Synthesis of Poly(oxoammonium salt)s and Their Electrical Properties in the Organic Thin Film Device

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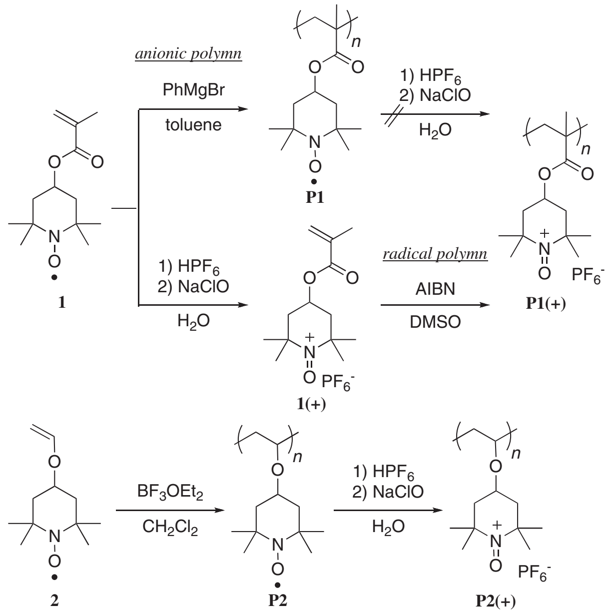
(Received September 8, 2009; CL-090816; E-mail: nishide@waseda.jp)

Two redox-active poly(oxoammonium salt)s were synthesized via chemical oxidation of a TEMPO-substituted polymer, or conventional radical polymerization of the oxoammonium monomer, respectively. The diode-structured thin film device composed of poly(oxoammonium salt) with radical conc. of 6–43% exhibited a resistive switching behavior (ON–OFF ratio $>10^3$), in contrast to the radical-free poly(oxoammonium salt), which revealed that the coexistence of radical/oxoammonium salts contributed to a significant change in *I*–*V* characteristics.

A rapid and reversible one-electron transfer of a nitroxide/oxoammonium redox couple has been utilized in wide applications such as metal-free redox catalysts for alcohol oxidation,[1] and electrode-active materials in the rechargeable batteries.[2,3] In situ formed oxoammonium salts serve as active species in the catalytic reactions, or hold the charged state of the battery. Recently, we have also reported the use of redox-active nitroxide radicals as a charge-transport material[4] or a key component of organic nonvolatile memory.[5] While charge-transfer (D/A) complexes[6] and organic semiconductors[7] have been extensively investigated as organic memory, redox-active radical polymers were employed in our memory device,[5] where in situ formation of oxoammonium cation (charge injection) and an electron self-exchange reaction between nitroxide/oxoammonium redox couples (charge transfer) play an important role. However, less attention has been paid to the electrical properties of poly(oxoammonium salt)s. We report here chemical synthesis of polymethacrylate and poly(vinyl ether) derivatives bearing oxoammonium salts, and their *I*–*V* characteristics in the organic thin film device.

Two synthetic strategies were examined for preparation of poly(oxoammonium salt)s: (a) chemical oxidation of a radical polymer and (b) radical polymerization of an oxoammonium monomer (Scheme 1). Poly(2,2,6,6-tetramethylpiperidine-*N*-oxyl methacrylate) **P1** was chemically oxidized using HPF$_6$ (1.5 equiv/TEMPO unit) and NaClO (0.5 equiv), however, the obtained polymer indicated side reactions on the ester moiety (decrease in $\nu_{C=O}$ absorbance at 1730 cm^{-1} in IR spectrum). The decrease in molecular weight after chemical oxidation also supported the degradation of **P1**.[9] Excess amount of oxidants are necessary for a quantitative chemical oxidation of the polymer however, which must be balanced to avoid side reactions.

As an alternative route to obtain the radical-free poly(oxoammonium salt) (radical conc. = 0%), we selected the radical polymerization of the oxoammonium methacrylate monomer **1(+)**. Less stoichiometric amount of oxidants [HPF$_6$ (0.8 equiv) and NaClO (0.24 equiv)] for the oxidation of 4-methacryloyloxy-TEMPO **1** avoided side reactions on the ester moiety, to give the corresponding oxoammonium salt **1(+)**. The purification procedure of the oxoammonium salts is not trivial due to their sensitivity to alcohols and amines, which leads to the facile regeneration of the TEMPO group.[1] Even a small amount of stabilizers or additives in conventional organic solvents (e.g. 0.5% ethanol in chloroform) regenerated TEMPO, which critically inhibited the following radical polymerization. All solvents were carefully purified, and used for monomer isolation, polymerization, and device fabrication. Repeated recrystallization from acetonitrile/toluene (1/5 v/v) yielded **1(+)** as yellow needle crystals.



Scheme 1. Synthesis of poly(oxoammonium salt)s.

The conventional radical polymerization of **1(+)** in DMSO using azobisisobutyronitrile (AIBN, 5 mol %) was carried out at 65 °C for 24 h under inert atmosphere. The reaction mixture was reprecipitated into dichloromethane to give the corresponding poly(oxoammonium salt) **P1(+)** ($M_n = 32000$, $M_w/M_n = 1.1$). The obtained polymer was soluble in acetonitrile and DMSO. The chemical structure was characterized by ^{1}H NMR, and the radical concentration was estimated by ESR spectrum to be 0%.[9]

The TEMPO-substituted poly(vinyl ether) **P2**[8] was also chemically oxidized with HPF$_6$ and NaClO, to give the corresponding poly(oxoammonium salt) **P2(+)** (Scheme 1). In contrast to polymethacrylate derivative, poly(vinyl ether) structure was durable under oxidation conditions (no significant deterioration in the molecular weight, Table 1). A quantitatively oxidized **P2(+)** was not obtained due to the low yield of the polymer reaction however, the remaining radical concentrations in **P2(+)** varied with the amount of chemical oxidants (Table 1). The radical polymer **P2** and the radical-rich **P2(+)** (Entry 4) was insoluble in organic solvents however the oxoammonium-rich **P2(+)**

Table 1. Oxidation conditions of **P2**

Entry	Oxidant/equiv		M_w	Radical conc. /%[a]
	HPF_6	NaClO		
1	1.50	0.48	96000	6
2	0.80	0.48	78000	23
3	0.80	0.24	83000	43
4	0.65	0.20	—[b]	—[b]

[a] Acetonitrile solution was characterized by ESR spectra. [b] Insoluble in organic solvent.

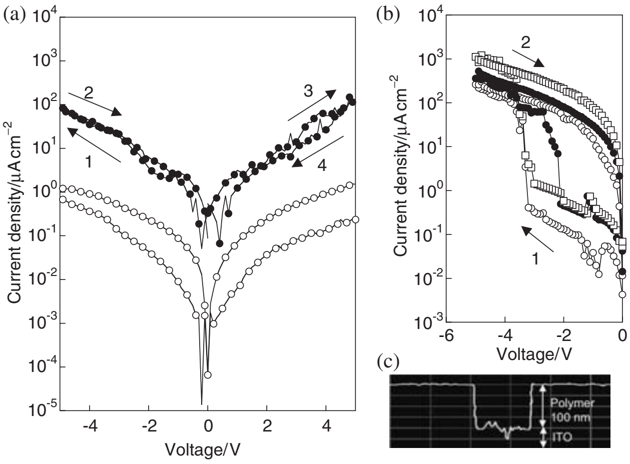


Figure 1. (a) *I–V* characteristics of the devices composed of **P1** (○) or **P1(+)** (●). (b) *I–V* characteristics of the devices composed of **P2(+)** with radical concentrations of 6 (○), 23 (●), and 43% (□). (c) Stylus surface profile of the **P2(+)** film. Film thickness was estimated from the scratched area.

(radical conc. <43%) showed improved solubility in acetonitrile and was employed in the thin film devices for further characterization.

The diode-structured thin film devices containing radical polymer **P1**, poly(oxoammonium salt)s **P1(+)** or **P2(+)** were fabricated via spin-coating of polymer solutions (1–2 wt %) onto an ITO/glass electrode, respectively, followed by vapor deposition of top Al electrode (150 nm). The contact stylus profile revealed a flat and uniform surface of the polymer layer (mean roughness <4 nm) and 100 nm in thickness after thermal annealing (100 °C, 10 h) (Figure 1c).

The typical *I–V* characteristics of the devices composed of **P1** or **P1(+)** are shown in Figure 1a. Upon application of bias in negative (0 to −5 V) and positive (0 to +5 V) directions, neither devices showed any resistance switching behavior. Poly(oxoammonium salt) **P1(+)** exhibited two orders of magnitude higher current density than the corresponding radical polymer **P1**, which was ascribed to the salt form.

On the other hand, the device composed of **P2(+)** showed a resistive switching behavior under application of increasing voltage (0 to −5 V) (Figure 1b). The current density drastically changed at ca. −3 V threshold voltage (ON–OFF ratio >10^3). While the current density of **P2(+)** at OFF state is comparable with that of radical polymer **P1**, the current density at ON state was three orders of magnitude higher than that of **P1**, and one order of magnitude higher than that of **P1(+)**, suggesting that coexistence of radical and oxoammonium moieties improved the electro-conductivity of the film. Upon application of the positive bias (0 to 5 V), the device was switched back to the high resistance (OFF) state. The device exhibited repeatable hysteretic curves, which promised its potential application as organic-based thin film memory. Further characterization will be reported in a future publication.

In summary, two redox-active poly(oxoammonium salt)s were chemically synthesized, and the *I–V* characteristics of the diode-structured thin film devices were investigated. The radical-free poly(oxoammonium salt) **P1(+)** showed higher current conductivity than the corresponding radical polymer **P1**. More curiously, poly(oxoammonium salt) with various radical concentrations, **P2(+)**, exhibited even higher current conductivity and an intriguing resistive switching behavior (organic memory property), which was ascribed to the coexistence of radical/oxoammonium salt in the thin film device.

This work was partially supported by Grants-in-Aid for Scientific Research (Nos. 19105003 and 21655043), the Global COE Program from MEXT, Japan, and the Research Project "Radical Polymers" at ARISE, Waseda Univ. T. S. acknowledges financial support from the Grants-in-Aid for Young Scientists (B) (No. A09324100).

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9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.