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Synthesis and dyeing performance of a novel polycarboxylic acid azo dye

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Abstract

A novel reactive polycarboxylic acid dye was synthesized by the reaction of polymaleic anhydride (PMA) with 3-methyl-1-(4-sulfonylphenyl)-4-(4-aminophenylazo)-2-pyrazoline-5-one. The structure of the novel dye was characterized by FTIR, UV–vis and ^{13}C NMR spectra. The dyeing properties of dye on cotton were tested, and the novel dye possessed high fixation and good fastness.

Keywords: Reactive polycarboxylic acid dye; Polymaleic anhydride; Dyeing

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It is well-known that reactive dyes are widely applied in printing inks [1–3] and dyeing of natural fabrics [4–8]. The research on this class of dyes has well been developed in the last fifty years. Aimed to further improve the fixation of reactive dyes, research has focused both on the use of alternative reactive groups and combinations of different reactive groups. Bi-functional reactive dyes have attracted considerable interest and have played an important role in the dye and dyeing chemistry [4,6,9]. The fixation of bi-functional reactive dyes can reach 80–90% [9–11]. Carboxylic acid groups were considered as substitute for conventional reactive groups, because carboxylic acid groups have the potential to react with the hydroxyl groups of cotton and the amino groups of wool, and reactive dyes containing carboxylic acid groups were developed by Oliveira and they were applied successfully to wool fibres [12,13]. Herein we reported synthesis of a new type reactive polycarboxylic acid dye, which was obtained by the reaction of polymaleic anhydride with azo chromophore. Because many reactive groups (carboxylic acid group) and chromophores are in one polymeric dye molecule, even only one reactive group reacted with fibre, many chromophores in the polymeric dye molecule can be linked to fibre by covalent bonding. The novel reactive polycarboxylic acid dye was applied to cotton, and the results showed that this novel polycarboxylic acid dye had good application prospects, because of their easy preparation method, high fixation and good fastness.

The synthetic route for polycarboxylic acid dye **5** was shown in Scheme 1. PMA was synthesized by radical polymerization of maleic anhydride in toluene [14], and benzoyl peroxide (BPO) was used as initiator. The yield of PMA was 90%, and its average number molecular weight was 1070. Intermediate **3** was synthesized by diazotization and coupling reaction with 4-nitroaniline as diazo component and 1-(4-sulfonylphenyl)-3-methyl-2-pyrazoline- 5-one as coupling component. 26 g (65 mmol) compound **3** and 150 mL water were added into a 500 mL three-necked flask

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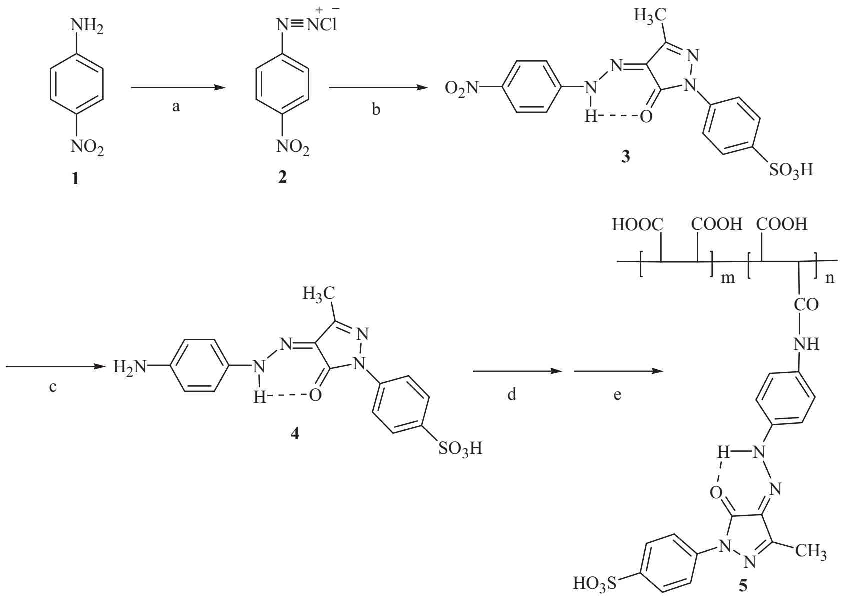

Scheme 1. Reaction conditions and reagents: (a) 35% HCl (aq.), $NaNO_2$, 0–5 °C, 0.5 h. (b) 3-methyl-1-(4-sulfophenyl)-2-pyrazoline-5-one, 15% Na_2CO_3 (aq.), 0–5 °C, 0.5 h, 96.9%. (c) $Na_2S{\cdot}9H_2O$, $NaHCO_3$, H_2O, 75 °C, 4 h, 89.4%. (d) PMA, KOAc, HAc, 120 °C, 8 h. (e) H_2O, 5% HCl (aq.), 5% Na_2CO_3 (aq.), 20 °C.

with a mechanical stirring bar, and heated to 75 °C. 22.6 g (130 mmol) sodium sulfide nonahydrate and 7.92 g (130 mmol) sodium bicarbonate was dissolved in 200 mL water, and this mixture was dropped into the flask within 1 h, and kept at 75 °C for 4 h, and the reaction termination was determined by TLC (isobutyl alcohol: *n*-propanol: ethyl acetate: water = 2:4:1:1). After the reaction was over, the pH of the mixture was adjusted to 5–6 with 5% hydrochloric acid, and intermediate **4** was obtained by filtering. The product was dried to a constant weight under vacuum for 24 h, the yield of the product was 89.4%. 2 g (6.83 mmol) compound **4** and 0.447 g (3.42 mmol) potassium acetate were dissolved in 10 mL acetic acid, 1.17 g PMA was added into the mixture, and then the temperature was increased to 120 °C and kept at the temperature for 8 h. The reaction termination was determined by TLC (isobutyl alcohol: *n*-propanol: ethyl acetate: water = 2:4:1:1). After that, the mixture was cooled to the room temperature and dissolved in 50 mL water, the pH of the solution was adjusted to 10–11 with 5% (wt/wt) sodium carbonate solution, and then reduced the pH using 5% hydrochloric acid. At last, polycarboxylic acid dye **5** was precipitated from the solution and obtained by filtration. FTIR 430 spectrophotometer, HP1100 mass spectrometer, HP-8453 UV–visible and Varian Inova 400 NMR were used to determine the structures of the intermediates and the dye.

The API–ES mass spectra of **3** gave the correct *quasi*-molecular ion peak at 402 ($[M-H]^-$). λ_{max} of **3** is 405 nm (H_2O). ^1H NMR (400 MHz, DMSO-d_6): δ 13.25 (s, 1H, NH), 8.31 (d, 2H, J = 8.8 Hz, aryl), 7.87 (d, 2H, J = 7.2 Hz, aryl), 7.85 (d, 2H, J = 8.0 Hz, aryl), 7.69 (d, 2H, J = 8.0 Hz, aryl), 2.33 (m, 3H, CH_3). ^{13}C NMR (400 MHz, DMSO-d_6): δ 11.71 (CH_3), 116.81 (aryl), 117.20 (aryl), 125.96 (aryl), 126.93 (aryl), 131.31 (aryl), 137.98 (aryl), 144.13 (aryl), 145.37 (aryl), 147.45 (C=N–NH), 149.57 ($[CH_3]C{=}N$, ring), 156.39 (C=O). FTIR (KBr): (–OH) 3434 cm^{-1}, (C=O on the pyrazolone group) 1671 cm^{-1}, (C=C of aromatic ring) 1593, 1500 and 1448 cm^{-1}, ($-NO_2$) 1559 and 1340 cm^{-1}, ($-SO_3H$) 1340 and 1150 cm^{-1}.

The API–ES mass spectra of **4** gave the correct *quasi*-molecular ion peak at 372 ($[M-H]^-$). λ_{max} of **4** is 450 nm (H_2O). ^1H NMR (400 MHz, DMSO-d_6): δ 13.63 (s, 1H, NH), 7.89 (d, 2H, J = 8.4 Hz, aryl), 7.65 (d, 2H, J = 8.0 Hz, aryl), 7.45 (d, 2H, J = 8.4 Hz, aryl), 6.65 (s, 2H, J = 8.0 Hz, aryl), 2.28 (m, 3H, CH_3). ^{13}C NMR (400 MHz, DMSO-d_6): δ 12.01 (CH_3), 114.87 (aryl), 117.03 (aryl), 118.41 (aryl), 125.16 (aryl), 126.87 (aryl), 130.86 (aryl), 138.81 (aryl), 144.31 (aryl), 148.43 (C=N–NH), 148.63 ($[CH_3]C{=}N$, ring), 157.67 (C=O). FTIR (KBr): (–OH) 3445 cm^{-1}, ($-NH_2$) 3352 cm^{-1}, (C=O on the pyrazolone group) 1658 cm^{-1}, (C=C of aromatic ring) 1593, 1500 and 1485 cm^{-1}, ($-SO_3H$) 1339 and 1155 cm^{-1}.

λ_{max} of compound **5** is 395 nm (H_2O). ^{13}C NMR (400 MHz, DMSO-d_6): δ 173.11–175.72 (C=O carboxylic group), 168 (C=O amide), 157.01 (C=O pyrazolone ring), 149.37 ($[CH_3]C{=}N$, pyrazolone ring), 147.1 (C=N–NH), 144.13

Table 1
Dyeing characteristics of dye 5 and some conventional reactive dyes.

Dye	Fixation (%)	Wash-fastness			Rub-fastness	
		Change	Cotton	Wool	Dry	Wet
Dye **5**	98.4	4	4–5	4–5	4–5	3–4
C.I. reactive yellow 17	78.2	4–5	4	4	4–5	3
C.I. reactive red 2	49.1	4	4	4	4	3–4
C.I. reactive blue 19	72.9	4–5	3–4	3–4	4	3–4

(C–N, pyrazolone ring), 141.38 (aryl), 139.12 (aryl), 138.54 (aryl), 128.08–129.92 (aryl), 127.47–127.66 (aryl), 126.82–126.95 (aryl), 124.75–124.89 (aryl), 116.97–117.23 (aryl), 33–45 (CH), 12.01 (CH_3), FTIR (KBr): (–OH) 3445 cm^{-1}, (C=O carboxylic group) 1712 cm^{-1}, (C=O amide group) 1658 cm^{-1}, (C=C of aromatic ring) 1593, 1500 and 1485 cm^{-1}, ($-SO_3H$) 1339 and 1155 cm^{-1}.

The synthesized compound **5** was applied to dyeing of cotton through a "3-dip-3-nip" padding operation at room temperature. The concentration of dye-bath was 0.5% (wt/wt), the dipping time of the dyed fibre in the padding bath containing compound **5** was 3 min, and the pressure on the mangle was adjusted to give 70% wet pick up. After the dyed fibre was dried at room temperature, it was dipped into the fixing-bath containing 1% (wt/wt) triethanolamine, 3% (wt/wt) dicyandiamine and 2% (wt/wt) zinc nitrate for 2 min and nipped once, the pressure on the mangle was adjusted to give approximately 80% wet pick up. Then the fibre was heated to 180 °C for 5 min. At last, the dyed fibre was rinsed completely with water. Dye fixation and fastness properties are shown in Table 1.

From Table 1, the overall fixation of dye **5** on cotton reached 98.4%. And when the cotton was dyed by the conventional reactive dyeing method using C.I. reactive yellow 17, C.I. reactive red 2 and C.I. reactive blue 19, and the fixation was only 78%, 49.1% and 72.9% [15–17], respectively. The wash fastness and rub fastness of dye **5** were as good as that from dyed cotton using conventional reactive dyes with the conventional reactive dyeing method.

In conclusion, the prepared dye **5** possesses competitive advantages of high dye fixation and good fastness and can be deemed promising in application.

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