mathrm{O-H}}$), 2978, 2941, 1728 ($\nu_{\mathrm{C=O}}$), 1467, 1363, 1317, 1245 ($\nu_{\mathrm{C-O}}$), 1175, 1112, 1050, 1012, 963, 898, 735. HRMS (CI): $[\mathrm{M+H}]^+$, found 521.3553. $\mathrm{C_{29}H_{49}N_2O_6}$ requires 521.3591.

5-Norbornene-2,2-dimethyl bis(2,2,6,6-tetramethylpiperidine-1-hydroxy 4-carboxylate) (**7′**) was synthesized from **7** in a manner similar to **1′**. Yield 100%, white solid, mp 142.5−143.5 °C. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 6.22 (1H, =CH−), 6.04 (1H, =CH−), 4.54−3.21 (5H, $-\mathrm{OCH_2}-$, −OH), 2.89 (1H, =CH−C*H*−), 2.82−2.43 (3H, =CH−C*H*−, −OCOCH⟨), 1.99−1.00 (36H, −C*H*$_2$$\mathrm{C(CH_3)_2}$−, $-\mathrm{OCH_2C}$C*H*$_2$⟨, =CH−CHC*H*$_2$CH⟨, ⟩$\mathrm{C(CH_3)_2}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 171.5, 171.3, 134.2, 130.2, 64.0, 63.1, 54.6, 43.4, 42.4, 42.2, 38.7, 37.84, 37.77, 31.1, 29.4, 28.6, 15.6. IR (KBr, cm^{-1}): 3445 ($\nu_{\mathrm{O-H}}$), 2974, 2937, 2873, 1728 ($\nu_{\mathrm{C=O}}$), 1469, 1372, 1315, 1242 ($\nu_{\mathrm{C-O}}$), 1196, 1162, 1041, 1014, 955, 728. HRMS (FAB): $[\mathrm{M+H}]^+$, found 521.3600. $\mathrm{C_{29}H_{49}N_2O_6}$ requires 521.3591.

Polymerization of norbornene monomers was carried with Grubbs second generation as a catalyst in dry $\mathrm{CH_2Cl_2}$ at 30 °C for 30 or 45 min under the following conditions: $[\text{monomer}]_0 = 1.0$ M, $[\text{catalyst}] = 10$ mM or $[\text{monomer}]_0 = 0.50$ M, $[\text{catalyst}] = 5.0$ mM. The polymers were isolated by precipitation in methanol.

IR (KBr, cm^{-1}) Data of the Polymers. Poly(**1**): 3500, 2976, 2945,1751, 1637, 1560, 1541, 1470, 1394, 1364, 1290, 1210, 1155, 1137, 983, 967, 935, 916, 874, 818, 766, 745, 711, 649, 564. Poly(**2**): 2976, 2941, 2363, 1732, 1465, 1364, 1178, 1010, 985, 752. Poly(**3**): 2976, 2941, 2363, 2328, 1734, 1466, 1364, 1177, 1010, 982. Poly(**4**): 3444, 2975, 2929, 1734, 1676, 1628, 1560, 1542, 1525, 1449, 1458, 1364, 1306, 1242, 1164, 1085, 1014, 937, 906, 743, 713, 582, 557. Poly(**5**): 3492, 2973, 2933, 1734, 1676, 1646, 1638, 1628, 1560, 1542, 1458, 1390, 1378, 1364, 1310, 1194, 1162, 1085, 1041, 1014, 968, 867, 850, 751, 648, 558. Poly(**6**): 3498, 2974, 2936, 1734, 1647, 1638, 1570, 1509, 1450, 1466, 1377, 1364, 1313, 1167, 1085, 1046, 1009, 968, 800, 741, 681, 557, 536. Poly(**7**): 3486, 2974, 2943, 1732, 1459, 1377, 1364, 1309, 1243, 1190, 1165, 1104, 1086, 1040, 970, 748, 680, 650, 557. Poly(**8**): 3444, 2973, 2945, 2863, 1733, 1458, 1390, 1377, 1363, 1308, 1243, 1195, 1166, 1012, 966, 755, 667, 647.

Fabrication and Electrochemical Properties of the Batteries. A coin-type cell was fabricated by stacking electrodes with porous polyolefin separator film. A cathode was prepared by pressing the composites of a polymer (10 wt %), carbon fiber (80 wt %), and fluorinated polyolefin binder (10 wt %) as described in a previous paper.[6c] The cathode was set to a coin-type cell with a lithium metal anode. A composite solution of ethylene carbonate/diethyl carbonate (30/70 v/v) containing 1 M $\mathrm{LiPF_6}$ was used as an electrolyte. Charge and discharge properties were measured at 25 °C using a computer-controlled automatic battery charge and discharge instrument (Keisokukiki, Co. Ltd., Battery Labo System BLS5500).

Theoretical Capacity of the Polymer-Based Cell. The theoretical capacity (C, in A h/kg) of an electroactive polymer is calculated from the polymer mass required per exchangeable unit charge.[21]

$$C\ (\mathrm{A\ h/kg}) = \frac{N_{\mathrm{A}}\mathrm{e}}{3600(M_{\mathrm{w}}/1000)}$$

where $N_{\mathrm{A}}e$ is the Faraday constant (96 484 C/mol), while M_{w} is the equivalent weight (or mass) of polymer in grams and defined as the molecular weight (molar mass) of the repeating unit of polymer divided by the number of electrons exchanged or stored by it (which may be a fractional number) or as the molecular weight of the set of repeating units exchanging (storing) one electron in polymers.

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Supporting Information Available: Single-crystal diffraction data of monomer **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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