Synthesis of 3,5-Dibromopyridines with $-NH(CH_2)_mSO_3Na$ ($m = 3$ and 4) Groups at the 2-Position of Pyridine and Use of the Dibromo Compound for Polymer Synthesis

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Reactions of 2-amino-3,5-dibromopyridine with sultones gave 3,5-dibromopyridines with $-NH(CH_2)_mSO_3Na$ ($m = 3$ and 4) groups at the 2-position of pyridine. The obtained compound served as a starting material for polypyridine with $-NH(CH_2)_mSO_3H$ side chains.

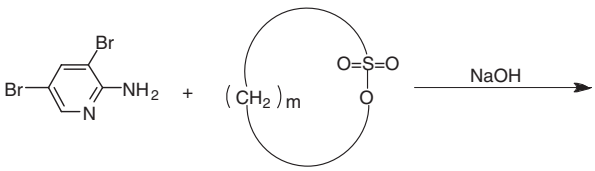
Polymer electrolytes with a sulfo group are attracting strong interest, because they serve as proton-conductive materials and are considered to be key compounds for fuel cells.[1] Various aromatic polymers with the sulfo group have been prepared, and most of them have the group attached at a benzene ring.

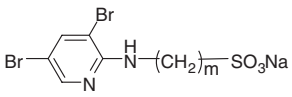
However, benzene rings are rather weak under oxidative conditions[2] which are necessary for fuel cells. For example, benzene rings are often cleaved under oxidative conditions.[2] By contrast, pyridine is stable against oxidation because of its electron-deficient nature,[3] and a CuCl/pyridine catalyst has been used as an oxidation catalyst of benzene derivatives.[2] Based on the reported stability of the pyridine ring against oxidation, it may be expected that polypyridines with the sulfo group serve as a stable polymer electrolyte under oxidative conditions. However, sulfonation of pyridine is usually not easy due to the electron-deficient nature of the pyridine ring and there is no precedent of polypyridine bearing the sulfo group.

Herein we report synthesis of the following 3,5-dibromopyridines with $-NH(CH_2)_mSO_3Na$ ($m = 3$ and 4; cf., eq 1) groups and use of the dibromopyridine as the starting monomer for sulfonated polypyridines. Dihaloaromatics and dihaloheterocycles can be converted to the corresponding polymers by organometallic dehalogenative polycondensations,[4] and by using the monomers shown in eq 1 polypyridine bearing the sulfo group has been synthesized for the first time as described in this paper. The obtained polymer actually showed excellent stability under Fenton oxidation conditions.

Results and Discussion

Reactions of 2-amino-3,5-dibromopyridine with 5-membered ring sultone and 6-membered ring sultone in the presence of NaOH according to eq 1 afforded the corresponding pyridine–$NH(CH_2)_mSO_3Na$ compounds.



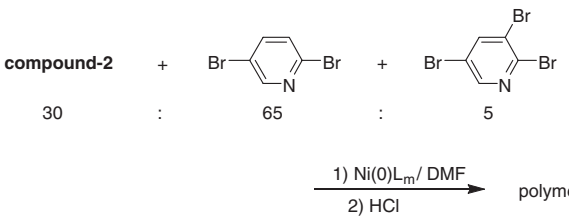


(1)

m=3 : **compound-1**
m=4 : **compound-2**

The products were characterized by elemental analysis, IR, and NMR. The N–H ^1H NMR signal of starting 2-amino-3,5-dibromopyridine at δ 6.47 (s, 2H) shifted to δ 6.65 (t, 1H) and δ 6.54 (t, 1H) for compound **1** and compound **2**, respectively, in DMSO-d_6. Sultones sometimes react at the N position of the pyridine ring to give pyridinium salts.[5] However, appearance of the N–H peak of compound **1** and compound **2** as a triplet unequivocally indicates that sultones reacted at the $-NH_2$ group to give the $-NH(CH_2)_mSO_3Na$ compounds. Although many reports have been published on the preparation of $-NH(CH_2)_mSO_3Na$ compounds by reaction of aliphatic amines and aromatic amines with sultones,[6] reports on the preparation of $-NH(CH_2)_mSO_3Na$ compounds of pyridine by reaction of aminopyridine and sultone have been limited.[7]

Dehalogenative copolymerization of compound **2**, 2,5-dibromopyridine, and 2,3,5-tribromopyridine using a zerovalent complex, Ni^0L_m, as a condensing agent[4,8] in dry DMF and ensuing treatment of the obtained polymer with hydrochloric acid gave a pyridine polymer having $-NH(CH_2)_mSO_3H$ side chains (cf., Experimental).[9a]



(2)

$Ni(0)L_m$: a mixture of bis(1,5-cyclooctadiene)nickel(0), $Ni(cod)_2$, and 2,2'-bipyridyl, bpy

Similar organometallic homopolymerization of 2,5-dibromopyridine using Ni^0L_m as the condensing reagent was reported.[9b] 2,3,5-Tribromopyridine was added to improve mechanical strength of the polymer by forming a branched structure. The polymer obtained without addition of 2,3,5-tribromopyridine was brittle. Bending of the main chain of the polymer at the branched unit seems to contribute to the mechanical strength of the polymer. The obtained polymer was soluble in formic acid. However, the polymer was not soluble in other solvents

Published on the web March 12, 2009; doi:10.1246/bcsj.82.413

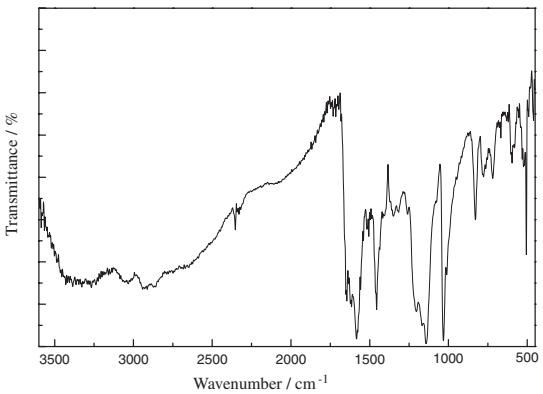


Figure 1. IR spectrum of the $-(CH_2)_4SO_3H$ polymer.

including acetic acid, trifluoroacetic acid, hexafluoro-*i*-propanol, and aqueous solutions of HCl and H_2SO_4. The polymer showed intrinsic viscosity $[\eta] = 0.38\,dL\,g^{-1}$ in formic acid at 30 °C. The $[\eta]$ value corresponds to a molecular weight of about 100000 of polystyrene.[10] Estimation of the molecular weight by gel permeation chromatography (GPC) was not possible due to the absence of a suitable solvent for GPC. When polymerization was carried out with a higher content of the $-NH(CH_2)_mSO_3Na$ monomer, the obtained polymer was highly soluble in water and isolation of the polymer by work-up, which included washing with an aqueous solution of disodium salt of ethylenediaminetetraacetic acid (EDTA), was difficult. The polymer prepared according to eq 2 was obtained in 87% yield based on the amount of carbon recovered. The polymer was soluble in formic acid, and casting from a formic acid solution of the polymer gave a cast film. Figure 1 shows the IR spectrum of the polymer. A strong peak characteristic of sulfonic acids[11] is observed at about 1200 cm^{-1}.

The cast film of the polymer showed tough resistance to Fenton's reagent[12] as expected. After the cast film was treated in a strong Fenton's reagent composed of 15% H_2O_2 and $FeSO_4$ (Fe: 20 ppm) at 60 °C for 3 h, the film became somewhat turbid. However, no obvious change in the shape of the film was observed. Under the strong oxidative conditions, aromatic polysulfonic acids containing a benzene ring are usually destroyed. For example, dark purple poly(2-methoxyaniline-5-sulfonic acid)[13] was destroyed completely in the same Fenton's reagent in about 5 min, and a colorless aqueous solution was obtained. The $(CH_2)_m$ group in the $-NH(CH_2)_mSO_3H$ side chain seems also to be stable under Fenton's conditions, similar to the stability of the CH_2 group in polyethylene and polypropylene toward Fenton's reagent.

As described above, new pyridine-based sulfonic acid Na salts with two polymerizable C–Br bonds have been synthesized, and the obtained polymer from the compound shows high stability under oxidative conditions, which is required for a polymer electrolyte for fuel cells.

Experimental

Materials and General Method. Commercially available 2-amino-3,5-dibromopyridine, sultones, 2,5-dibromopyridine, 2,3,5-tribromopyridine, $Ni(cod)_2$, and bpy were used as purchased. The polymerization expressed by eq 2 was carried out under nitrogen using Schlenk technique. ^{1}H NMR spectra were recorded on a JEOL JNM-EX300 spectrometer.

Preparation of Monomers. 2-Amino-3,5-dibromopyridine (10 g, 40 mmol) and 1,3-propanesultone (4.88 g, 40 mmol) were added to a mixture of dry DMF (30 mL) and NaOH (1.6 g, 40 mmol) at room temperature (rt), and the reaction mixture was stirred for 77 h at 120 °C. Addition of an excess amount of acetone led to precipitation of a yellowish white precipitate, which was purified by column chromatography on a SiO_2 column (eluent = 3:1 mixture of $CHCl_3$ and MeOH) to obtain a yellow powder of compound **1**. Yield: 5.15 g (33%); mp 308 °C. Anal. Calcd for $C_8H_9Br_2N_2NaO_3S$: C, 24.26; H, 2.29; Br, 40.35; N, 7.07; S, 8.10%. Found: C, 23.76; H, 2.69; Br, 38.87; N, 6.89; S, 7.77%. The compound may contain hydration water; e.g., calcd for $C_8H_9Br_2N_2NaO_3S \cdot 0.5\,H_2O$: C, 23.72; H, 2.49; Br, 39.46; N, 6.92; S, 7.92%. ^{1}H NMR (300 MHz, D_2O): δ 7.74 (d, $J = 2.1$ Hz, 1H), 7.57 (d, $J = 2.1$ Hz, 1H), 3.26 (t, $J = 6.9$ Hz, 2H), 2.84 (m, 2H), 1.87 (m, 2H).

In D_2O, the N–*H* NMR peak was not observed presumably due to rapid hydrogen exchange between N–*H* and D_2O. In DMSO-d_6, CH_2 peaks at about δ 3.3 and δ 2.45 overlapped with solvent impurities (DMSO-d_5 and H_2O). However, the N–*H* signal is clearly observed as a triplet by coupling with NH–CH_2 protons. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.09 (d, $J = 1.8$ Hz, 1H), 7.96 (d, $J = 1.8$ Hz, 1H), 6.65 (t, $J = 5.8$ Hz, 1H, –NH), 1.81 (m, 2H).

Compound **2** (yellow powder) was prepared analogously by using 2-amino-3,5-dibromopyridine (2.0 g, 7.9 mmol), 1,4-butanesultone (1.09 g, 8.0 mmol), and NaOH (0.32 g, 8.0 mmol) in 6 mL of DMF. Yield: 46%; mp 310 °C. Anal. Calcd for $C_9H_{11}Br_2N_2NaO_3S$: C, 26.36; H, 2.70; Br, 38.97; N, 6.83; S, 7.82%. Found: C, 26.53; H, 3.02; Br, 38.85; N, 6.91; S, 7.63%. The compound may contain hydration water. ^{1}H NMR (300 MHz, D_2O): δ 7.82 (d, $J = 2.1$ Hz, 1H), 7.75 (d, $J = 2.1$ Hz, 1H), 3.20 (t, $J = 6.7$ Hz, 2H), 2.79 (m, 2H), 1.61 (m, 4H).

^{1}H NMR (300 MHz, DMSO-d_6): δ 8.09 (d, $J = 2.1$ Hz, 1H), 7.95 (d, $J = 2.1$ Hz, 1H), 6.54 (t, $J = 5.6$ Hz, 1H, –NH), 1.57 (m, 2H).

Polymerization. Dehalogenative polycondensation of a 30:65:5 mixture of monomer **2**, 2,5-dibromopyridine, and 2,3,5-tribromopyridine was carried out as follows. A DMF (20 mL) solution of monomer **2** (215 mg, 0.52 mmol), 2,5-dibromopyridine (269 mg, 1.1 mmol), and 2,3,5-tribromopyridine (28 mg, 0.089 mmol) was added to a dry DMF (20 mL) solution containing $Ni(cod)_2$[4] (960 mg, 3.5 mmol), bpy (550 mg), and 1,5-cyclooctadiene (0.43 mL) at rt, and the reaction mixture was stirred at 60 °C for 5 days. After cooling to rt, acetone was added, and the precipitate was separated by filtration. The brown powder was washed with a hot (80 °C) aqueous solution of disodium salt of ethylenediaminetetraacetic acid (EDTA·2Na), a hot (80 °C) aqueous solution of EDTA·2Na and NaOH, a hot (80 °C) aqueous solution of NaOH, and water (25 °C) in that order. The powder was treated with diluted (ca. 2 M) hydrochloric acid, washed with water, and dried under vacuum to obtain 174 mg of the brown polymer; yield 87% (based on the amount of carbon recovered). Calculated contents of C, H, N, and S for the composition of $(C_9H_{12}N_2O_3S)_{0.3}(C_5H_3N)_{0.65}(C_5H_2N)_{0.5}$ which is based on the feeding ratios of the monomers are: C, 60.84; H, 4.65; N, 14.88; S, 7.86%. However, found contents of C, H, N, and S were: C, 64.15; H, 4.55; N, 15.08; S, 6.86%. The higher observed carbon content and lower observed sulfur content than those of the respective calculated contents suggested somewhat higher reactivity of 2,5-dibromopyridine than that of monomer **2**. The polymer contained only a small amount of Br (0.09%), indicating

that the dehalogenative polycondensation proceeded smoothly. A portion (about 1/4) of the polymer was soluble in formic acid, and casting a formic acid solution of the polymer gave a polymer film.

We are grateful to Mrs. S. Shiozaki and Mr. N. Kumagai of our laboratory for experimental support and helpful discussion.

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