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Novel Synthesis of Electroresponsive Poly(thiophenylene) through a Michael-Type Addition

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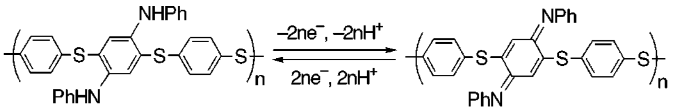
ABSTRACT



A novel poly(thiophenylene) having *N*,*N*′-diphenyl-1,4-phenylenediamine (PDA) as a redox unit was synthesized through a Michael-type addition. This polymerization proceeded at room temperature without catalysts. The polymer obtained acted as a good electroresponsive material with moderate thermostability.

Electroresponsive polymers have attracted the attention of many researchers because of the wide applications in electrical engineering. Recent interest has been stimulated by the potential use of such polymers as electrode materials in batteries and in capacitor, sensor, and electronic displays. Up to now π-conjugated polymers have been developed for this purpose due to their high electrical conductivity;[1] however, they lack chemical and thermal stabilities and also moldability. Themostable polymers with redox activity have been strongly desired for electronic devices with good reliability for long-term use. One approach for an alternate material is the introduction of a redox active center onto thermostable aromatic polymers.[2] Poly(thiophenylene) (PPS) is well-known to exhibit good thermal stability, moldability, and chemical resistance as an excellent engineering plastic.[3] Although these properties make PPS a high performance polymer, it is difficult to synthesize under mild conditions. Much effort has been exerted in the development of a new synthetic method.[4]

Recently, polyaniline as a emeraldine base, which has a quinoid imine oxidative state form, has been shown to react with nucleophiles such as amines and mercaptans at room temperature.[5] This reaction is noteworthy for the arylsulfide bond formation through the nucleophilic substitution of a mercaptan on the imine compounds. We now report a successful attempt to synthesize an electroresponsive PPS containing *N*,*N*′-diphenyl-1,4-phenylenediamine (PDA) units at room temperature. This process involves a Michael-type

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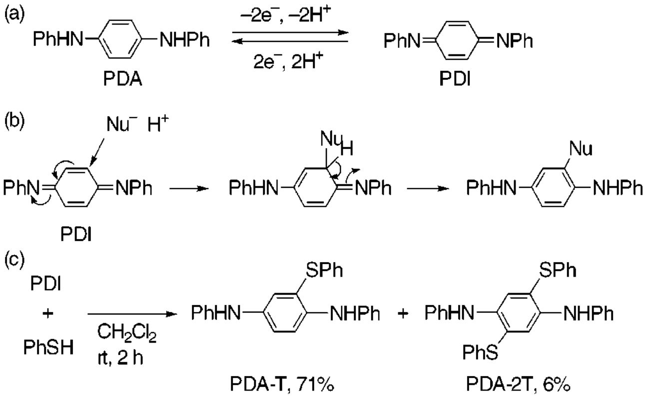
addition on the compounds having a double bond with an electron-attractive group.[6]

N,*N*′-Diphenyl-1,4-phenylenediamine (PDA) is a redox-active unit of polyaniline and is converted to *N*,*N*′-diphenyl-1,4-phenylenediimine (PDI) by chemical or electrochemical oxidation as shown in Scheme 1a. A Michael-type addition of nucleophiles to PDI was confirmed to proceed at room temperature (Scheme 1b).

Scheme 1. (a) Reversible Redox between PDA and PDI. (b) The Michael-Type Addition Mechanism to PDI. (c) The Control Reaction of Thiophenol with PDI



The control reaction of PDI with thiophenol was carried out in dichloromethane for 2 h at room temperature (Scheme 1c). The 2-phenylthio-PDA (PDA-T) and 2,5-bis(phenylthio)-PDA (PDA-2T) were isolated by silica gel column chromatography in 71 and 6% yields, respectively.[7] A Michael-type addition of thiophenol to the quinoid ring of PDI gave PDA-T. On the other hand, PDA-2T was formed via the addition of thiophenol to PDI-T, which was the oxidized form of PDA-T. Since PDA-T has lower oxidation potential (0.23 V vs SCE at pH 1.3) than that of PDA (0.28 V), some amount of PDI acts as an oxidant of PDA-T. As a result, PDA as the reduced form of PDI was detected in a 17% yield in this reaction. In other words, more than 94% of PDI was converted in this reaction. Diphenyl disulfide as a side product was detected only in very small amounts on the basis of HPLC. These results suggested that the nucleophilic addition quantitatively proceeded.

The nucleophilic reaction was demonstrated by a controlled experiment using PDI. The electronic absorption attributed to PDI at 450 nm gradually decreased with the addition of the nucleophile during the reaction. Kinetic analysis of its UV−vis spectra reveals that mercaptans such as thiophenol, hexadodecyl mercaptan, and methyl mercaptan quantitatively react with PDI. Their reactions obey pseudo-first-order kinetics, where the rate constant for thiophenol and dodecyl mercaptan were found to be 2.62×10^{-2} s^{-1} and 2.8×10^{-4} s^{-1}, respectively. Other nucleophiles such as sodium methoxide (5.0×10^{-3} s^{-1}) and butylamine (2.62×10^{-2} s^{-1}) were also confirmed to react with the imine compounds.

A solvent effect was observed during the nucleophilic reaction (Figure 1). The rate constant in dichloromethane is 4 times greater than that in *N*-methylpyrrolidone (NMP). The reaction rapidly proceeds in a nonpolar solvent by preventing the stabilization of the nucleophile by solvation.

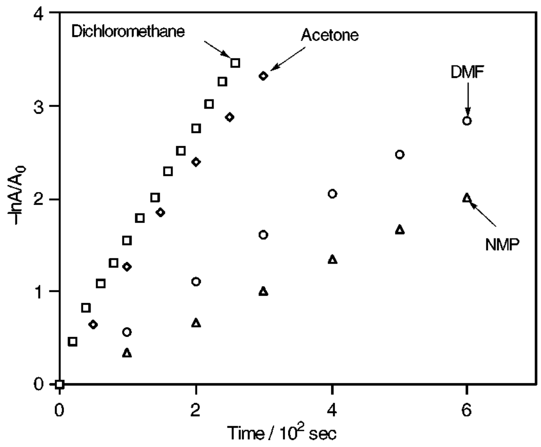


Figure 1. Solvent effect in the reaction of PDI with thiophenol.

A combination of ^{1}H−COSY and NOESY revealed that PDA-2T was a disubstituted PDA with phenylthio groups at the 2- and 5-positions. A nuclear Overhauser effect (NOE) between the proton (a singlet peak at 6.98 ppm) on the central phenyl ring and the proton (7.23 ppm) of the thiophenylene ring at the *o*-position was observed. These results supported the idea that 2,3- and 2,4-bis(phenylthio)-PDA were difficult to form in this reaction. It is suggested that thiophenol was preferentially substituted at the 5-position of the central phenyl ring of PDI-T due to the steric hindrance and electron-donating effect of the phenylthio group. This means that the Michael-type addition should afford a linear thiophenylene polymer in a polymerization reaction.

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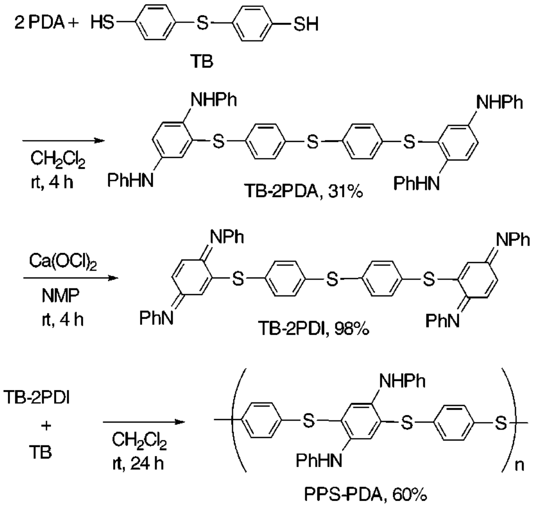
(7) **Synthesis of PDA-T and PDA-2T.** Thiophenol (55.1 mg, 0.5 mmol) was dissolved in dichloromethane (50 mL). In the solution, *N*,*N*′-diphenyl-*p*-phenylenediimine (PDI, 129 mg, 0.5 mmol) dissolved in dichloromethane (50 mL) was added using an additional funnel. The reaction mixture was stirred at room temperature for 2 h. The orange color of the solution changed to yellow. The solution was concentrated, and PDA-T (131 mg, 71%, brown viscous liquid) and PDA-2T (11.3 mg, 6%, yellow crystal) were isolated by silica gel column chlomatography (hexane:dichloromethane = 3:1−1:1). **PDA-T**: ^{1}H NMR (400 MHz, DMSO-d_6, TMS standard, 30 °C, ppm) δ 8.06 (s, 1H), 7.34 (m, 5H), 7.32 (s, 1H), 7.18 (d, 1H, $J = 8.79$ Hz), 7.14 (m, 4H), 6.97 (dd, 2H, $J = 2.44, 8.79$ Hz), 6.90 (d, 2H, $J = 8.31$ Hz), 6.86 (d, 1H, $J = 2.44$ Hz), 6.81 (d, 2H, $J = 8.30$ Hz), 6.74 (t, 1H, $J = 7.81$ Hz), 6.70 (t, 1H, $J = 7.32$ Hz); ^{13}C NMR (100 MHz, DMSO-d_6, TMS standard, 30 °C, ppm) δ 145.92, 143.47, 139.53, 134.25, 133.92, 131.26, 130.42, 129.51, 129.01, 128.89, 128.38, 124.25, 119.42, 119.27, 118.24, 117.55, 116.04, 114.98; IR (KBr) 3389 (NH), 1496 (phenyl); EI-MS 368 $[M]^+$. Anal. Calcd for $C_{24}H_{20}N_2S$: C, 78.22; H, 5.47; N, 7.60. Found: C, 77.84; H, 5.11; N, 7.35. **PDA-2T**: ^{1}H NMR (400 MHz, DMSO-d_6, TMS standard, 30 °C, ppm) δ 7.43 (s, 2H), 7.33 (m, 8H), 7.23 (m, 2H), 7.09 (t, 4H, $J = 7.81$ Hz), 6.98 (s, 2H), 6.77 (d, 4H, $J = 7.82$ Hz), 6.72 (t, 2H, $J = 7.32$ Hz); ^{13}C NMR (100 MHz, DMSO-d_6, TMS standard, 30 °C, ppm) δ 144.28, 136.91, 133.90, 130.85, 129.56, 128.87, 127.61, 127.44, 123.79, 119.32, 116.15; IR (KBr) 3366 (NH), 1507 (phenyl); EI-MS 476 $[M]^+$. Anal. Calcd for $C_{30}H_{24}N_2S_2$: C, 75.59; H, 5.08; N, 5.88. Found: C, 75.57; H, 4.71; N, 5.89.

As a synthetic strategy of the desired polymer, we selected polyaddition of 4,4′-thiobisbenzenethiol (TB) to PDI-end-capped TB (TB-2PDI) as shown in Scheme 2.

Scheme 2. Synthesis of Poly(thiophenylene) through a Michael Addition



TB-2PDA, which is the reduced form of TB-2PDI, was synthesized by reaction of PDI (1.0 mmol) with TB (0.5 mmol) in dichloromethane at room temperature for 2 h.[8] The TB-2PDA was isolated by silica gel column chromatography in a 31% yield. The obtained TB-2PDA was quantitatively converted to the imine (TB-2PDI) by oxidation with Ca(OCl)$_2$. The polymerization of TB-2PDI with TB proceeded in dichloromethane at room temperature for 24 h to give the corresponding polymer (PPS−PDA).[9] The orange color of the mixture disappeared during the polymerization due to the reduction of the imine to the amine structure. The mixture was poured into methanol to precipitate the polymer. The PPS−PDA was isolated in a 60% yield as a white powder and was soluble in dichloromethane, DMSO, THF, and NMP. The molecular weight (M_w) was determined to be 5.4×10^3 on the basis of GPC ($M_w/M_n = 1.52$). The temperatures for a 10% weight loss ($Td_{10\%}$) and glass transition were 362 and 131 °C, respectively. The amine group (3386 cm^{-1}) was confirmed by the IR spectrum.

Polymerization via a Michael-type addition was also confirmed by ^{1}H NMR measurement.[10] A phenylthio-PDA unit and a bis(phenylthio)-PDA showed large differences in the chemical shifts of peaks attributed to the amine protons. In the spectrum of PDA-T, two peaks attributed to two amine protons appeared at 8.06 and 7.32 ppm (Figure 2a). Similarly to PDA-T, two peaks attributed to four amine protons at 8.08 and 7.32 ppm were confirmed in the spectra of TB-2PDA (Figure 2c). On the other hand, one peak attributed to two amine protons appeared at 7.43 ppm in the spectrum of PDA-2T (Figure 2b). These spectra show that a peak around 8.0 ppm in a phenylthio monosubstituted PDA unit disappears in a disubstituted one. Therefore, no peaks around 8.0 ppm in the spectrum of PPS−PDA support conversion of the PDA units in TB-2PDA to disubstituted ones by polymerization on the basis of Michael-type addition (Figure 2d).

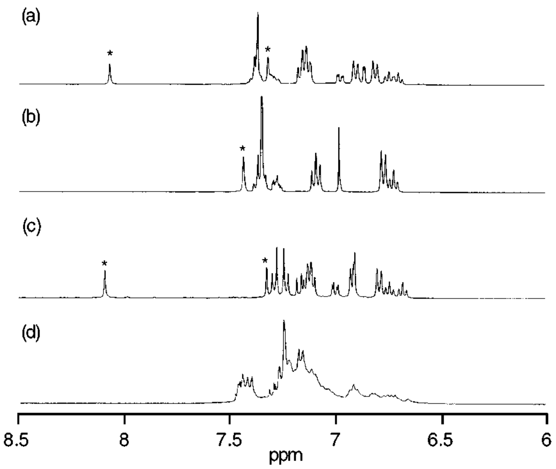


Figure 2. The ^{1}H NMR spectra (400 MHz, DMSO-d_6) of (a) PDA-T, (b) PDA-2T, (c) TB-2PDA, and (d) PPS−PDA. The marked peaks (*) are attributed to amine protons.

The electrochemical response of PPS−PDA was confirmed using the electrode modified by the polymer film (1.6×10^{-8} unit mol/cm^2). The polymer shows a redox activity in an acidic atmosphere (pH 0−4), which is similar to that of PDI. A redox couple was observed at 0.48 V vs SCE at pH 0.19 (Figure 3a). The redox cycle was stable for more than 10^2 scans. The scanning rate in cyclic voltammetry is

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(8) **Synthesis of TB-2PDA**. 4,4′-Thiobisbenzenethiol (TB, 0.123 g, 0.5 mmol) was dissolved in dichloromethane (50 mL). In this solution, PDI (0.260 g, 1.0 mmol) dissolved in dichloromethane (100 mL) was added using an additional funnel. The reaction mixture was stirred at room temperature for 2 h. The orange color of the solution changed to yellow. The solution was concentrated, and TB-2PDA (112 mg, 31%, brown yellow solid) was isolated by silica gel column chromatography (hexane:dichloromethane = 3:1−1:1). **TB-2PDA**: ^{1}H NMR (400 MHz, DMSO-d_6, TMS standard, 30 °C, ppm) δ 8.08 (s, 2H), 7.32 (s, 2H), 7.28 (d, 4H, J = 8.31 Hz), 7.23 (d, 4H, J = 8.31 Hz), 7.17 (d, 2H, J = 8.30 Hz), 7.13 (t, 4H, J = 7.32 Hz), 7.11 (t, 4H, J = 7.32 Hz), 7.00 (dd, 2H, J = 2.45, 8.79 Hz), 6.92 (d, 4H, J = 7.32 Hz), 6.91 (d, 2H, J = 2.45 Hz), 6.79 (d, 4H, J = 7.81 Hz), 6.74 (t, 2H, J = 7.32 Hz), 6.68 (t, 2H, J = 7.32 Hz); ^{13}C NMR (100 MHz, DMSO-d_6, TMS standard, 30 °C, ppm) δ 145.76, 143.39, 139.53, 134.33, 134.25, 133.28, 131.54, 131.44, 129.19, 129.00, 128.84, 124.27, 119.87, 119.35, 118.27, 117.94, 116.17, 115.00; IR (KBr) 3390 (NH), 1499 (phenyl); FAB-MS 766 [M]$^+$. Anal. Calcd for $C_{48}H_{38}N_4S_3$: C, 75.16; H, 4.99; N, 7.31. Found: C, 75.11; H, 4.69; N, 7.06.

(9) **Synthesis of PPS−PDA**. TB-2PDA (0.153 g, 0.2 mmol) was dissolved in *N*-methylpyrrolidone (NMP, 4 mL). Calcium hypochlorite (0.172 g, 1.2 mmol) was added, and the solution was stirred at room temperature for 4 h. The orange color of the solution changed to yellow. The reaction mixture was reprecipitated in water, and TB-2PDI (0.150 g, 98%, orange powder) was isolated by filtration. The oxidized one was dissolved in dichloromethane (25 mL). In the solution, TB (50 mg, 0.2 mmol) dissolved in dichloromethane (25 mL) was added using an additional funnel. The solution was stirred at room temperature for 24 h. The orange color of the solution changed to white. The reaction mixture was reprecipitated in methanol, and PPS−PDA (60%, yellow powder) was isolated by filtration. **PPS−PDA**: ^{1}H NMR (400 MHz, DMSO-d_6, TMS standard, 30 °C, ppm) δ 7.5−6.6 (m); IR (KBr) 3386 (NH), 1495 (phenyl).

(10) The PDA units of the compounds obtained are gradually oxidized to PDI in the air with moisture, but they are stable over 6 months in a refrigerator.

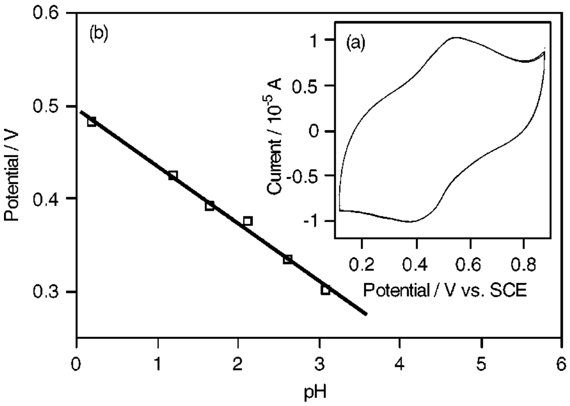

Figure 3. (a) Cyclic voltammograms of PPS−PDA coated on a glassy carbon electrode in 0.2 M Na_2SO_4/H_2SO_4 aqueous solution (pH 0.19) and (b) the Nernst plots.

proportional to the oxidation and reduction peak potentials. These results mean that excellent redox activity was maintained even in the thiophenylene polymer. The redox potentials depend on the pH in the mixture, which means that the electron-transfer process is associated with proton transfer. On the basis of the Nernst plots, the slope in the redox reaction was determined to be ca. −60 mV/pH (Figure 3b). These results indicate that the redox process involves two electrons and two proton transfers per unit. The PPS−PDA promotes a two-electron transfer accompanied by a two-proton transfer and acts as a good electroresponsive material.

We developed a novel synthetic method for redox-active poly(thiophenylene)s via a Michael-type addition. This polymerization proceeded under mild conditions without catalysts. The polymers obtained were good electroresponsive materials. With this polymerization method, various redox-active polymers are expected to be synthesized.

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