## Click Synthesis and Reversible Electrochromic Behaviors of Novel Polystyrenes Bearing Aromatic Amine Units

### Yongrong Li,<sup>1</sup> Tsuyoshi Michinobu<sup>2,3</sup>

<sup>1</sup>Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

<sup>2</sup>Global Edge Institute, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

<sup>3</sup>PRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Saitama, Japan

Correspondence to: T. Michinobu (E-mail: michinobu.t.aa@m.titech.ac.jp)

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ABSTRACT: Novel electrochromic polymers were prepared by the click postfunctionalization of poly(4-azidomethylstyrene) with alkyne-containing aromatic amine units in the presence of Cu(I) catalysts. Two kinds of aromatic amine units, tris(4-alkoxyphenyl)amine and N, N, N', N'-tetraphenyl-*p*-phenylenediamine, were introduced into polystyrene side chains, which were completely characterized by gel permeation chromatographymultiangle light scattering, nuclear magnetic resonance, and infrared spectroscopies, and elemental analysis. Thermal analyses demonstrated the high stability with the decomposition temperatures exceeding 300 °C even after postfunctionalization. The UV-vis absorption spectra of the polymer thin films revealed negligible absorption in the visible region, as reasonably confirmed by visual observation. The polymer thin films were prepared by spray-coating on an indium tin oxide-coated glass plate. Cyclic voltammograms of these films exhibited an-

**INTRODUCTION** Solution-processable electrochromic polymers are an important class of materials for the applications to electrochromic displays and mirrors, smart windows, and information storage.<sup>1</sup> Promising building blocks are mainly classified into metallo-supramolecular polymers and organic aromatic polymers.<sup>2</sup> In contrast to the metal-containing materials, purely organic polymers that display perfectly reversible redox activities are limited. For example, Reynolds et al.<sup>3</sup> reported a series of conjugated polymers composed of 3,4-dioxythiophene- and 3,4-dioxypyrrole-based main chains capable of undergoing reversible discoloration upon oxidation and coloration upon reduction. The colors in the neutral (reduced) state are controlled by designing the polymer structures because of the ease of structural tuning of the organic materials. Donor-acceptor alternating structures are such an example of the spectral/band gap engineering.<sup>4</sup>

Another class of promising organic polymers is aromatic polyamines that display coloration upon oxidation and discoloration upon reduction.<sup>5</sup> It is known that unsubstituted odic peaks ascribed to the oxidation of the side-chain aromatic amine moieties. The tris(4-alkoxyphenyl)amine unit displayed one-step oxidation at 0.287 V (vs. Ag/AgCl), while the N,N,N,N-tetraphenyl-p-phenylenediamine unit showed twostep oxidations at 0.297 and 0.641 V. These oxidation processes produced new colors of the polymer films. The former triarylamine-based chromophore provided a blue color after the oxidation, while the latter phenylenediamine-based chromophore showed a potentially controlled green and dark blue colors. The reversibility and switching behaviors of these color changes were also comprehensively investigated. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 2111– 2120, 2012

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triphenylamine moieties readily dimerize upon a one-electron oxidation forming N, N, N', N'-tetraphenylbenzidine units.<sup>6</sup> Therefore, the appropriate molecular design is required to enhance the chemical stability of the oxidized states. Introduction of electron-donating substituents into the *p*-positions of the triphenylamine moieties effectively improves the lifetime of the oxidized states. Further improvement is usually achieved when p-phenylenediamine structures with lower oxidation potentials are adopted. This molecular design of aromatic amines has indeed been used in the development of hole-transporting materials and organic ferromagnetic polymers.<sup>7</sup> Also, Liou et al.<sup>8</sup> successfully applied the redox characteristics of the aromatic amines to designing novel electrochromic polyamines. They reported a series of polyamides and polyimides incorporating the aromatic amine moieties into the main chain. Because of the excellent engineering plastic features, the polymers displayed a high thermal stability, good film formation capability, and reversible electrochromism.

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Recently, we reported a new concept of click postfunctionalization using Cu(I)-catalyzed azide-alkyne cycloaddition,<sup>9</sup> accessible from readily available azide-functionalized polymers as a precursor, and various alkyne-containing small molecules as a functional reactant.10 Using this method, the desired functional groups can be introduced into the polymer side chains in quantitative yields without the production of any byproducts. The significant advantage of using this method is the straightforward derivatization from a single precursor polymer, which allows the systematic investigation of its various properties in a short time period. In other words, the repetition of tedious polymerization and purification processes is not required in order to prepare multiple polymer samples. We now report the postfunctional quantitative introduction of aromatic amine-based electrochromophores into a polystyrene precursor.<sup>11</sup> Two different electrochromophores were designed and their electrochromic behaviors comprehensively compared.

#### **EXPERIMENTAL**

#### Materials

All reagents were purchased form Kanto, Tokyo Kasei, Wako, and Aldrich and used as received. 4-{[*tert*-Butyl(dimethyl) silyl]oxy}aniline (1),<sup>12</sup> (4-{[4-(diphenylamino)phenyl](phenyl) amino}phenyl)methanol (5),<sup>12</sup> and poly(4-azidomethylstyrene) (7)<sup>13</sup> were synthesized according to the reported method.

#### Measurements

<sup>1</sup>H- and <sup>13</sup>C-NMR spectra were measured on a JEOL model AL300 spectrometer at 20 °C. Chemical shifts are reported in parts per million downfield from SiMe<sub>4</sub>, using the solvent's residual signal as an internal reference. The resonance multiplicity is described as s (singlet), br s (broad singlet), d (doublet), and m (multiplet). Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded on a JASCO FT/IR-4200 spectrometer. Gel permeation chromatography (GPC) was measured on a JASCO system equipped with polystyrene gel columns using THF as an eluent at the flow rate of 1.0 mL min<sup>-1</sup>. Absolute molecular weights were determined by using the detector miniDAWN Tristar. Elemental analyses were conducted on a PerkinElmer 2400-SeriesII CHNS/O Analyzer. Thermogravimetric analysis (TGA) was carried out on a Seiko SII TG 6220 under nitrogen flow at the heating rate of 10 °C min<sup>-1</sup>. Absorption spectra of spectroelectrochemistry experiments were measured on an Agilent 8453 UV-vis spectrophotometer. Other UV-vis-near infrared spectra in solutions were recorded on a JASCO V-670 spectrophotometer. Potential applications were performed using a cyclic voltammetry setup at 20 °C in dehydrated CH<sub>3</sub>CN-containing 0.1 M (nC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NClO<sub>4</sub> in threeelectrode cell. The working, reference, and auxiliary electrodes were an indium tin oxide (ITO), Ag/AgCl/CH<sub>3</sub>CN/  $(nC_4H_9)_4NPF_6$ , and a platinum wire, respectively. All potentials are referenced to the Ag/AgCl (Ag/Ag<sup>+</sup>) couple unless otherwise stated. Polymer thin films were prepared on an ITO electrode (10  $\Omega$ , about 0.8  $\times$  2.5 cm<sup>2</sup>) by spray-coating of polymer solutions (2.0 g  $L^{-1}$  in THF), followed by drying in vacuo at 50 °C.

# 4-{[*tert*-Butyl(dimethyl)silyl]oxy}-*N*,*N*-bis(4-methoxyphe-nyl)aniline (2)

Tris(dibenzylideneacetone)dipalladium(0) (Pd<sub>2</sub>(dba)<sub>3</sub>; 93.5 mg, 0.102 mmol), and tri-*tert*-butylphosphine (P(*t*Bu)<sub>3</sub>; 114 mg, 0.610 mmol) were dissolved in dry toluene (80 mL) under N<sub>2</sub>. After stirring for 10 min at 20 °C, **1** (2.27 g, 10.2 mmol), 4-bromoanisole (5.70 g, 30.5 mmol), and sodium *tert*-butoxide (NaO*t*Bu; 2.34 g, 24.4 mmol) were added. The solution was stirred at 100 °C for 15 h. After cooling to 20 °C, the reaction mixture was diluted with toluene (100 mL) and washed with brine (100 mL × 2). The toluene layer was dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation and column chromatography (SiO<sub>2</sub>, hexane/ethyl acetate = 4:1) afforded the desired product (2.2 g, 51%) as a yellow solid.

<sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta$  0.14 (s, 6 H), 1.01 (s, 9 H), 3.31 (s, 6 H), 6.72 (m, 4 H), 6.79 (m, 2 H), and 7.07 (m, 6 H). <sup>13</sup>C NMR (75 MHz,  $C_6D_6$ ):  $\delta$ -4.39, 23.19, 25.85, 54.99, 115.00, 120.86, 124.66, 125.64, 140.75, 142. 44, 151.31, and 156.86. Infrared (IR; neat): 2953, 2830, 1498, 1456, 1436, 1238, 1039, 906, 843, 818, 804, and 778 cm<sup>-1</sup>. MALDI-TOF MS (dithranol): *m/z*: calcd for  $C_{26}H_{33}NO_3Si^+$ : 435.22 g mol<sup>-1</sup>; found: 434.2 g mol<sup>-1</sup> [*M*-H]<sup>+</sup>.

### 4-[Bis(4-methoxyphenyl)amino]phenol (3)<sup>14</sup>

To a solution of **2** (1.50 g, 3.44 mmol) in THF (30 mL), tetrabutylammonium fluoride (1 M in THF, 7 mL) was added under air. The mixture was stirred at 20 °C for 20 min. Column chromatography (SiO<sub>2</sub>, hexane/ethyl acetate = 2:1) afforded the desired product (1.0 g, 90%) as yellow oil.

<sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta$  3.31 (s, 6 H), 3.80 (br s, 1 H), 6.46 (m, 2 H), 6.72 (m, 4 H), and 7.04 (m, 6 H). IR (KBr): 3387, 1497, 1462, 1441, 1233, 1178, 1104, 1033, and 824 cm<sup>-1</sup>. MALDI-TOF MS (dithranol): *m/z*: calcd for  $C_{20}H_{19}NO_3^+$ : 321.14 g mol<sup>-1</sup>; found: 320.15 g mol<sup>-1</sup> [*M*-H]<sup>+</sup>.

## 4-Methoxy-*N*-(4-methoxyphenyl)-*N*-[4-(prop-2-yn-1-yloxy) phenyl]aniline (4)

A solution of **3** (500 mg, 1.56 mmol),  $K_2CO_3$  (500 mg, 4.68 mmol), and KI (51.0 mg, 0.312 mmol) in dry DMF (30 mL) was heated to 80 °C under  $N_2$  for 1 h. Propargyl bromide (222 mg, 1.87 mmol) was slowly added over 0.5 h. The reaction mixture was stirred at 80 °C for 2 days. After cooling to 20 °C, water (100 mL) was added, and the crude product was extracted with  $CH_2CI_2$ . Column chromatography (SiO<sub>2</sub>, hexane/ethyl acetate = 4:1) afforded the desired product (460 mg, 85%) as brown viscous liquid.

<sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta$  1.98 (s, 1 H), 3.31 (s, 6 H), 4.18 (s, 2 H), 6.70 (m, 4 H), 6.79 (m, 2H), and 7.03 (m, 6 H). <sup>13</sup>C NMR (75 MHz,  $C_6D_6$ ):  $\delta$  55.02, 56.03, 75.41, 79.27, 115.02, 116.14, 124.60, 125.59, 142.36, 143.43, 153.31, and 155.79. IR (KBr): 3281, 2119, 1497, 1462, 1441, 1234, 1212, 1177, 1105, 1030, and 824 cm<sup>-1</sup>. MALDI-TOF MS (dithranol): *m/z*: calcd for  $C_{23}H_{21}NO_3^+$ : 359.15 g mol<sup>-1</sup>; found: 358.15 g mol<sup>-1</sup> [*M*—H]<sup>+</sup>.



**SCHEME 1** Synthesis of aromatic amine moieties: (a) 4-bromoanisole, NaOtBu, Pd<sub>2</sub>(dba)<sub>3</sub>, P(tBu)<sub>3</sub>, and toluene, 100 °C, 24 h; (b) ( $nC_4H_9$ )<sub>4</sub>NF, THF, 20 °C, 2 h; (c) BrCH<sub>2</sub>C=CH, K<sub>2</sub>CO<sub>3</sub>, KI, DMF, N<sub>2</sub>, 80 °C, 48 h; (d) DCC, DMAP, HC=C(CH<sub>2</sub>)<sub>3</sub>COOH, CH<sub>2</sub>Cl<sub>2</sub>, 20 °C, 16 h.

#### 4-{[4-(Diphenylamino)phenyl](phenyl)amino}benzyl hex-5-ynoate (6)

To a solution of 5-hexynoic acid (204 mg, 1.35 mmol) in  $CH_2Cl_2$  (13 mL) at 0 °C, *N,N'*-dicyclohexylcarbodiimide (DCC; 306 mg, 1.48 mmol), 4-dimethylaminopyridine (DMAP; 16.5 mg, 0.135 mmol), and **5** (1.2 g, 2.7 mmol) were added. The reaction mixture was allowed to warm to 20 °C and stirred for 16 h. After the filtration of white precipitates, the solvent was evaporated and column chromatography (SiO<sub>2</sub>, CHCl<sub>3</sub>/ hexane = 4/1) afforded the desired product (530 mg, 74%) as a brown solid.

<sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.69 (m, 2 H), 1.77 (m, H), 2.00 (m, 2 H), 2.25 (m, 2 H), 5.01 (s, 2 H), 6.91 (m, 3 H), 7.02 (m, 4 H), and 7.20 (m, 14 H). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ 17.83, 23.85, 32.83, 65.91, 69.50, 83.24, 122.85, 123.05, 123.56, 124.30, 124.43, 125.70, 126.03, 129.57, 129.60, 130.06, 130.39, 143.01, 143.68, 148.13, 148.32, 148.35, and 172.24. IR (neat): 3287, 3034, 2934, 2118, 1731, 1587, 1502, 1487, 1310, 1265, 1150, 829, 752, 694, and 626 cm<sup>-1</sup>. MALDI-TOF MS (dithranol): m/z: calcd for C<sub>37</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>: 536.25 g mol<sup>-1</sup>; found: 535.4 g mol<sup>-1</sup> [*M*—H]<sup>+</sup>.

#### **P1**

To a solution of **7** (146 mg, 0.92 mmol per repeat unit) in DMF (12 mL), **4** (330 mg, 0.92 mmol), sodium ascorbate (18.2 mg, 0.092 mmol), and copper(II) sulfate pentahydrate (11.4 mg, 0.046 mmol) were added under argon. The mixture was stirred at 20 °C for 24 h. The solution was poured into MeOH/CH<sub>2</sub>Cl<sub>2</sub> (10/1). The precipitate was filtered, washed with MeOH, and dried under vacuum, yielding the pale yellow solid (395 mg, 83%).

<sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta$  0.65 (br s, 5n H), 3.37 (s, 6n H), 5.04 (br s, 3n H), 6.74 (br s, 6n H), 6.88 (br s, n H), and 7.03 (br s, 9n H). IR (neat): 3034, 2932, 1501, 1503, 1462,



#### P2

To a solution of **7** (146 mg, 0.92 mmol per repeat unit) in DMF (12 mL), **6** (490 mg, 0.92 mmol), sodium ascorbate (18.2 mg, 0.092 mmol), and copper(II) sulfate pentahydrate (11.4 mg, 0.046 mmol) were added under argon. The mixture was stirred at 20 °C for 24 h. The solution was poured into MeOH/CH<sub>2</sub>Cl<sub>2</sub> (10/1). The precipitate was filtered, washed with MeOH, and dried under vacuum, yielding the pale yellow solid (530 mg, 84%).

<sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta$  0.64 (br s, 3n H), 2.02 (br s, 2n H), 2.31 (br s, 2n H), 2.72 (br s, 2n H), 4.89 (br s, 4n H), 6.83 (m, 4n H), 6.95 (m, 8n H), and 7.07 (m, 12 nH). IR (neat): 3034, 2923, 2097, 1731, 1588, 1503, 1489, 1264, 753, and 694 cm<sup>-1</sup>. Elemental analysis: calcd for ( $C_{46}H_{41}N_5O_2$ )<sub>n</sub>: C 79.40, H 5.94, N 10.06, O 4.60; found: C 79.50, H 5.49, N 10.41%.

#### **RESULTS AND DISCUSSION**

#### Synthesis of Aromatic Amine Moieties

Triarylamine derivatives have traditionally been synthesized by Ullmann chemistry, while the recent progress in the Pdcatalyzed cross-coupling reactions enabled the high yielding and large-scale production of various aromatic amine molecules.<sup>15</sup> Therefore, we prepared the redox-active aromatic amine moieties, tri(4-alkoxyphenyl)amine and N,N,N',N'-tetraphenyl-*p*-phenylenediamine units, by the Pd-catalyzed reactions. Starting from 4-{[*tert*-butyl(dimethyl)silyl]oxy}aniline **1**, the Pd-catalyzed amination with the twofold 4-bromoanisole constructed the triarylamine framework **2** in 51% (71% yield for each amination reaction; Scheme 1). Deprotection





**FIGURE 1** <sup>1</sup>H NMR spectra of (a) **4** and **P1** and (b) **6** and **P2** in  $C_6D_6$  at 20 °C. The residual  $C_6H_6$  and water contamination are marked as \* and #, respectively.

of the tert-butyl(dimethyl)silyl group followed by the Williamson reaction with propargyl bromide yielded the alkynefunctionalized tris(4-alkoxyphenyl)amine unit 4. The total yield of the three steps was 40%. The hydroxyl group-functionalized N,N,N',N'-tetraphenyl-p-phenylenediamine 5 was prepared from 4-bromotriphenylamine via the two-step Pd-catalyzed amination reactions according to a literature method.<sup>12</sup> Similar to the synthesis of **4**, the Williamson reaction was attempted. However, this reaction was not successful in this case. Therefore, the hydroxyl group of 5 was esterified under standard conditions using DCC and DMAP, for conversion into the alkyne functionality. The desired compound 6 was obtained in a moderate yield of 74%. The total yield to produce this molecule from commercially available compounds was 46%. The chemical structures of the two aromatic amine chromophores were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR, IR, and MALDI-TOF mass measurements.

#### **Polymer Synthesis**

The azide-functionalized polystyrene derivative **7** was selected as a readily available precursor polymer. The absolute molecular weight  $(M_n)$  and the polydispersity  $(M_w/M_n)$  determined by gel permeation chromatography-multiangle light scattering (GPC-MALS; multiangle light scattering) were 15,400 and 1.71, respectively. The presence of the azide group was confirmed by the strong vibration peak at 2095 cm<sup>-1</sup> of the IR spectrum (Fig. 1), and the azide content in the repeat unit was determined to be 96% from the elemental analysis.

The new alkyne-functionalized aromatic amines 4 and 6 were subjected to the click postfunctionalization of 7 in the presence of a Cu(I) catalyst in DMF, yielding new polystyrene derivatives **P1** and **P2**, respectively (Scheme 2). Although a

new Cu catalyst was developed for the homogeneous reaction in organic solvent media,<sup>16</sup> the initial combination of CuSO<sub>4</sub>·5H<sub>2</sub>O and sodium ascorbate effectively promoted the cycloaddition between the azide moieties of 7 and the terminal alkyne of the aromatic amine units. The GPC-MALS measurements revealed a reasonable molecular weight increase. It should be noted that relative molecular weights determined by the comparison to standard polystyrenes were not reliable in this case probably due to the strong adhesive feature of the functionalized polystyrenes P1 and P2. The  $M_{\rm n}$  and  $M_{\rm w}/M_{\rm n}$  values were 77,500 and 1.44 for **P1** and 98,100 and 1.29 for P2, respectively (Table 1). The absence of the terminal alkynes and azide groups in P1 and P2 was confirmed by the <sup>1</sup>H NMR and IR spectra. Because P2 showed a gradual color change in chloroform, the NMR spectra were taken in deuterized benzene or dimethyl sulfoxide. In the <sup>1</sup>H NMR spectra, the terminal alkyne proton peaks detected at 1.98 and 1.74 ppm for 4 and 6, respectively,



**SCHEME 2** Synthesis of **P1** and **P2** by click postfunctionalization: (a)  $CuSO_4$ :5H<sub>2</sub>O, sodium ascorbate, DMF, 24 h.

TABLE 1	Summary	of Molecu	ılar Weig	ghts and	d Therma	a
Propertie	s of the Po	olymers				

Polymer	<i>M</i> <sub>n</sub> <sup>a</sup>	$M_{\rm w}/M_{\rm n}^{\rm a}$	<i>T</i> <sub>5%</sub> (°C) <sup>b</sup>	T <sub>g</sub> (°C) <sup>c</sup>
7	15,400	1.71	-	-
P1	77,500	1.44	308	113
P2	98,100	1.29	331	97

<sup>a</sup> Molecular weights determined by GPC-MALS (multiangle light scattering).

 $^{\rm b}$  The 5% weight loss temperatures determined by TGA at the heating rate of 10  $^{\circ}\text{C}$  min  $^{-1}.$ 

 $^{\circ}$  Glass transition temperatures determined by DSC at the scanning rate of 10  $^{\circ}C$  min  $^{-1}.$ 

completely disappeared after the postfunctionalization, despite the occurrence of partial broadening (Fig. 1). Moreover, in the IR spectra, both the strong azide vibrational peak at 2095 cm<sup>-1</sup> of **7** and the alkyne C—H and C≡C vibrational peaks detected at 3281 and 2119 cm<sup>-1</sup> for **4** and at 3287 and 2118 cm<sup>-1</sup> for **6** apparently disappeared after the postfunctionalization. As an example, the IR spectra of **4**, **7**, and **P2** are depicted in Figure 2. More importantly, elemental analyses revealed the content of the pendent aromatic amine units to be 98.5% for **P1** and 98.0% for **P2** from the C/N ratio. All these results strongly support the occurrence of the quantitative click postfunctionalization.

#### **Thermal Properties**

Thermal stability is very important when practical applications are considered. To determine the thermal properties of the postfunctionalized polymers **P1** and **P2**, TGA and differential scanning calorimetry measurements were performed at the scanning rate of 10 °C min<sup>-1</sup> under flowing nitrogen. The thermal analysis data are summarized in Table 1, and the TGA curves are depicted in Figure 3. Both postfunctionalized polymers are thermally stable and the 5% decomposition temperatures ( $T_{5\%}$ ) of **P1** and **P2** were 308 and 331 °C, respectively. The residual soot amounts of **P1** and **P2** at 500







FIGURE 3 TGA curves of P1 and P2 measured at the heating rate of 10  $^\circ C\ min^{-1}$  under flowing nitrogen.

°C were 57.2 and 65.3%, respectively. The high-char yields of these polymers could be explained by their high aromatic contents. The glass transition temperatures ( $T_g$ ) of **P1** and **P2** were 97 and 113 °C, respectively. These values are comparable to the reported  $T_g$  of polystyrene, ensuring that this postfunctionalization does not lower the thermal stabilities of the precursor polymers.

#### **Optical and Electrochemical Properties**

Both **P1** and **P2** are soluble in the common organic solvents, such as toluene, benzene, chlorobenzene, *o*-dichlorobenzene, THF, and dichloromethane at room temperature. However, they are insoluble in some polar solvents, such as acetonitrile and dimethyl sulfoxide, at room temperature. The presence of the clear solubility boundary made it possible to prepare thin films of these polymers by a spray-coating method on an ITO substrate and undergo electrochemical measurements in the thin-film states.

The UV-vis absorption and fluorescence spectra of **P1** and **P2** were measured both in THF and in the thin-film state, and the data are summarized in Table 2. These optical properties are ascribed to the side-chain aromatic amine units, because the precursor polystyrene did not provide these spectra. The absorption spectrum of **P1** in THF showed a well-defined main peak (longest wavelength absorption maximum:  $\lambda_{max}$ ) at 298.5 nm accompanied by a weak long wavelength shoulder peak, characteristic of the  $\pi-\pi^*$  and  $n-\pi^*$  transitions of the tris(4-alkoxyphenyl)amine units (Fig. 4).<sup>17</sup>

**TABLE 2** Summary of the optical properties of the functionalized polystyrenes

		In THF	Film		
Polymer	λ <sub>max</sub> (nm)	λ <sub>em</sub> (nm) [λ <sub>ex</sub> (nm)]	Stokes shift (cm <sup>-1</sup> )	λ <sub>max</sub> (nm)	λ <sub>em</sub> (nm) [λ <sub>ex</sub> (nm)]
P1	298.5	398.5 [298.5]	8406	302.5	400.0 [302.5]
P2	314.0	401.0 [314.0]	6910	322.5	401.5 [322.5]



FIGURE 4 Normalized UV-vis absorption [(a) in THF; (c) in film] and fluorescence spectra [(b) in THF; (d) in film] of P1 and P2.

The  $\lambda_{\rm max}$  of P2 was detected at 314.0 nm in THF. This value bathochromically shifted compared to that of P1 due to the extended aromatic moiety. However, the emission maxima  $(\lambda_{em})$  of **P1** and **P2** in THF appeared at similar positions of 398.5 and 401.0 nm, respectively. Accordingly, the Stokes shift of **P1**, calculated from the  $\lambda_{max}$  and  $\lambda_{em}$  values, was 8406 cm<sup>-1</sup>, which was greater than that of **P2** (6910 cm<sup>-1</sup>). The optical band gaps of P1 and P2, determined from the end absorptions in THF, were 3.22 (385 nm) and 3.26 eV (380 nm), respectively. The polymer thin films, prepared by casting the solutions onto a quartz plate, displayed a slight bathochromic shift in both  $\lambda_{max}$  and  $\lambda_{em}$  compared to the solution spectra. The most significant shift was observed for the  $\lambda_{\text{max}}$  value of **P2** (8.5 nm), suggesting the strong aggregation propensity of the larger aromatic chromophores in the side chains. Although a broadening of the end absorptions also occurred, the main peaks remained in the UV region, thereby maintaining its visual transparency.

Cyclic voltammograms (CVs) of these polymer films were measured in a poor solvent, dry  $CH_3CN$ , with 0.1 M  $(nC_4H_9)_4NClO_4$  as the supporting electrolyte. The redox potentials and the calculated energy levels are listed in Table 3. The polymer films were prepared by the spray coating of the THF solutions onto an ITO-coated glass plate. Because they were almost insoluble in  $CH_3CN$ , the redox behavior in the film states was directly evaluated using the ITO as a working electrode. Solution CVs of the aromatic polyamines are usually measured at the scanning rate of 50–100 mV s<sup>-1</sup>, but it was found that the polymer films peel off the ITO surface when scanned at this rate. Decreasing the scanning rate solved this problem. The most suitable scanning rate was

eventually determined to be 1 mV s<sup>-1</sup>. The exfoliation of the polymer films was probably due to the partial solubilization of the formed polycations in CH<sub>3</sub>CN, although it was unclear by visual observation.

The redox activities of these polymers originate from the side-chain aromatic amine moieties. The **P1** film displayed a single well-defined oxidation peak at 0.289 V (vs.  $Ag/Ag^+$ ), ascribed to one-electron removal from the tris(4-alkoxyphe-nyl)amine moiety [Fig. 5(a)]. Although the anodic current intensity of the oxidation process was greater than the cathodic one of the corresponding reduction process, no new oxidation peaks appeared even after the repeated scans. The repeated scans led to a gradual decrease in the anodic current intensity and the current intensities of both oxidation and reduction finally became almost the same, again supporting the partial solubilization of the polymer films when they were oxidized. This result basically suggested no side

**TABLE 3** Summary of the redox potentials and energy levels of the functionalized polystyrenes

Polymer	E <sub>ox,1</sub> (V) <sup>a</sup>	E <sub>ox,2</sub> (V) <sup>a</sup>	Opt. BG (eV) <sup>b</sup>	HOMO (eV) <sup>c</sup>	LUMO (eV) <sup>d</sup>
P1	0.287	-	3.22	-4.98	-1.76
P2	0.297	0.641	3.26	-5.08	-1.82

<sup>a</sup> Potentials versus Ag/Ag<sup>+</sup> in CH<sub>3</sub>CN with 0.1 M (nC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NClO<sub>4</sub>.

<sup>b</sup> Optical band gap.

 $^{\rm c}$  Calculated from the  $E_{\rm ox,1}$  values on the basis of Fc/Fc^+ = -4.8 eV. Fc/ Fc^+ = 0.1 V (vs. Ag/Ag^+).

<sup>d</sup> Calculated from the HOMO levels and the optical band gaps.



**FIGURE 5** Cyclic voltammograms (CVs) of the thin films of (a) **P1** and (b) **P2** on an ITO-coated glass plate in CH<sub>3</sub>CN containing 0.1 M ( $nC_4H_9$ )<sub>4</sub>NCIO<sub>4</sub> at the scanning rate of 1 mV s<sup>-1</sup>. Potentials versus Ag/Ag<sup>+</sup>.

reactions under the measurement conditions, which was confirmed by the reversible electrochromic behavior (vide infra). The **P2** film also exhibited strong oxidation peaks at 0.297 and 0.641 V. The first oxidation potential ( $E_{\text{ox},1}$ ) was attributed to the one-electron removal from the *p*-phenylenediamine unit forming an aminium cationic radical. A further electron removal occurred at the second oxidation potential ( $E_{\text{ox},2}$ ) yielding a bication. Similar to **P1**, the repeated scanning of the CV curves did not provide a new peak, thus showing the high potential of **P2** as a solution-processable electrochromophore.

The electronic energy levels, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), of **P1** and **P2** were estimated from the combination of the redox potentials and optical band gaps. The HOMO levels of **P1** and **P2** were determined to be -4.98 and -5.08 eV, respectively, on the basis of ferrocene/ferrocinium (Fc/Fc<sup>+</sup>) = -4.8 eV. The LUMO levels of **P1** and **P2**, calculated from the determined HOMO levels and the optical band gaps, were -1.76 and -1.82 eV, respectively. These values are comparable to those of reported aromatic polyamines.<sup>5,8</sup>

#### **Electrochromic Properties**

Based on the optical and electrochemical studies, the electrochromic behavior of the polymer thin films was evaluated. Spectroelectrochemistry was used to monitor the spectral changes in the electrochromic films of P1 and P2. The spraycoated thin films on the ITO-coated glass plate together with the reference and counter electrodes were placed in a 1-cm cuvette. The UV-vis-near infrared spectra were measured in  $CH_3CN$ -containing 0.1 M ( $nC_4H_9$ )<sub>4</sub>NClO<sub>4</sub> at 20 °C. When potentials more positive than 0.20 V (vs. Ag/Ag<sup>+</sup>) were applied to the thin film of P1, new absorption bands centered at 390 and 720 nm appeared, resulting in the film's color change from almost transparent to blue (Fig. 6).<sup>17</sup> Considering the CV curve, this color change is ascribed to the generation of the aminium cationic radical, and this radical showed a sufficient stability in the solid state. In the case of the P2 film, two-step color changes upon electrochemical oxidation were observed (Fig. 7). The application of a 0.15 V potential produced new bands centered at 405 and 820 nm. The lower-energy band at 820 nm is characteristic of the

aminium cationic radical of the N,N,N',N'-tetraphenyl-*p*-phenylenediamine unit.<sup>18</sup> The intensity of these bands increased as more positive potentials were applied up to 0.45 V, leading to a green film. The significant persistency of the aminium cationic radical realized the high stability of the green color. However, the further increase in the applied potentials led to a decrease in the peak intensities at 405 and 820 nm and the appearance of another new peak at 620 nm, resulting in a dark blue film. The second color change in the **P2** film is attributed to the oxidation from the aminium cationic radical to the bication. The presence of the isosbestic points



**FIGURE 6** Electrochromic behavior of the **P1** film on the ITOcoated glass plate in  $CH_3CN$ -containing 0.1 M ( $nC_4H_9$ )<sub>4</sub>NCIO<sub>4</sub> at applied potentials from 0 to 0.40 V (vs. Ag/AgCI).





**FIGURE 7** Electrochromic behavior of the **P2** film on the ITO-coated glass plate in  $CH_3CN$ -containing 0.1 M ( $nC_4H_9$ )<sub>4</sub>NClO<sub>4</sub> at applied potentials (a) from 0 to 0.45 V and (b) from 0.45 to 0.9 V (vs. Ag/AgCl).

basically suggests no side reactions during these oxidation steps under the stated measurement conditions. The stability of the electrochemically generated poly(cationic radical)s was estimated from the time-dependent UV-vis-near infrared spectral changes of the thin films on the ITO plate. Both poly (cationic radical)s were almost persistent under the inert atmosphere, while the half-lives of the poly(cationic radical)s of **P1** and **P2** under air were 69 and 231 h, respectively.

Reversible color production by the desired potential applications is essential for the fabrication of practical electrochromic devices. For both the **P1** and **P2** films, the UV-vis-near infrared spectral changes in the oxidation process from the neutral polyamines to the aminium cationic radicals were fully reversible when slow scanning rates were adopted. Fast scanning of the potentials induced peeling of the films from the ITO electrode, as indicated in the CV measurements. To gain insight into the film stability and coloring mechanism in detail, the response time and switching processes were investigated. The absorbance ascribed to the aminium cationic radicals was monitored as a function of time by UV-visnear infrared spectroscopy, and the absorbance profiles of the **P1** and **P2** films are shown in Figures 8 and 9, respectively. The pulse time for the **P1** film at 720 nm and for the **P2** film at 820 nm was determined to be 20 and 50 s,



**FIGURE 8** Current consumption (upper) and absorbance change (lower) at 720 nm upon eletrochromic switching between 0 and 0.27 V of the **P1** film (~1  $\mu$ m thickness) on the ITO-coated glass plate (coated area: 2.5 cm  $\times$  0.8 cm).



**FIGURE 9** Current consumption (upper) and absorbance change (lower) at 820 nm upon eletrochromic switching between 0 and 0.28 V of the **P2** film (~1  $\mu$ m thickness) on the ITO-coated glass plate (coated area: 2.5 cm  $\times$  0.8 cm).

respectively, due to the starting point of the absorbance saturation. The switching time was evaluated as 90% of the full switch, because it is difficult to perceive any further color change by the naked eye beyond this point. The results revealed that the switching times of the coloring and bleaching process for the P1 film at 720 nm (blue color) were 6.2 and 3.2 s, respectively. In the case of the P2 film at 820 nm (green color), the slower coloring process of 11.1 s and faster bleaching process of 1.8 s were observed. These values are comparable to the reported values, supporting the clear correlation between the response time and chemical structures.<sup>19</sup> Importantly, these experiments revealed that the color changes are reversibly achieved by applying cyclic scans of potential pulses between the oxidation voltages and the corresponding reduction voltages. The 100 cycle experiments suggested that the decrease in the oxidized absorbance was merely 5% for the P1 film and 12% for the P2 film, which were consistent with the repeated scans of the CV curves. Unfortunately, the second color change of the P2 film from green to dark blue was not fully reversible upon repeated pulse applications. The absorbance at 620 nm became lower as more pulses were applied (not shown), probably because of the undesired side reaction caused by the unsubstituted para-positions of the triarylamine unit.

#### CONCLUSION

We have developed a straightforward method for introducing active electrochromophores into the reactive polystyrene using the conventional click chemistry reaction. The total synthetic yields of the aromatic amine-based electrochromophore moieties amounted to 40-46%, suggesting the applicability to large-scale synthesis. The tris(4-alkoxyphenyl)amine-based chromophore displayed a one-step color change from transparent to blue, while the N,N,N',N'-tetraphenyl-pphenylenediamine-based chromophore showed two-step changes from transparent to green and finally to dark blue. The production processes of the blue and green colors were reversible due to the high chemical stability of the carefully designed aminium cationic radicals. This useful postfunctionalization methodology based on the combination of click chemistry and electrochromism will be applied to a wide variety of polymers and material surfaces.

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