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Synthesis and Properties of Polyacetylene and Polynorbornene Derivatives Carrying 2,2,5,5-Tetramethyl-1-pyrrolidinyloxy Moieties

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ABSTRACT: PROXYL-containing propargyl ester $HC{\equiv}CCH_2OCO$-3-PROXYL (**1**), *N*-propargylamide $HC{\equiv}CCH_2NHCO$-3-PROXYL (**2**), 1-pentyne-4,4-dimethyl ester $HC{\equiv}CCH_2C(CH_3)(CH_2OCO\text{-3-PROXYL})_2$ (**3**), and norbornene diester monomers NB-2,3-*exo,exo*-$(CH_2OCO\text{-3-PROXYL})_2$ (**4**), NB-2,3-*endo,endo*-$(CH_2OCO\text{-3-PROXYL})_2$ (**5**), and NB-2,2-$(CH_2OCO\text{-3-PROXYL})_2$ (**6**) (NB = norbornene, PROXYL = 2,2,5,5-tetramethyl-1-pyrrolidinyoxy) were polymerized to afford novel polymers containing the PROXYL radical at high densities. While **1** and **2** provided polymers with number-average molecular weights of 3300−29 800 in 60−65% yields in the presence of a Rh catalyst, monomers **4**−**6** gave polymers with number-average molecular weights up to 209 000−272 000 in 90−94% yields with a Ru catalyst. The formed polymers were thermally stable up to ca. 220 °C according to TGA and soluble in common organic solvents including toluene, $CHCl_3$, and THF. Poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) hardly exhibited absorption above 400 nm, which corresponds with their very light color. The oxidation/reduction gaps in the cyclic voltammograms of the present polymers were as small as 0.072−0.092 V, indicating large electrode reaction rates. All the PROXYL-containing polymers demonstrated the reversible charge/discharge processes, whose capacities were larger than 85 A h/kg. In particular, the maximum capacity of poly(**1**)- and poly(**4**)-based cells reached 117 and 107 A h/kg, which practically coincided with the theoretical capacity values (119 and 109 A h/kg, respectively).

Introduction

Stable organic radicals have been utilized in the studies of spin-trapping,[1] spin-labeling,[2] organic ferromagnetism,[3] and so forth. Among them, nitroxyl radicals such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2,2,5,5-tetramethyl-1-pyrrolidinyloxy (PROXYL) are well-known and have found applications in a variety of fields, including spin-labels to study the conformation and structural mobility of biological systems,[4] scavengers of unstable radical species,[5] and oxidizing agents.[6] Polymers carrying stable organic radicals have been intensively investigated in the fields of electron spin resonance[7] and molecular motion[8] and frequently employed as functional materials such as polymeric stabilizers,[9] oxidants of alcohols,[10] and spin- and charge-storage materials.[11] Among these applications, polymers having radicals have been extensively studied in the search for organic ferromagnetic materials,[12] e.g., poly(triphenylamine-*alt*-phenylenevinylene)s,[13] poly(9,10-anthryleneethynylene),[14] poly(phenylacetylene),[15] and dendritic−macrocyclic poly(arylmethyl) polyradical.[16] Charge-storage materials based on polyradicals such as TEMPO- and PROXYL-carrying polymers can be applied to cathode-active materials in organic radical batteries. To the best of our knowledge, however, the synthesis and battery properties of this type of polymers have been scarcely investigated.[17]

Poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA) has been prepared by the polymerization of a methacrylate monomer having the corresponding amine group followed by oxidation to generate the radical in the polymer.[17] This polymer was examined as a material for organic radical batteries which would be quickly chargeable and have a high power density.[18] It was found that this polymer contained ca. 70% of radical against the theoretical value and that the batteries using this polymer showed an average discharge voltage of 3.5 V and a discharge capacity of 77 A h/kg (70% of the theoretical value). Thus far, polymers carrying nitroxide free radicals have usually been synthesized by an indirect method, i.e., synthesis of precursor polymers having the corresponding amino group, followed by the oxidation to afford polymers containing stable radicals.[17] The indirect route is adopted due to lack of capability of radical-bearing monomers to undergo radical polymerization. However, this method is often accompanied by incomplete oxidation, resulting in the less than quantitative incorporation of the radical into the polymers. A feasible approach to circumvent this problem is to polymerize free-radical-containing monomers with transition-metal catalysts, which are not affected by the radicals in the monomers.

We have recently studied the preparation and charge/discharge properties of a series of polyacetylenes and polynorbornenes containing TEMPO groups to find that the discharge capacity of the cell fabricated with poly(NB-2,3-*endo,exo*-$(COO\text{-4-TEMPO})_2$) reaches the theoretical value (109 A h/kg) anticipated for the molecular structure.[19] Polymers containing PROXYLs are promising candidates as cathode-active materials in quickly chargeable/dischargeable and high power density batteries. However, the synthesis of polymers containing PROXYLs and their application to a rechargeable battery has not been reported so far.

The present paper deals with the synthesis of PROXYL-carrying polymers by direct polymerization of PROXYL-containing acetylenes and norbornenes (Scheme 1) with transition-

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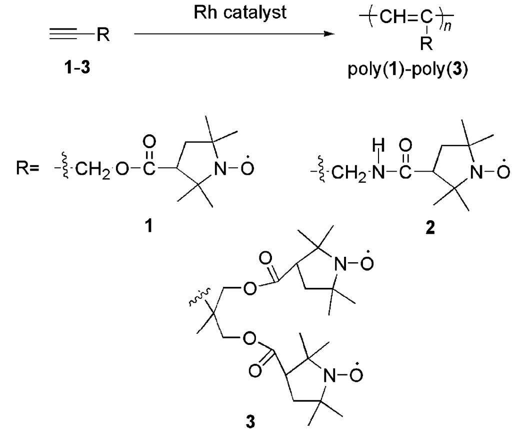
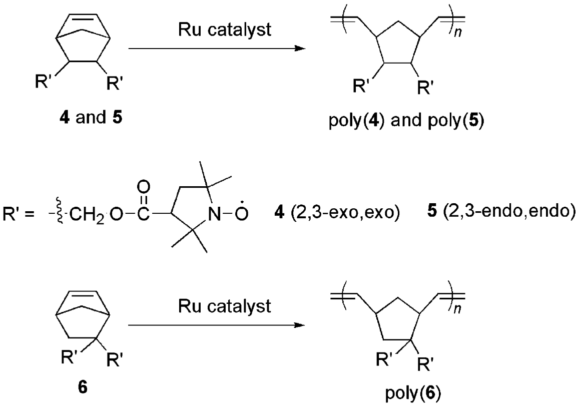
Scheme 1



(a) Polymerization of PROXYL-containing acetylene monomers



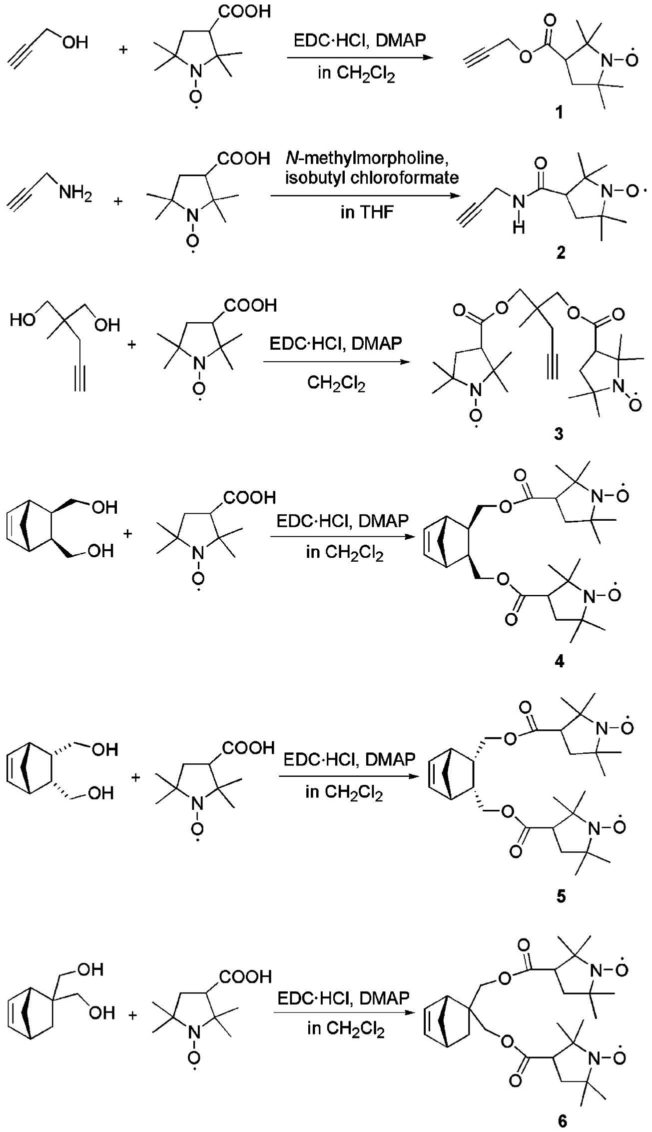
(b) Polymerization of PROXYL-containing norbornene monomers

metal catalysts, elucidation of the fundamental properties, and the evaluation of their performance as cathode-active materials in organic radical battery.

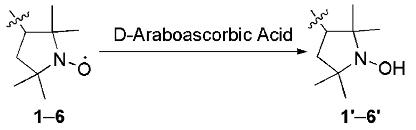
Results and Discussion

Monomer Synthesis. The synthetic routes for monomers **1**−**6** have been illustrated in Scheme 2. Acetylenic ester and amide monomers, namely 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy propargyl ester (**1**) and 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy *N*-propargylamide (**2**), were synthesized by condensation of the carboxy group of 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy (3-carboxy-PROXYL) with the hydroxy or amino group of propargyl compounds. 1-Pentyne-4,4-dimethyldi(2,2,5,5-tetramethyl-1-pyrrolidinyloxyl carboxylate) ($HC{\equiv}CCH_2C(CH_3)(OCO\text{-}3\text{-}PROXYL)_2$ (**3**) was prepared by condensation of the carboxy group of 3-carboxy-PROXYL with the hydroxyl groups of 1-pentyne-4,4-dimethanol. Norbornene diester monomers, namely 5-norbornene-2-*exo*,3-*exo*-dimethyldi(2,2,5,5-tetramethyl-1-pyrrolidinyloxy carboxylate) (**4**), 5-norbornene-2-*endo*,3-*endo*-dimethyldi(2,2,5,5-tetramethyl-1-pyrrolidinyloxy carboxylate) (**5**), and 5-norbornene-2,2-dimethyldi(2,2,5,5-tetramethyl-1-pyrrolidinyloxy carboxylate) (**6**), were synthesized by condensation of the hydroxy groups of norbornene derivatives and 3-carboxy-PROXYL. The monomers were purified by silica gel column chromatography eluted by ethyl acetate/*n*-hexane (1/4 volume ratio) or recrystallization using ethyl acetate/*n*-hexane (1/1 volume ratio). The presence of free radicals did not allow measuring the NMR spectra of the monomers. Hence, they were converted to the corresponding hydroxyamine derivatives (**1′**−**6′**; Scheme 3) according to the literature method,[10c] and the ^1H and ^{13}C NMR spectra of these derivatives were measured, which supported that the monomers possessed the expected structures (see the Experimental Section). Further confirmation for the structures of the monomers was furnished by IR spectra and elemental analysis.

Scheme 2



Scheme 3



Polymer Synthesis. The polymerization of acetylenic monomers **1**−**3** was carried out using $(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ as a catalyst at 30 °C for 24 h, the results of which are summarized in Table 1. Polymerizations of **1** were performed in toluene, $CHCl_3$, and THF, and the reaction mixtures were poured into a large excess of diethyl ether to give pale yellow powdery polymers. The polymer yields were in the range 41−60%, and the polymers possessed M_n of 16 200−29 800. Among them, the polymerization in THF gave the best results with respect to polymer yield and the M_n, and the same behavior was observed for monomer **2**; i.e., polymer yield (65%) and M_n (3300) were highest in THF solution. This monomer hardly polymerized in toluene, which is attributable to the strong interaction between the Rh metal and the amide group in

Table 1. Polymerization of Monomers 1 and 3 with (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$]^a

			polymer^b		
run	monomer	solvent	yield, %	M_n^{c}	M_w/M_n^{c}
1	**1**	toluene	41	16200	1.79
2	**1**	$CHCl_3$	59	19300	1.69
3	**1**	THF	60	29800	1.63
4	**2**	toluene	trace		
5	**2**	$CHCl_3$	55	1500	1.40
6	**2**	THF	65	3300	1.20
7	**3**	THF	20	3700	1.73

[a] Polymerized at 30 °C for 24 h; $[M]_0 = 0.25$ M, [Rh] = 2.5 mM. [b] Diethyl ether-insoluble part. The color of the polymers was pale yellow. [c] Determined by GPC eluted with THF, using a polystyrene calibration.

Table 2. Polymerization of Monomers 4−6 with the Grubbs Second Generation Catalyst^a

		polymer^b		
run	monomer	yield, %	M_n^{c}	M_w/M_n^{c}
1	**4**	94	272 300	3.53
2	**5**	90	210 600	3.67
3	**6**	95	209 000	4.24

[a] Polymerized in CH_2Cl_2 at 30 °C for 2 h; $[M]_0 = 0.50$ M, [Ru] = 5.0 mM. [b] Diethyl ether-insoluble part. The color of the polymers was gray. [c] Determined by GPC eluted with THF, polystyrene calibration.

nonpolar toluene. However, the polymerization of **3** hardly afford polymer probably owing to the steric hindrance of substituted groups.

Table 2 summarizes the conditions and results of ring-opening metathesis polymerization (ROMP) of norbornene monomers **4**−**6** using the Grubbs second generation catalyst in CH_2Cl_2 at 30 °C for 2 h. The polymerization mixtures became deep yellow within 30 min and gradually turned dark brown with the concomitant increase of viscosity. After polymerization, the reaction mixture was poured into a large amount of diethyl ether to precipitate the formed polymers. Gray solid polymers were obtained in 90−95% yields, whose M_n values were as high as 209 000−272 300. Both yield and M_n of the polymers scarcely changed even though the polymerization time was prolonged beyond 2 h.

Structure of the Polymers. Poly(**1**) and poly(**2**) exhibited no IR absorptions due to the stretching vibrations of C≡C and H−C≡, indicating that the ordinary acetylene polymerization took place. Polymerization of monomers **4**−**6** most likely takes place by ROMP of the norbornene moiety, although no clear information was obtained by IR spectroscopy. Strong absorption maxima at 1364 cm^{-1} assignable to the nitroxyl radical were observed in the IR spectra of all the polymers, indicating the presence of PROXYL moiety in the polymers.

Properties of the Polymers. Poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) were soluble in relatively nonpolar common organic solvents including toluene, $CHCl_3$, CH_2Cl_2 and THF but insoluble in *n*-hexane and diethyl ether. TGA traces of the present polymers are shown in Figure 1. The temperatures for 5% weight loss for poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) were around 220−250 °C under air. All the polymers containing PROXYLs decomposed in similar fashions regardless of the main-chain structure (polyacetylene and polynorborene), suggesting that the thermolysis of the polymers initially occurs at the ester linkage which connects PROXYL moiety to the main chain, followed by the decomposition of the double bonds in the main chain.

Figure 2 depicts the UV−vis spectra of poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) in $CHCl_3$, along with those of monomers **1**, **2**, and **4**−**6** for comparison. In all these spectra, the PROXYL

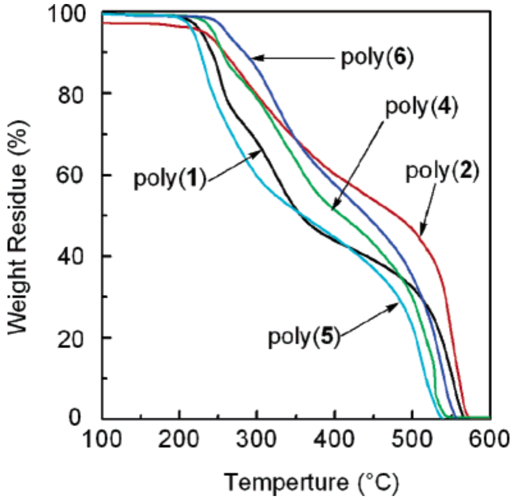


Figure 1. TGA curves of poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) measured at a heating rate of 10 °C /min in air. Poly(**1**): run 3, Table 1; poly(**2**): run 6, Table 1; poly(**4**)−poly(**6**): Table 2.

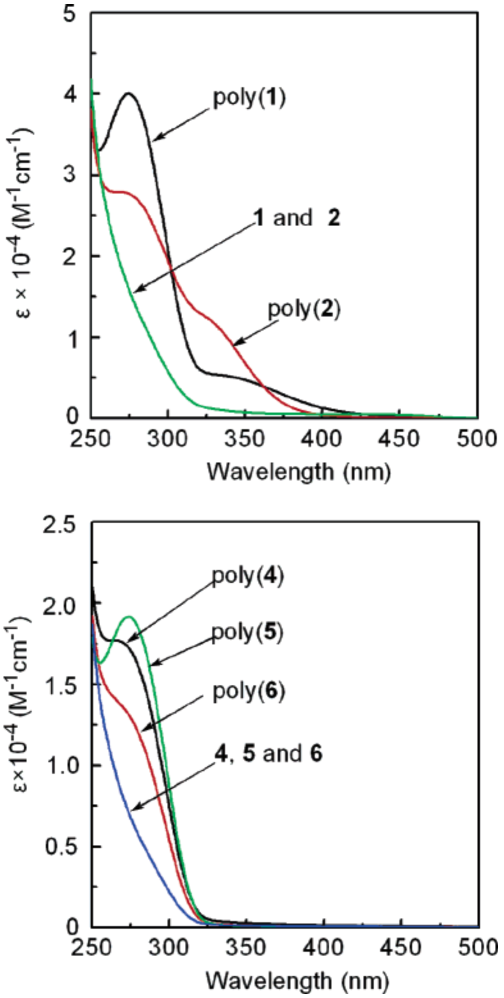


Figure 2. UV−vis spectra of **1**, **2** and **4**−**6** and poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) measured in $CHCl_3$. Concentration: **1** and poly(**1**): 4.46×10^{-5} M; **2** and poly(**2**): 4.48×10^{-5} M; **4**−**6** and poly(**4**)−poly(**6**): 2.04×10^{-5} M. Poly(**1**): run 3, Table 1; poly(**2**): run 6, Table 1; poly(**4**)−poly(**6**): Table 2.

moiety displays no absorption above 325 nm, which accounts for the almost white color of the monomers. Poly(**1**) and poly(**2**) with pale yellow color exhibited absorptions in the range 325−450 nm, which should originate from the conjugated polyacetylene main chain, while monomers **1** and **2** showed no

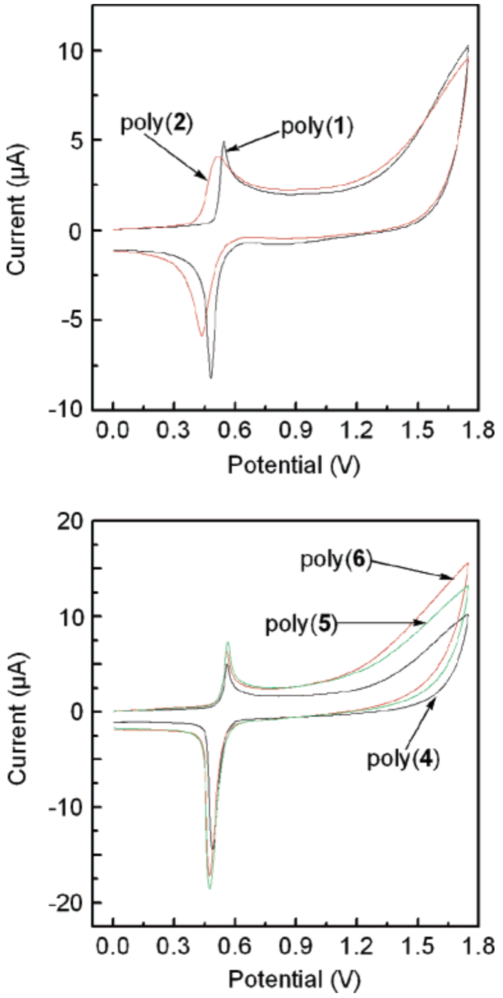


Figure 3. Cyclic voltammograms of poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) measured at a scan rate of 0.01 V/s vs Ag/Ag$^+$ in TBAP solution. Poly(**1**): run 3, Table 1; poly(**2**): run 6, Table 1; poly(**4**)−poly(**6**): Table 2.

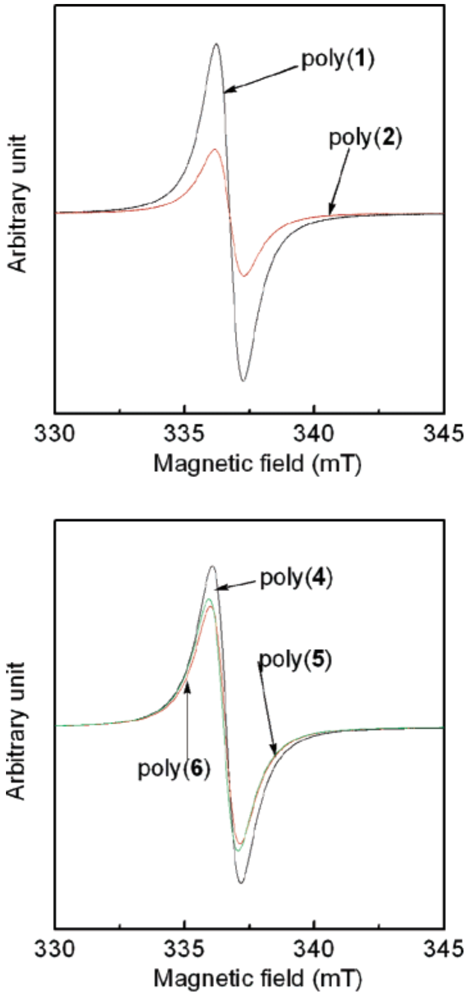


Figure 4. ESR spectra of poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) measured in the powdery state. Poly(**1**): run 3, Table 1; poly(**2**): run 6, Table 1; poly(**4**)−poly(**6**): Table 2.

absorption in this region. The observation that no absorption was seen above 325 nm in poly(**4**)−poly(**6**) is consistent with their nonconjugated main chain.

The cyclic voltammetry (CV) curves of poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) at the first cycle are shown in Figure 3. Reversible oxidation and reduction based on the PROXYL radical are observed for all the polymers. Poly(**1**) exhibits an oxidation potential peak at 0.55 V vs Ag/Ag$^+$ and a reduction potential peak at 0.47 V vs Ag/Ag$^+$, while poly(**2**) shows the corresponding peaks at 0.52 and 0.44 V, respectively. Poly(**4**)−poly(**6**) showed similar oxidation peaks at 0.56, 0.57, and 0.56 V and the corresponding reduction peaks at 0.49, 0.48, and 0.47 V, respectively. It is noted that the distances between the oxidation and reduction peak potentials of poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) are 0.080, 0.081, 0.072, 0.090, and 0.092 V, respectively, at a sweep rate of 0.01 V/s, which are by far smaller than those of other electroactive organic materials such as PTMA (ca. 0.146 V),[17c] disulfide compounds (ca. 0.10−0.20 V),[20] and conducting polymers (ca. 0.20−0.80 V).[21] The small gaps between the reduction and oxidation peaks generally imply large electrode reaction rates of the polymers, which suggests that these polymers will exert high power rates in the charge/discharge processes of battery under the constant battery process conditions. Poly(**1**), poly(**2**), and poly(**4**) show larger oxidation/reduction rates among the present polymers because the separation of its oxidation and reduction peak potentials is 0.072−0.081 V and smaller. Therefore, the poly(**1**)-, poly(**2**)-, and poly(**4**)-based batteries will exhibit high power−rate performance in the charge/discharge process. Although CV scans were continued in five cycles, the oxidation and reduction peaks of poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) scarcely changed, indicating that the electrochemical properties of these PROXYL-containing polymers are sufficiently stable.

Figure 4 depicts the electron spin resonance (ESR) spectra of poly(**1**), poly(**2**), and poly(**4**)−poly(**6**). All the ESR spectra exhibited a sharp singlet signal based on the PROXYL moiety with the ESR *g*-factor of 2.0063, which is slightly larger than 2.0055 for a typical nitroxyl radical of the TEMPOL (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl) crystal, probably because of the interaction with the polymer backbone. The spin concentrations determined with X-band ESR were approxi-

Table 3. Magnetic Properties of Polymers

polymer	no. of free radicals per monomer unit	Curie−Weiss temp (K)	ESR *g*-factor	ESR line width (G) ∼50 MHz	 ∼9400 MHz
poly(**4**)	2.06 ± 0.10	2.2	2.0063	15.4	9.6
poly(**5**)	1.99 ± 0.10	2.2	2.0063	15.6	9.7

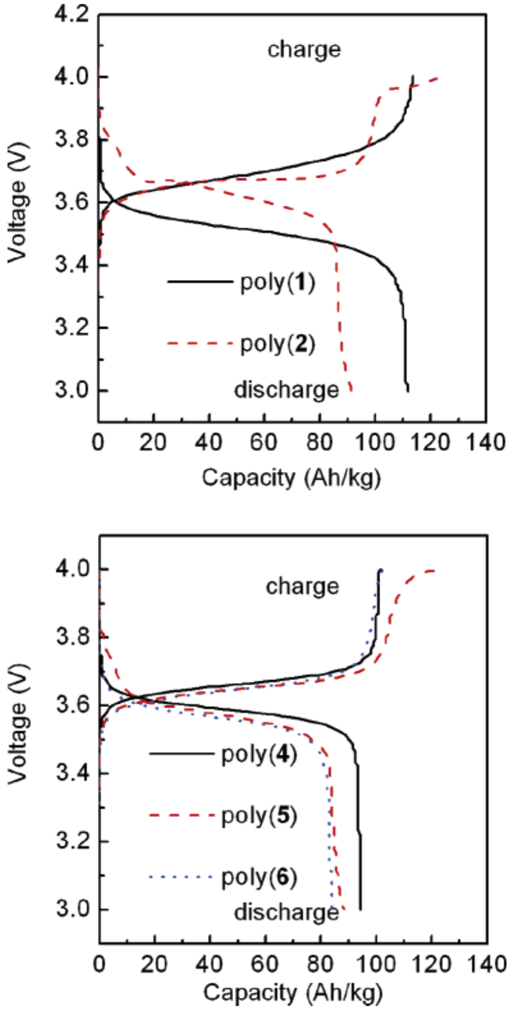


Figure 5. Charge/discharge curves of poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) at a current density of 0.089 mA/cm^2 (100 mA /g$_{\text{cathode active material}}$) in a voltage range of 3.0−4.0 V. Poly(**1**): run 3, Table 1; poly(**2**): run 6, Table 1; poly(**4**)−poly(**6**): Table 2.

mately in the range 0.7 × 10^{21}−4.2 × 10^{21} spins/g, indicating that the local spin concentrations within the macromolecular domain are high. More precise determination was carried out for poly(**4**) and poly(**5**) with both SQUID susceptometer and ESR at low frequency (Table 3). Quite interestingly, it is clear that each repeating unit of both polymers possess around two radicals, namely quantitative amounts of spins, based on the PROXYL moiety. The Curie−Weiss temperature of 2.2 K is lower than 7 K for the TEMPOL crystal, suggesting anisotropic magnetic interaction between the PROXYL radicals of the polymers, in comparison with the 3D magnetic interaction in the TEMPOL crystal. The strong frequency dependence of the ESR line widths is also an indication of the anisotropic magnetic interaction, typical of the quasi-1D spin systems in the polymers.[22]

Coin-type cells were fabricated using poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) as cathodes, and the charge/discharge curves of the cells were observed at a constant current density of 0.089 mA/cm^2 in the voltage range 3.0−4.0 V. Figure 5 shows clear voltage plateaus in both charge and discharge curves with all the cells, implying that the polymers are usable as cathode-active materials of a rechargeable battery. The plateau voltages of the charge/discharge processes are in the range 3.4−3.8 V starting at ∼3.6 V, which corresponds to the redox potential of the PROXYL radical. It is reasonable to assume that the charge process at the cathode is oxidation of PROXYL (**7**) in the polymers to oxoammonium salt (**8**), and the discharge process is the reverse reaction, namely, reduction of the salt (Scheme 4). Taking into account that one PROXYL moiety provides one electron in this redox process, we can estimate the theoretical capacities of the cells fabricated with poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) to be 109−120 A h/kg (Table 4). Evaluating from the values at 3 V in Figure 5, the initial discharge capacities of the cells fabricated with poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) are determined to be 85−117 A h/kg per polymer weight at a current density of 0.089 mA/cm^2.

Scheme 4

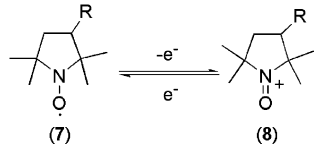


Table 4. Capacity Data of Polymers

polymer	m/e[a]	theor capacity, A h/kg[b]	obsd capacity, A h/kg[c]	obsd capacity/ theor capacity, %
poly(**1**)[d]	224.3	119.6	117.2	98.0
poly(**2**)[d]	223.1	120.0	94.7	78.9
poly(**4**)	245.2	109.3	107.0	98.0
poly(**5**)	245.2	109.3	89.0	81.4
poly(**6**)	245.2	109.3	84.9	77.7

[a] The molecular weight per exchangeable unit. [b] Theoretical capacity (A h/kg), namely specific charge (in A h/kg), was calculated according to ref 28. [c] Observed capacity (A h/kg): initial discharge capacity at a current density of 0.089 mA/cm^2, cutoff at 2.5 V. [d] Poly(**1**) sample from run 3 in Table 1 and poly(**2**) sample from run 6 in Table 1.

The experimentally observed discharge capacity of poly(**1**) was 98% of the theoretical capacity, while that of poly(**2**) was no more than 79% of the theoretical capacity (Table 4). It is interesting to note that the observed discharge capacity of poly(**1**) and poly(**2**), 117 and 95 A h/kg, are much higher than those of the TEMPO-containing counterparts (66 and 81 A h/kg, respectively).[19,23] The average value of two experiments (103 and 111 A h/kg) for the capacity of poly(**4**)-based cell was 107 A h/kg, which reaches 98% of the theoretical capacity value (109 A h/kg). This ratio is the same as that of poly(**1**), indicating that poly(**1**) and poly(**4**) exhibit high capacity which will lead to a wide range of potential applications as a power source. On the other hand, the capacities of the poly(**5**)- and poly(**6**)-based cells remained 89 and 85 A h/kg, respectively, clearly lower than that of the poly(**4**)-based counterpart. This seems to be due to the difference in spatial arrangement of the PROXYL radicals; more specifically, a spatial arrangement that places the PROXYL groups far apart seems to favor a high capacity, as in the case of TEMPO-carrying polynorbornenes.[19] Another possible reason for the difference in capacity is a difference in the macroscopic aggregation state (e.g., the size and hardness of polymer powders) but not in the spin concentration (because the spin concentrations of poly(**4**) and poly(**5**) are both quantitative). The capacities of the corresponding TEMPO-containing polymers for poly(**4**)−poly(**6**) are 68, 78, and 45, respectively,[24] which are obviously smaller than those of poly(**4**)−poly(**6**). The result that the PROXYL-containing polymers, poly(**1**), poly(**2**), and poly(**4**)−poly(**6**), display larger capacities than the TEMPO-bearing counterparts indicates that the PROXYL moiety is more efficient to achieve large capacity than is TEMPO.

Figure 6 depicts the charge/discharge curves of poly(**1**) observed at different currents. The charge and discharge capacities gradually decreased with increasing current, which is attributable to the polarization of PROXYL. A useful capacity

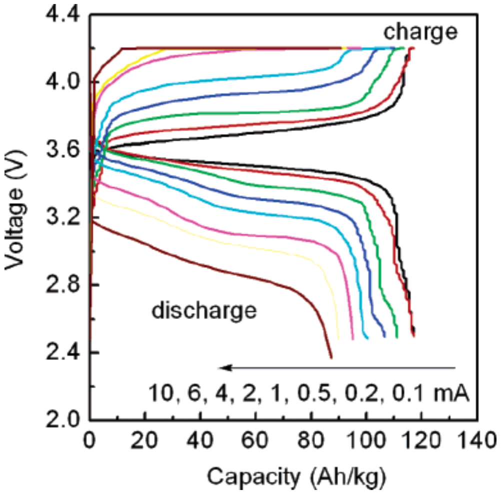


Figure 6. Charge/discharge curves of poly(**1**) at different currents in a voltage range of 2.5−4.2 V. Poly(**1**): run 3, Table 1.

of ca. 87 A h/kg was attained at 10 C mA, which corresponds to 74% of the discharge capacity at 0.1 C mA, indicating that the poly(**1**)-based cell displays the excellent charge/discharge characteristics under the extremely large currents. The poly(**4**)-based cell exhibited a similar performance to that of poly(**1**), whereas poly(**2**), poly(**5**), and poly(**6**) showed inferior properties under large currents.

Figure 7 depicts the relationship between capacity and discharge rate of poly(**1**), poly(**2**), and poly(**4**)−poly(**6**). In this figure, C is the unit for the current expressed as multiple of the nominal capacity of the cell, which was ca. 0.2 mA. The large capacity of poly(**1**) was maintained fairly well even though the discharge rate was increased to 80 C. By contrast, the capacity of poly(**2**) and poly(**4**)−poly(**6**) decreased considerably with increasing discharge rate. This means that a large current is available in the discharge of poly(**1**).

Figure 8 illustrates the cycle performance of the poly(**1**), poly(**2**), and poly(**4**)−poly(**6**)/Li batteries, in which charging and discharging were repeated at a 0.089 mA/cm^2 current density under application of 3.0−4.0 V cell voltages. The cell using poly(**1**) retained about 85% of the capacity after 100 cycles. Poly(**2**) exhibited a different cycle performance; namely, the increase in capacity was observed during the initial 30 cycles, which appears to arise from the increase in the contact surface between the electrode and the electrolyte probably because of swelling of the polymer. The discharge capacity of poly(**4**) did not deteriorate even after 100 cycles, whereas the capacities of the poly(**5**) and poly(**6**) cells decreased to about 65 and 75% of the initial values, respectively. It seems that the cycle lives of poly(**1**), poly(**2**), and poly(**4**)-based cells are comparable to that of the reported PTMA system.[17]

As discussed above, poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) can be applied to the cathode-active materials in organic radical batteries as charge-storage materials, which are promising as quickly chargeable/dischargeable and high power density batteries. Among the present polymers, poly(**1**) exhibited a high capacity up to 117 A h/kg, which is observed even at a high discharge rate up to 80 °C. On the other hand, poly(**4**) is characterized by a high capacity up to 107 A h/kg, which is kept even after 100 cycles.

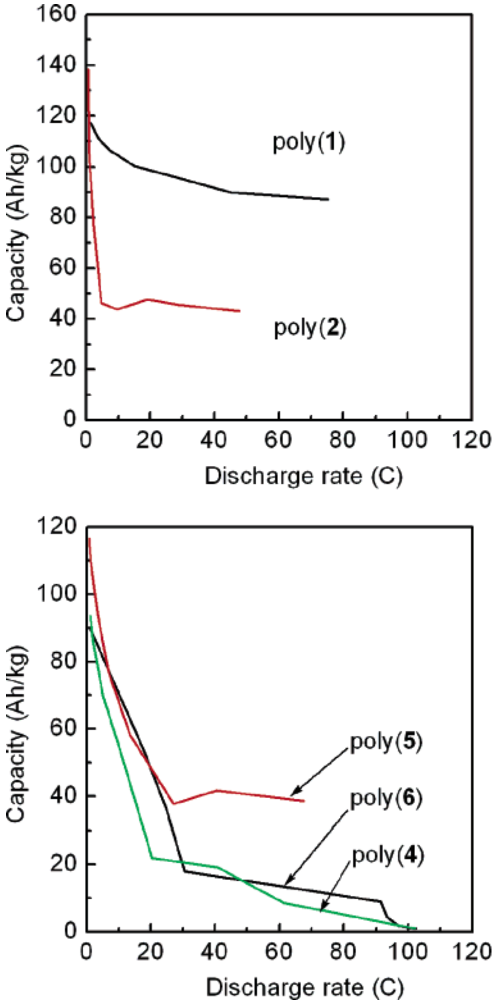


Figure 7. Dependence of capacity on discharge rate of poly(**1**), poly(**2**), and poly(**4**)−poly(**6**). Poly(**1**): run 3, Table 1; poly(**2**): run 6, Table 1; poly(**4**)−poly(**6**): Table 2.

Conclusions

In the present research, we synthesized a group of monomers containing PROXYL, **1**−**6**, and polymerized them with rhodium and ruthenium catalysts. While acetylenic monomers **1** and **2** yielded polymers with M_n of 3300−29 800 in 60−64% yields, norbornene derivatives **4**−**6** gave polymers with M_n of 209 000−272 000 in 90−94% yields. The formed polymers were thermally stable and soluble in common organic solvents. The separations of the oxidation and reduction potential peaks of these polymers in CV were by far smaller than those of other electroactive organic materials, indicative of high power rate in the charge/discharge processes of battery. The ESR spectra of poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) exhibited a sharp singlet, and poly(**4**) and poly(**5**) possessed practically quantitative amounts of free radicals based on the PROXYL moiety, namely, around two spins per repeating unit. The capacity of poly(**1**)-based cell was as large as 117 A h/kg, corresponding to 98% of the theoretical capacity value (119 A h/kg). The cell fabricated with poly(**4**) as cathode demonstrated a promising cycle life; i.e., the discharge capacity did not deteriorate even after 100 cycles. The discharge rate of the poly(**1**)-based cells could be much faster than those of other polymers. Charge-storage materials based on poly(**1**), poly(**2**), and poly(**4**)−poly(**6**) can be applied to cathode-active materials in organic radical batteries. The high capacity and excellent charging and discharging characteristics of poly(**1**) indicate that a wide array of potential applications are expected as a power source for this type of polymer.

Experimental Section

Measurements. IR spectra were measured using a JASCO FT/IR-4100 spectrophotometer. Melting points (mp) were measured

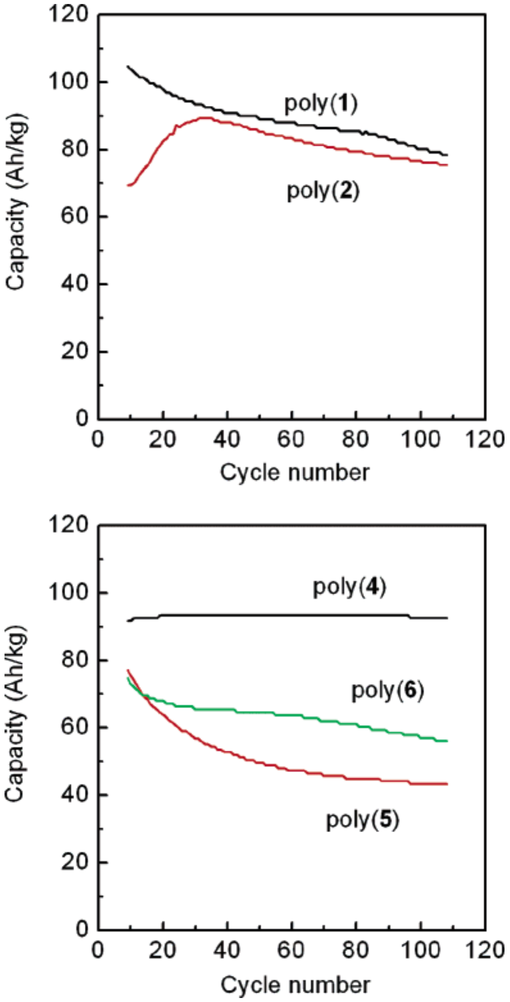


Figure 8. Dependence of capacity on cycle number of poly(**1**), poly(**2**), and poly(**4**)−poly(**6**). Charging and discharging were repeated at a 0.089 mA/cm^2 current density in a range of 3.0−4.0 V cell voltage. Poly(**1**): run 3, Table 1; poly(**2**): run 6, Table 1; poly(**4**)−poly(**6**): Table 2.

on a Yanaco micro melting point apparatus. Elemental analysis was done at the Kyoto University Elemental Analysis Center. The number- and weight-average molecular weights (M_n and M_w, respectively) 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 at 40 °C with a polystyrene calibration. Thermal gravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA-7 thermal analyzer. ESR spectra were measured on a JEOL JES-FR30 type X-band (9.48 GHz) spectrometer. 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.[25] Cyclic voltammograms were observed with an HCH Instruments ALS600A-n electrochemical analyzer. The measurements were carried out with a modified ITO substrate as the working electrode coupled with a Pt plate counter electrode and an Ag/AgCl reference electrode, using a solution of a polymer (1 mM) and tetrabutylammonium perchlorate (TBAP, 0.1 M) in CH_2Cl_2.

Materials. Solvents used for polymerization were distilled before use according to the standard procedures. The Grubbs second generation catalyst was purchased from Materia, Inc., and used as received. 3-Carboxy-PROXYL (TCI), propargyl alcohol (Aldrich), propargylamine (Aldrich), 5-norbornene-2-*exo*,3-*exo*-dimethanol (Aldrich), 5-norbornene-2-*endo*,3-*endo*-dimethanol (Aldrich), 5-norbornene-2,2-dimethanol (Aldrich), *N*-(3-(dimethylamino)propyl)-*N*′-ethylcarbodiimide hydrochloride (EDC•HCl; Eiweiss Chemical Corp.), 4-(dimethylamino)pyridine (DMAP; Wako), *N*-methylmorpholine (Wako), and isobutyl chloroformate (Wako) were purchased and used without further purification. 1-Pentyne-4,4-dimethanol and (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] were synthesized according to the literature.[26,27]

Monomer Synthesis. 1 was prepared as follows: 3-Carboxy-PROXYL (500 mg, 2.68 mmol) was added to a solution of EDC•HCl (796 mg, 3.04 mmol) and DMAP (37 mg, 0.34 mmol) in CH_2Cl_2 (15 mL) at room temperature. Propargyl alcohol (170 mg, 3.04 mmol) was added to the solution, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was washed with water (20 mL) three times, and the organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed by rotary evaporation to afford the crude product. It was purified on a silica gel column with a hexane/ethyl acetate mixture (4/1 volume ratio) as eluent. A pale yellow liquid of **1** was obtained in 89% yield (500 mg). IR (KBr, cm^{-1}): 3294 ($\nu_{\mathrm{H-C\equiv}}$), 2976, 2935, 2873, 2127 ($\nu_{\mathrm{C\equiv C}}$), 1746 ($\nu_{\mathrm{C=O}}$), 1463, 1365($\nu_{\mathrm{N-O}}$), 1305, 1291, 1194, 1168 ($\nu_{\mathrm{C-O}}$), 1017, 958, 686, 648. Anal. Calcd for $C_{12}H_{18}NO_3$: C, 64.26; H, 8.09; N, 6.25. Found: C, 64.20; H, 8.17; N, 6.24.

2 was prepared as follows: *N*-Methylmorpholine (272 mg, 2.68 mmol) was added to a solution of 3-carboxy-PROXYL (500 mg, 2.68 mmol) in THF (10 mL) at room temperature. Isobutyl chloroformate (366 mg, 2.68 mmol) was added to the solution to precipitate *N*-methylmorpholine hydrochloride as a white mass. Then, propargylamine (148 mg, 2.68 mmol) was added, and the resulting mixture was stirred at room temperature overnight. The precipitate was removed by filtration, and the filtrate was concentrated by rotary evaporation. The residue was dissolved in ethyl acetate (20 mL) and washed with water three times and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed to afford the crude product. It was purified by recrystallization from hexane/ethyl acetate (1/1 volume ratio). A pale yellow solid of **2** was obtained in 83% yield (500 mg); mp 102−103 °C. IR (KBr, cm^{-1}): 3328 ($\nu_{\mathrm{N-H}}$), 3214 ($\nu_{\mathrm{H-C\equiv}}$), 2977, 2932, 2117 ($\nu_{\mathrm{C\equiv C}}$), 1702, 1661 ($\nu_{\mathrm{C=O}}$), 1528 ($\delta_{\mathrm{N-H}}$), 1364 ($\nu_{\mathrm{N-O}}$), 1327, 1258, 1173, 1150, 1041, 709, 647. Anal. Calcd for $C_{12}H_{19}N_2O_2$: C, 64.55; H, 8.58; N, 12.55. Found: C, 64.27; H, 8.44; N, 12.51.

3 was synthesized from 1-pentyne-4,4-dimethanol and 2 equiv of 3-carboxy-PROXYL in a manner similar to **1**. Yield 74%, pale yellow liquid. IR (KBr, cm^{-1}): 3462, 3275, 2975, 2934, 2120, 1735 ($\nu_{\mathrm{C=O}}$), 1458, 1379, 1363 ($\nu_{\mathrm{N-O}}$), 1303, 1254, 1193, 1152, 1104, 1067, 1012, 781, 697, 647. Anal. Calcd for $C_{25}H_{40}N_2O_6$: C, 64.63; H, 8.68; N, 6.03. Found: C, 64.27; H, 8.44; N, 6.31.

4 was synthesized from 5-norbornene-2-*exo*,3-*exo*-dimethanol and 2 equiv of 3-carboxy-PROXYL in a manner similar to **1**. Yield 88%, pale yellow liquid. IR (KBr, cm^{-1}): 3465, 3058, 2970, 2934, 2871, 1734 ($\nu_{\mathrm{C=O}}$), 1560, 1541, 1462, 1422, 1363 ($\nu_{\mathrm{N-O}}$), 1303, 1253, 1197, 1163, 1104, 1067, 1005, 780, 730, 699, 646. Anal. Calcd for $C_{27}H_{42}N_2O_6$: C, 66.10; H, 8.63; N, 5.71. Found: C, 66.22; H, 8.61; N, 5.47.

5 was synthesized from 5-norbornene-2-*endo*,3-*endo*-dimethanol and 2 equiv of 3-carboxy-PROXYL in a manner similar to **1**. Yield 75%, pale yellow liquid. IR (KBr, cm^{-1}): 3450 ($\nu_{\mathrm{O-H}}$), 3059, 2976, 2975, 2933, 1735 ($\nu_{\mathrm{C=O}}$), 1637, 1574, 1464, 1422, 1363 ($\nu_{\mathrm{N-O}}$), 1325, 1303, 1253 ($\nu_{\mathrm{C-O}}$), 1195, 1163, 1149, 1105, 1067, 1047, 1005, 949, 754, 666, 640. Anal. Calcd for $C_{27}H_{42}N_2O_6$: C, 66.10; H, 8.63; N, 5.71. Found: C, 65.92; H, 8.60; N, 5.64.

6 was synthesized from 5-norbornene-2,2-dimethanol and 2 equiv of 3-carboxy-PROXYL in a manner similar to **1**. Yield 82%, pale yellow liquid. IR (KBr, cm^{-1}): 3450, 3061, 2972, 2934, 2878, 1738 ($\nu_{\mathrm{C=O}}$), 1634, 1571, 1464, 1422, 1363 ($\nu_{\mathrm{N-O}}$), 1303, 1255, 1193, 1150, 1104, 1067, 1004, 952, 754, 720, 700, 657. Anal. Calcd for $C_{27}H_{42}N_2O_6$: C, 66.10; H, 8.63; N, 5.71. Found: C, 65.82; H, 8.67; N, 5.57.

Since it was impossible to measure the NMR spectra of the monomers, the ^{1}H and ^{13}C NMR spectra of the hydroxyamine compounds (**1′**−**6′**; Scheme 3) were examined, whose data are as follows. **1′**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.72−4.62 (m, 2H, CH_2CMe_2), 2.84 (s, 1H, HC≡), 2.40 (qu, 1H, CHC≡O), 1.82 (s, 2H, CH$_2$O), 1.35 (s, 3H, CH$_3$), 1.23 (s, 3H, CH$_3$), 1.17 (s, 3H, CH$_3$), 1.06 (s, 3H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 162.3 (C≡O), 83.4 (CH$_2$*C*≡), 74.6 (≡CH), 67.3 (CH*C*Me$_2$), 62.1 (CH$_2$*C*Me$_2$), 53.7 (CH$_2$O), 51.6 (*C*HC≡O), 36.9 (*C*H$_2$CMe$_2$), 26.4 (CH$_2$C*Me*$_2$), 25.5 (CHC*Me*$_2$). **2′**: ^{1}H NMR (400 MHz, CDCl$_3$, δ): 4.02−3.99 (m, 2H, CH$_2$N), 2.61 (qu, 1H, CHC≡O), 2.17 (s, 1H, HC≡), 2.0−1.37 (m, 2H, CH$_2$CMe$_2$), 1.36−1.12 (m, 12H, 4Me). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 159.9 (C≡O), 83.1 (CH$_2$*C*≡), 74.3 (≡CH) , 60.5 (CH*C*Me$_2$), 56.1 (CH$_2$*C*Me$_2$), 36.3 (*C*H$_2$C≡), 32.3 (*C*H$_2$CMe$_2$), 23.3 (CH$_2$C*Me*$_2$), 16.9 (CHC*Me*$_2$). **3′**: ^{1}H NMR (400 MHz, CDCl$_3$, δ): 3.85−4.05 (m, 4H, 2CCH$_2$O), 2.74 (s, 2H, 2COCHCMe$_2$), 2.23 (s, 2H, CH$_2$C≡), 1.97−2.08 (m, 4H, 2CH$_2$-CMe$_2$), 1.74 (s, 1H, HC≡), 1.29 (s, 3H, CCH$_3$), 0.99−1.18 (m, 24H, 8Me). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 173 (C≡O), 78.8 (CH$_2$*C*≡), 69.6 (≡CH), 66.7 (C*C*H$_2$O), 62.2 (CH*C*Me$_2$) 52.6 (CH$_2$*C*Me$_2$), 36.7 (*C*HCO), 36.1 (CH*C*H$_2$CMe$_2$), 31.7 (CH$_3$*C*CH$_2$), 26.6 (*C*H$_2$C≡), 19.3 (CH$_2$C*Me*$_2$), 18.6 (CHC*Me*$_2$), 7.52 (CH$_3$*C*CH$_2$). **4′**: ^{1}H NMR (400 MHz, CDCl$_3$, δ): 6.15 (s, 2H, −CH≡), 3.80−3.62 (m, 4H, 2CH$_2$O), 2.87 (brs, 2H, 2═CHC*H*), 2.10 (s, 2H, 2C*H*CH$_2$O), 1.97 (s, 2H, 2CHC═O), 1.79 (brs, 2H, CHC*H*$_2$CH), 1.43−1.29 (m, 4H, 2CH$_2$CMe$_2$), 1.19 (s, 24H, 8Me). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 166.8 (2C═O), 133.2 (2C═), 61.9 (2CH*C*Me$_2$), 56.2 (2CH$_2$*C*Me$_2$), 40.6 (2CH$_2$O), 39.8 (CH*C*H$_2$CH), 38.5 (2═CH*C*H), 35.7 (2CH*C*HCH$_2$), 28.1 (2*C*HC≡O), 17.0 (2*C*H$_2$-CMe$_2$), 15.0 (2CH$_2$C*Me*$_2$), 10.0 (2CHC*Me*$_2$). **5′**: ^{1}H NMR (400 MHz, CDCl$_3$, δ): 6.14 (s, 2H, −CH≡), 4.05−3.72 (m, 4H, 2CH$_2$O), 2.87 (brs, 2H, 2CHC═), 2.50 (s, 2H, 2CHC*H*CH$_2$), 1.97 (s, 2H, 2CHC═O), 1.79 (s, 2H, CHC*H*$_2$CH), 1.54 (s, 4H, 2C*H*$_2$-CMe$_2$), 1.20 (m, 24H, 8Me). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 164.9 (2C═O), 130.1 (2C═), 70.2 (2CH$_2$O), 59.1 (2CH*C*Me$_2$), 54.4 (2CH$_2$*C*Me$_2$), 43.0 (CH*C*H$_2$CH), 39.8 (2═C*C*H), 39.6 (2CH*C*HCH$_2$), 34.6 (2*C*HC═O), 15.3 (2*C*H$_2$CMe$_2$), 8.9 (2CH$_2$C*Me*$_2$), 8.3 (2CHC*Me*$_2$). **6′**: ^{1}H NMR (400 MHz, CDCl$_3$, δ): 6.19 (m, 2H, CH≡CH), 4.06−3.69 (m, 4H, 2CH$_2$O), 2.87 (s, 2H, 2═CC*H*), 2.68 (s, 2H, ═CCC*H*$_2$), 2.00 (s, 2H, 2CHC═O), 1.79 (s, 2H, CHC*H*$_2$-CH), 1.53 (s, 4H, 2C*H*$_2$CMe$_2$), 1.20 (s, 24H, 8Me). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 160.3 (2C═O), 127.8 (C≡C), 58.4 (2*C*H$_2$O), 57.3 (2CH*C*Me$_2$), 50.0 (2CH$_2$*C*Me$_2$), 37.1 (CH*C*H$_2$CH), 36.8 (═C*C*HC), 35.9 (═C*C*HCH$_2$), 32.0 (O≡C*C*HCH$_2$), 26.1 (═CC*C*CH$_2$), 23.1 (2*C*H$_2$CMe$_2$), 10.9 (═CC*C*H$_2$C), 8.7 (2CH$_2$C*Me*$_2$), 3.9 (2CHC*Me*$_2$).

Polymerization. Polymerizations of acetylenic monomers **1**−**3** were carried out with (nbd)Rh$^+$[η^6-C$_6$H$_5$B$^-$(C$_6$H$_5$)$_3$] as a catalyst in dry toluene, CHCl$_3$, or THF at 30 °C for 24 h under the following conditions: $[\text{monomer}]_0 = 0.25$ M, $[\text{catalyst}] = 2.5$ mM. After polymerization, the resultant solution was poured into a large amount of diethyl ether to precipitate the formed polymer. It was filtered and then dried under reduced pressure.

Polymerizations (ROMP) of norbornene monomers **4**−**6** were carried with the Grubbs second generation catalyst in dry CH$_2$Cl$_2$ at 30 °C for 2 h under the following conditions: $[\text{monomer}]_0 = 0.50$ M, $[\text{catalyst}] = 5.0$ mM. The polymerization was quenched by adding *tert*-butyl vinyl ether (0.20 mL) and stirring the mixture at room temperature for 1 h. The polymers were isolated by precipitation in diethyl ether.

IR (KBr, cm^{-1}) Data of the Polymers. Poly(**1**): 3455, 2974, 2932, 2872, 1736, 1462, 1380, 1364, 1302, 1254, 1187, 1147, 1104, 1066, 997, 948, 877, 852, 747, 698, 668, 647, 561. Poly(**2**): 3450, 3321, 3058, 2975, 2932, 1657, 1533, 1462, 1364, 1302, 1225, 1169, 1149, 1105, 1035, 889, 852, 747, 689, 671, 654, 630. Poly(**4**): 3459, 2975, 2933, 1734, 1637, 1463, 1422, 1362, 1303, 1255, 1191, 1165, 1146, 1104, 1066, 1007, 947, 777, 695, 669, 649. Poly(**5**): 3455, 2973, 1736, 1637, 1560, 1541, 1464, 1422, 1363, 1303, 1254, 1192, 1147, 1104, 1067, 1003, 969, 838, 779, 754, 699, 670, 641. Poly(**6**): 3450, 2975, 1736, 1637, 1560, 1464, 1422, 1364, 1303, 1255, 1191, 1146, 1104, 1066, 1005, 779, 743, 700, 657, 646.

Fabrication and Electrochemical Properties of the Batteries Using the Polymers. A coin-type cell was fabricated by stacking electrodes with porous polyolefin separator films. A cathode was formed 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.[19] The cathode was set to a coin-type cell possessing a lithium metal anode. A composite solution of ethylene carbonate (30 vol %)/diethyl carbonate (70 vol %) containing 1 M of LiPF$_6$ was used as an electrolyte. Charge/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 Polymer-Based Cell. The theoretical capacity (in A h/kg) of an electroactive polymer is calculated from the polymer mass or volume required per exchangeable unit charge.[28]

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

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 kg 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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