Design, Synthesis, and Application of Amphoteric Macromolecular Dyes with Controllable Solubility

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ABSTRACT: A series of amphoteric macromolecular dyes were designed and synthesized from poly(acrylamide-*co*-vinylamine) oligomer and reactive dyes. The structure of the synthesized dyes was characterized by fourier transform infrared spectra, mass spectra, and ultraviolet–visible spectroscopy analysis. The solubility of the dyes was also investigated. The results showed that the solubility of the dyes can be controlled by tuning the ratio of amino to sulfonate groups in amphoteric macromolecular dyes. Based on the results of controllable solubility conducted by visible light transmittance measurements, amphoteric macromolecular dyes were used to dye cotton fiber; the fixation of the dye on cotton was more than 95% when crosslinking agent was added. The dyed samples exhibited good fastness to washing and rubbing. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41120.

INTRODUCTION

Unlike other dyes, reactive dyes can be fixed on fibers through the formation of covalent bonds, thereby solving the problem of dyed fibers with poor fastness to washing and rubbing. Reactive dyes have been extensively applied in the textile industry. However, the hydrolysis of the reactive groups during storage, transportation, and application decreases the fixation of reactive dyes on cotton fiber, which is only 50–80%.[1] Hydrolyzed reactive dyes in aqueous solution waste resources and pollute the environment. Therefore, different methods have been studied to remove residual dyes and clear dyeing wastewater, such as adsorption, flocculation, and oxidation.[2–4] Although adsorption, flocculation, and oxidation treatments are helpful to the environment, their energy consumption and cost are high. When dyes can be completely fixed on fibers, or can be recycled and reused after application; then, the utility of the dyes can be maximized and environmental pollution caused by dyeing wastewater can be resolved.

Over the last two decades, researchers have been trying to achieve high fixation of reactive dyes on fibers.[5–7] Lewis et al. developed various novel reactive dyes with high fixation to fiber, and created a polyfunctional reactive dye containing two dichloro-s-triazine residues linked by aliphatic amino groups through a third triazine system to the chromophoric residue.[7] The polyfunctional reactive dye had 93% total dyeing fixation efficiency on cellulose. Cid et al. used fluorotriazine reactive

dyes to dye cotton in supercritical carbon dioxide; the results showed outstanding dye fixation on cotton.[8] Our research group has prepared various polymeric crosslinking dyes by incorporating hydrophobic chromophore, such as 2,4-dinitrochlorobenzene, 1,4-dihydroxyanthraquinone, chlorosulfonate benzoyl H-acid, and 4-(4-chlorosulfonyl-phenylhydrazono)−3-methyl-1-phenyl-5-pyrazolone, on polyallylamine, polyvinylamine, or polyethylene polyamine.[9–12] In these polymeric dyes, water-soluble polyamine was used as the main train. Parts of the amino groups in the polyamine are kept to react with the crosslinking agent. Polymeric crosslinking dyes can be fixed on cotton and silk with high fixation by covalent bonds with the crosslinking agent acting as a bridge between the fiber and the dye molecule. Few dyes can be found in dyeing wastewater. The solubility of polymeric crosslinking dyes is afforded by amino groups. However, these dyes have poor solubility in alkali conditions, or when the chromophore is strongly hydrophobic. In addition, the dissolved state of polymeric crosslinking dyes is difficult to control. Controllable solubility of dyes is highly useful in the selection of pH value and applied conditions for the dyeing and fixing process and makes the recycling and reusing of dyes possible.

An amphoteric macromolecule is a polymer containing cationic and anionic groups. Amphoteric macromolecules have an isoelectric point (IEP) that can be tuned by varying the ratio of cationic to anionic groups. IEP is intimate to the aggregation behavior in water, surface tension, and phase behavior of amphoteric
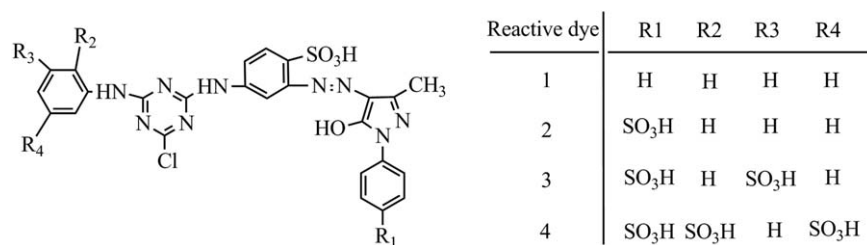
Reactive dye	R1	R2	R3	R4
1	H	H	H	H
2	SO_3H	H	H	H
3	SO_3H	H	SO_3H	H
4	SO_3H	SO_3H	H	SO_3H

Figure 1. Structures of the designed four reactive dyes.

macromolecules.[13–16] Therefore, change of the ratio of cationic to anionic groups is a significant and useful tool to control the solubility of amphoteric macromolecule. In this study, four reactive dyes with different numbers of sulfonate groups were designed (Figure 1). Amphoteric macromolecular dyes were also synthesized by grafting reaction of poly(acrylamide-co-vinylamine) oligomer with reactive dyes. This study aims to investigate the solubility of dyes by changing the ratio of amino to sulfonate groups in the amphoteric macromolecular dyes. The dyeing and fixing process of amphoteric macromolecular dyes on cotton fiber was investigated using controllable solubility as the theoretical basis.

EXPERIMENTAL

Materials and Characterization

Poly(acrylamide-co-vinylamine) (PAV) oligomer (GPC, $M_n = 603$, PDI = 1.69) with 75% amino group content was prepared using the Hofmann degradation of polyacrylamide according to a previous study.[17] Reactive dyes 2 and 3 (C. I. Reactive Yellow 2) were prepared according to the literature.[18,19] The cyanuric chloride (2, 4, 6-trichlorotriazine) used was of analytical grade. 3-Methyl-1-(4-sulfophenyl)−5-pyrazolone (98%), 3-methyl-1-phenyl-5-pyrazolone (99%), 2-amino-1, 4-benzenedisulfonic acid (98%), and 2, 4-diaminobenzenesulfonic acid (98%) were obtained from Shanghai Dyestuff Company and used without purification. The crosslinking agent M was prepared according to the literature,[20] and its structure is shown in Figure 2. All other chemicals were analytical grade and used without purification.

IR spectrum was registered with FTIR-430 Spectrophotometer (Japan) in the scanning range of 4000–400 cm^{-1} using a KBr pellet method. UV-visible spectra were carried out in deionized water at room temperature using Agilent 8453 UV-Vis spectrometer. Mass spectra were recorded at CID = 50–200 V with an HP 1100 HPLC/MS system from Hewlett Packard, USA.

Synthesis

Preparation of Reactive Dye 1. Cyanuric chloride (0.0103 mol), ice, and water were stirred for 30 min in a 150 mL beaker, and
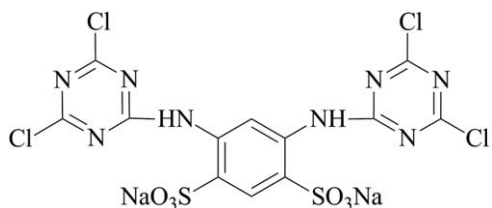

Figure 2. Structure of crosslinking agent M.

then 0.01 mol solution of 2, 4-diaminobenzenesulfonic acid was added slowly. The reaction was performed at 0–5°C and pH = 4–5. Thin layer chromatography (TLC) was used to monitor the completion of the reaction ($R_f = 0.75$, Silica GF254, n-PrOH : i-BuOH : EtOAc : H$_2$O, 2 : 4 : 1 : 3, v/v). After the reaction was completed, 2.5 mL of concentrated hydrochloric acid and 0.0105 mol of NaNO$_2$ were added into to the solution, and the diazotization reaction was continued for 30 min until no reaction to the Erich reagent was detectable. Excess nitrous acid was decomposed using sulfamic acid. The resultant diazo compound was added to a 0.01 mol 1-phenyl-3-methyl-5-pyrazolone solution in 25 mL of water at 0–5°C and pH of 6.5–7.0. The reaction was completed after 2 h. Afterwards, 0.01 mol aniline was added, and the temperature was increased to 30–40°C and pH 6.0–6.5 for 2 h. The product was collected by filtration, washed with water for several times, and then dried in vacuum (Yield: 91%). $R_f = 0.82$, λ_{max} (H$_2$O : DMF = 1 : 1, v/v) = 398 nm. The atmospheric pressure chemical ionization mass spectrometer (APCI-MS) showed peaks at 576.1 for [M–H]$^-$.

Preparation of Reactive Dye 4. The first condensation reaction of cyanuric chloride and 2-amino-1, 4-benzenedisulfonic acid was essentially the same as that of the reactive dye 1 (TLC control, R_f of the first condensation product was 0.82). Then, a solution of 2, 4-diaminobenzenesulfonic acid (0.01 mol) was added slowly. The reaction was performed at 40°C and pH = 5–6. TLC was used to monitor the completion of the reaction ($R_f = 0.42$). The diazotization and coupling reactions of the second condensation product were the nearly same as that of the Reactive dye 1 except that the 1-phenyl-3-methyl-5-pyrazolone was replaced by 3-methyl-1-(4-sulfophenyl)−5-pyrazolone (Yield: 87.4%). $R_f = 0.35$, λ_{max} (H$_2$O) = 393 nm. APCI–MS: 492.3 ([M − 4H + 3Na]$^{2-}$/2), 278.5 ([M − 4H + Na]$^{3-}$/3), 271.2 ([M − 4H]$^{3-}$/3).

Preparation of Amphoteric Macromolecular Dyes. The synthetic scheme of amphoteric macromolecular dyes is illustrated in Figure 3. PAV (20 mmol) was dissolved in 20 mL of water (for PAV-RY1 and PAV-RY2, PAV was dissolved in DMSO and H$_2$O mixture, 1 : 1, v/v) and the pH value was adjusted to 10.0–11.0 by 10% NaOH. Solution of reactive dye (reactive dyes 1 and 2 were dissolved in DMSO and H$_2$O mixture, 1 : 1, v/v) was added slowly when the temperature was heated to 70°C. The system was kept at 70°C with pH of 10.0–11.0 until the reaction was completed. The TLC method was used to monitor the completion of the reaction (R_f of the amphoteric macromolecular dyes was 0.0). The resultant macromolecular dye solution was adjusted to pH 2 using 6 mol/L of HCl. The macromolecular dye
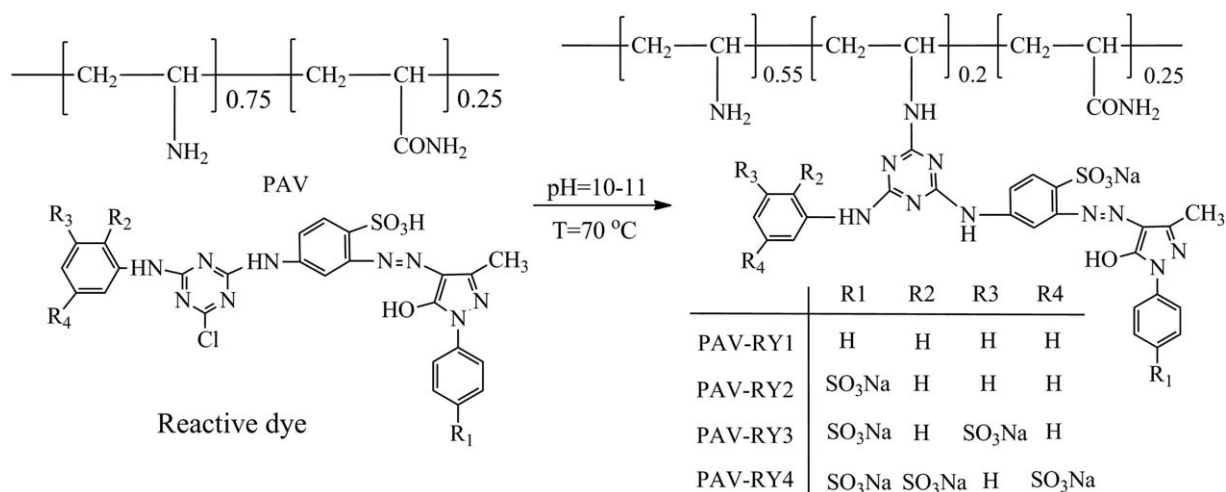
Figure 3. Synthesis of the amphoteric macromolecular dyes.

solution was then poured into 200 mL methanol, and the yellow precipitate was collected. The final product was obtained after drying the precipitate under vacuum at 40°C for 24 h.

Experiment of Controllable Solubility

Solubility Behavior. The solubility behavior of the amphoteric macromolecular dye solutions were determined by visible light transmittance measurements carried out at a wavelength of 600 nm at 25°C as functions of pH value using an Agilent 8453 UV–visible spectrophotometer.

Zeta Potential Experiment. Zeta potential experiment on the amphoteric macromolecular dye solutions was conducted as functions of pH value with a ZETASIZER nano series Nano-ZS90 from Malvern Instruments Corp. All samples were measured at 25°C, and the reported values were based on five measurements with 20 cycles each.

Dyeing and Fixing Process. Dyeing cotton using the amphoteric macromolecular dyes was carried out through "two-dip–two-nip" operation performed at room temperature. The fiber was dipped in the dye bath containing 3% (wt/wt) amphoteric macromolecular dye at a liquor-to-goods ratio of 20 : 1 for 3 min, and the fiber was then nipped with 70% wet pick-up. After drying at room temperature, the dyed fiber was dipped into the crosslinking bath consisting of 20 g/L crosslinking agent for another 2 min, and then nipped once with 70% wet pick-up. Afterward, the fiber was heated to 60°C in an oven for 10 min. Finally, the dyed fabrics were soaped with 5‰ OP-10 solution (95°C) completely, rinsed with water, and then air dried.

Measurement of Dye Fixation and Fastness Testing. The fixation of the amphoteric macromolecular dyes on cotton was calculated by determining the reflectance (R) of the dyed samples at the wavelength of maximum absorption on a Pye-Unicam SP8400 Spectrophotometer. The color yield (K/S) was calculated according to the Kubelka–Munk equation [eq. (1)]. K/S values were measured twice: before soaping treatment [$(K/S)_b$] and after soaping treatment [$(K/S)_a$]. Percent fixation of the dye was calculated as follows [eq. (2)].

$$K/S = (1-R)^2/2R \qquad (1)$$

$$\text{Dye fixation (\%)} = \left[(K/S)_a/(K/S)_b\right] \times 100 \qquad (2)$$

The color fastness of the dyed fabrics was tested according to the Chinese Criteria methods, which include fastness to light [GB/T 8427-87], washing [GB/T 3921-97], and rubbing [GB/T 3920-97]. The light fastness was carried on a Light and Weather-Fastness Tester Heraeus 150S. The rubbing fastness was tested on a Circular Rub Fastness Tester YG571B. The washing fastness was tested in a standard bath. All the samples were evaluated and given the appropriate grading using the Standard Gray Scales.

RESULTS AND DISCUSSION

Design of Amphoteric Macromolecular Dyes

The solubility behavior of the amphoteric macromolecules can be tuned by changing the ratio of the anionic to cationic groups. The cationic and anionic groups for the prepared amphoteric macromolecular dyes in this study are amino and sulfonate groups, respectively. Although the ratio of amino to sulfonate groups can be manipulated by controlling the degree of substitution (DS), the chromophore in polyamine crosslinking dyes should retain enough content to fulfill their actual application on fibers. In addition, the residual amino groups that react with the crosslinking agent should be enough to enable high fixation of the amphoteric macromolecular dyes to the fibers. Hence, tuning the ratio of amino to sulfonate groups by controlling the DS is not the initial choice. The number of sulfonate groups in the reactive dye can be easily controlled by choosing a different aryl sulfonate. Therefore, we designed four yellow reactive dyes (reactive dyes 1, 2, 3, and 4) containing the same chromophore with different numbers of sulfonate groups. The number of sulfonate groups in reactive dyes 1, 2, 3, and 4 is 1, 2, 3, and 4, respectively. At fixed DS, the designed reactive dyes can be selected as candidates for tuning the ratio of amino to sulfonate groups in the amphoteric macromolecular dyes.

Synthesis of Amphoteric Macromolecular Dyes

The primary amino group has high activity as a nucleophilic reagent, and can easily react with reactive dyes. A pH value of

Table I. The Data of the Amphoteric Macromolecular Dyes

Sample	Degree of substitution (%)	λ_{max} (H$_2$O)	ε (L·g^{-1}·cm^{-1})	Isoelectric point (IEP)	Yield (%)
PAV-RY1	20	396	18.1[a]	8.2	96.4
PAV-RY2	20	392	16.5	6.1	95.4
PAV-RY3	20	390	15.7	2.4	96.7
PAV-RY4	20	390	15.1	–	95.1

[a] Determined in DMF : H$_2$O = 1 : 1(v : v).

10 is required to enable the amino groups of PAV to dissociate fully.[21] Reactive dyes 1 and 2 are poorly soluble in water; thus, PAV-RY1 and PAV-RY2 cannot be successfully synthesized in water. However, the reaction can be completed in the presence of DMSO and a water mixture solvent (v : v = 1 : 1). TLC exhibited that the reaction was completed quantitatively. The R_f of the prepared amphoteric macromolecular dye is 0.0, and the R_f of reactive 1, reactive 2, reactive 3, and reactive 4 is 0.82, 0.59, 0.53 and 0.35, respectively. During the reaction, we did not find the hydrolytic product of reactive dye by TLC. Table I shows the results and data of the products.

FT-IR spectrum was used to further confirm whether or not the reactive dyes had been successfully grafted on the PAV. FI-IR spectra of PAV-RY1, PAV-RY2, PAV-RY3, and PAV-RY4 are shown in Figure 4. The absorption bands created by s-triazine ring exist at 1497 cm^{-1}. The absorption bands at 1402 and 1338 cm^{-1} were assigned to the pyrazole ring, whereas the absorption bands at 1163 and 1030 cm^{-1} indicated the presence of sulfonate groups. Meanwhile, it can be clearly found that with the increase of the amounts of sulfonate groups (from PAV-RY1 to PAV-RY4), the intensity of absorption bands at 1163 and 1030 cm^{-1} became stronger.

Controllable Solubility of Amphoteric Macromolecular Dyes

The solubility behavior of dyes is important in their application. For example, when these dyes are used for dying fibers, the concentration needed is about 1 g/L by exhaustion method.[22] However, 20–50 g/L concentration of dye is needed when using the tie-dyed method.[1,9] Therefore, research on solubility behavior can provide directions on how dyes can be efficiently applied.

Figure 5 illustrates the transmittance and zeta potential of the amphoteric macromolecular dyes (1 g/L) in 0.01 N NaCl. The soluble pH value of PAV-RY1, PAV-RY2, PAV-RY3, and PAV-RY4 is above 10, 8.5, 6.5, and 4.5, respectively. This can be explained from the changes of the ratio of sulfonate to amino groups in amphoteric macromolecular dyes. In PAV-RY1, PAV-RY2, PAV-RY3, and PAV-RY4, this ratio is 0.36, 0.73, 1.09, and 1.45, respectively. Amino groups are mainly in form of —NH$_2$ when pH value of the solution is above 10 and sulfonate groups are negative (—SO$_3^-$) at pH > 1. Therefore, PAV-RY1 can be soluble when the pH value of the solution is above 10.

Figure 5. Transmittance (a) and zeta potential of amphoteric macromolecular dyes (b) (1 g/L) in 0.01 N NaCl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
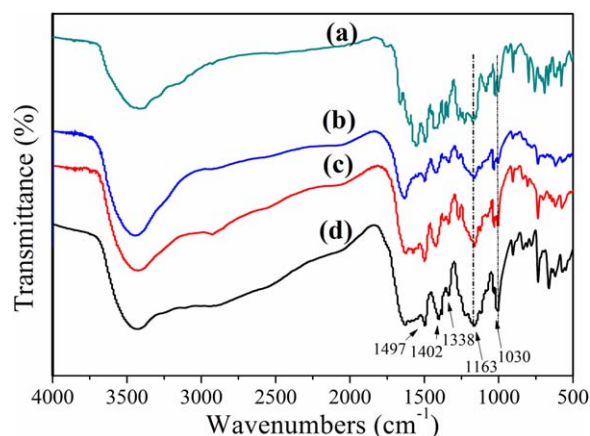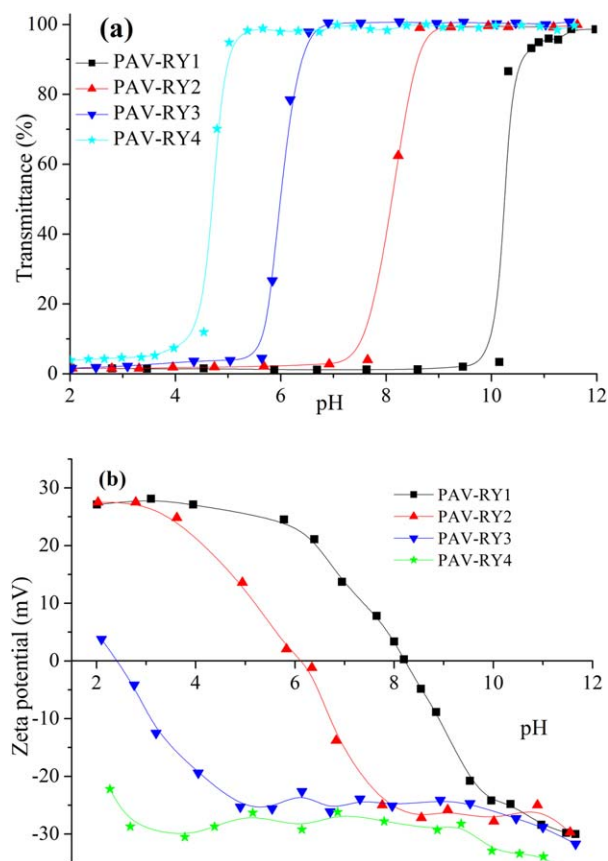
Figure 4. FT-IR spectra of PAV-RY1 (a), PAV-RY2 (b), PAV-RY3 (c), and PAV-RY4 (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
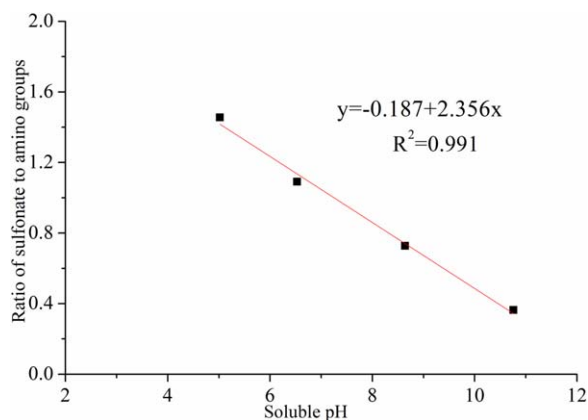
Figure 6. Relationship between the ratio of sulfonate and amino groups and soluble pH value. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

At pH < 10, the protonated amino groups were interacted with sulfonate groups, so the intermolecular interaction favored the aggregation of the amphoteric macromolecular dye. With the increase of the sulfonate groups in the amphoteric macromolecular dye, the amphoteric macromolecular dye was more hydrophilic so that its soluble pH value decreased. Especially in PAV-RY4, the ratio of sulfonate to amino groups is 1.45, and the amounts of sulfonate groups are much larger than that of amino groups. Beside the interaction of the protonated amino groups with the sulfonate groups, the amounts of the residual

sulfonate groups helped to make the amphoteric macromolecular dye soluble. Therefore, it is evident that PAV-RY4 can be soluble at pH > 4.5.

Given the occurrence of complexation by intra- and intermolecular interaction and the overall charge neutralization near the isoelectric point, the amphoteric macromolecular dyes formed aggregates. However, the IEP of PAV-RY1, PAV-RY2, and PAV-RY3 is about 8.2, 6.1, and 2.4, respectively. No IEP of PAV-RY4 was found [Figure 5(b)]. The aggregates of the amphoteric macromolecular dyes still exist when the pH value of the aqueous solution deviates from the IEP by approximately two units because of the presence of aromatic rings, which are similar to the polyampholyte containing aromatic rings.[13] The hydrophobicity of the chromophore and aromatic rings is strong to ensure that the prepared amphoteric macromolecular dyes are insoluble when the pH of the aqueous solution falls below the IEP. Interestingly, the soluble pH value of PAV-RY1, PAV-RY2, PAV-RY3, and PAV-RY4 was linearly increased with the decrease of the ratio of sulfonate to amino groups in their structure (Figure 6). Therefore, solubility can be controlled by changing the ratio of sulfonate to amino groups in the amphoteric macromolecular dyes.

Figure 7 shows the transmittance of amphoteric macromolecular dyes at high concentration (20 and 50 g/L). Compared with the low concentration (1 g/L), the soluble pH value of the amphoteric macromolecular dyes was correspondingly raised to above 12, 10.5, 9.0, and 7.5 for PAV-RY1, PAV-RY2, PAV-RY3, and
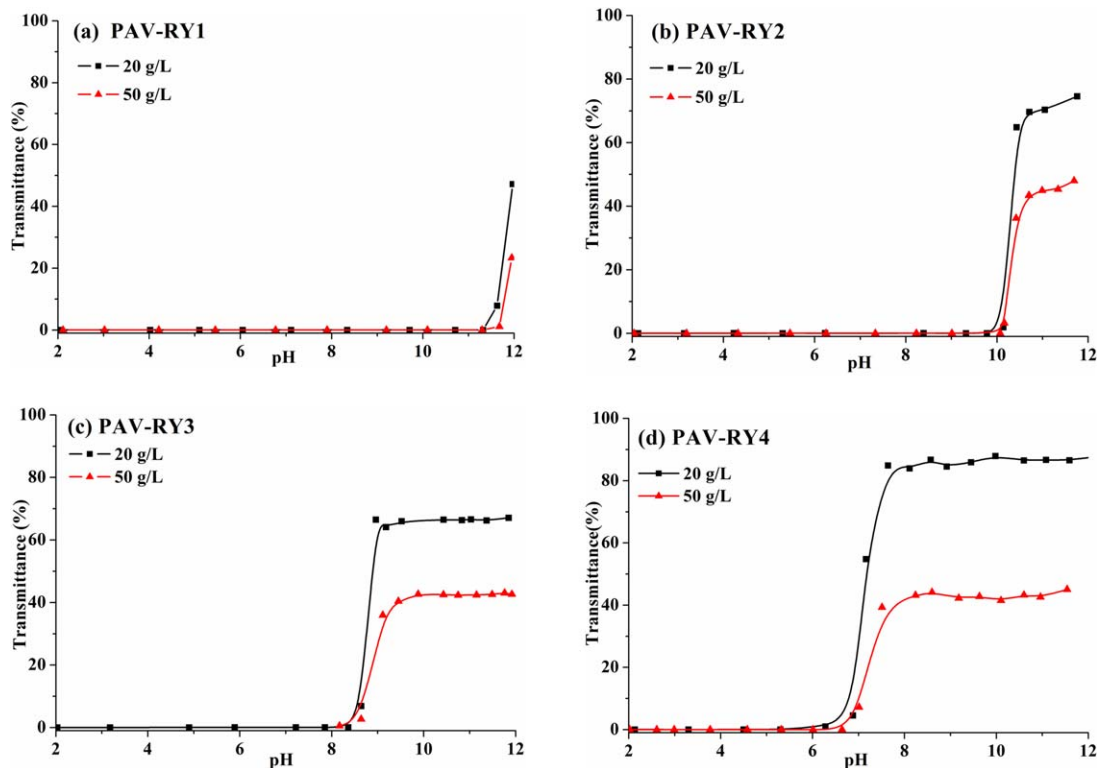

Figure 7. Transmittance of PAV-RY1–PAV-RY4 (20 and 50 g/L) at different pH values. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Directions of the Controllable Solubility on Dyeing and Fixing Process

Sample	Soluble pH (20–50 g/L)	Insoluble pH (1.0 g/L)	pH value of the dyeing bath	pH value of the crosslinking bath
PAV-RY1	≥12	<10	12	6–7
PAV-RY2	≥10.5	<8	10.5	6–7
PAV-RY3	≥9.0	<6	9.0	5–6
PAV-RY4	≥7.5	<4	7.5	3–4
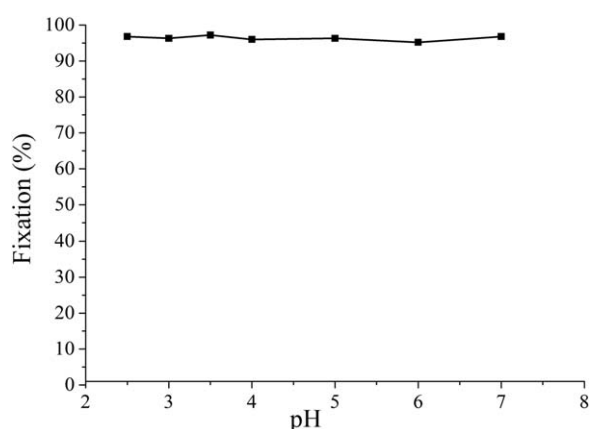
Figure 8. Relationship between the pH value of crosslinking bath and fixation of PAV-RY-2 on cotton.

PAV-RY4, respectively (2–3 units). The intermolecular interaction of the amphoteric macromolecular dyes increased quickly with increasing concentration, making the dyes aggregate easily.

Application of Controllable Solubility on Dyeing and Fixing Process

The solubility behavior of dyes is an important key factor in their application. The controllable solubility of amphoteric macromolecular dyes was used for the direct dyeing and fixing process on cotton fiber (Table II). The pH value of the dyeing bath containing 3% (wt/wt) of PAV-RY1, PAV-RY2, PAV-RY3, and PAV-RY4 was selected based on the soluble pH region of the corresponding dyes at high concentration through the tie-dyed method. After the dyed fibers were dried at room temperature, the dye should be fixed on the fiber by the crosslinking agent. To prevent the amphoteric macromolecular dye from dissolving in the crosslinking bath, the pH value of the crosslinking bath should be selected according to the insoluble pH region at low

concentration. Taking PAV-RY2 as an example, the pH value of the PAV-RY2 dyeing bath must be above 10.5 and its crosslinking bath must have a pH below 8.0. Hence, the final pH value of the PAV-RY2 dyeing bath is 10.5 and the fixing process can be completed at neutral pH value.

The relationship between the pH value of the crosslinking bath and fixation of PAV-RY-2 on cotton fiber was investigated to further confirm the above assumption (Figure 8). In the experiment, the PAV-RY-2 on dyed cotton fiber began to dissolve in the crosslinking bath when pH value of the bath was above 8.0. Hence, the fixation of PAV-RY-2 on cotton fiber in a crosslinking bath with pH < 8 was investigated. When the pH value of the crosslinking bath is lower than 8, fixation of PAV-RY-2 on cotton fiber was about 97%. Therefore, studies on controllable solubility can provide directions for the dyeing and fixing process.

Fastness Properties of Amphoteric Macromolecular Dyes on Cotton

Fastness properties of PAV-RY-1, PAV-RY-2, and PAV-RY-3 on cotton are listed in Table III. Fixation of PAV-RY-1, PAV-RY-2, and PAV-RY-3 is above 95.7%. The rub and wash fastness of the amphoteric macromolecular dyes reached grades 3–4 and 4–5, respectively. This result is attributed to the fact that amphoteric macromolecular dyes are fixed on the fiber by covalent bonds with the crosslinking agent acting as a bridge between the fiber and the dye molecule. However, fixation of PAV-RY-4 on cotton was only 65.4%. Fixation of amphoteric macromolecular dyes decreased with the increment of sulfonate groups in the chromophore. Therefore, the low fixation of PAV-RY-4 on cotton may be attributed to the large steric hindrance that prevents crosslinking agent M from reacting with the amino groups in PAV-RY-4. Although our prepared amphoteric macromolecular dyes cannot be completely fixed on fibers, recycling and reusing

Table III. Fixation and Fastness Properties of the Amphoteric Macromolecular Dyes

Sample	Fixation (%)	Light fastness	Rub fastness		Wash fastness	Staining	
			Dry	Wet	Alteration	Cotton	Silk
PAV-RY1	97.1	4–5	4	3–4	4–5	4–5	4–5
PAV-RY2	96.8	4–5	4	3–4	4–5	4–5	4–5
PAV-RY3	95.7	4–5	4	3	4–5	4–5	4–5
PAV-RY4	65.4	–	–	–	–	–	–

the amphoteric macromolecular dyes is feasible because of their controllable solubility.

CONCLUSIONS

Four amphoteric macromolecular dyes were designed and prepared by grafting PAV oligomer with reactive dyes. Controllable solubility of amphoteric macromolecular dyes was achieved by tuning the ratio of sulfonate to amino groups. The pH value of the dyeing and fixing process was selected based on the results of controllable solubility. Fixation of PAV-RY-1, PAV-RY-2, and PAV-RY-3 (synthesized from PAV oligomer and reactive dyes with 1, 2, and 3 sulfonate groups, respectively) reached above 95%, and the rub and wash fastness reached grades 3–4 and 4–5, respectively.

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