Articles

Synthesis of Disulfide-Containing Aniline and Copolymerization with Aniline

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ABSTRACT: A novel disulfide-containing aniline, 1,4-dihydrobenzo[*d*][1,2]dithiin-5-ylamin (**1**), was synthesized by the alkylbromination of 1,2-dimethyl-3-nitrobenzene, followed by the formation of a disulfide bond via thioesterification and then the reduction of the nitro group. The monomer showed a reductive and oxidative potential of the disulfide bond at −0.63 and 1.25 V (vs Ag/Ag^+), respectively. Although the monomer showed the oxidative potential of aniline at 0.85 V (vs SCE), the electro- or chemical-oxidative polymerization of the monomer resulted in the formation of only the oligomer, suggesting that the disulfide-containing condensed ring would prevent further propagation of the polymerization due to steric hindrance. However, the nearly ideal copolymerization of **1** with aniline (An) was carried out by chemical oxidative polymerization. The resulting copolymers (**1**/An = 1/1 and 2/1, by mole) had weight-averaged molecular weights ($\bar{M}_w$) of 10 000 and 6600, respectively, and good redox activities coupled with those of the polyaniline and disulfide group. The copolymer showed conductivities of 5.1×10^{-2} S/cm for 1/1 and 1.3×10^{-2} S/cm for 2/1 after being redoped with camphorsulfonic acid. It is suggested that these copolymers might be good candidates for the cathode materials of secondary polymer batteries.

Introduction

Some organic compounds having two mercapto groups have become possible cathode materials with a high energy density for energy storage devices,[1] because the two mercapto groups undergo intermolecular disulfide bonding to become polydisulfides, accompanied by the two-electron oxidation per one disulfide bond and reductive depolymerization in reverse. However, the slow redox reaction at ambient temperature and the insulative property of the polydisulfides require a high temperature and the addition of some conducting materials, resulting in a low energy density.[2−4] Furthermore, the depolymerized monomers will diffuse and escape from the electrode, resulting in a low cycling stability. For example, many researchers that studied 2,5-dimercapto-1, 3, 4-thiadiazole as a monomer found that it needed to be combined with other conducting materials.[5−7] Though 2,2′-dithiodianiline (DTDAn) was polymerized by electro- or chemical oxidative polymerization to form a polymer having both the redox activity of the disulfide bond and the electron conductivity of polyaniline, the polymer showed a low electric conductivity and a low disulfide density due to the interpolymer disulfide bond.[8]

In this paper, we synthesized a new aniline derivative, which had a condensed aliphatic ring containing one disulfide bond to obtain an electron-conductive polymer with a high disulfide density. The polyaniline was expected to perform the reversible ring-opening reduction of the disulfide bond in each monomer unit, leading to a high Coulombic efficiency. We also studied the copolymerization of the aniline derivative with normal aniline using physicochemical and electrochemical analyses.

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Experimental Section

Measurements. Infrared spectra were measured with a JASCO FT/IR-410 by using KBr pellets, and UV−vis spectra were recorded on a Shimadzu UV 2000. The ^1H and ^{13}C NMR of the $CDCl_3$ solutions were recorded on a JEOL LA-500. The solid-state ^{13}C NMR spectra of the copolymer were recorded on a JEOL GSX-400. Elemental analyses (C, H, N, S, halides) of the polymer were performed using a Yanagisawa MT3 CHN and a Metrohm 645 Multi-DOSIMAT. XPS were carried out using a JEOL JPS 90MX with a Mg Kα X-ray source (1253.6 eV photons). The disulfide bond of S 2p core-level photopeak at 164.5 eV in the copolymers was referenced to the C 1s neutral carbon photopeak at 284 eV. Thermogravimetric analysis of the polymer was carried out with a Seiko TG/DTA 220 under a nitrogen atmosphere at a heating rate of 20 °C/min. The conductivity of the polymer was measured as pellets or films by a Kyowariken K-750RS using the four-probe method. Cyclic voltammograms (CV) were measured using a BAS 100B with a standard three-electrode system. A platinum wire (diameter: 0.05 cm, length: 0.50 cm) or a carbon sheet (0.01 cm^2) was used as the working electrode, and Ag/Ag^+ or SCE electrodes were used as the reference electrodes.

Materials. The monomer of 1,4-dihydrobenzo[*d*][1,2]dithiin-5-ylamin (**1**) with a intramolecular disulfide group was synthesized according to Scheme 1 with modification of the method as previously reported.[9] A 1,2-dimethyl-3-nitrobenzene as the starting material and *N*-bromosuccinimide (NBS) were purchased from Tokyo Chemical Industry Co., and used without further purification. 2,2′-Azobis(isobutyronitrile) (AIBN) was purchased from the Aldrich Co., and recrystallized twice from ethanol before use. Potassium thioacetate (KSAc) from

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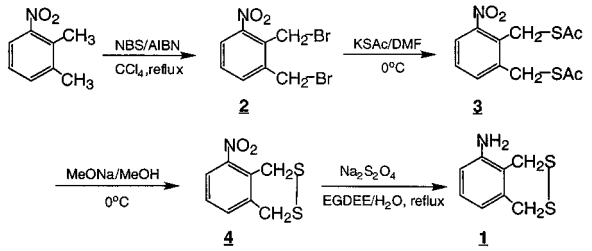
Scheme 1. Synthetic Scheme of BTMAn (1)



the Aldrich Co. was used in a way to limit water absorption. Sodium methoxide (MeONa), sodium disulfite ($Na_2S_2O_4$), and other guaranteed commercial solvents such as carbon tetrachloride (CCl_4), dimethylformamide (DMF), methanol, and ethylene glycoldiethyl ether (EGDEE) were purchased from the Kanto Chemical Co. and used without further purification. Aniline (An) was purchased from the Kanto Chemical Co., and used after vacuum distillation. Other solvents for the electrochemical analysis of the polymer such as acetonitrile (AN), DMF, ethylene carbonate (EC) and propylene carbonate (PC) were used after vacuum distillation and kept under a nitrogen atmosphere. Ammonium peroxodisulfate (APS) as an oxidant for the chemical oxidative polymerization and camphorsulfonic acid (CSA) were purchased from the Kanto Chemical Co., and used as received. Lithium perchlorate ($LiClO_4$) and lithium hexafluorophosphate ($LiPF_6$) as electrolytes for CV measurements were purchased from the Kanto Chemical Co. and used after recrystallization.

Synthesis of 2,3-Bis(bromomethyl)nitrobenzene (2). 1,2-Dimethyl-3-nitrobenzene (25.0 g, 16.7 mol) and NBS (58.9 g, 33.1 mol), as a bromination reagent, were dissolved in 250 mL of CCl_4 containing AIBN (1.5 g, 9.1 mmol), as a radical initiator, and heated to reflux (75 °C) for 12 h. The reaction mixture was then cooled, and any floating materials were filtered off. The solution was extracted with chloroform and washed with water. After evaporating the chloroform, the resulting yellowish oil was recrystallized from cold methanol using dry ice/methanol. A white precipitate of **2** was obtained in a 46% yield: mp 55.4−56.7 °C; FT-IR (KBr) 2970, 2881 (ν_{C-H}), 1526, 1361 ($\nu_{N=O}$), 623 (ν_{C-Br}) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.46−7.89 (m, 3H, phenyl), 4.69 (s, 2H, 2-methylene), 4.86 (s, 2H, 3-methylene) ppm; ^{13}C NMR ($CDCl_3$) δ 120−137 (6C, phenyl), 32, 35 (2C, 2,3-dimethyl) ppm.

Synthesis of Thioacetic Acid 2-Acetylsulfanylmethyl-6-nitrobenzyl Ester (3). 2 (10.0 g, 32.0 mmol) was dissolved in DMF (40 mL) below 10 °C (ice bath) under a nitrogen atmosphere, and KSAc (9.1 g, 80 mol) in the same solvent (40 mL) was added to it within 5 min. After the mixture was stirred for 1 h, 40 mL of H_2O was added to the solution to stop the reaction. The solution was then extracted with chloroform and washed with water. A yellowish oil formed after being recrystallized from methanol, and then **3** was obtained with a 72% yield as a light yellow solid: mp 81.6−82.7 °C; FT-IR (KBr) 2954, 2872 (ν_{C-H}), 1526, 1357 ($\nu_{N=O}$), 1688 ($\nu_{C=O}$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.46−7.89 (m, 3H, phenyl), 4.19 (s, 2H, 2-methylene), 4.37 (s, 2H, 3-methylene), 2.36 (s, 6H, methyl) ppm; ^{13}C NMR ($CDCl_3$) δ 194 (6C, methyl), 125−140 (6C, phenyl), 26.5, 30.6 (2C, 2,3-dimethyl) ppm.

Synthesis of 5-Nitro-1,4-dihydrobenzo[*d*][1,2]dithiine (4). 3 (5.0 g, 16.7 mmol) was dissolved in dry methanol (60 mL) and stirred with an ice bath under a nitrogen atmosphere, and MeONa (2.3 g, 41.8 mmol) in the same solvent (40 mL) was added to it. The reaction was completed within 4 h, which resulted in a brownish transparent solution. Not only deacetylation but also disulfide formation were performed during the reaction. One hundred milliliters of water was then added to the mixed solution for the deactivation of the remaining MeONa. The resulting brownish liquid **4** (yield: 52%) was obtained by extraction with chloroform. FT-IR (neat) 2960, 2866 (ν_{C-H}), 1521, 1355 ($\nu_{N=O}$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.73−7.26 (m, 3H, phenyl), 4.22 (s, 2H, 2-methylene), 4.18 (s, 2H, 3-methylene) ppm; ^{13}C NMR ($CDCl_3$) δ 125−140 (6C, phenyl), 26.5, 30.6 (2C, 2,3-dimethyl) ppm.

Synthesis of 1,4-dihydrobenzo[*d*][1,2]dithiin-5-ylamin (1). 4 (5.0 g, 23.5 mmol) was reduced with $Na_2S_2O_4$ (14.3 g, 82.2 mmol) in the mixed solution of EGDEE (150 mL) and water (150 mL). After the solution was refluxed for 2 h, 1 N HCl (50 mL) was added for the deactivation of any excess $Na_2S_2O_4$. The solution was then cooled to room temperature and poured into cold water that produced a yellowish powderlike precipitate. After conversion of the ammonium salt to the amino group by the addition of K_2CO_3, the extract from chloroform **1** was obtained with a yield of 85% as a yellowish oil. FT-IR (neat) 3431, 3353, 1624 (ν_{N-H}), 3056, 2890 (ν_{C-H}), 1455 (ν_{CH2-H}), 779 (δ_{C-H}), 706 (ν_{C-H}) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.5−7.0 (m, 3H, phenyl), 3.7 (s, 2H, broad, NH_2), 3.5 (s, 2H, CH_2) and 3.6 (s, 2H, CH_2) ppm; ^{13}C NMR ($CDCl_3$) δ 114−144 (6C, phenyl), 36.2 and 28.5 (2C, dimethylene) ppm; UV (MeOH) 244 (E_2 absorption band), 297 (*B* absorption band) nm.

Polymerization of 1 and Copolymerization of 1 with Aniline. The yellowish oil of **1** was dispersed in a 2 N HCl solution to obtain a white suspension. A 2 N HCl solution of aniline was added to the suspension at the molar ratios of [**1**]/[An]: 2/1, 1/1, or 1/2. After the addition of APS as an oxidant to the suspension, it gradually turned to a green transparent solution with vigorous stirring, and then a green precipitate formed after 24 h. The precipitation regarded as an emeraldine salt was filtered and washed with distilled water and then methanol. The conversion of the emeraldine salt to an emeraldine base was carried out by stirring for 12 h in a 1 N ammonium solution. The polymer was washed several times with distilled water and then with methanol, and dried in vacuo for 12 h at 70 °C. For the conductivity measurement, the emeraldine base was redoped with 1 M H_2SO_4 or 1 M CSA.

Cyclic Voltammetry of 1 and Electropolymerization. CV of the monomer was carried out in a 0.1 M $LiClO_4$/DMF solution with a Pt wire as the working electrode. The electropolymerization of **1** or copolymerization of **1** with aniline was performed by cyclovoltammetric or potentiostatic methods with 0.2 M **1** and 0.1 M $HClO_4$ in AN/H_2O (1/1 by vol.) using a Pt wire or a carbon sheet as the working electrodes. CV of the copolymers was done in 1.0 M $LiClO_4$/AN or 1.0 M $LiPF_4$/(EC + PC) with a copolymer-coated Pt wire as the working electrode.

Results and Discussion

Synthesis of 1 and its Polymerization. We first attempted to brominate 2,3-dimethylaniline with NBS and AIBN in CCl_4. However, only a trace amount (yield <5%) of 2,3-bis-bromomethylaniline was formed, and the other positions of the phenyl ring such as the 4- or 6-positions were substituted with bromine due to the electron-donation of the amino group. Next, when we changed the aniline to the nitrobenzene, we successfully obtained **2** in the relatively high yield of 46% under the conditions of 75 °C and 12 h. The byproducts were the one-substituted form (ca. 30%) and the three-substituted form (ca. 10%). The yield of **2** was dependent on the reaction temperature and time.

The thioacetylation of **2** by KSAc resulted in **3** with a yield of 72%; KSAc is so sensitive to air and moisture that the reaction should be undertaken under an inert atmosphere with dried solvent. The deacetylation of **3** and the subsequent disulfide formation (**4**) were successfully performed with MeONa in dried MeOH. Since the deacetylation was carried out step-by-step, the complete deacetylation depended on the reaction time. The nitro group was reduced to the amino group (**1**) with $Na_2S_2O_4$ in a EGDEE/H_2O (1/1) mixed solution along with preserving the disulfide groups. The yield was 85%.

The ^1H and ^{13}C NMR spectra of **1** are shown in Figure 1. In the ^1H NMR spectrum, the protons of the two methylene groups are divided into two peaks of 3.7 and

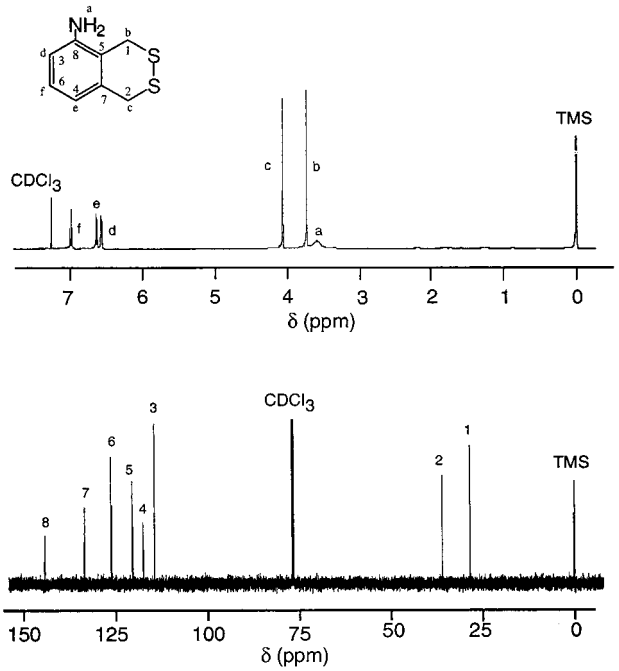


Figure 1. ^{1}H and ^{13}C NMR spectra of **1** in $CDCl_3$.

4.1 ppm. The methylene group next to the electron-donating amino group slightly shifts to a lower magnetic field. The protons of the phenyl ring were confirmed to be between 6.5 and 7.0 ppm. The amino protons were confirmed as a broad peak at 3.6 ppm. In the ^{13}C NMR spectum, the signals of 28.5 and 36.2 ppm are clearly identified as the *o*- and *m*-methylene carbons, respectively. The six signals of the phenyl carbons are detected at 114.7, 117.9, 120.7, 126.5, 133.8, and 144.6 ppm as identified in Figure 1.

In the UV−vis spectum of **1** in AN (data not shown), the E_2 ($\pi-\pi^*$) absorption peak of the phenyl ring is located at 243 nm, which is higher than that of aniline (231 nm) and significantly broadened. The *B* absorption band of 297 nm also shifts to a higher wavelength (281 nm for aniline). It might be due to the effect of substitution at the ortho and meta positions of the aniline structure because 3-methylmercaptoaniline also shows the corresponding peaks at 244 and 299 nm, respectively.

The product obtained by the chemical oxidative polymerization of **1** was a brownish powder and had a good solubility in the common solvents such as methanol, acetone, AN, etc. The number-averaged molecular weight of the polymerization measured by GPC was 300−400, which is attributed to the dimer or trimer. The steric hindrance of the disulfide group should restrict the propagation of the polymer chain. Similar results were reported for the polymerization of the anilines substituted with bulky or electron-withdrawing groups such as nitroaniline,[10] 3-ethylaniline,[11] and 2,3-xylidine.[12]

Figure 2 shows the CV of **1** with a Pt wire as the working electrode in a 0.1 M $LiClO_4$ DMF solution. In the first potential sweep from 0 to −1.0 V (vs Ag/Ag^+), a single and sharp reduction peak is observed at −0.63 V. This peak is attributed to the reduction of the disulfide bond to the ring-opened dithiolate anions. On the other hand, as shown in Figure 2a, two oxidation peaks were observed at 1.0 and 1.25 V during the potential sweep from −1.0 to +1.5 V (vs Ag/Ag^+) and showed good redox activity with the scan times. These

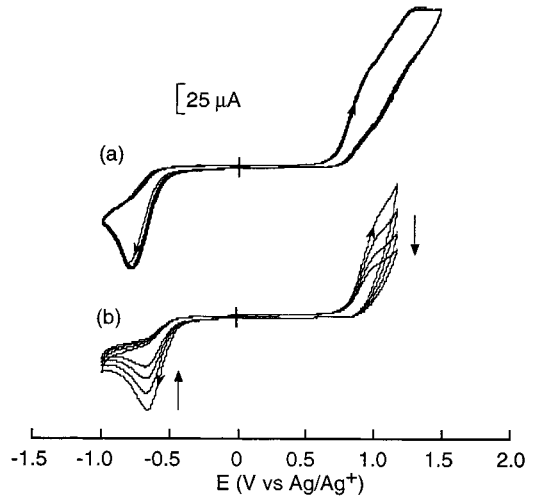


Figure 2. Cyclic voltammograms of 0.2 M **1** with Pt wire as the working electrode in 0.1 M $LiClO_4$/DMF solution on the range (a) from −1.0 to +1.5 V, and (b) from −1.0 to +1.2 V at a scan rate of 100 mV/s.

oxidation peaks would be attributed to the oxidation peak of the aniline monomer and the reoxidation peak of the dithiolate anions, respectively. We found the reduction of the disulfide bond and the oxidation of the thiolate anion in the CV when the sweep range was between −1.0 and +1.5 V and not between −1.0 and 1.2 V (Figure 2b), indicating that the oxidation peak of the thiolate anions should exist between 1.2 and 1.5 V. Therefore, we could identify it as the peak at 1.25 V.

We tried the electro-oxidative polymerization of **1** using CV during the forward potential sweep from −0.2 to 1.2 V with 0.2 M **1** in a 0.1 M $HClO_4$ AN/H_2O (1/1 by vol.) mixed solution where a carbon sheet was used as the working electrode. There was a clear oxidation peak of the monomer at 0.83 V (vs SCE) in the first scan. The new redox couple at 0.67 V (E_{oxi}) and 0.16 V (E_{red}) (vs SCE) would be attributed to the oligomer of **1**. However, no current increase in the redox couple was observed after the second scan, indicating no propagation of the polymerization.

Copolymerization of 1 with Aniline. 1 was mixed with aniline (An) at the molar ratios of 2/1, 1/1, and 1/2 in a 2 N HCl aqueous solution. The oxidation of the solution was carried out using APS as the oxidant. The copolymers in an emeraldine-based state were mainly soluble (ca. 3.0 mg/1 mL of solvent) in NMP, DMSO, and DMF with similar solubility to that of PAn, however, the copolymers were insoluble in chloroform, AN, and acetone. The color of the PAn solution was blush violet, whereas the copolymers were more darkish violet with the increasing ratio of **1**. The solubility of the copolymers decreased with the ratio of **1** when compared with the other aniline copolymers having aniline derivatives substituted with aliphatic hydrocarbons.[12,13] It is suggested that the condensed aliphatic heterocyclic group might not contribute to the solubility increase of PAn.

The DMF solution of the copolymers was applied to GPC for the molecular weight measurement. As listed in Table 1, copolymers with relatively high molecular weights were obtained from the copolymerization. PAn showed the wide polydispersity (M_w/M_n) of 6.9 due to the polymerization in low temperature (5 °C).[14] The degree of polymerization of the polymers is related to the composition, namely, the average molecular weight

Table 1. Characterization of the Copolymers and the Related Homopolymers in an Emeraldine Base State

polymer or copolymer	ratios of [**1**]/[An]	yield (%)	av mol wt[a]			elem anal. of S atom (%)[b]	
			$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	calcd	found
homopolymer	1/0	10	3.7×10^2	3.2×10^2	1.2	35	
copolymer 2	2/1	34	6.6×10^3	3.3×10^3	2.0	23	22
copolymer 1	1/1	44	9.7×10^3	4.2×10^3	2.3	21	15
copolymer 0.5	1/2	55	1.3×10^4	4.7×10^3	2.7	16	13
PAn[c]	0/1	67	5.0×10^4	7.3×10^3	6.9	0	

[a] DMF soluble part of emeraldine base polymer. [b] Calculated by N atom; was used to reference due to water contents.[16,17] [c] Synthesized under the same conditions.

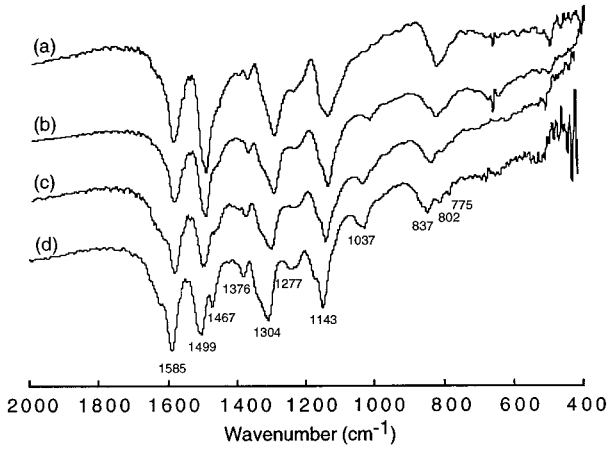


Figure 3. FT-IR spectra of (a) PAn, (b) copolymer 0.5, (c) copolymer 1, and (d) copolymer 2 base forms.

and polydispersity increases with the increasing ratio of An as well as the yield of the precipitates. The resulting copolymers (**1**/An = 1/1 and 2/1, by mole) had the weight-averaged molecular weights ($\bar{M}_w$) of 10 000 and 6600, respectively. From the elemental analyses of the copolymers, the sulfur content in the copolymer increases with the increasing feed ratio of **1**. For example, copolymer 2 contains a sulfur content of 22% compared to the calculated value of 23%.[15,16] This indicates that the combination of **1** and An shows the nearly ideal copolymerization reactivity. Though the homopolymerization of **1** was impossible, its copolymerization with An could be ideally performed because An and oligoanilines would favor the coupling with **1**. As mentioned above, the copolymerization of the substituted aniline with aniline was strongly affected by the electron state and steric factors of the substituents. For examples, electron-donating alkyl substituents that stabilize the cation free radical intermediates during the copolymerization had a higher reactivity than An.[13] On the other hand, the copolymerization reactivity of 2,3-xylidine with a large steric hindrance was lower than that of aniline.[12]

Figure 3 shows the FT-IR spectra of the PAn and copolymers (emeraldine base) with different ratios of [**1**]/[An]. The main bands of the copolymers are the same as those of the PAn (a); bands at 1585, 1499, and 1376 cm^{-1} are assigned to the stretching bands of the quinoid and benzenoid ring, and the C−N stretching band of the quinoid imines, respectively.[17−19] The higher intensity of the benzenoid peak when compared to that of the quinoid peak of the PAn suggests that the benzenoid structure would be a major structure. Furthermore, the strong 1304 cm^{-1} band of the copolymers indicates the C−N stretching band of quinoid−benzenoid−quinoid conjugation. It was also reported that the 1376 and 1304 cm^{-1} peaks in the copolymers were attributed to the C−C stretching of quinoid with the C−H bending and

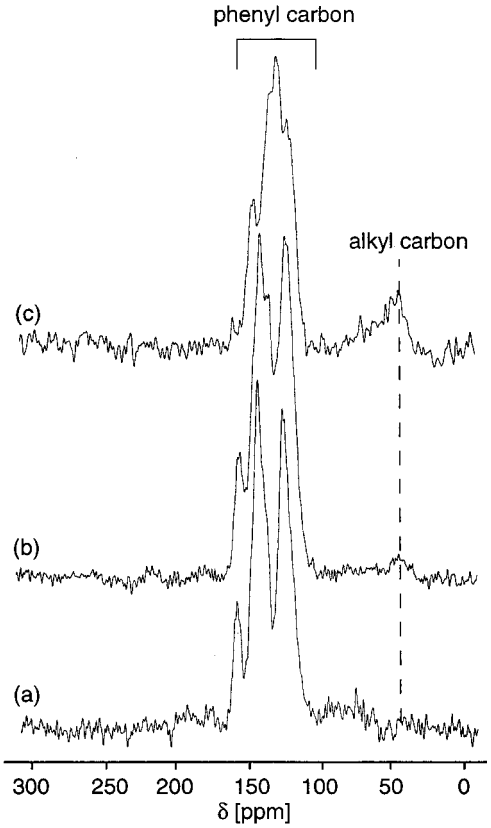


Figure 4. Solid-state ^{13}C NMR spectra of (a) PAn, (b) copolymer 1, and (c) copolymer 2 base forms.

the C−C stretching of benzenoid with the C−H bending, respectively.[19,20] The aromatic C−H out-of-plane (para substituents) bending appears at 837 cm^{-1}.[17] The weak bands of 1467 and 775 cm^{-1} assigned to C−S stretching bands are observed in the copolymers. With the increasing ratio of **1**, new bands appeared and grew at 1037, 802, and 837 cm^{-1} which are considered as the aromatic C−H in-plane and out-of-plane bending vibration of a tetrasubstituted benzene ring and the C−H out-of-plane bending vibration with a para-substituted polyaniline, respectively.[12,18] There is no other band attributed to the S=O (1100 cm^{-1}) peaks of the sulfone or sulfonate groups, indicating that the disulfide groups were well protected from further oxidation. Moreover, it is interesting that the quinoid band becomes larger than the benzenoid band in the copolymer with the increasing molar ratio of **1**, suggesting a more quinoid structure in the copolymers.

The solid-state ^{13}C NMR spectrum of PAn is compared with that of the polymers as shown in Figure 4. The peaks of the emeraldine-based PAn (Figure 4a) are identified as 122 and 124 (−C=C− of benzenoid rings), 142 (−C−NH−), 137 (−C=C− of quinoid rings), and 157 ppm (>C=N−) in accordance with the assignment in

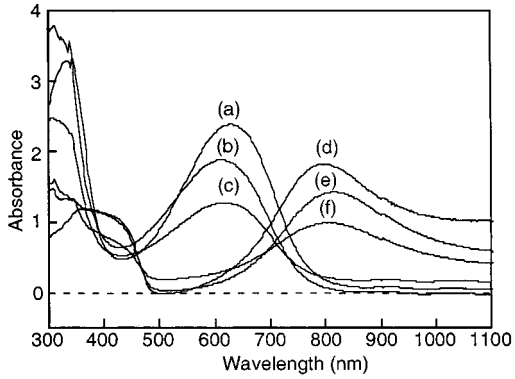


Figure 5. UV-visible spectra of (a) PAn, (b) copolymer 1, (c) copolymer 2 base forms and H_2SO_4-doped forms of (d) PAn, (e) copolymer 1, (f) copolymer 2.

previous papers.[22] In the case of the polymers, new methylene carbon peaks are confirmed at 40 and 45 ppm, and they increase with increasing ratio of **1**. At the same time, the resolution of the phenyl ring peaks is reduced due to the overlap of the peaks from **1** and An. These results indicate that the polymers were the copolymers of **1** and An. As shown in Figure 4c, the quinoid carbon (−N═C<) peak at 157 ppm for PAn becomes smaller for copolymer 2, and a new peak found at 161 ppm would be attributed to the quinoid carbon of **1**. Peaks at 145 and 147 ppm would be attributed to the C═C of the quinoid rings where the methylene groups are introduced.[22,23] The other carbon peaks in the copolymers are too indistinct to identify them in these ^{13}C NMR spectra. Furthermore, XPS of these copolymers (deprotonated forms) indicated that S 2p core-level photopeaks at 164.5 eV were increased with the increasing ratio of **1**.

The UV−vis spectra of PAn and copolymers in an emeraldine-base state and a re-doped state with sulfuric acid are shown in Figure 5. PAn in the emeraldine-base state (a) showed the typical absorption peaks at 340 nm ($\pi-\pi^*$ transition) and 628 nm (n−π^* transition).[17,18] The copolymers in the emeraldine-base state showed similar spectra to that of PAn. However, a blue shift and a decrease in the absorbance are common characteristics of the copolymers (312, 614 nm for the copolymer 1 (b), 310, 616 nm for the copolymer 2 (c)). These results suggest that the copolymerization of **1** could give more constrained π-conjugated polymers and a shorter chain length. It was reported that both the π-conjugation length and the redox potentials of the substituted π-conjugated copolymers would be affected by the nature and the position of the substituents of the ring.[24,25]

In the doped state of the PAn (d) and the copolymers (e, f), a significant red shift would occur due to the protonation of the imino site and polaron bands over 800 nm. The absorbance of the copolymers also decreases as well as in the case of the emeraldine-base state.

From the TGA curves of PAn or the copolymers under a nitrogen atmosphere, PAn is stable up to 450 °C, and the stability decreased when An was copolymerized with **1**. The copolymers seem to have two or three weight loss points compared with PAn.[26−28] The first weight loss of 1−5% observed around 150 °C should be due to the elimination of water and/or solvent such as NMP trapped in the polymer chains. The second significant weight loss in the range of 170−250 °C might be explained in terms of the chemical decomposition of the copolymers such as the exclusion of the side chains or hydrogen, followed by cross-linking between copolymer chains.[12] The 10% weight loss decomposition temperatures ($T_{d10\%}$) of the copolymers are listed in Table 2. The copolymers are significantly less stable because of the thermal cleavage of the S−C bond to generate H_2S.

Table 2. Electrical Conductivity and Thermal Stability (T_d) of the Copolymers and Related Homopolymers

polymer or copolymer	ratios of [**1**]/[An]	conductivity (S/cm)[a] H_2SO_4 doped	conductivity (S/cm)[a] CSA doped	T_d (°C)[b]
homopolymer	1/0			
copolymer 2	2/1	3.3×10^{-3}	1.3×10^{-2}	233
copolymer 1	1/1	6.7×10^{-3}	5.1×10^{-2}	288
copolymer 0.5	1/2	6.7×10^{-2}	3.2×10^{-1}	321
PAn	0/1	4.0×10^{-1}	1.0×10^{1}	465

[a] Pressed pellet was used after emeraldine base polymer re-doped with H_2SO_4 and CSA. [b] 10% weight loss temperatures of the emeraldine base forms.

As shown in Table 2, the conductivities of the PAn and copolymers significantly improved when doped with CSA compared with those doped with H_2SO_4. PAn showed an improvement in the conductivity from 4.0×10^{-1} to 10 S cm^{-1}. MacDiarmid et al. proposed that the tremendously high conductivity of the PAn/CSA (*m*-cresol) system could be explained in terms of "expanded coil structure" and "secondary doping effect".[29] In the copolymers, the conductivity is improved more than 1 order of magnitude by doping with CSA. However, the conductivity of the copolymers decreased with the increasing molar ratios of **1**. The decreased molecular weight as shown in Table 1 and the influence of the bulky condensed aliphatic heterocyclic substituent would explain such a conductivity decrease.

In the CV of these copolymers, we could not find that the disulfide cleavage potential around −0.63 V, which was confirmed for the monomer in the same CV conditions. The disulfide cleavage potential of the copolymer 2 was shifted to −0.14 V (vs Ag/Ag^+) near the redox peak of PAn when a carbon sheet was used as the working electrode. It can be explained that the "electrocatalytic effect" of the redox of polyaniline chain would act on the redox of the disulfide bond. Naoi et al. showed that the disulfide cleavage at −0.8 V of the DTDAn monomer was shifted to +0.2 V after polymerization due to the electrocatalytic effect of the polyaniline chains.[6−8] The self-doping/dedoping by thiolate anions following to the redox of the disulfide bonds would also relate to such a potential shift.

Figure 6 shows the CV of the PAn and copolymers on the polymer-coated Pt wire as the working electrode in a 1.0 M $LiClO_4$/AN solution with the potential range from −0.2 to +1.2 V. PAn (a) shows two typical redox couples under acidic conditions at 0.15 (first) and 0.80 V (second) attributed to its redox states by the applied potential.[18] In the copolymers, with the increasing ratio of **1**, the two redox couples approached each other, like a single couple around 0.65 V as shown in copolymer 2. As mentioned above, since the redox of the disulfide bond should be shifted to the positive potential, the redox potential of the copolymer 2 in the potential range from −0.2 to 1.2 V would involve the redox of the disulfide bond. Scheme 2 shows the proposed redox scheme of the copolymer 2.

In Figure 7 is shown the CV of the copolymer 2 with the increasing scan rate. Since the increase in the scan rate linearly increases the output current, it is implied

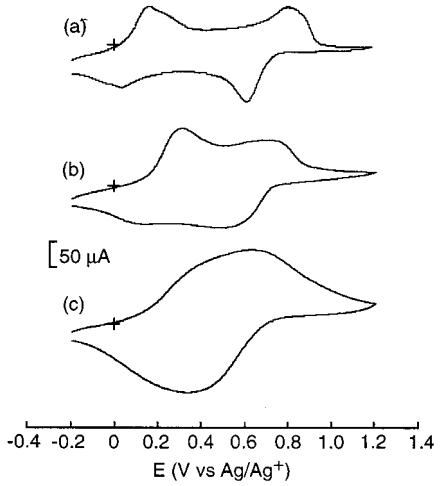


Figure 6. Cyclic voltammograms of (a) PAn, (b) copolymer 1, and (c) copolymer 2 base forms with the polymer-coated Pt wire as the working electrode in 0.1 M $LiClO_4$/acetonitrile; scan rate 100 mV/s.

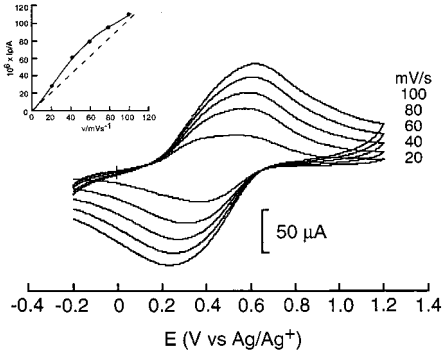
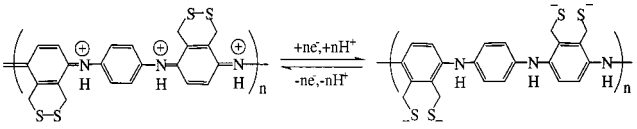


Figure 7. Cyclic voltammograms of copolymer 2 by scan rates from 20 to 100 mV/s with the polymer-coated Pt wire as the working electrode in 0.1 M $LiClO_4$/acetonitrile.

Scheme 2. Redox Scheme of Copolymer 2



that the copolymer has a good redox activity. It is also noted that it has more than twice the Coulombic capacity compared to that of PAn as calculated from the CV in a 1.0 M $LiPF_6$/(EC + PC) solution. Though further investigations concerning CV are now in progress, the results suggest that the copolymer might be a good cathode material for secondary batteries having a high energy density.

Conclusion

A novel aniline derivative (**1**) having a disulfide ring was synthesized and forced to polymerize by chemical or electrochemical-oxidation. However, the dimer or trimer of **1** was obtained due to the steric effects of the substituent. We found that **1** was quantitatively copolymerized with aniline by chemical oxidative polymerization. The resulting copolymers have relatively high conductivities around 10^{-2} S/cm and good redox properties by coupling of the redox activities of the disulfide and polyaniline. We are now investigating the copolymerization conditions, which afford a higher conductivity and exploring the possibility of their use as cathode materials in the polymer secondary batteries.

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