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Optical switching and anion-induced chromogenic application in conjugated polyazomethine derivatives

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ABSTRACT

New azomethine-containing conjugated polymers linked with fluorene and/or quinoxaline units were synthesized via Suzuki-coupling reaction in the presence of palladium(0) catalyst followed by hydrogenation and polymer reaction with cyclohexanone. The polymer exhibited red absorption color of red and intense red emission in chloroform solution. The polymers in solid state showed instantaneous color change when exposed to acid gas and recovered their initial colors rapidly when kept in air. Using pH-control, reversible optical switching was accomplished in the presence of trifluoroacetic acid (TFA) and triethylamine as an acid and a base, respectively. Diverse colors were demonstrated when exposed to a variety of anions, especially iodide and acetate ions, with the TFA-treated polyazomethines mainly because of difference in proton abstraction ability as well as conformational changes of molecular backbone.

1. Introduction

Recently considerable interest has been focused on the investigation of polymer sensors that exhibit a change of their absorption and emission characteristics in response to external stimuli such as heat [1], light [2], and chemicals [3]. Among various kinds of polymer sensor systems, π-conjugated polymers with inherent absorption and emission characteristics lead to versatile uses in optical and fluorescent sensors for chemicals [3a,4] as well as biological molecules [5]. $\pi-\pi^*$ Transitions of conjugated polymers with aromatic or heterocyclic units generally result in the low optical band gap at visible region. As a result, significant interest in chromogenic and fluorogenic sensors based on the conjugated polymers is rapidly growing in industrial process, environmental monitoring, and physiological detection [3a,6].

It is well-known that the development of selective optical signaling systems for anions is an emerging field of research in supramolecular photochemistry. Some examples of selective chemosensors based on small molecules were reported for fluoride, nitrate, and cyanide [7]. Though ionochromic sensing for anions of conjugated polymers were described in detail upto now [8], it is still challenging to develop new anion sensing optical sensory polymers.

Among biologically relevant anions, iodide is particularly attracting due to importance in energy transduction in organisms and in controlling metabolic processes [7c,9a]. Iodine is used in synthesizing organic chemicals, in manufacturing dyes, in medicine, in agricultural fertilizers, and in analytical chemistry [9b,9c].

Polyazomethine, known as polyimine or poly(Schiff base) is one of the less studied π-conjugated polymers with respect to its electronic, optical, and nonlinear optical properties [10]. The incorporation of nitrogen atom into the conjugated structure is another attempt to investigate the electronic and optical properties of these materials.

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Furthermore, the poor processability of conjugated polymers can be greatly improved introducing CH=N group instead of CH=CH group.

Herein, we are reporting a synthesis of new polyazomethine derivatives which can easily detect the presence of anions via optical methodology of simple protonation-deprotonation step. Protonation of polyazomethines serve as a simple optical sensor protocol, in which chromatic change occurs via proton abstraction by anions. This simple and rapid methodology is based on the difference in the proton abstraction ability and in conformational alteration in the main chain of polyazomethine derivatives. Proton-induced chromatic change was investigated in terms of reversible solid state acid gas sensing as well.

2. Experimental

2.1. Characterization

^{1}H and ^{13}C NMR spectra were collected on a Bruker DRX 300 spectrometer using tetramethylsilane as an internal standard (Korea Basic Science Institute). IR spectra were recorded on a Mattson Genesis II spectrometer. UV–vis absorption spectra were obtained from a PerkinElmer Lambda 35 spectrometer at room temperature. Fluorescence spectra were taken from a PerkinElmer LS 45 spectrometer with a xenon lamp as a light source. Gel permeation chromatography (GPC) was carried out to determine the molecular weight of polymers using tetrahydrofuran (THF) as an eluent after calibration with standard polystyrenes.

2.2. Materials

All the chemicals and reagents were purchased from Aldrich and used as received unless otherwise specially noted. THF used as a solvent was purified by a conventional distillation method with sodium/benzophenone. Precursor polymers **P1**, **P2**, **P4** and **P5** were synthesized according to previously published method [8c,11]. **P1** was synthesized via Suzuki-coupling polymerization with **1** and 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) **2** under nitrogen in the presence of palladium catalyst. **P1** was hydrogenated with lithium aluminum hydride to obtain **P2**. With similar procedure, **P5** could be obtained via Suzuki-type polymerization of **1**, **2**, and **3** followed by reduction of **P4** with lithium aluminum hydride.

P2 FT-IR (KBr pellet, cm^{-1}): ν 3432.6 (NH_2), 2927.4 (sp^2 C–H), 1612.2 (C=N), 1367.2 (C=C), 1232.2 ($-CH_2-$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ *8.1–7.9* (m, 8H), 3.75 (s, 4H), 2.1 (s, 4H), 1.2–0.7 (m, 22H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.96, 141.15, 136.55, 132.74, 128.68, 128.20, 124.33, 123.41, 109.85, 55.68, 40.53, 31.75, 30.00, 29.95, 24.28, 22.80, 14.25. Anal. Calcd. (%) for $C_{31}H_{38}N_2$: C, 84.88; H, 8.73; N, 6.39. Found: C, 84.02; H, 9.01; N, 6.80.

P5 FT-IR (KBr pellet, cm^{-1}): ν 3469 (NH_2), 2927–2856 (sp^2 C–H), 1610 (C=N), 1367 (C=C), 1226 ($-CH_2-$). ^{1}H NMR ($CDCl_3$, ppm): δ *8.1–7.3* (m, 26H), 3.75 (s, 4H), 2.1 (s, 4H), 1.2–0.7 (m, 22H). ^{13}C NMR ($CDCl_3$, ppm): δ 152.48, 151.62, 151.33, 139.05, 136.55, 133.30, 130.41, 128.92, 128.52, 128.33, 128.25, 124.31, 123.44, 120.25, 109.87, 55.65, 40.48, 31.80, 30.15, 24.33, 22.88, 14.25. Anal. Calcd. (%) for $C_{38.28}H_{41.12}N_2$: C, 86.79; H, 7.76; N, 5.29. Found: C, 84.48; H, 9.11; N, 6.04.

2.3. Synthesis of ***P3*** and ***P6***

To a round-bottom flask containing 25 mL of cyclohexanone was added **P2** (0.075 g, 0.17 mmol) or **P5** (0.1 g, 9.51×10^{-5} mol). The reaction mixture was stirred for 72 h at room temperature. After the reaction, the reaction mixture was poured slowly into 120 mL of methanol and the precipitates were isolated by filtration. The solid polymer was washed with methanol and acetone several times, filtered, and finally dried in a vacuum oven.

P3 FT-IR (KBr pellet, cm^{-1}): ν 3464, 2924, 2850, 1608, 1562, 1458, 1388, 1110, 957, 774. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ *8.1–7.9* (m, 8H), 1.9–0.7 (m, 46H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 207.12, 159.68, 151.70, 141.25, 136.11, 135.69, 130.88, 127.47, 123.63, 120.14, 107.71, 55.35, 40.61, 33.55, 32.96, 31.80, 30.19, 30.07, 29.91, 28.79, 24.33, 22.95, 14.24.

P6 FT-IR (KBr pellet, cm^{-1}): ν 3471, 2924, 2850, 1608, 1562, 1458, 1411, 1377, 1126, 1006, 975, 817, 763. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ *8.1–7.3* (m, 8H), 1.9–0.7 (m, 46H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 207.09, 159.70, 151.64, 151.40, 141.60, 141.24, 139.91, 139.53, 139.08, 130.88, 130.47, 130.27, 130.02, 128.92, 128.56, 128.36, 127.43, 125.92, 123.64, 120.03, 119.59, 107.67, 55.48, 55.36, 42.19, 40.56, 34.07, 33.54, 32.95, 32.12, 31.80, 31.10, 30.19, 30.07, 29.90, 29.55, 28.77, 28.25, 27.22, 25.39, 25.21, 24.40, 22.91, 14.22.

3. Results and discussion

It is well-known that the Suzuki cross-coupling reaction is a versatile method for formation of a carbon-carbon bond, which can be applied to polymerization reaction. In our previous article, we described a new sensory polymers containing ortho-diaminophenylene group for fluoride anion sensing through this simple preparation method [8c]. It is well-known that the conjugated polymer with diamino group in its main chain is not easy to prepare because the diamino group is a good nucleophile, thus it is difficult to control in metal-catalyzed polymerization condition such as Suzuki-type reaction. Poly(benzothiadiazole-*co*-9,9-dihexylfluorene) (**P1**) and poly[(benzothiadiazole-*alt*-9,9-dihexylfluorene)-*co*-(quinoxaline-*alt*-9,9-dihexylfluorene) (**P4**) were synthesized via Suzuki-coupling reaction in the presence of palladium(0) catalyst as shown in Scheme 1. Detailed characterization of such polymers were illustrated in our previous article including the molar ratio (m and n found to be 0.48 and 0.52, respectively), molecular weight (M_n 8010 and M_w 13,500 for **P1**; M_n *5350* and M_w 10,100 for **P4**), and other spectroscopic results such as IR and UV absorption.

By simple polymer reduction reaction with $LiAlH_4$, **P1** and **P4** were easily converted to **P2** and **P5**, respectively, and subsequently free amines on the polymer main chain of **P2** and **P5** were readily reacted with cyclohexanone to