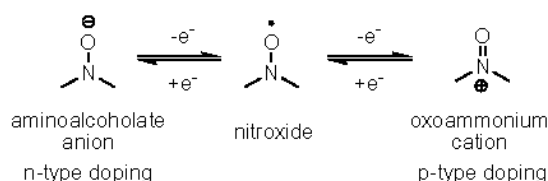


## Radical Polymers and Organic Radical Battery

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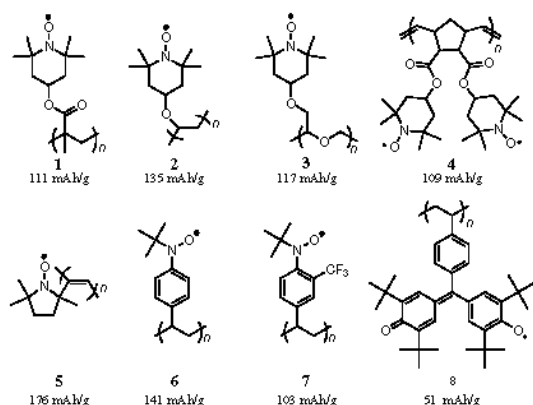
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Organic radical polymers bear multi-unpaired electrons, and are usually chemically reactive. However, they could be converted into stable materials by designing their molecular structures.<sup>1,2)</sup> Some of nitroxide polymers displayed a reversible and very rapid redox to form their oxoammonium salts (a p-type doping, in Scheme 1), with which an organic-cathode was fabricated.<sup>3-5)</sup> Other radical polymers were rapidly and reversibly reduced to their aminoalcoholate form (a n-type doping) and anode-active. The very rapid redox or one-electron transfer of the radical polymers (electron-transfer rate constant =  $10^{-1}$  cm<sup>2</sup>/s, apparent diffusion constant of charge transfer =  $10^{-8}$  cm<sup>2</sup>/s) enabled a dramatically high power-rate performance during the charging and discharging process of the battery.<sup>6)</sup> No deterioration both in the capacity and the power-rate was observed up to 10,000 charging and discharging cycles. The surprisingly long cyclability was ascribed to the simple electron transfer reaction and to the amorphous electrode structure.



**Scheme 1.** P- and n-type redox couples of nitroxide radical

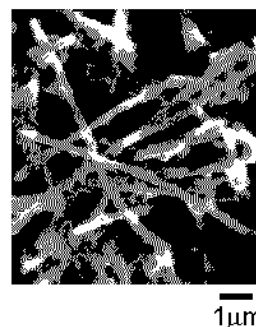
We have synthesized a series of nitroxide polymers: The polymer involves the radical moiety with a high density and allows molding of electrodes. The radical polymers were obtained by the polymerization of the precursor monomers, followed by the oxidation reaction of the precursor polymers. The radical polymers were also prepared by the anionic polymerization or Ru-catalyzed metathesis polymerization of the radical monomer. Molecular weight of the radical polymers was  $> 10^4$ , and the radical content was almost 100% as shown by the chemical structure.



**Scheme 2.** P- and n-type radical polymers

Nitroxide polymers were thermally stable at high temperature: For example, a 10% weight decrease of poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) **1** occurred at 263°C. The radicals on the **1** polymer were almost stable up to this thermal decomposition temperature of the polymer. This radical concentration remained unchanged for over 1 year under ambient conditions. The radical polymers displayed appropriate solubility in organic solvents and were insoluble in electrolyte solutions such as ethylene carbonate and diethyl carbonate with LiPF<sub>6</sub>.

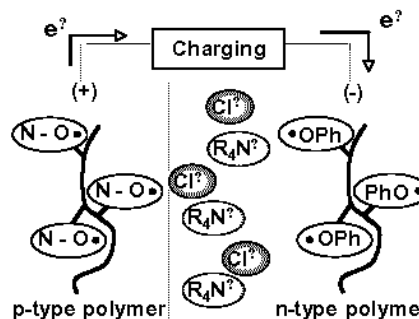
The radical polymers themselves did not show sufficient electric conductivity; therefore, the radical polymer was mixed with 20-50 wt% graphite fibers to give a cathode electrode. A SEM image of the composite electrode (Figure 1) reveals that a graphite nanofiber with a diameter of 150 nm is thoroughly covered with a thin (50-100 nm thick) radical polymer layer.



**Figure 1.** A SEM image of the radical polymer/carbon composite electrode.

*In situ* ESR signals supported ESR-silent oxoammonium formation on the anodic side and regeneration of the nitroxide radical with very high concentration on the cathodic side. The redox potential of the composite electrode were 0.76 V vs. Ag/AgCl (3.58 V vs. Li/Li<sup>+</sup>) for **1**, 0.75 V vs. Ag/AgCl (3.57 V vs. Li/Li<sup>+</sup>) for **4**, and 0.20 V vs. Ag/AgCl (3.15 V vs. Li/Li<sup>+</sup>) for **8**. The narrow peak separation of the redox waves of the radical polymer even in the form of the electrode was attributable to fast electrode reaction kinetics, which afforded the capability for a high power rate in the charging and discharging processes of the battery.

This paper shows a series of our radical polymers (Scheme 2), to describe molecular structure-relationships in energy-density and power-rate performances as the electrode-active material. Environmentally-benign features of the totally organic-based battery (Figure 2) are strong advantage against metal-based conventional batteries. The use of organic radical polymers can open the possibility to design a next generation secondary battery.



**Figure 2.** A totally organic-derived radical battery

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