Synthesis of Polyaniline with Low Polydispersity by Using a Supramolecular Ionic Assembly as the Reaction Medium

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Conducting polymers (CPs) are an important class of optoelectronic materials that have a number of advantages as organic substances; namely, they are designable, flexible, processible, and lightweight. These attractive features have enabled the fabrication of new organic electronic devices, such as light-emitting diodes, photovoltaics, transistors, and actuators.[1] Polythiophenes (PTs), polyfluorenes (PFs), poly-(phenylene vinylene)s (PPVs), and polyanilines (PANIs) are all representative CPs, and some are currently at a practical application stage. To design and synthesize CPs with desired functions, factors related to not only the electronic properties of the π-conjugated systems but also the structural characteristics, such as the regioregularity and polydispersity, are important because these structural qualities determine the aggregation morphology and thus affect the bulk properties.[2] However, such controlled polymerization has not been regarded as feasible because CPs are typically synthesized through step-growth mechanisms. The polydispersity index (PDI) of step-growth polymerization is predicted to be 2.0 when the monomer conversion is 100%.

In 2004, the groups led by Yokozawa[3] and McCullough[4] reported independently that a nickel-catalyzed coupling reaction of 3-alkylthiophene-based monomers proceeded in chain-growth manner, giving regioregular poly(3-alkyl thiophene)s with a PDI of close to unity. Recent development of this method has further enabled the controlled polymerization of other CPs, such as polyphenylenes (PPs)[5] and PFs.[6] Furthermore, Yu and Turner[7] have succeeded in ring-opening metathesis polymerization (ROMP) of [2.2]paracyclophanedienes, which afforded soluble PPVs with a PDI of 1.2. Accordingly, the chain-growth polymerization of CPs has opened new doors in synthetic polymer chemistry and organic electronics.[8] However, in principle, the concept cannot be applied to the polymerization of aniline[9] because it proceeds through the oxidative coupling of anilinium salts.

Recently, Lo and Sleiman[10] reported nucleobase-templated synthesis of poly(phenylene ethynylene)s (PPEs). Importantly, the PDI values of the daughter polymer (that is, PPE) were close to unity, copying that of the template polymer despite the step-growth nature of Sonogashira coupling polymerization. Furthermore, other templating approaches using porous coordination polymers (PCPs)[11] and block copolymer micelles[12] were found to be effective. In such unique reaction media, the propagation reaction occurred preferentially against other side reactions and achieved a low PDI value. However, examples of conjugated polymer synthesis are still limited.

Inspired by the development of these templating approaches, we decided to pursue the synthesis of PANI with a low PDI value, because PANI is one of the remaining CPs for which such a polymerization has not yet been established. The template-assisted polymerization of aniline has been widely examined;[13] however, previous research focused on creating PANI nanostructures that replicated the template structures, and a characterization of the PANI including PDI values has not been performed in detail. Herein, we present a supramolecular ionic assembly composed of an anionic π-conjugated backbone and anilinium cations that could provide a unique polymerization medium in which the anilinium cations are concentrated and aligned. Remarkably, the oxidative polymerization of aniline using the supramolecular template yielded PANI with a PDI value as low as 1.3 ($M_n = 20500$).

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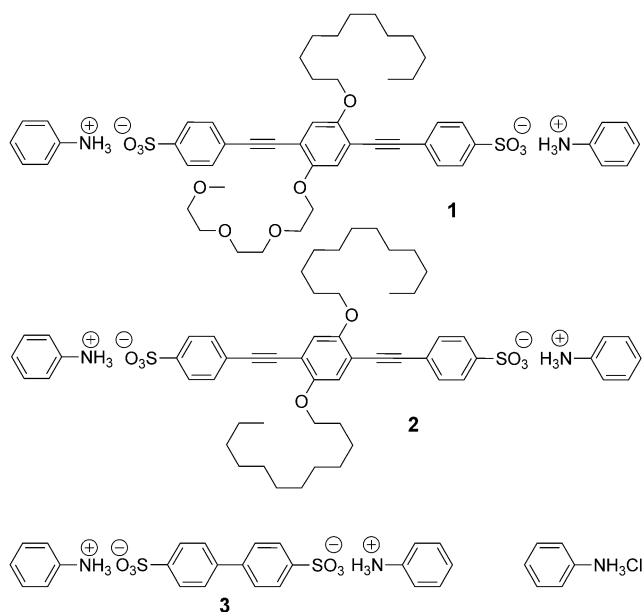
Scheme 1. Structures of compounds **1**, **2**, and **3**. Anilinium chloride was used for comparison.

Figure 1. a) An SEM image of a freeze-dried sample of **1** prepared in water: [**1**] = 0.2 mM, pH 2.5. b) The dynamic light scattering profile of the supramolecular assembly of **1** prepared in water: [**1**] = 0.2 mM, pH 2.5.

We designed and synthesized oligo(phenylene ethynylene) (OPE)-based anionic molecules that have anilinium cations not only as counterions but also as monomers (Scheme 1). To tune the balance between the hydrophobicity and hydrophilicity of the molecules, which is essential for self-assembly in water,[14] we introduced triethylene glycol and dodecyl chains in **1** and two dodecyl chains in **2**. Compound **3** was prepared for control experiments and is analogous to **1** and **2** but does not assemble in water owing to its compact structure. All the compounds are characterized using the usual methods (see Supporting Information).

We prepared the supramolecular assembly by dissolving **1** in water under sonication and maintaining the solution at 5 °C. Figure 1a shows a scanning electron microscope (SEM) image of a freeze-dried sample of the supramolecular assembly of **1** ([**1**] = 0.2 mM, pH 2.5). We observed rectangular structures with a width of about 200–400 nm. X-ray diffraction (XRD) measurements indicated that the assembly had a crystalline nature, although a detailed characterization was difficult owing to the complicated XRD profile (Supporting Information, Figure S1). The size of the supramolecular assembly in solution was also evaluated using dynamic light scattering (DLS; Figure 1b). The average size was about 300–500 nm, which is consistent with that observed in the SEM images. Compound **2** ([**2**] = 0.2 mM) was too hydrophobic and could not be dissolved in water. In contrast, composite **3** ([**3**] = 0.2 mM) was soluble but did not form any supramolecular assembly.

Figure 2 shows the variable-temperature (VT) ultraviolet (UV) absorption spectra of the supramolecular assembly of **1**. By lowering the temperature of the solution of **1** from 75 to 5 °C, a red-shift in the π–π* transition of OPE in **1** from 363 to 368 nm with isosbestic points was observed
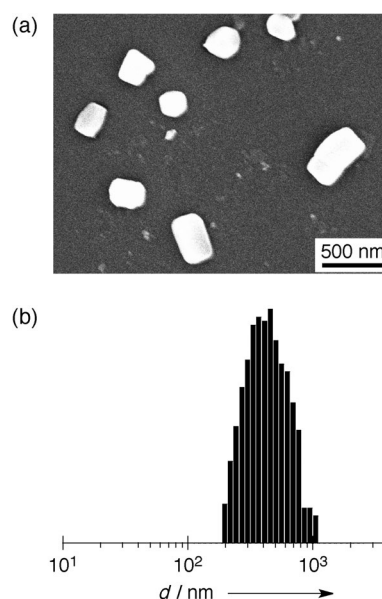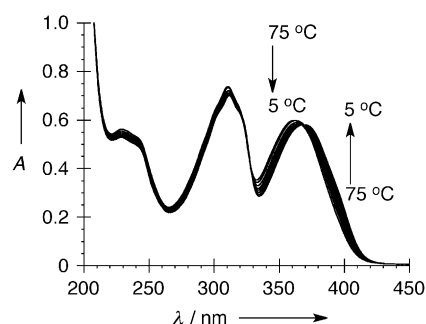

Figure 2. Changes to the UV absorption spectrum of the supramolecular assembly of **1** in water as the assembly is cooled from 75 to 5 °C: [**1**] = 0.2 mM, pH 2.5, l = 1 mm.

along with a new shoulder band at 399 nm. This indicates the formation of a supramolecular assembly of OPE chromophores[15] at 5 °C.

We also conducted variable-temperature (VT) ^{1}H NMR measurements of the supramolecular assembly of **1**. Figure 3a shows partial ^{1}H NMR spectra of **1**, for which the proton signals of the OPE backbone became broad for temperatures below 45 °C, indicating the formation of the supramolecular assembly. Importantly, a shift in the proton signals of the anilinium cation in **1** was scarcely observed during this process, while the chemical shifts of those in anilinium chloride and compound **3** moved to higher frequencies (a lower magnetic field) upon cooling (Figure 3b; Supporting Information, Figure S2). The change in the chemical shifts with temperature is rationalized by the hydration-induced shift of the free anilinium cations. These results in turn suggest that within the anionic supramolecular assembly of **1**, anilinium monomers would form contact ion pairs with the
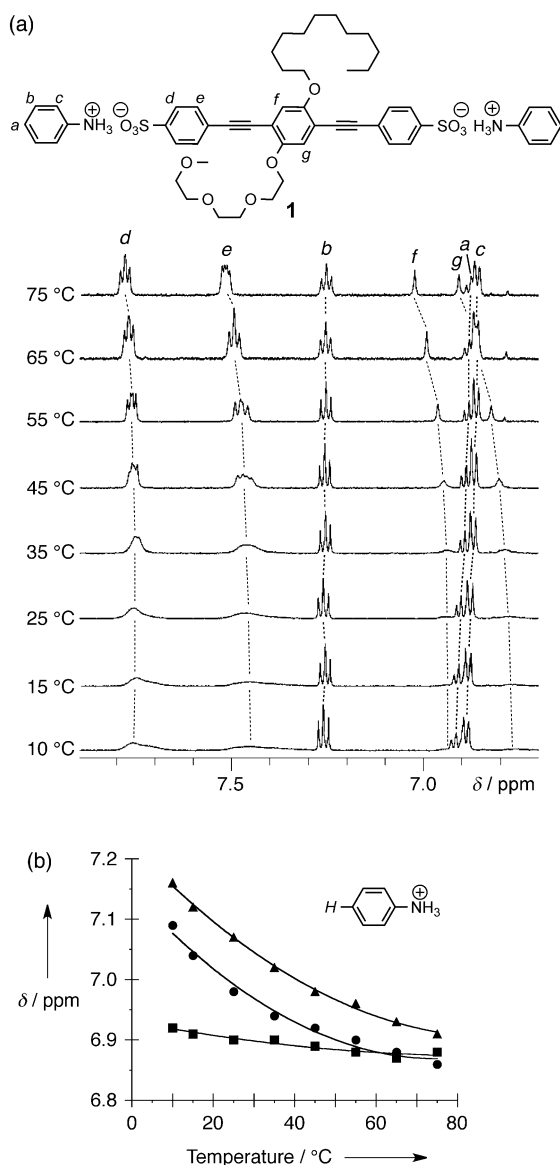
(a)

(b)

Figure 3. a) Changes to the ^{1}H NMR spectrum of the supramolecular assembly of **1** in water with temperature: Sodium [2,2,3,3-D$_4$]-3-3-(trimethylsilyl) propanoate was used as an internal standard; [**1**] = 0.2 mM, pD = 2.5. b) Plots of the chemical shifts of p-H in anilinium salts against temperature: anilinium chloride (▲ [anilinium chloride] = 0.4 mM, pD = 2.5), compound **3** (● [**3**] = 0.2 mM, pD = 2.5), and compound **1** (■).

anionic OPE backbone. Therefore, the supramolecular assembly of **1** provides the anilinium monomers with different surroundings from those in the bulk solution. We expect that oxidative polymerization of aniline in such a unique reaction medium can afford PANI in a controlled manner.

With the above information in mind, we conducted oxidative polymerization of aniline. We added ammonium persulfate (APS, 0.4 mM, 1.0 equiv/aniline) to a solution of the supramolecular assembly of **1** (0.2 mM, pH 2.5, 0–5 °C). The mixture was stirred for 24 h at 0–5 °C, yielding a green-colored solution without any precipitation. An absorption spectrum of the resultant solution showed maximum absorption
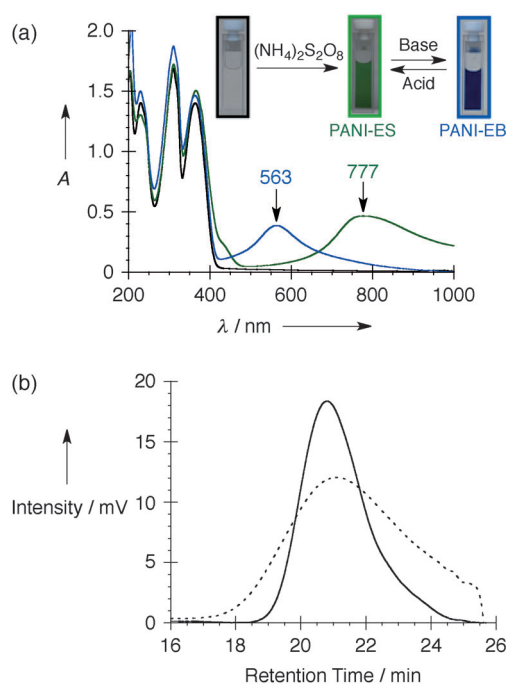
(a)

(b)

Figure 4. a) Absorption spectra of **1** (black line), PANI-ES (green line), and PANI-EB (blue line) obtained through the templating approach. PANI-ES and PANI-EB were diluted from 1 mL to 4 mL by addition of H$_2$O (3 mL); l = 1 cm. (b) GPC profiles of the PANI-EB obtained through the templating approach (——) and commercially available PANI-EB (----, PDI (M_w) > 1.8 (20 000)).

at a peak wavelength (λ_{max}) of 777 nm (1.6 eV), which is attributable to the emeraldine salt form of PANI (namely, PANI-ES; Figure 4a). Importantly, neither anilinium chloride nor compound **3** could be polymerized under the same conditions, which is probably due to the low monomer concentration and temperature ([anilinium cation] = 0.4 mM, 0–5 °C, pH 2.5). We infer from this that the supramolecular template can locally concentrate the monomers and facilitate the polymerization. The addition of potassium hydroxide solution rendered the resultant solution basic and dedoped the PANI-ES, transforming it into the emeraldine base form [(PANI-EB), λ_{max} = 563 nm (2.2 eV)] without any precipitation. The PANI-EB was then precipitated out by adding dimethylformamide (DMF) to the PANI-EB solution, filtered, and washed with methanol and water, and freeze-dried (yield 85 %). The anionic template was readily isolated from the filtrate by evaporating solvents, and it can be re-used for further synthesis of polyaniline after complexation with anilinium cations.[16]

Solid-state ^{15}N NMR spectrum of the resultant PANI-EB with anionic OPE showed a single peak at 70.75 ppm, which is most likely due to rapid imine–amine interconversion at room temperature, and peaks assignable to the branched structures were not detected (Supporting Information, Figure S3).[17] A gel permeation chromatography (GPC) profile of the obtained PANI-EB is shown in Figure 4b. Remarkably, the polydispersity of our PANI-EB was narrow with a PDI of about 1.3 (M_n = 20 500, calculated using polystyrene

standards). This value is significantly smaller than that of commercially available PANI-EB (PDI (M_w) = 1.8 (20 000)). Among several syntheses of PANI-EB under identical conditions of [**1**] = 0.2 mM at 0–5 °C, variations of ±6 % in the obtained M_n value were observed (Supporting Information, Table S1). It should be mentioned that the length of the PANI calculated from the M_n value is not consistent with the size of the supramolecular assembly of **1** (Figures 1 a,b). A similar inconsistency between the M_n value and template size has also been observed in other systems.[18] Therefore, we expect that the supramolecular assembly plays an important role in influencing the polymerization kinetics rather than defining the length of the PANI by copying its size.

The time evolution of the polymerization, starting with the addition of one equivalent of APS toward aniline, was therefore monitored using absorption spectroscopy (Figure 5). After an induction period of 4 h, features related
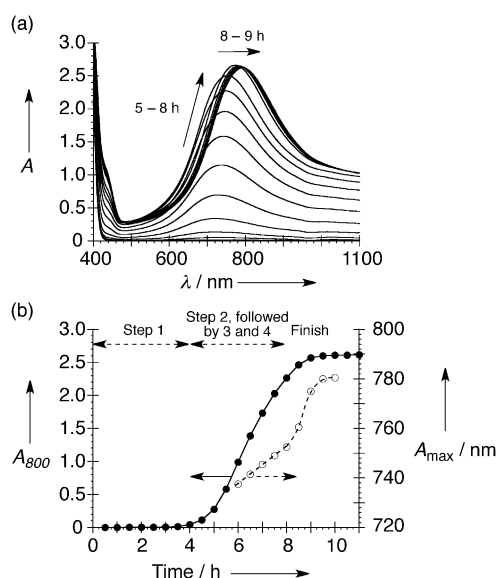

Figure 5. a) Changes to the absorption spectrum observed during polymerization. b) Plots of the absorbance at 800 nm (●) and absorption maximum against time (○: [**1**] = 0.2 mM, [APS] = 0.4 mM, pH 2.5 at 5 °C, l = 1 cm.

to the absorption of the pernigraniline form of PANI (PANI-PN) appeared in the spectra and gradually increased in strength. This process was accompanied by a small peak shift from 700 nm to 740 nm, which is indicative of the formation and elongation of π-conjugated systems. The increase in the absorbance was eventually saturated and the λ_{max} shifted to 777 nm, at which point the polymerization finished (Figure 5 b). The peak shift observed in the last stage of the polymerization indicates the transformation of PANI-PN to PANI-ES. This kinetic analysis of the PANI formation is consistent with the reported mechanism[19] and is explained as follows (Scheme 2 a). An induction period is observed because the initiation step (that is, oxidation of the anilinium monomer) is generally slow (step 1). Once polymerization has commenced (step 2), PANI-PN is the main

form in the redox equilibrium because PANI-ES can be easily oxidized into PANI-PN (step 3). During polymerization, the oxidation of the monomer is mediated by the redox couple of PANI-PN and PANI-ES (step 4), which accelerates the polymerization. Polymerization ends when all the APS is consumed; consequently, only the PANI-ES remains in the solution, upon which the absorption maximum shifts from 740 nm (PANI-PN) to 777 nm (PANI-ES). The PANI-ES can be dedoped and transformed into PANI-EB, accompanied by a color change from green to blue, by treatment with potassium hydroxide solution (step 5). Interestingly, the polymerization took place even with the addition of only 0.2 equiv of APS (Supporting Information, Figure S4). Moreover, the addition of another 0.2 equiv of APS restarted the polymerization. If the APS oxidizes the anilinium monomers randomly and sparsely in the supramolecular assembly of **1**, polymerization should not take place with a deficiency of APS. Therefore, it should be reasonable to conclude from these results that the polymerization proceeds at the surface of the supramolecular assembly of **1**. We deduce that the PANI-ES, polymerized at the surface, would dissociate from the supramolecular assembly along with anionic PPEs as solubilizing agent, which then exposes a fresh surface of anilinium monomers for subsequent polymerization. Accordingly, a plausible mechanism for the controlled polymerization using the supramolecular reaction medium is depicted in Scheme 2 b. As discussed, the anilinium monomer is oxidized by the PANI-PN. Because the diffusion of anilinium monomer would be suppressed in the supramolecular assembly, the propagation reaction should occur at the chain end of PANI (Step 4 in Scheme 2 b). Such a kinetically controlled process is likely to give rise to the narrow polydispersity of the resultant PANI. Given this plausible mechanism, the temperature and concentration should influence the quality of the resultant PANI, as these factors will affect not only the formation of supramolecular assembly (Supporting Information, Table S1 and Figure S5) but also the polymerization kinetics. In fact, as the polymerization temperature or concentration of **1** was increased, M_n and the PDI also increased. Under such conditions, even anilinium chloride could be polymerized in some degree, and such bulk polymerization would deteriorate the structural quality of PANI. The relationships between the concentration of **1**, M_n, and PDI are shown in Figure 6. The PDI value can be as low as 1.3 provided that the concentration of **1** is kept below 1 mM.

As M_n and the structural quality of CPs profoundly influence the electrical properties,[1g,20] we measured the conductivity of the PANI-ES obtained from the supramolecular ionic assembly of **1**. PANI-ES films were prepared from PANI-EB (PDI = 1.3, M_n = 20 500) by doping with camphorsulfonic acid (CAS) in *meta*-cresol; this sample was dropcast onto a silicon wafer (see the Supporting Information). We measured the electrical conductivity of the PANI-ES film to be 190 S cm^{-1} at 25 °C using a four-terminal technique (Supporting Information, Figure S6). In contrast, the conductivity of the commercially available sample, doped by

(a)

(b)
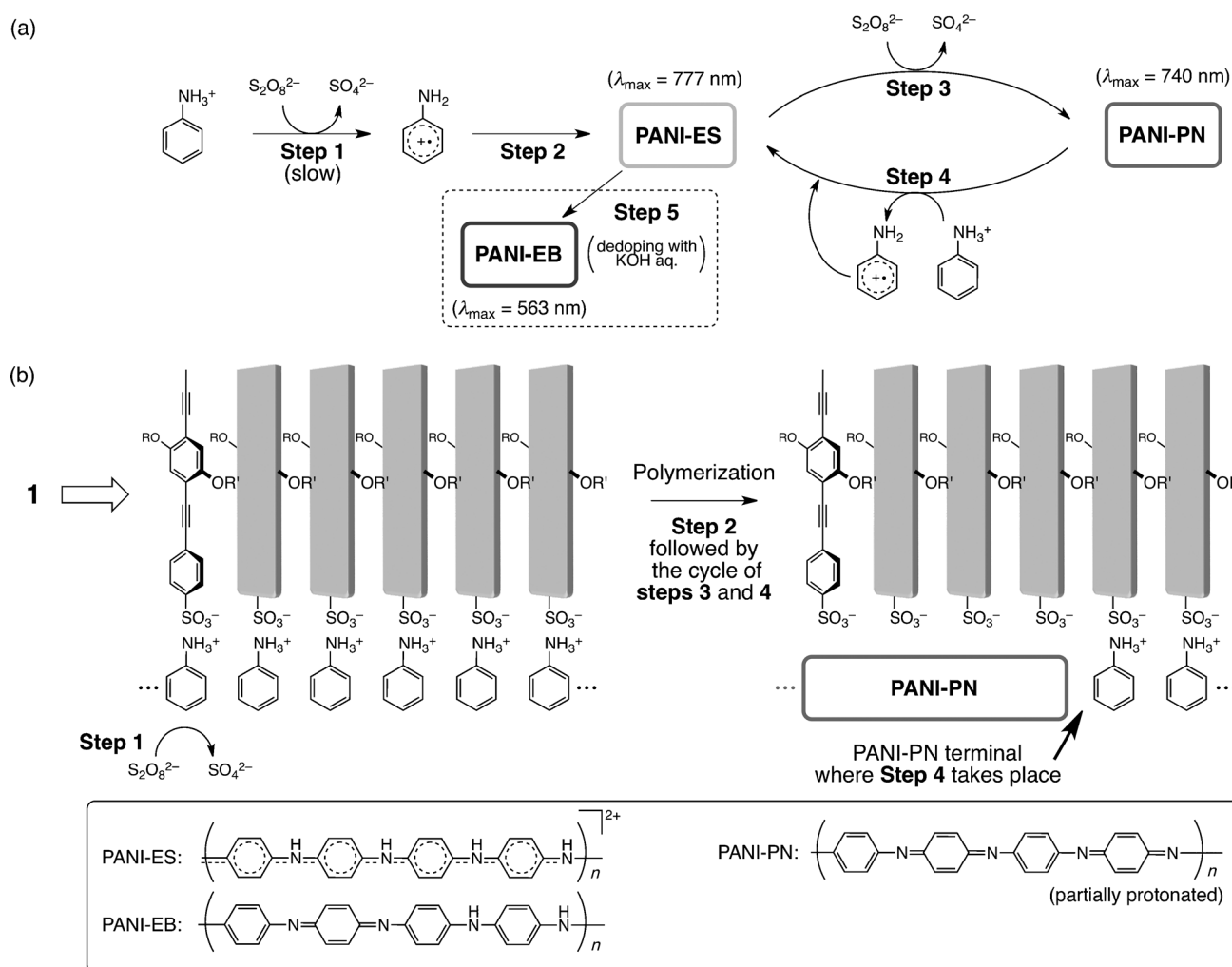
Scheme 2. The oxidative polymerization process of aniline and a plausible mechanism in this system.
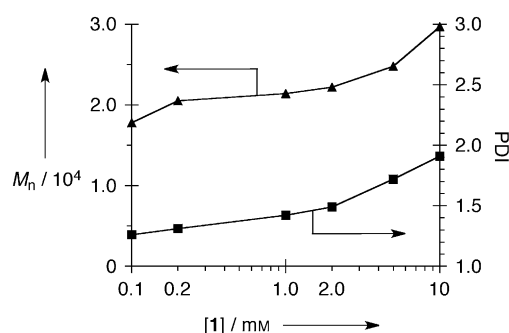

Figure 6. Plots of M_n (▲) and the PDI (■) of PANI as a function of the concentration of **1**.

the same procedure, was evaluated to be 28 S cm^{-1} (its GPC is shown in Figure 4b). In the case for PANI, there is a relationship between the M_n and the electrical conductivity;[20a–d] our system would contribute to reveal the correlation between the PDI of PANI and the electrical conductivity.

In conclusion, we have demonstrated oxidative polymerization of aniline using a supramolecular ionic assembly as a reaction medium, which afforded PANI-EB with $M_n = 20\,500$ and a PDI of 1.3. We deduce that anilinium monomers form contact ion pairs with the anionic OPE backbone and are locally concentrated along the ionic assembly of **1**; such a situation eventually enables the facilitation of the polymerization reaction and would suppress side reactions. The conductivity of the PANI-EB doped with CAS in *meta*-cresol was estimated to be 190 S cm^{-1}, which was higher than commercially available PANI. At this stage, we have not succeeded in controlling M_n significantly; however, the control of supramolecular ionic assemblies would lead to the synthesis of higher molecular weight PANI-ES with a low PDI, which should exhibit better conductivity. Our approach basically permits the utilization of this unique ionic assembly for the synthesis of other conducting polymers. Such research is now in progress.

COMMUNICATION

Experimental Section

All of the starting materials and solvents were purchased from Aldrich, Wako Chemicals, Kanto Chemicals, and Tokyo Chemicals and used as received. ^1H NMR and ^{15}N NMR analyses were carried out with a Bruker Biospin DRX-600 (600 MHz) and JASTEC-500 with JEOL ECA500 spectrometer, respectively. Chemical shifts were reported in parts per million (ppm) downfield from sodium [2,2,3,3-D$_4$]-3-(trimethylsilyl)propionate (0 ppm for ^1H) as the internal standard. UV/Vis and UV/Vis–NIR absorption spectra were obtained using Hitachi U-2900 and Shimadzu UV-3600 spectrophotometers, respectively. Number-average molecular weight (M_n) and polydispersity index (PDI) were determined by a gel permeation chromatography (GPC, Tosoh HLC-8220GPC equipped with two Shodex GPC LF-804 columns) in DMF using polystyrene as a standard. Field-emission scanning electron microscope (FE-SEM) images were collected on a Hitachi 4800. Compound **1** was synthesized according to Scheme S1 in the Supporting Information.

Acknowledgements

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