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Dye-incorporated water-soluble polymer via click triazole formation

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ABSTRACT

A click triazole-polymerization is proposed for the synthesis of a water-soluble polymer dye. 4,4′-Diazidostilbene-2,2′-disulfonate (DASS) sodium salt reacted with a diacetylenic derivative of para-methyl red (PMR) in water, which was catalyzed by copper (I) ion or accelerated under ultrasound irradiation. DASS formed a soluble polymer with a carboxylate salt of PMR showing a water solubility of 120 g/100 mL but it generated an insoluble polymer with an alkyl ammonium salt. The prepared polymeric dye underwent color transition at pH 5–6, which is higher than that of PMR and similar to that of ortho-methyl red (OMR). The quinonoid canonical structure of PMR generated a purple water solution and was dominant in the polymer solution at pH below 5. Intra-molecular hydrogen bonding between the triazoles and azo nitrogens was presumed to have induced the formation of the quinonoid structure. The color change of the polymer was reproducible during successive up/down pH cycles.

1. Introduction

Extensive research has been conducted to investigate polymer dyes and their applications such as fiber, hair dyes, solid-state polymeric dye lasers, and chromatography [1–3]. Organic dyes have been modified for electric and optical processes with polymer backbones [4–6]. Physical and chemical polymer bonding sometimes improves the inherent optical properties of organic dyes [7,8]. Some inter- and intra-molecular interactions of dyes contribute to specific applications such as sensor, switches and semiconductors [9]. Most neutral organic dyes are soluble in organic solvents and transformed for water-media uses. Hydrophilic polymer encapsulation is a useful approach for water applications such as drug delivery or tracers [10,11]. Another is the host-guest concept, where a guest dye is surrounded by hosts such as cyclodextrin [12] or dendrimer [13]. The direct synthesis of water-soluble polymer dyes remains an issue because of functional group tolerance.

In the research, hydrophilic click polymers were developed for water-soluble dyes via polymerization with a water-soluble, difunctional monomer of 4,4′-diazidostilbene-2,2′-disulfonate (DASS) sodium salt. DASS has been used as a photo-cross-linking agent to interconnect polymer chains under UV radiation [14,15] and has often been introduced to improve the polymer membrane in a fuel cell [16]. Two azido groups of DASS are known to undergo a click reaction with triple bonds to generate water-swelling polymers. The repeating unit with two sulfonate ions is chemically stable, hydroscopic and transparent in visible wavelengths. The triazole linker is able to hold protons in an acidic solution and to enhance the ion mobility of the membrane. Furthermore, a dye-attached polymer as a pH indicator enables visual pH sensing or tracing in water applications [17–19]. Therefore, the synthesis of click polymers of DASS and a dye is valuable in numerous applications. Dipolar azo dyes have vivid colors due to their π-conjugated structures. Some azo compounds such as methyl orange or methyl red (MR) are a popular acid-base indicator with the protonation-deprotonation of the azo group and amino nitrogen as well as carboxylic and sulfonic acid for specific color changes [20,21]. The basic strength of various nitrogen atoms and thereby thermodynamic equilibrium decides the transition pH of the indicator.

2. Experimental detail

2.1. Material and instrumentations

The starting materials and reagents were used as purchased from Aldrich Chemical Co., except for 4,4′-diazidostilbene-2,2′-disulfonic acid disodium salt tetrahydrate (DASS) purchased from Fluka. ^{1}H and ^{13}C NMR spectra were recorded on 300 MHz and 75 MHz Varian NMR spectrometer system, respectively. IR spectra were measured on a Thermo Nicolet FT-IR. The molecular weight of

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small molecules was recorded on an Agilent 1200LC/1100 MSD SL mass spectrometer. Elemental analyses were carried out using a LECO 932 CHNS elemental analyzer. UV–Vis spectra were measured on a Varian Cary 5000 spectrometer. Aqueous GPC measurement was carried out using sulfonated-DVB column (Jordi-Gel Aqueous GPC Column, using 0.2 M aqueous sodium acetate and THF) to give molecular weights calibrated by poly(acrylic acid) standards. Thermal analyses of polymers were conducted on a Mettler Toledo TGA/SDTA 851e analyzer. The ultrasound (20 kHz) was generated using a VCX-500P Ultrasonic Processor (SONICS). The pH was kept with buffer using HCl/Na_2HPO_4 and NaOH/$NaHCO_3$.

2.2. Preparation of ***1a***

A 50 mL-round bottom flask was charged with 0.76 g (5.0 mmol) of methyl 4-hydroxybenzoate, propargyl bromide (6 mmol), and N,N-dimethyl formamide (DMF, 10 mL). The mixture was stirred with potassium carbonate (0.83 g) over 12 h at room temperature. The resulting mixture was poured into water (100 mL) and extracted twice with diethyl ether (200 mL × 2). The combined organic layer was washed with 150 mL of water and dried over $MgSO_4$. The solution was concentrated and purified by a chromatographic separation using ethyl acetate (EA)/hexane (1/7, v/v) to afford **1a** (73% yield, white powder).

^{1}H NMR ($CDCl_3$): $\delta = 7.99$ (d, 2 H), 6.98 (d, 2 H), 4.73 (s, 2 H), 3.87 (s, 3 H), 2.58 (s, 1 H). ^{13}C NMR ($CDCl_3$): $\delta = 166.9$, 161.3, 131.8, 123.6, 114.7, 78.0, 76.4, 56.0, 52.2. IR (KBr): 3176 (s, C_{sp}–H), 2120 (C_{sp}–C_{sp}), 1709 (carbonyl), 1281 (C–O) cm^{-1}. LC-MS: *m*/*z* 190.06 $[M]^+$.

2.3. Preparation of ***1b*** (R = CH_3) and ***1b*** (R = H or Na)

1a (0.382 g, 2.00 mmol) and DASS (0.536 g, 1.00 mmol) were placed in a 25 mL-round bottom flask charged with tetrahydrofuran (THF)/water (4.5 mL/1.5 mL). To the reaction was added $CuSO_4$ (50 mg) and sodium ascorbate (80 mg) at room temperature. The reaction mixture was stirred for 3 days at room temperature. After removing the volatile solvents, the residue was treated with methanol (10 mL) and then the insoluble solid was filtered out using a filter paper. The resulting mixture was purified by a chromatographic separation using EA/methanol (4/1, v/v)to afford **1b** (R = CH_3, yellow powder, 45%). **1a** (2.00 mmol) was treated with NaOH (2.4 mmol) in water (6 mL) for 4 h and then reacted with DASS (0.536 g, 1.00 mmol) in the presence of $CuSO_4$ (50 mg) and sodium ascorbate (80 mg) for 12 h at 60 °C to yield **1b** (R = H or Na).

^{1}H NMR (R = CH_3, CD_3OD): $\delta = 8.77$ (s, 2 H), 8.46 (s, 2 H), 8.32 (s, 2 H), 8.23 (s, 2 H), 8.03 (s, 2 H), 8.01 (s, 2 H), 7.18 (s, 2 H), 5.36 (s, 4 H), 3.87 (s, 6 H). IR (KBr): 1707, 1605, 1509, 1437, 1250 cm^{-1}. UV (H_2O): $\lambda_{max} = 327$, 253 nm. ESI–MS (negative matrix), *m*/*z*: 800.77 $[M - 2Na]^+$. Anal. Calcd for $C_{36}H_{28}N_6Na_2O_{12}S_2$: C, 51.06; H, 3.33; N, 9.93, S, 7.57. Found: C, 51.00; H, 3.29; N, 9.88; S, 7.62.

2.4. Preparation of ***3a***

A 500 mL-round bottom flask was charged with methyl 3,5-dihydroxybenzoate (5.04 g, 30 mmol) and acetone (100 mL). After being completely dissolved, propargyl bromide (8.88 mL, 80%), K_2CO_3 (8.29 g), and tetrabutylammonium bromide (TBAB, 0.97 g) were successively added. The reaction mixture was refluxed for 48 h and then cooled to room temperature. The resulting mixture was poured into water (100 mL) and extracted with EA (300 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to give crude **2a** (methyl 3,5-bis(2′-propynyloxy)benzoate). The crude (**2a**) was re-dissolved in THF (40 mL) and mixed with aqueous NaOH solution (3.0 M, 15 mL) and methanol (10 mL) at room temperature. After being stirred for 12 h, the solution was neutralized with aqueous HCl (35%, 3.4 mL) and precipitated with additional water (40 mL) to afford **3a** (overall 74% yield, white powder).

2a: ^{1}H NMR ($CDCl_3$): $\delta = 7.31$ (s, 2 H), 6.83 (s, 1 H), 4.75 (s, 4 H), 3.91 (s, 3 H), 2.58 (s, 2 H). ^{13}C NMR ($CDCl_3$): $\delta = 166.7$, 158.7, 132.3, 109.0, 107.7, 78.2, 76.3, 56.3, 52.7. LC-MS, *m*/*z*: 245.02 $[M + 1]^+$. Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.84; H, 4.98.

3a: ^{1}H NMR ($CDCl_3$): $\delta = 7.38$ (s, 2 H), 6.89 (s, 1 H), 4.76 (s, 4 H), 2.59 (s, 2 H). ^{13}C NMR (CD_3OD): $\delta = 168.0$, 158.9, 132.7, 108.8, 106.8, 78.2, 76.1, 55.7. IR (KBr): 3350–2700 (br, CO_2H), 3294, 2115, 1688 (C=O), 1609, 1246 cm^{-1}. LC–MS, *m*/*z*: 231.01 $[M + 1]^+$. Anal. Calcd for $C_{13}H_{10}O_4$: C, 67.82; H, 4.38. Found: C, 67.77; H, 4.19.

2.5. Preparation of water-soluble polymer ***3b***

In a 25 mL-round bottom flask were placed **3a** (0.46 g, 2.00 mmol) and NaOH (80 mg) in water (8 mL). After adding DASS (1.08 g, 2.00 mmol), $CuSO_4$ (52 mg), and sodium ascorbate (80 mg), the mixture was warmed to 60 °C and agitated for 48 h to yield a ball-shaped, phase-separated mass. The solid was dissolved in water (30 mL) and precipitated by the addition of ethanol (150 mL) and keeping at low temperature. The solid was filtered and vacuum-dried to afford polymer **3b** (65% yield, yellow powder).

^{1}H NMR (D_2O): $\delta = 8.44$–8.30 (br, 2 H), 8.28–7.96 (br, 2 H), 7.95–7.40 (br, 5 H), 7.34–6.95 (br, 3 H), 6.91–6.52 (br, 2 H), 5.39 (d, 1 H), 5.14–4.97 (br, 2 H). IR (KBr): 1640, 1385, 1203 cm^{-1}. UV (H_2O): $\lambda_{max} = 342$ nm. Anal. Calcd for $C_{27}H_{17}N_6Na_3O_{10}S_2$: C, 45.13; H, 2.38; N, 11.70; S, 8.93. Found: C, 45.05; H, 2.36; N, 11.85; S, 8.96.

2.6. Preparation of a quaternary ammonium bromide ***4a***

Methyl 3,5-bis(2′-propynyloxy)benzoate **2a** (2.44 g, 10.0 mmol) was dissolved in THF (30 mL) and treated with $LiAlH_4$ (0.19 g) for 1 h. Methanol (5 mL) and water (100 mL) were added to decompose any excess $LiAlH_4$. The resulting mixture was extracted with EA, dried over $MgSO_4$, filtered, and concentrated to afford a crude alcohol. Triphenylphosphine (2.62 g, 10 mmol) was dissolved in anhydrous dichloromethane (30 mL) and bromine (0.26 mL) was slowly added at 0 °C. The milky bromophosphonium bromide solution was mixed with the crude alcohol under nitrogen atmosphere at 0 °C. After being stirred for 1 h, the mixture was concentrated and mixed with diethyl ether (50 mL). The resulting mixture was filtered to remove triphenylphosphonium oxide and organic layer was concentrated. A column chromatographic separation using EA/hexane (1/7, v/v) afforded 1-bromomethyl-3,5-bis(2′-propynyloxy)benzene in overall 68% yield.

^{1}H NMR ($CDCl_3$): $\delta = 6.64$ (s, 2 H), 6.56 (s, 1 H), 4.68 (s, 1 H), 4.42 (s, 2 H), 2.58 (s, 2 H). ^{13}C NMR ($CDCl_3$): $\delta = 154.2$, 138.6, 120.8, 108.0, 70.0, 69.7, 57.6, 34.8. LC–MS, *m*/*z*: 278.01 $[M]^+$.

1-Bromomethyl-3,5-bis(2′-propynyloxy)benzene (1.39 g) was dissolved in triethylamine (10.0 mL) and refluxed for 24 h. The resulting mixture was concentrated, rinsed with anhydrous ether, and dried under vacuum in an oven at 50 °C to afford **4a** (88% yield, hydroscopic solid).

^{1}H NMR (D_2O): $\delta = 6.80$ (s, 2 H), 6.75 (s, 1 H), 4.80 (s, 4 H), 4.35 (s, 2 H), 3.22 (q, 6 H), 3.09 (s, 2 H), 1.38 (t, 9 H). ^{13}C NMR (D_2O): $\delta = 158.5$, 130.0, 112.6, 105.1, 100.2, 78.7, 77.5, 56.5, 52.9, 46.9, 7.4. IR (KBr): 3176 (s, C_{sp}–H), 2120 (C_{sp}–C_{sp}), 1599 (C=C) cm^{-1}. LC–MS, *m*/*z*: 300.20 $[M - Br]^+$. Anal. Calcd for $C_{19}H_{25}BrNO_2$: C, 60.16; H, 6.64; N, 3.69. Found: C, 60.13; H, 6.53; N, 3.58.

2.7. Preparation of water-soluble polymer ***4b***

A 25 mL-round bottom flask was charged with **4a** (0.758 g, 2.00 mmol), DASS (1.08 g, 2.00 mmol), and water (8 mL). After

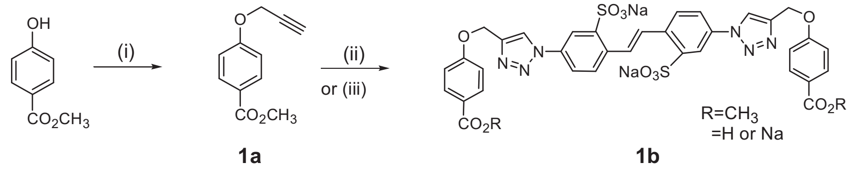

Fig. 1. Click reaction for water-soluble molecule **1b**: (i) propargyl bromide and K_2CO_3 in DMF, (ii) DASS/$CuSO_4$/sodium ascorbate in water/THF (r.t.), and (iii) NaOH and then DASS/$CuSO_4$/sodium ascorbate in water (60 °C).

adding $CuSO_4$ (52 mg) and sodium ascorbate (80 mg), the mixture was warmed to 60 °C and agitated for 24 h, yielding a phase-separated mass. The solid was washed with water (30 mL) and methanol (30 mL) and then vacuum-dried to afford insoluble polymer **4b** (90% yield).

IR (supplementary data). Anal. Calcd for $C_{33}H_{34}BrN_7Na_2O_8S_2$: C, 46.81; H, 4.05; N, 11.58; S, 7.57. Found: C, 46.66; H, 4.01; N, 11.44; S, 7.49.

2.8. *Preparation of **5***

In a 100 mL-round bottom flask were placed N-phenyldiethanolamine (3.82 g, 95%), propargyl bromide (80%, 8.88 mL), KOH (3.37 g), and TBAB (1.29 g) and dissolved in dimethyl sulfoxide (DMSO, 35 mL). The reaction mixture was stirred for 24 h at 60 °C and poured into 100 mL of water. The mixture was extracted with EA, dried over $MgSO_4$, and filtered. The concentrated crude was purified by a chromatographic separation using EA/hexane (1/4, v/v) to afford **5** (55% yield, viscous liquid).

^{1}H NMR ($CDCl_3$): $\delta = 7.28$ (d, 2 H), 6.60 (d, 2 H), 6.31 (s, 1 H), 4.15 (s, 4 H), 3.67 (m, 4 H), 3.58 (m, 4 H), 2.44 (s, 2 H). IR (KBr): 3180 (s, C_{sp}–H), 2120 (C_{sp}–C_{sp}) cm^{-1}. ^{13}C NMR ($CDCl_3$): $\delta = 146.9$, 132.2, 113.8, 108.2, 79.9, 75.1, 67.4, 58.7, 54.2. LC–MS, *m/z*: 257.18 [M]$^+$.

2.9. *Preparation of **5a***

Ethyl 4-aminobenzoate (98%, 1.05 g, 6.22 mmol) was dissolved in acetic acid (2.4 mL) and aqueous HCl (35%, 0.7 mL). Aqueous $NaNO_2$ (7.46 mmol) was added at 0 °C to yield a yellow solid. After being stirred for 30 min, a methanol solution of **5** was slowly added and reacted for 2 h at room temperature. The mixture was poured into water (50 mL) under vigorous agitation and filtered to afford a reddish yellow solid. Further purification was performed by column chromatography using EA/hexane (1/2, v/v) to afford pure **5a** (red powder) in 44% yield.

^{1}H NMR ($CDCl_3$): $\delta = 8.14$ (d, 2 H), 7.88 (m, 4 H), 6.81 (d, 2 H), 4.38 (m, 4 H), 4.18 (d, 4 H), 3.75 (m, 4 H), 2.45 (s, 2 H), 1.41 (t, 3 H). ^{13}C NMR ($CDCl_3$): $\delta = 166.5$, 155.9, 151.1, 143.9, 130.7, 126.0, 122.2, 111.8, 79.7, 75.2, 67.5, 61.3, 58.7, 51.4, 14.6. IR (KBr): 3180 (s, C_{sp}–H), 2120 (C_{sp}–C_{sp}), 1700 (carbonyl), 1280 (C–O) cm^{-1}. LC–MS, *m/z*: 434.18 [M + 1]$^+$. Anal. Calcd for $C_{25}H_{27}N_3O_4$: C, 69.27; H, 6.28; N, 9.69. Found: C, 69.26; H, 6.28; N, 9.65.

2.10. *Preparation of **5b***

Ethyl 4-aminobenzoate (98%, 1.03 g, 6.00 mmol) was dissolved in acetic acid (2.4 mL) and aqueous HCl (35%, 0.7 mL). Aqueous $NaNO_2$ (7.50 mmol) was added at 0 °C to yield a yellow solid. After additional stirring for 30 min, a methanol solution of N,N-bis(2-hydroxyethyl)aniline (95%, 0.95 g) was slowly added and reacted for 2 h at room temperature. The mixture was poured into water (50 mL) under vigorous agitation and filtered to afford a reddish solid. Further purification was performed by column chromatography using EA/hexane (2/1, v/v). The solid (1.07 g, 3.00 mmol) was dissolved in THF (3 mL) and mixed with an aqueous NaOH solution (3.0 M, 2 mL) and methanol (3 mL). After stirring for 2 h at 50 °C, the resulting mixture was cooled to room temperature, neutralized with aqueous HCl solution (3.0 M, 2.0 mL), and precipitated with additional water (15 mL). The solid was filtered and vacuum-dried at 60 °C to afford **5b** (overall 42% yield, red powder).

^{1}H NMR (DMSO-d6): $\delta = 8.16$ (d, 2 H), 7.82 (m, 4 H), 6.91 (d, 2 H), 3.75 (m, 4 H, CH–O), 3.65 (m, 4 H, CH–N), 3.55 (br, 2 H, O–H). ^{13}C NMR (DMSO-d6): $\delta = 168.1$, 157.1, 152.8, 143.4, 131.9, 131.8, 127.0, 122.5, 114.8, 59.0, 53.5. LC–MS, *m/z*: 330.12 [M + 1]$^+$. Anal. Calcd for $C_{17}H_{19}N_3O_4$: C, 62.00; H, 5.81; N, 12.76. Found: C, 61.95; H, 5.77; N, 12.74.

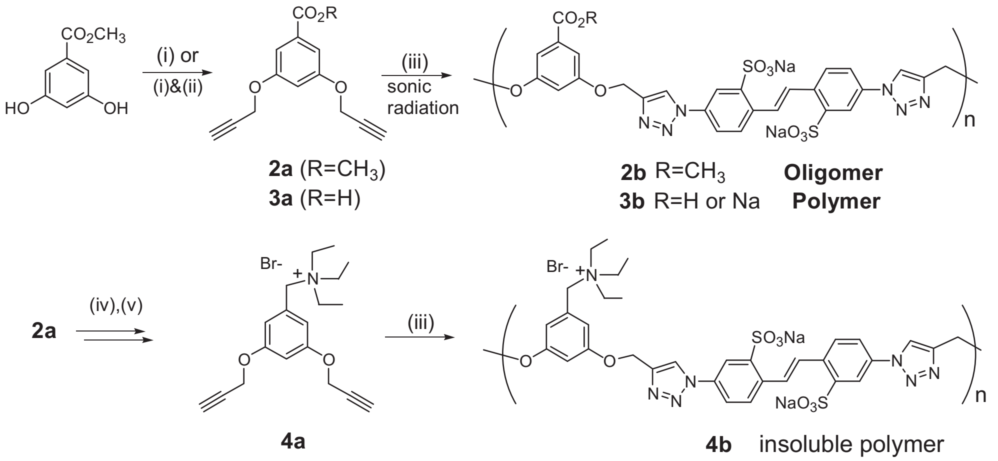

Fig. 2. Preparation of water-soluble click polymers: (i) propargyl bromide/K_2CO_3/TBAB in refluxing acetone, (ii) NaOH and then HCl, (iii) NaOH and then DASS/$CuSO_4$/sodium ascorbate in water (60 °C), (iv) $LiAlH_4$ in THF and then Br_2/PPh_3 in CH_2Cl_2, and (v) refluxing in Et_3N.

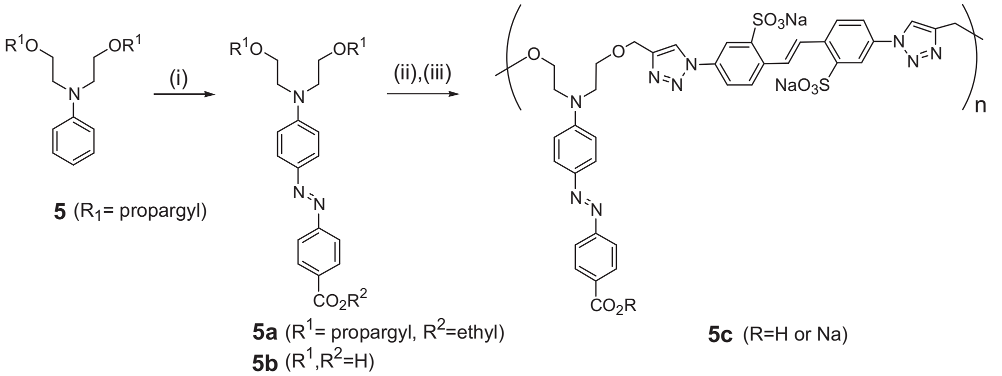

Fig. 3. Preparation of water-soluble polymer dye: (i) ethyl 4-aminobenzoate, HCl(aq), $NaNO_2$, and acetic acid/water, (ii) NaOH in THF/water, (iii) and DASS/$CuSO_4$/sodium ascorbate in water/THF (60 °C).

2.11. Preparation of water-soluble polymer dye ***5c***

5a (0.866 g, 2.00 mmol) was dissolved in THF (4 mL) and stirred for 2 h with aqueous NaOH solution (3 M, 0.67 mL) at 50 °C. To the resulting mixture were added DASS (1.07 g, 2.00 mmol), $CuSO_4$ (52 mg), and sodium ascorbate (80 mg). The reaction mixture was agitated at 60 °C for 48 h and then filtered and concentrated under reduced pressure. The resulting crude polymer was purified by precipitation using methanol to afford **5c** (75% yield, red powder).

^1H NMR (D_2O) $\delta = 8.17$ (m, 2 H), 8.05 (s, 2 H), 7.85 (d, 2 H), 7.38–7.67 (m, 2 H), 7.23 (d, 2 H), 6.42 (br m, 2 H), 4.69 (d, 2 H), 4.44–4.56 (m, 6 H), 3.41–3.78 (m, 6 H), 1.83 (s, 1 H). IR (KBr): 1599, 1552, 1496, 1385, 1203 cm^{-1}. UV (H_2O): $\lambda_{max} = 325, 462$ nm. PL (H_2O, radiated at 462 nm) λ_{max}: 367, 401, 577, 643 nm. Anal. Calcd for $C_{37}H_{30}N_9Na_3O_{10}S_2$: C, 49.72; H, 3.38; N, 14.10; S, 7.18. Found: C, 49.58; H, 3.32; N, 14.03; S, 7.10.

3. Results and discussion

A water-soluble polymer dye was synthesized via the click polymerization of a water-soluble segment and a dye. The Huisgen cycloaddition reaction of azide and alkyne is a representative click-reaction with a high reaction conversion required for polymerization [22]. Aqueous Cu(I) was used to catalyze the reaction and guide selective 1,4-triazole formation from the click reaction. A preliminary study was performed for water-media click polymerization with water-soluble DASS and an alkyne. Methyl 4-hydroxybenzoate was derived with a propargyl group and treated with DASS under the copper catalytic condition. A co-solvent system of THF and water (3/1, v/v) was used in the reaction due to an organic soluble alkyne, **1a**, as illustrated in Fig. 1. A single product, **1b**, was generated over 3 days at room temperature and confirmed with ^1H-NMR analysis using deuterium oxide. A peak at δ 5.36 was assigned to protons from two triazole rings. IR analysis revealed the complete disappearance of the strong azide band (2200 cm^{-1}) and terminal alkyne C–H band (3300 cm^{-1}). The reaction with a sodium salt of **1a** was completed within 12 h.

Based on this result, click polymerization was investigated with DASS. Methyl 3,5-dihydroxybenzoate was derived with two propargyl groups. The click polymerization with organic soluble **2a** afforded oligomers as shown in Fig. 2. The absorption band of the azide was observed from the IR analysis of the oligomeric product and still remained for a long reaction period of 5 days. Thus, **2a** was hydrolyzed to enhance solubility in water before polymerization. An equimolar mixture of **3a** and DASS was agitated under the same click reaction condition for 48 h, when resulting polymer showed no azide band in the IR spectrum. The ^1H-NMR spectrum of the polymer proved the triazole formation in agreement with the result of the preliminary study. When the reaction was irradiated with ultrasound at 20 kHz [23], the polymerization was accelerated to completion in 10 h. The sonic wave radiation was ineffective for the polymerization without the copper catalyst and unreacted monomers were almost recovered over 10 h. Because the carboxylate salt of alkyne, **3a**, was soluble in basic water, a quaternary ammonium salt was considered for neutral pH media. The $LiAlH_4$ reduction and bromination of **2a** provided an ammonium bromide, **4a**, after refluxing in triethylamine. The polymerization of **4a** and DASS proceeded faster than that of **3b** in the catalytic condition. Monitoring of the azide band in the IR spectrum revealed its disappearance after 24 h. Unfortunately, the separated polymeric product dissolved in neither water nor organic solvents, which was attributed to the formation of zwitterions by losing NaBr from **4b**.

These water-soluble polymers led us to focus on the synthesis of a water-soluble polymer dye. MR is an azo-coupled, dipolar dye that is used as a pH indicator and coloring agent for bacteria detection [24]. MR analogue **5a** was prepared through a para-azotization from a dipropargyl compound **5**. Alkali-hydrolysis of **5a** and successive polymerization with equimolar DASS afforded polymer dye **5c** after neutralization as described in Fig. 3. The polymer exhibited an excellent water solubility of ca.120 g/100 mL (25 °C, yellow color in water). An IR absorption spectrum showing no azide absorption indicated successful polymerization.

The inherent viscosity of the polymer was in the range 0.27–0.28 dL/g at 25 °C and was stable up to 267 °C by a thermal gravimetric analysis. Aqueous GPC analysis was performed to give relative molecular weights calibrated by poly(acrylic acid) standards. The GPC results of three polymers are summarized in Table 1

Table 1
Analytic data of the prepared polymers.

Polymers	GPC analysis[a]			TGA[c]
	Mn (kg/mol)	Mw (kg/mol)	PDI[b]	5% loss (°C)
2b	3.8	5.3	1.4	294
3b	16.2	25.9	1.6	320
3b[d]	10.7	19.3	1.8	–
5c	13.4	21.4	1.6	267

[a] The number average molecular weight (Mn) and the weight average molecular weight (Mw) were calibrated by poly(acrylic acid) standards.

[b] Polydispersity.

[c] Thermal gravimetric analysis.

[d] Polymerization irradiated with ultrasound (20 kHz).

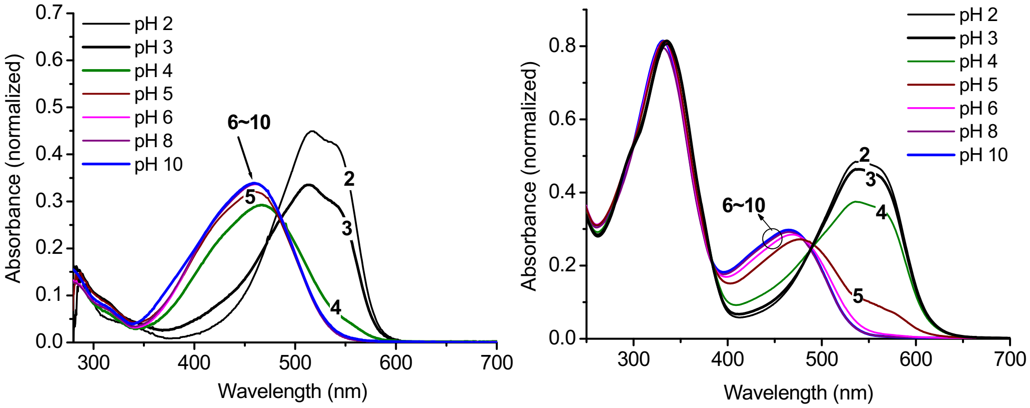

Fig. 4. UV–Vis absorption spectra of dye **5b** (left) and polymer dye **5c** (right) and their pH dependence.

along with thermal gravimetric analysis. Neutral alkyne monomer **2a** generated oligomer **2b** of low molecular weight and anionic monomer **3a** evidently led to the formation of polymer **3b** of high molecular weight. The ultrasound-assisted polymerization provided the polymer of lower molecular weights than other polymerization.

MR has a tri-basic activity due to three nitrogen atoms (neutral-MR, monoprotonated-HMR, diprotonated-H2MR) and a specific color change according to the equilibrium state in pH media [20]. HMR has a strong absorption at around 520 nm due to quinonoid canonical structures while neutral or anionic MR has a strong absorption at around 430 nm. The color transition of methyl red occurs over a pH range of 4.2–6.3 [25]. Ortho-substituted carboxylic acid on the MR (OMR) participates in intra-molecular hydrogen bonding between the carboxylic proton and the azo group, thereby yielding a stable planar structure [21]. Para-substituted carboxylic acid on the MR (PMR) has a similar color change at lower pH because of the absence of intra-molecular hydrogen bonding. Water-soluble dye **5b**, being analogous to PMR, was analyzed with UV–Vis spectroscopy at the various buffered pHs. A color transition of **5b** was observed in the pH range of 3–4 and an isosbestic point at 485 nm indicated a protonation-deprotonation equilibrium in Fig. 4. The pH behavior indicates that **5b** is more basic than previous PMR having pK_a of ca. 2 [26]. The UV–Vis absorption of polymer dye **5c** was similarly compared under pH conditions. A strong absorption at 330 nm was definitively attributed to a DASS unit by the similar observation with a simple polymer **3b** and was used as an internal standard for the pH comparison. As the pH was lowered, the band intensity at 489 nm decreased and a new band was developed at 540–560 nm by the protonation at an azo nitrogen of the dye. The absorption bands of the polymer were red-shifted by ca. 20 nm from the similar bands of the dye **5b** but the isosbestic point was retained. Surprisingly, the color transition of the polymer dye was observed at pH 5 with the broad band combining two absorptive bands. The protonation on an azo nitrogen seems to be accelerated in the polymer. Thus, the following mechanism of a structure presented in Fig. 5 can be proposed with reasonable assurance: protonation preferentially proceeds at triazole groups [27] of the polymer backbone and the resultant triazolium proton may induce hydrogen bonding with a neighboring azo group. This triazole-induced hydrogen bond was considered to have a similar mechanistic effect of ortho-carboxylic acid in OMR yielding a quinonoid structure, which has a transition pH range of 4.2–6.3 [20,21,25]. The apparent color change of the polymer dye was observed at a pH range of 5–6, in marked contrast to the pH range of 3–4 for dye **5b**. Fig. 5 shows the color change of the polymer dye according to pH. The purple color at pH 5 was similar to that of dye **5b** at pH 3.

The H-bonding contribution of a quinonoid canonical structure was further investigated with a simple molecule through NMR analysis. Dye **6** was prepared and treated with deuterium chloride (supplementary data) to induce intra-molecular H-bonding. Fig. 6 compares ^{13}C-NMR spectra of **6** and **6a**. Three peaks assigned to aromatic carbons (C14, C15, C16) of **6** were strongly affected by H-bonding. The acid treatment of **6** led to color change similar to **5c** from yellow to purple. Protonated **6a** showed a red-shifted absorption spectrum as being compared with **6**, which is attributed to the formation of a quinonoid structure.

The transition range of the polymer dye was similar to that of OMR as a pH indicator but the color was different. The transition was reproducible during successive up/down pH cycles. The distinct color change and water solubility of the polymer dye were considered useful as much as OMR to detect an end point during the analytic titration.

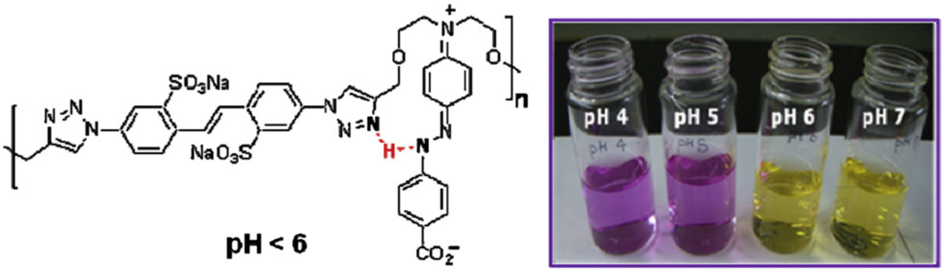

Fig. 5. The proposed hydrogen bonding domination at pH <6 and color change of **5c** at various pHs.

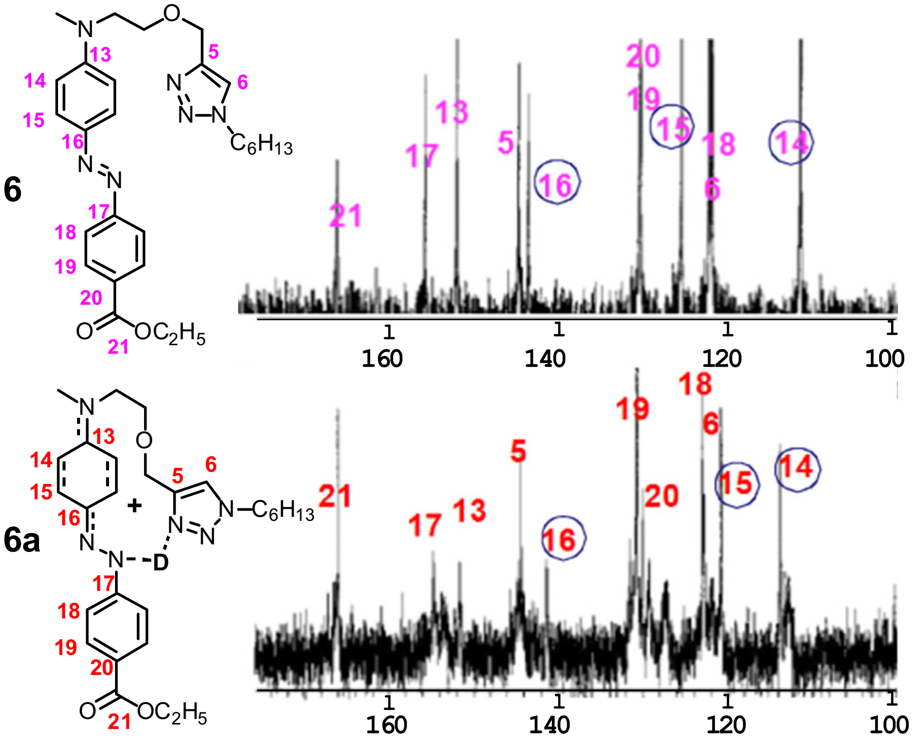

Fig. 6. ^{13}C-NMR spectral shift of a dye (**6**) by hydrogen bonding.

4. Conclusion

A water-soluble polymer dye was developed via click polymerization. 1,2,3-Triazole was formed by the reaction between a difunctional dye and DASS in which two sulfonate groups provided the water solubility of the polymer dye. A PMR analogue in the polymer showed a color transition pH similar to that of OMR at pH 5–6. Triazole groups were proposed to be involved in intramolecular H-bonding with an azo nitrogen, leading to the preferential formation of a quinonoid canonical structure. The polymer dye exhibited a purple color at pH below 5 and a yellow color at pH above 6, and this color transition was critical and reproducible toward successive pH change.

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Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.dyepig.2012.01.012.

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