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# Highly conductive polyaniline copolymers with dual-functional hydrophilic dioxyethylene side chains

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# ABSTRACT

We investigated new highly conductive polyaniline copolymers bearing a small amount of dualfunctional hydrophilic dioxyethylene side chains, which can act as a stabilizer in a heterogeneous dispersion medium in polymerization and a reactive dispersant in polar solvents. Compared to the unsubstituted polyaniline, new polyaniline copolymers maintained their high electrical conductivity of 485 S/cm with camphorsulfonic acid dopant in *m*-cresol. Moreover, in the alcoholic butoxyethanol solvent with a dodecylbenzenesulfonic acid dopant, new polyaniline copolymers showed enhanced dispersion abilities with very small particle sizes of <10 nm and exhibited a high electrical conductivity of 13 S/cm, which is significantly higher than polyanilines in an organic aliphatic alcoholic solvent ( $10^{-6} \sim 1$  S/cm). Therefore, new polyaniline copolymers are very interesting materials for electronic applications.

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# 1. Introduction

Conducting polymers have attracted considerable interest for applications, such as organic electrodes for electronic devices including organic photovoltaics and organic light emitting diodes, sensors, anti-corrosion coating, and EMI shielding [1,2]. In particular, polyaniline with high electrical conductivity has been widely investigated [3,4]. However, the low processability of conducting polyaniline in common organic solvents due to its low dispersion ability (or low solubility), has limited these practical applications [3]. Many approaches have investigated improvement of the processability of polyanilines including the introduction of highly soluble substituted groups, such as alkyl, alkoxy and fluorine groups and oxyethylene groups (or polyethylene glycol)by chemical modification of the aniline monomer or post-modification of the emeraldine base (EB) form of the polyanilines [5-9] and graftcopolymerization of polyanilines onto highly soluble polymers, polystyrene sulfonic acid [10]. However, the chemical substitution of polyaniline results in a dramatic decrease in its electrical conductivity in organic solvents compared to unsubstituted polyaniline [6–9]. Even with an optimized dopant and good solvent system, in many cases, the substituted polyanilines exhibit low electrical conductivity of  $10^{-6} \sim 20$  S/cm [5–10].

Here, we report new highly conductive polyaniline copolymers with a small amount of dual-functional hydrophilic dioxyethylene side chains (see Fig. 1a), which can act as a stabilizer in a heterogeneous dispersion medium during polymerization, as well as a reactive dispersant in polar solvents. Compared to unsubstituted polyaniline, new polyaniline copolymers S2 maintained their high electrical conductivity of 485 S/cm with camphorsulfonic acid (CSA) dopant in *m*-cresol. Moreover, in alcoholic butoxyethanol solvent with a dodecylbenzenesulfonic acid (DBSA) dopant, new polyaniline copolymers showed enhanced dispersion abilities with very small particle sizes of <10 nm and exhibited a high electrical conductivity of 13 S/cm, which is significantly higher than conventional polyanilines in an organic aliphatic alcoholic solvent.

# 2. Experimental section

The chemicals used were obtained from mainly Sigma–Aldrich (aniline, ammonium persulfate, 2-aminophenol, diethyleneglycol monomethyl ether, *p*-toluene sulfonic chloride, sodium hydride (60% dispersion in mineral oil), tetrahydrofuran (99.9%), (1S)-(+)-10-camphorsulfonic acid), Shinyo Pure Chemicals (sodium



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**Fig. 1.** (a) Chemical structure of the LE form of the S2 polyaniline copolymer with a dioxyethylene side chain. (b) Schematic diagram of self-stabilized effect of dual-functional monomers in the SSDP method. (c) SEM images of the as-synthesized S2-2 (upper) and unsubstituted PANI (lower) emeraldine salt (ES) particles at a reaction temperature of 0 °C.

bicarbonate), TCI (potassium-tert-butoxide), Samjung (trifluoroacetic acid), and Samchun (35% HCl, NH<sub>4</sub>OH, H<sub>2</sub>SO<sub>4</sub> (95%)).

# 2.1. Synthesis of monomer

An aniline monomer 2-(2-(2-methoxyethoxy)ethoxy)benzenamine (M2) with a dual-functional dioxyethylene side chain was prepared using the following procedure (see Scheme 1). The <sup>1</sup>H-NMR spectra were recorded on a Varian 400 MHz and the chemical shifts reported in ppm ( $\delta$ ) relative to (CH<sub>3</sub>)<sub>4</sub>Si.

*tert-Butyl 2-hydroxyphenylcarbamate*: 2-Aminophenol (10.9 g, 0.1 mol) dissolved in THF (250 mL) was mixed with NaHCO<sub>3</sub> (8.8 g, 0.15 mol) dissolved in deionized water (250 mL). Di*-tert*-butyl dicarbonate (*t*-BOC: 22.7 g, 0.1 mol) was then added to the resulting solution and stirred for 10 h. The resulting brown solution was evaporated to remove the THF solvent and produce a light brown



Scheme 1. Synthetic route for aniline monomer M2 with a dual-functional dioxyethylene side chain.

solid. (Yield = 82%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$ ): 8.145 (s, 1H, -NH), 7.095–6.845 (m, 4H, Ar), 6.675 (s, 1H, -OH), 1.530 (s, C(CH<sub>3</sub>)<sub>3</sub>).

2-(2-Methoxyethoxy)ethyl 4-methylbenzenesulfonate: Diethyleneglycol monomethyl ether (12 g, 0.12 mol) with 4-toluenesulfonyl chloride (TsCl:19 g, 0.1 mol) was dissolved in THF (200 ml). The NaH (5.5 g, 0.12 mol) was then added slowly to the resulting solution and stirred for 3 h. The resulting light-purple solution was filtered to remove the remaining sodium hydride. The yellow solution was extracted by dichloromethane. (Yield = 84%), <sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$ ): 7.793, 7.772 (d, 2H, Ar), 7.341, 7.321 (d, 2H, Ar), 4.176–4.152 (m, 2H, -CH<sub>2</sub>), 3.697–3.674 (m, 2H, -CH<sub>2</sub>), 3.586–3.575 (m, 2H, -CH<sub>2</sub>), 3.571–3.356 (m, 2H, -CH<sub>2</sub>), 3.347 (s, -CH<sub>3</sub>), 2.448 (s, -CH<sub>3</sub>, Ar).

tert-Butyl 2-(2-(2-methoxy)ethoxy)phenylcarbamate: tert-Butyl 2-hydroxyphenylcarbamate (10.45 g, 0.05 mol) with potassium tert-butoxide (6.1 g, 0.055 mol) was dissolved in THF (200 mL) and the mixture stirred at 40 °C under a N<sub>2</sub> atmosphere. 2-(2-Methoxyethoxy) ethyl 4-methylbenzenesulfonate (15.07 g, 0.055 mol) in THF (50 mL) was then added drop wise for 30 min using a dropping funnel. The mixture was stirred for 3 days and the resulting brown solution was filtered to remove the remaining potassium-*tert*-butoxide. The brown solution was then separated by ethyl acetate and water. (Yield = 62%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$ ): 8.064 (s, -NH), 7.803,7.782 (d, 1H Ar), 7.342, 7.321 (d, 1H Ar), 6.971–6.859 (m, 4H Ar), 4.204–4.151 (m, CH<sub>2</sub>), 3.866–3.842 (m, CH<sub>2</sub>), 3.731–3.715 ((m, CH<sub>2</sub>), 3.614–3.572 (m, CH<sub>2</sub>), 3.439 (s, -CH<sub>3</sub>), 1.582 (s, C(CH<sub>3</sub>)<sub>3</sub>).

2-(2-(2-Methoxyethoxy)ethoxy)benzenamine (M2): tert-Butyl 2-(2-(2-methoxyethoxy) ethoxy) phenylcarbamate (6.24 g, 0.02 mol) with trifluoroacetic acid (TFA: 4.56 g, 0.04 mol) in dichloromethane (40 mL) was stirred at 40 °C for 3 h. The NaHCO<sub>3</sub> was added to neutralize the trifluoroacetic acid, and the product was extracted with dichloromethane and water. (Yield = 71%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$ ): 6.809–6.697 (m, 4H Ar), 4.173–4.148 (m, CH<sub>2</sub>), 3.869–3.844 (m, CH<sub>2</sub>), 3.724–3.708 (m, CH<sub>2</sub>), 3.701–3.573 (m, CH<sub>2</sub>), 3.596 (s, –CH<sub>3</sub>).

#### 2.2. Synthesis of new polyaniline copolymers

New polyaniline copolymers S2 with a hydrophilic side chain and unsubstituted polyanilines PANI were synthesized by the chemical oxidation of aniline with ammonium persulfate (APS) as the oxidant [11]. An example synthesis of the S2-2 copolymer follows: the reactor was cooled to 0 °C with an HCl solution and chloroform and kept at that temperature for 30 min. Purified aniline and new synthesizing monomer M2 were added to the solution (aniline: M2 monomer = 100:2 in molar ratio) and the ammonium persulfate (APS) dissolved in HCl was added drop wise. The solution color changed from brown to blue after 3 h. Polymerization was performed for 12 h. The polymer powders were filtered and washed with dichloromethane and acetone and dried in a vacuum oven. Dried polyaniline (ES form) was dedoped to the emeraldine base (EB) form using ammonium hydroxide for 24 h. This EB powder was dried for 48 h in a vacuum oven. IR: quinoid ring  $(1592 \sim 1578 \text{ cm}^{-1})$ , benzoid ring  $(1535 \sim 1495 \text{ cm}^{-1})$ , C=N stretching  $(1310 \sim 1290 \text{ cm}^{-1})$ , aromatic C–H in-plane bending  $(1170 \sim 1000 \text{ cm}^{-1})$ , C–H out-of-plane bending  $(830 \text{ cm}^{-1})$ , C–O stretching  $(1300-1000 \text{ cm}^{-1})$ .

# 2.3. Elemental analysis of S2 copolymers

Based on elemental analysis (EA) for C, H, and N in the EB form of the S2 copolymers, the molar ratio of the dual-functional monomer M2 with a hydrophilic dioxyethylene group to the unsubstituted aniline monomer was calculated. The EA for S2-2 polymerized at 0 °C was C 74.47%, H 4.99% and N 14.02%. As shown in the figure below, when x:y = 1 : 5.7, the experimental results were well agree with those calculated C 74.47%, H 4.96% and N 14.02%, corresponding to that the molar ratio of M2 monomer to unsubstituted aniline monomer (M2:aniline = 3.9:100 (molar ratio)). The S2-2 and S2-10 polymerized at -10 °C, with a final molar ratio of M2 monomer to unsubstituted aniline monomer of M2:aniline = 3.7:100 and 18.3:100, respectively. solvent, its dual-functional polar side chain can act as a selfdispersion agent in the organic polar solvent, which lead to enhanced processability. Since the electrical conductivity of the substituted polyaniline decreased dramatically with increasing side chain length [6], as short as possible polar side chain with sufficiently high hydrophilicity (two -(CH<sub>2</sub>CH<sub>2</sub>O)- units) were thus introduced.

Fig. 1a shows the chemical structure of the new polyaniline copolymer (S2) with a dioxyethylene side chain in the leucoemeraldine (LE) base form. The dual-functional aniline monomer M2 was synthesized by a reaction of 2-aminophenol with diethyleneglycol monomethyl ether (see Scheme 1). Large amounts of substituted aniline monomers in the copolymer lead to a decrease in electrical conductivity [5–10]. Therefore, only a small amount of dual-functional aniline monomer M2 was used for copolymerization. The S2-2 and S2-10 copolymers stand for feeding aniline: M2 molar ratio = 100:2 and 100:10, respectively. For polymerization, the SSDP method with ammonium persulfate oxidant in a non-polar chloroform/polar water biphasic system was used, as repor-



#### 2.4. Sample preparation and electrical conductivity measurements

To form the conducting emeraldine salt (ES), the nonconducting emeraldine base (EB) of S2 copolymers and unsubstituted polyaniline (PANI) were first grinded with a dopant for 30 min and slowly added to corresponding solvent: *m*-cresol for camphorsulfonic acid (CSA) (aniline: CSA = 2:1 molar ratio) and butoxyethanol (BuEtOH) for dodecylbenzenesulfonic acid (DBSA) (aniline: DBSA = 2 : 1.5 molar ratio). The conducting thick films were casted onto slide glass at 50 °C from the prepared solution. The electrical conductivity of the substituted and unsubstituted polyaniline ES films, with sample widths of 1 mm and thicknesses from few micrometers to 30 µm was measured by a four-line method at room temperature with a Keithley 237 picoamperometer. The distance between each electrodes was 1 mm. To reduce contact resistance between the polyaniline film and gold wire electrode, graphite glue was used.

# 3. Results and discussion

Recently, a new polymerization method, self-stabilized dispersion polymerization (SSDP) method [11] based on a heterogeneous solvent system without a stabilizer, was developed. The resulting polyaniline exhibited high electrical conductivity and metallic transporting properties [12]. The self-stabilizing effect of the monomer anilinium chloride on the interface of the biphasic organic/aqueous solvent system [12] lead to a lower degree of chemical structural defects (i.e., lower ortho-linked defects) [13]. Here, an aniline analogous monomer 2-(2-(2-methoxyethoxy) ethoxy)benzenamine (M2) [14] with a dual-functional dioxyethylene side chain was used to enhance the self-stabilizing effects of the monomer during polymerization (see Fig. 1). Owing to the high hydrophilicity of the dioxyethylene groups, the polar sidechains could enhance the self-stabilizing effects of the anilinium monomer during polymerization in a heterogeneous biphasic nonpolar chloroform/polar water solvent system, as shown in Fig. 1b. Moreover, when the polyaniline copolymer polymerized using M2 monomer is conducting emeraldine salt (ES) form in an organic ted in Ref. [11,12]. For comparison, unsubstituted polyaniline (henceforth, noted PANI) was synthesized under identical experimental conditions.

In polyaniline, these physical properties and electrical conductivity show wide variations depending on the polymerization temperature [15]. First, the effect of the polymerization temperature was examined on a small scale in a 1L reactor. Similar experimental conditions, such as amount of reagents and solvents, reaction time, impeller shape, stirring speed and reactor, were used to eliminate the influence of other experimental parameters. To screen the polymerization temperature for S2 copolymers with high electrical conductivity, S2 copolymers were polymerized with different reaction temperatures for a reaction time of 12 h. Conducting S2 copolymer films were prepared using the synthesized S2 EB copolymers doped with camphorsulfonic acid (CSA) in *m*-cresol (aniline: CSA = 2:1 in molar ratio). The dopant/solvent (CSA/m-cresol) system used for the polyaniline was reported to produce the highest electrical conductivity due to the primary and secondary doping effects [3,11]. Fig. 2 shows the electrical conductivity measured using a four-line method [12] as a function of the reaction temperature for S2-2 and S2-10. The inherent viscosity relative to the molecular weight was measured using an Ubbelohde viscometer with S2 EB copolymers in sulfuric acid at 30 °C and plotted together with the electrical conductivity, as shown in Fig. 2.

In unsubstituted PANI, the highest conductivity was obtained at a reaction temperature of -25 °C, despite the low reaction rate [11]. However, the S2 copolymers were not polymerized at this reaction temperature due to steric hindrance of the dioxyethylene sidechains. The electrical conductivity of the S2 copolymers as a function of the reaction temperature showed similar trends to their inherent conductivity; the electrical conductivity decreased with decreasing inherent viscosity as shown in Fig. 2. The S2-2 copolymers showed approximately one order of magnitude higher electrical conductivity than the S2-10 copolymers. Moreover, the S2 copolymers synthesized at a polymerization temperature of 0 °C exhibit the highest electrical conductivity. It was attributed that the polymerization temperature of 0 °C may be lowest temperature having moderated molecular weight to overcome the steric hindrance of the dioxyethylene side-chains. Therefore, the S2-2 copolymer synthesized with smaller amounts of the dual-functional monomer at a polymerization temperature of 0  $^{\circ}$ C was further investigated.

S2-2 copolymers were polymerized at 0 °C in a relatively largescale reactor with a 5-L capacity. The EB form of the S2-2 copolymer showed a molecular weight of  $M_n = 69,600$  and  $M_w = 215,000$ , confirmed by gel permeation chromatography (GPC) in *N*-methylpyrrolidone (NMP) and an inherent viscosity of 1.04 in sulfuric acid at 30 °C. Unsubstituted PANI polymerized at 0 °C under identical conditions, such as amount of reagents and solvents, reaction time, stirring speed and reactor as described above, showed a similar molecular weight of  $M_n = 71,000$  and  $M_w = 266,100$  and a similar inherent viscosity of 1.05.

Scanning electron microscopy (SEM) and elemental analysis (EA) were performed to examine the self-stabilizing effects of the anilinium chloride M2 monomer at the interface of a biphasic non-polar chloroform/polar water solvent system in the SSDP method (see Fig. 1b). Based on EA for C, H, and N in the EB form, the molar ratio of the dual-functional monomer M2 with hydrophilic dioxyethylene group to unsubstituted aniline monomer in the S2-2 copolymer was M2:aniline = 3.9:100 (molar ratio), which was higher than the feeding ratio in polymerization (M2:aniline = 2:100 (molar ratio)). This higher ratio of M2 than feeding ratio in polymerization was also observed in the S2-10 copolymer (see Experimental section). In the synthesized S2



**Fig. 2.** Electrical conductivity with CSA/m-cresol and the inherent viscosity of the EB form as a function of the reaction temperature for a reaction time of 12 h for (a) S2-2 and (b) S2-10.

copolymers, the higher molar ratio of the M2 monomer than the feeding ratio is related to the higher hydrophilicity of the M2 monomer with dioxyethylene groups compared to that of unsubstituted aniline monomer. In the SSDP method, the anilinium salts were polymerized dominantly in the interfaces between the water and chloroform phases [11,12]. The higher hydrophilicity of the M2 monomer enhanced the self-stabilizing effect during biphasic polymerization, and consequently the M2 monomers participated more in the polymerization process at the interface between the water and chloroform phases.

SEM confirmed the enhancing self-stabilizing effect of the M2 monomer bearing a dioxyethylene side chain. Fig. 1c shows the SEM images of the as-synthesized S2-2 (upper) and PANI (lower) emeraldine salt (ES) particles, which were doped with HCl. The S2-2 copolymers formed much thinner skins compared to that of PANI, with a thickness of ~200 nm and ~3  $\mu$ m for S2-2 and PANI, respectively. The S2-2 polymers were polymerized mainly at the interfaces between the water and chloroform phases. The thinner skin of the S2-2 morphology can more readily assist in the dispersion process with small particle sizes than the thicker skin of the PANI.

Although the stabilizing effects of the M2 monomer and the thinner skin morphology of the S2-2 copolymers were enhanced, they showed an electronic structure similar to PANI. As shown in Fig. 3, the absorption spectra of the EB form in N-methylpyrrolidone (NMP) and ES doped with CSA in *m*-cresol of both S2-2 and PANI were similar. Both the S2-2 and PANI conducting ES forms showed a well-developed "free-carrier tail" in the near-infrared region, which is characteristic of highly conducting materials [3b]. As expected in the linear absorption properties, the S2-2 copolymers bearing side-chains exhibited high electrical conductivity: at a polymerization temperature of 0 °C and doped with CSA in the m-cresol system, S2-2 and unsubstituted PANI films had a conductivity of 485 and 160 S/cm, respectively. Therefore, the S2-2 copolymers bearing hydrophilic side-chains maintained the high electrical conductivity of unsubstituted PANI and exhibit significantly higher electrical conductivity than other substituted polyanilines  $(10^{-6} \sim 20 \text{ S/cm})$  [5–10].

In order to examine the dispersion ability of the S2-2 polymers in common organic solvents, the dispersion solution in aliphatic alcoholic solvent was prepared by stirring and milling. The S2-2 copolymer doped with dodecylbenzenesulfonic acid (DBSA) was added to butoxyethanol (BuEtOH) (aniline : DBSA = 2:1.5 M ratio). The S2-2/DBSA/butoxyethanol solution exhibited high dispersion abilities and a high solid content: the solid content in the solution was 1.6 wt% and 0.8 wt% after 5.0 and 1.2  $\mu$ m PTFE filtration, respectively. Fig. 4a and b show transmission electron



**Fig. 3.** Absorption spectra of the emeraldine base (EB) and emeraldine salt (ES) of the S2-2 copolymer and PANI.



**Fig. 4.** S2-2 ES polyaniline nanoparticles in a butoxyethanol solution: (a) TEM image, (b) SEM image of the nanoparticles spin-coated on a silicon wafer, (c) schematic diagram of well-dispersed S2-2 nanoparticles in a polar organic solvent.

microscopy (TEM) and SEM images of S2-2 polyaniline nanoparticles after 1.2  $\mu$ m filtration. The samples for the SEM image were prepared by spin-coating onto a silicon wafer with diluted solution. The images clearly confirm that the size of the nanoparticles was <10 nm. The SEM image of the S2-2 sample filtered with 5.0  $\mu$ m PTFE filters was similar to that from filtration with 1.2  $\mu$ m, except for the small amount of aggregates. Even with a small amount of M2 monomer with a hydrophilic side chain, the nanoparticles of the S2-2 copolymer in butoxyethanol were well dispersed without a dispersing agent. This was attributed to two effects: 1) the as-synthesized morphology with a thinner skin (~200 nm) forms nanoparticles more readily than unsubstituted PANI with a thicker skin (Fig. 1c); 2) the hydrophilic dioxyethylene groups on the S2-2 polymers act as self-dispersion agents, as shown in Fig. 4c.

The linear absorption curve of the S2-2 nanoparticles/butoxvethanol solution (Fig. 3) revealed a well-developed polaron band in the near-infrared region. The electrical conductivity of the S2-2 films doped with DBSA in butoxyethanol was approximately 13 S/ cm, significantly higher than the polyanilines in an organic aliphatic alcoholic solvent  $(10^{-6} \sim 1 \text{ S/cm})$ . The high electrical conductivity of the S2-2 copolymers in an alcoholic solvent was attributed to these dispersion characteristics with the particle size. The electrical conductivity of the conducting polymers is related not only to the chemical structure, but also to the dispersion characteristics including the particle size and solubility. With polyanilines having the same chemical structure and molecular weight, in good solvent system, polyanilines exhibit better dispersion abilities with smaller particle sizes (or better solubility) than in a poor solvent system, resulting in higher electrical conductivity, so-called secondary doping effect [3,16]. Therefore, the high dispersion ability of the S2-2 copolymers with small particle sizes (<10 nm) in alcoholic solvent leads to high electrical conductivity.

# 4. Conclusion

We have investigated new highly conductive polyaniline copolymers S2 that bear a small amount of dual-functional hydrophilic dioxyethylene side chains, which act both as a stabilizer in a heterogeneous dispersion medium in polymerization and a reactive dispersant in polar solvents. Compared to unsubstituted polyaniline PANI, the new polyaniline copolymers S2 maintain their high electrical conductivity, but showed enhanced dispersion abilities in organic alcoholic solvents with very small particle sizes of <10 nm. Therefore, polyaniline copolymers S2 are very interesting materials for electronic applications.

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