Multifunctional Water-soluble Polymeric Fluorescent Whitening Agents Based on 4,4'-Bis (1,3,5-Triazinyl)-Diamino Stilbene-2,2'-Disulfonic Acid Structure

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A series of multifunctional water-soluble polymeric fluorescent whitening agents (PFWAs, 5a-f) based on 4,4'-diamino-stilbene-2,2'-disulfonic acid (DSD acid)-triazine structure were successfully synthesized using a nucleophilic substitution reaction with cyanuric chloride, DSD acid, amino compounds, polyethylene glycol (PEG), and/or polyvinyl alcohol (PVA) as raw materials. The structure of the PFWAs was characterized by FT-IR, and the substitution degree was calculated from the results of an elemental analysis. The optical properties of the PFWAs were measured by the UV-vis spectra and fluorescence spectra when the PFWAs were applied to paper fiber to serve the roles of light stabilizer, fluorescent whitener, and surface-sizing agent. Then the performance of the PFWAs on paper was evaluated by measuring the surface strength and smoothness of paper, brightness degree of paper, and the yellowness value (value of PC) of paper. The results indicated that the PFWAs had better light stability in water solution than that of a conventional fluorescent whitening agent (FWA) as a light stabilizer. According to the surface-sizing experiment and UV aging experiment, it was concluded that not only could the PFWAs enhance the surface strength and smoothness of paper, but also have a better effect on anti-UV aging than that of FWA as a light stabilizer and fluorescent whitener agent.

Keywords: Fluorescent whiteners; Yellowing inhibitor; Polymer; Light stability; Surface sizing agent

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INTRODUCTION

Fluorescent whitening agents (FWAs) are primarily applied to textiles and papers to enhance their whiteness and brightness by increasing the UV-blocking properties through absorbing light in the near ultraviolet region and re-emitting light at a longer wavelength in the blue and visible region (Grabtchev 1994; Hussain *et al.* 2012; Paulsson and Parkas 2012; Zhang *et al.* 2013). The triazine-aminostilbene fluorescent whiteners based on 4,4'-diamino-stilbene-2,2'-disulfonic acid (DSD acid) are an important class of fluorescent whitening agents that includes a great conjugated system with double carbon bonds. They are widely used to create intense and bright white shades when evenly applied to the paper surface (Grabtchev 1994; Um *et al.* 2007). A large number of FWAs in this class are well-known to researchers, containing different amino and alkoxy derivatives in the triazene ring.

Hussain *et al.* (2009b) reported the synthesis of a series of stilbene-triazine compounds, and their performance on cotton fiber as UV-absorbing and FWAs was evaluated. These compounds showed a high degree of whiteness with moderate UV-blocking properties and fair to fairly good fastness properties. Lee *et al.* (2005) reported various disodium 4,4'-bis(1,3,5-triazin-6-yl)-diaminostilbene-2,2'-disulfonate derivatives which were asymmetrically substituted on both triazine moieties. The derivatives showed higher dyeing properties than the fluorescent whitening agent, CI86. However, the above reported FWAs are mainly used to treat cotton, and the effect is poor when applied to paper. The authors' research team has been committed to the high yield of pulp paper whitening for many years and revealed that the FWAs exhibited cis-trans isomerism while irradiated by natural light, which implies poor light stability; this is one of the main problems in the current application (Liu 2011; Xu 2013; Liu *et al.* 2015; Zhang *et al.* 2016a, 2016b).

The triazine-aminostilbene fluorescent whitener with the trans-conformers could emit fluorescence. This works because the benzene ring of the trans-conformers is in the same plane and the p electrons overlap in the π conjugated system. In general, the triazine-aminostilbene fluorescent whiteners with trans-conformers in ground state were more stable than that with cis-conformers (Gegiou *et al.* 1968). However, the main production in the photo reaction is completely different from the thermal reaction (Saltiel *et al.* 1979). Therefore, triazine-aminostilbene fluorescent whiteners with trans-conformers in ground state can reverse to the cis-conformers under natural light irradiation. According to previous research, these issues are caused by the structure of triazine-aminostilbene fluorescent whiteners, in which there exists a C=C bond, and the molecular configuration will turn around the C=C bond when the FWAs acquire energy (Liu and Zhang 2010; Fedorenko *et al.* 2014). For this reason, triazine-aminostilbene fluorescent whiteners generally have cis-isomers and trans-isomers in their structures, and only the trans-configuration can have emission fluorescence.

Herein, the practical applications of them are limited, especially in advanced paper applications. Based on the research mentioned above, the preparation of fluorescence emitted and light stabilized FWAs has become intriguing and full of challenges. Zhang *et al.* (Xie *et al.* 2009; Liu and Zhang 2011; Xiang *et al.* 2014) prepared many kinds of triazine-stilbene fluorescent whitening agents that include different substitutes in the triazine rings to improve their light stability. Grabachev I *et al.* (2000) prepared a polymeric fluorescent whitener by fixing a DSD acid-triazine monomer onto the long chain of styrene or acrylonitrile (Grabtchev 1994; Grabchev and Philipova 1998; Grabchev 2000; Hussain *et al.* 2009a). These methods have played a positive role in the optical stability of the fluorescent whitener. However, the fluorescent whitening agents mentioned above have poor water-solubility and single function, which also restricts the practical applications in the paper industry. Therefore, the synthesis of a water-soluble and multifunctional polymeric fluorescent whitening agent remains a great challenge.

With the objective to resolve the above problems, a series of multifunctional water-soluble polymeric fluorescent whitening agents based on 4,4'-diamino-stilbene-2,2'-disulfonic acid (DSD acid)-triazine structure was successfully synthesized in this work. The triazine-stilbene fluorescent whitener monomers were modified by polyethylene glycol and polyvinyl alcohol to increase the water solubility of FWAs and the surface strength of paper.

EXPERIMENTAL

Materials

The main raw chemicals used to synthesize the PFWAs (5a-f) and FWA were as follows: 4,4'-diaminostilbene-2,2'-disulfonic acid (DSD acid, $C_{14}H_{14}N_2O_6S_2$, 95%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), cyanuric chloride ($C_3Cl_3N_3$, 99%, Aladdin Industrial Corporation, Shanghai, China), sodium hydroxide (NaOH), absolute ethyl alcohol (C_2H_6O), N,N-dimethylformamide (DMF), triacetonediamine ($C_9H_{20}N_2$), monoethanolamine (C_2H_7NO), morpholine (C_4H_9NO), sulfanilic acid ($C_6H_7NO_3S$), aniline (C_6H_7N), and polyethylene glycol-200 (PEG, $HO(CH_2CH_2O)_nH$), polyvinyl alcohol-1788 (PVA, $[C_2H_4O]_n$) (analytical grade, Tianli Chemical Reagent Co. Ltd, Tianjin, China). The pulp used for the paper was poplar chemi-mechanical pulp (CMP, Yueyang Paper Ltd., Yueyang, China).

Methods

Synthesis of the (monochloro-sym-triazinyl) products

The polymeric fluorescent whitening agents PFWAs (5a through 5f) and FWA were prepared by three-step synthetic routes as summarized in Fig. 1. In a 250-mL round-bottom flask equipped with a stirring bar, pH meter, thermometer, and a reflux condenser, 40 mL acetone was added, and the flask was wrapped with ice. To this stirred system, 24.9 mmol cyanuric chloride was added. Then, 12.45 mmol DSD acid dissolved with 10 % (w/v) aqueous sodium hydroxide was slowly dropped in the above system at 0 °C to 5 °C through external cooling, while maintaining the pH between 5 and 6 *via* the addition of 10% (w/v) aqueous sodium hydroxide. The reaction mixture was stirred for 1 h while testing for the disappearance of the disodium salt of DSD acid by a TLC analysis and iodine spot test. The temperature was then increased to 10 °C. 20 mL acetone solution of 24.9 mmol amino compound (R) were added and then stirred for 2 h to 3 h at a pH of around 6 to 7. In this process, the temperature would gradually rise to approximately 35 °C to 40 °C. The reaction mixture was stirred constantly until the disappearance of amino compound (based on the TLC analysis) and the system was cooled to room temperature. After through which the resulting suspension was filtered, repeatedly washed with acetone, and vacuum-dried at 40 °C. The (monochloro-sym-triazinyl) products from step 2 were obtained.

Synthesis of the PFWAs (5a-f) and FWA

A 250-mL reaction flask equipped with a condenser and a stirring bar was charged with 2.63 mmol of the above-mentioned product, 30 mL anhydrous DMF, and stirred until the reaction mixture was dissolved. The temperature of the vigorously stirred mixture was increased to 95 °C to 100 °C, and the excess polymer (R1) was gradually added while maintaining the pH at 7.5 to 8.5 through the addition of 10% (w/v) aqueous sodium hydroxide. After the addition of the aqueous polyvinyl alcohol solution was complete and the pH was not lowered, the product was cooled to room temperature, distilled under reduced pressure, repeatedly washed with acetone, and vacuum-dried at 40 °C. The FWA and PFWAs (5a through 5f) were prepared. The substituents (R and R_1) and yield are shown in Table 1.

Synthesis of the compound 5a: IR (KBr): ν = 3444 cm^{-1} (NH Stretch); 3026 cm^{-1} (C=CH Stretch); 2945 cm^{-1}, 2863 cm^{-1}(CH_3 Stretch); 2937 cm^{-1} (CH_2 Stretch); 1419 cm^{-1}, 1378 cm^{-1} (CH_3 Bend); 1082 cm^{-1} (C-O-C Stretch); 1419 cm^{-1}, 1378 cm^{-1}(-CH_3 Stretch); 713 cm^{-1}(-CH_2- Stretch); 545 cm^{-1}(N-C Stretch).

Synthesis of the compound 5b: IR (KBr): ν = 3451 cm^{-1} (NH Stretch); 3026 cm^{-1} (C=CH Stretch); 1083 cm^{-1} (C-O-C Stretch); 834 cm^{-1}(C-H Stretch of Benzene Ring P-substituted); 711 cm^{-1}(-CH_2- Stretch); 559 cm^{-1}(N-C Stretch).

Synthesis of the compound 5c: IR (KBr): ν = 3444 cm^{-1} (NH Stretch); 3072 cm^{-1}, 3008 cm^{-1} (C=CH Stretch); 2959 cm^{-1}, 2866 cm^{-1} (CH_3 Stretch); 2910 cm^{-1} (CH_2 Stretch); 1105 cm^{-1}, 1074 cm^{-1} (C-O-C Stretch); 725 cm^{-1}(-CH_2- Stretch); 542 cm^{-1}(N-C Stretch).

Synthesis of the compound 5d: IR (KBr): ν = 3446 cm^{-1} (NH Stretch); 3286 cm^{-1} (-OH Stretch); 3114 cm^{-1} (C=CH Stretch); 2967 cm^{-1}, 2888 cm^{-1} (CH_3 Stretch); 2944 cm^{-1} (CH_2 Stretch); 1123 cm^{-1}, 1077 cm^{-1} (C-O-C Stretch); 728 cm^{-1}(-CH_2- Stretch); 541 cm^{-1} (N-C Stretch).

Synthesis of the compound 5e: IR (KBr): ν = 3512 cm^{-1} (NH Stretch); 3315 cm^{-1} (-OH Stretch); 3026 cm^{-1} (C=CH Stretch); 2946 cm^{-1}, 2863 cm^{-1} (CH_3 Stretch); 1083(C-O-C Stretch); 1417 cm^{-1}, 1373 cm^{-1} (-CH_3 Stretch); 714 cm^{-1}(-CH_2- Stretch); 545 cm^{-1} (N-C Stretch).

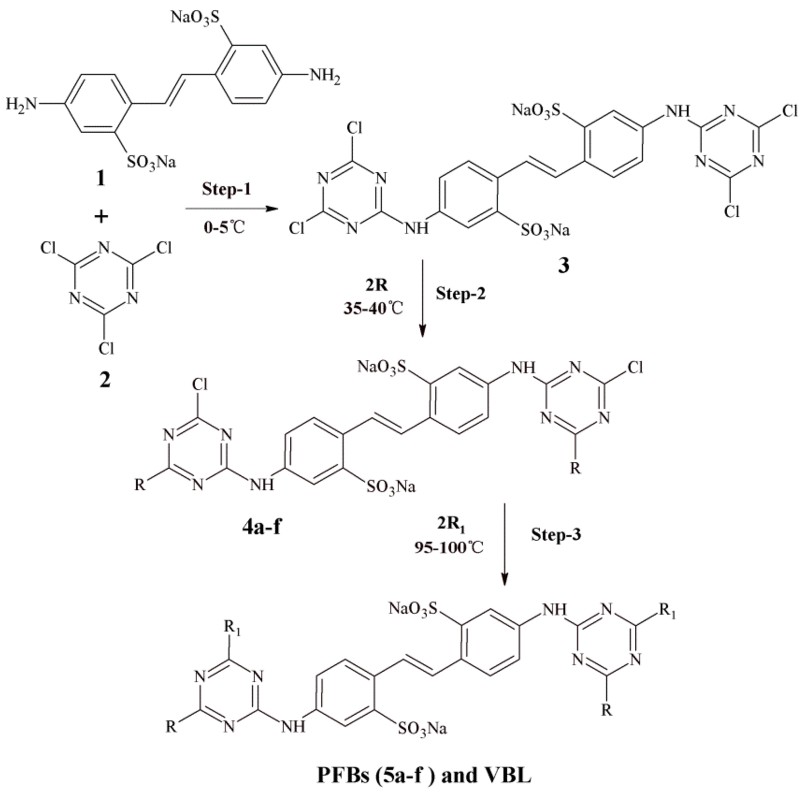
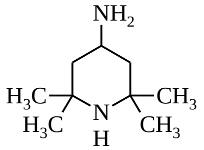
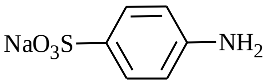
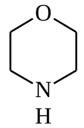
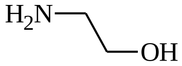
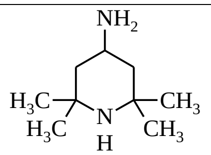
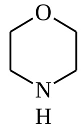
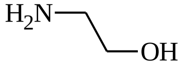
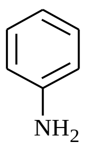


Fig. 1. Schematic diagram of synthetic route of PFWAs (5a-f) and FWA

Synthesis of the compound 5f: IR (KBr): ν = 3465 cm^{-1} (NH Stretch); 3278 cm^{-1} (-OH Stretch); 3077 cm^{-1} (C=CH Stretch); 2861 cm^{-1} (CH_3 Stretch), 2915 cm^{-1} (CH_2 Stretch),1415 cm^{-1} (CH_3 Bend); 1072 cm^{-1} (C-O-C Stretch); 711 cm^{-1} (-CH_2- Stretch); 543 cm^{-1} (N-C Stretch).

Synthesis of the compound FWA: IR (KBr): ν = 3423 cm^{-1} (NH Stretch); 3295 cm^{-1} (-OH Stretch); 3085 cm^{-1} (C=CH Stretch); 2964 cm^{-1}, 2867 cm^{-1}, (CH_3 Stretch), 2938 cm^{-1} (CH_2 Stretch),1178 cm^{-1} (C-O Stretch); 543 cm^{-1} (N-C Stretch).

Table 1. Substituent of PFWAS and FWA

Compounds	R	R_1	Yield (%)
5a		PEG-200	91
5b		PEG-200	87
5c		PEG-200	56
5d		PEG-200	75
5e		PVA-1788	88
5f		PVA-1788	67
FWA			83

Characterization

The FT-IR (KBr, σ/cm^{-1}) spectra were obtained using a VECTOR-22 (Bruker Corporation, Berlin, Germany) instrument. The UV-vis spectra were obtained on a Cary 100 UV-Visible spectrophotometer (Agilent, Santa Clara, USA) with an integrating sphere detector, and barium sulfate ($BaSO_4$) was used as the reflectance standard material. Elemental analysis was characterized by a Vario EL III automatic analyzer (ELMENTAR, Hanau, Germany). The fluorescence spectra were measured on a fluorescence phosphor thermoluminescence spectrometer (HORIBA, Paris, France). The brightness was recorded on a ZB-A colorimeter (Hangzhou Zhibang Instrument Co., Ltd., Hangzhou, China). The UV accelerated aging test was completed by using a ZN-100N desktop UV light resistance climate chamber (Xi'an Tongsheng Instrument

Manufacturing Co., Ltd., Xi'an, China). Patterns used in the experiment were obtained by a paper machine (Shaanxi University of Science and Mechanical Equipment Factory, Xi'an, China). The surface strength and smoothness of paper were measured by the J-IGT350 printability tester (Sichuan Changjiang Instrument Co., Ltd., Sichuan, China) and an electronic smoothness tester (Changchun Instrument Co., Ltd., Changchun, China).

Applied experiment of paper coating- Preparation of the handsheets for test

The poplar chemi-mechanical pulp was dispersed into the distilled water and the percentage of pulp was adjusted to 10% in mass fraction. Then the H_2O_2 (1%), EDTA (0.05%), and sodium silicate ($Na_2SiO_3{\cdot}9H_2O$, 0.5%) were introduced into the solution in sequence and the pH was adjusted to 9 to 10. After that, the above solution was kept in a constant temperature (70 °C) with 90 min for the reaction and then washed until neutral with distilled water. The pulp solution was used to make the handsheets (100 $g{\cdot}m^{-2}$) and cut it into pieces (68 mm × 73 mm). The surface-sizing material was prepared after adding the synthesized compounds into the solution. The sizing materials were coated on the handsheets used the coating machine with an opaque background and the samples were dried at room temperature (Zhang *et al.* 2016b).

UV accelerated aging test

The brightness of the hand sheets was measured by a ZB-A colorimeter (Hangzhou Zhibang Instrument Co., Ltd., Hangzhou, China) at λ = 457 nm. The brightness numerical value was the average value of 5 times the determination. Paper anti-UV aging testing was performed using a ZN-100N UV light resistant climate chamber (tube of UV-340). The test conditions were as follows: 25 °C, wavelength of the UV lamp was 340 nm, output power was 5.3 $mW{\cdot}cm^{-2}$, radiation for 28 h, and the distance between the samples and the lamp was 30 cm. The whiteness of the samples was determined at the set interval.

Surface sizing experiment

The PFWAs (5a through 5f) and FWA were added into deionized water at concentrations of 0.8 wt.%. The papers were coated with the solutions in a coating machine, and dried in the glazing machine. The surface strength and smoothness of papers were measured by the J-IGT350 printability tester (Sichuan Changjiang Instrument Co. Ltd., Sichuan, China) and an electronic smoothness tester (Changchun Instrument Co. Ltd., Changchun, China). According to the national standard methods GB/T 22365 (2008), GB/T 456 (2002), as well as Shi and He (2003), all of the quality indicators of the patterns were measured.

RESULTS AND DISCUSSION

Hydrophilic Properties

Figure 2 (upper part) shows the water-solubility of PFWAs and FWA and the lower portion of Fig. 2 exhibits their fluorescence property. As shown, the water-solubility of polymers was high, as indicated by clear solutions, while the aqueous solution of FWA was cloudy. Additionally, the aqueous solution on the bottom of 5a and 5e contained small amounts of insoluble solids. However, the aqueous solution of the other products was transparent without any impurities. After comparing 5a through 5f and FWA, it was found that PEG and PVA improved the water-solubility of stilbene type fluorescent whitening agent and had a positive effect. However, the aqueous solution of 5a and 5e had a small amount of precipitation present, which was due to the poorly water-soluble compound, piperidine amine. Using UV light to irradiate the aqueous solution of the products revealed that all of the aqueous solution emitted blue light. The fluorescence intensity of 5d was the strongest one and that of FWA was the weakest. The results revealed that the performance of PEG and PVA on the water solubility and fluorescence intensity of stilbene-type fluorescent whitening agent had positive effect.

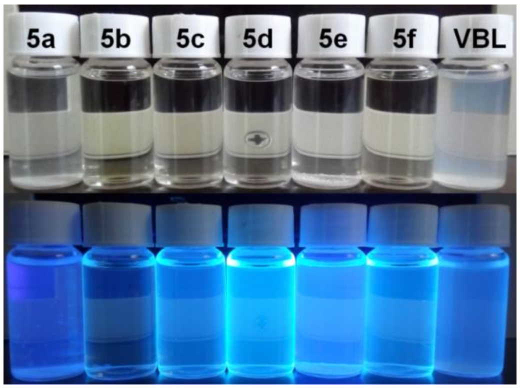


Fig. 2. Water-solubility of PFWAs and FWA

Elemental Analysis

The elemental analysis results of compounds 5a through 5f were obtained using a Vario EL III automatic analyzer, ELMENTAR, Hanau, Germany. Acetanilide (ACET) was the standard sample and the operating temperatures were 950 °C (furnace 1), 500 °C (furnace 2), and 0 °C (furnace 3). Each sample was loaded approximately 2 mg to 3 mg. The results of the elemental analysis are shown in Table 2.

Table 2. Elemental Analysis Results of PFWAs

Compounds	Elemental Analysis Calculated N of 4a-f (%)	Found N, C, H of PFWAs (%)			Degree of Substitution (%)
		N	C	H	
5a	17.67	12.74	40.82	5.871	24.28
5b	12.71	8.512	28.52	3.704	17.01
5c	17.22	10.97	33.00	4.415	19.72
5d	18.40	13.37	33.15	3.625	30.29
5e	17.67	11.45	41.10	6.029	0.7506
5f	17.22	10.16	29.83	3.825	0.6897

Table 2 clearly shows the contents of the various elements (N, C, and H) in the compounds 5a through 5f. The degree of substitution (DS) of the fluorescent monomers on polymers was obtained based on the nitrogen content of the compound using Eq. 1 (for compounds 5a through 5d) and Eq. 2 (for compounds 5e through 5f),

$$DS = \frac{1000N}{14n_N - N(M_S - 1)} \tag{1}$$

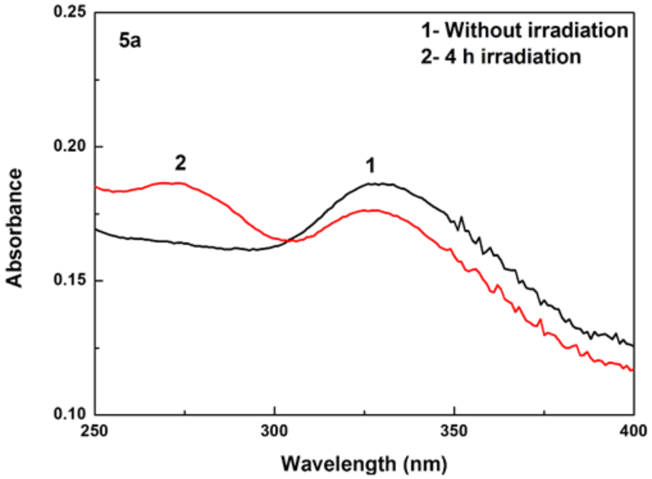
$$DS = \frac{100 M_Z N}{14 n_N - N(M_S - 1)} \qquad (2)$$

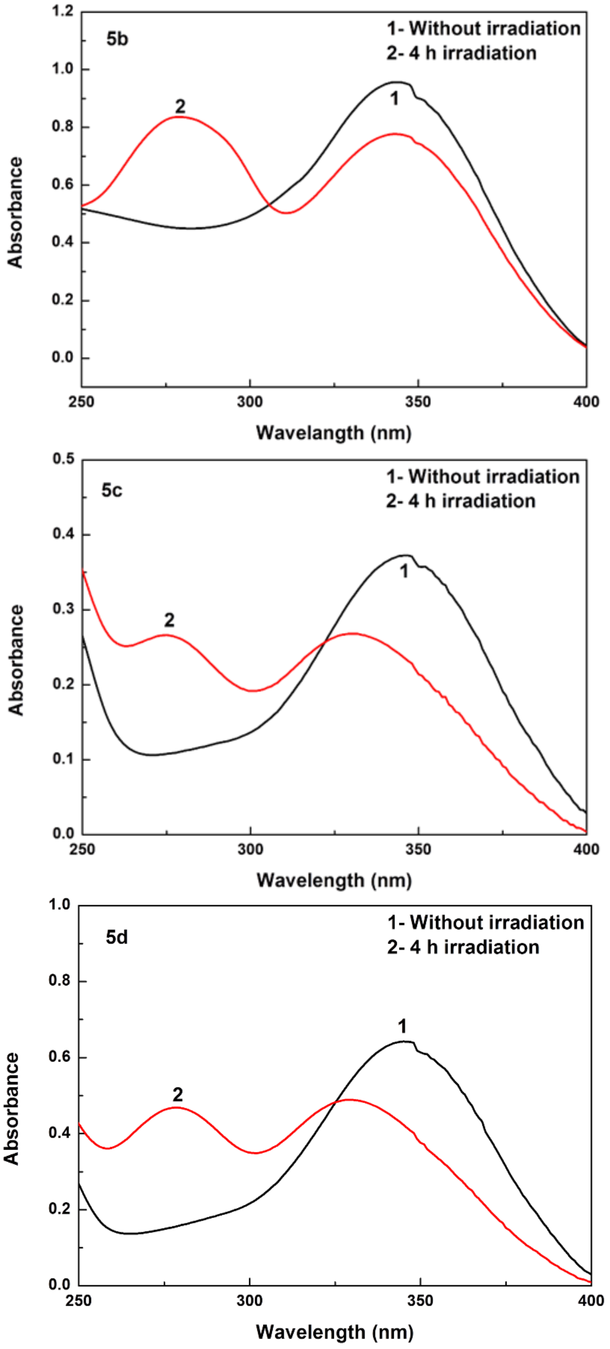
where N denotes the nitrogen content of the compound in mass fraction (%), n_N is the number of nitrogen atoms in the fluorescent monomer, M_S is the molecular weight of the fluorescent monomer (amu), M_Z in Eq. 1 denotes the molecular weight of one-half PEG molecules (M_Z = 100 amu), and M_Z in Eq. 2 is the molecular weight of constitutional unit of PVA.

The DS listed in Table 2 shows that in every 50 PEG molecules of the compounds 5a through 5d, there were 24.28, 17.01, 19.72, and 30.29 hydroxyl groups that were substituted by the fluorescent monomers, respectively. Also, per 100 PVA hydroxyl groups of the compound 5e and 5f, there were 0.7506 and 0.6897 hydroxyl groups substituted by the fluorescent monomers, respectively. This indicated that the fluorescent monomer was more likely to replace the hydroxyl group in the PEG molecule than the PVA molecule. This phenomenon may have been because the distance of the PVA hydroxyl molecules was too close, which resulted in too large of a steric hindrance, and PEG did not present this problem.

UV Spectra

The UV-vis spectra of samples 5a through 5f and FWA were obtained using a concentration of 5 × 10^{-6} g·mL^{-1} in deionized water in a quartz cell (1.0 cm). The spectra were recorded at room temperature, the scan range was from 200 nm to 600 nm and the scanning speed was 5 nm/min. The light stability and cis-trans isomerization of PFWAs and FWA was measured and analyzed by the UV-vis spectra, as shown in Fig. 3.




5b
1- Without irradiation
2- 4 h irradiation
1
2
Absorbance
0.0
0.2
0.4
0.6
0.8
1.0
1.2
250
300
350
400
Wavelangth (nm)
5c
1- Without irradiation
2- 4 h irradiation
1
2
Absorbance
0.0
0.1
0.2
0.3
0.4
0.5
250
300
350
400
Wavelength (nm)
5d
1- Without irradiation
2- 4 h irradiation
1
2
Absorbance
0.0
0.2
0.4
0.6
0.8
1.0
250
300
350
400
Wavelength (nm)

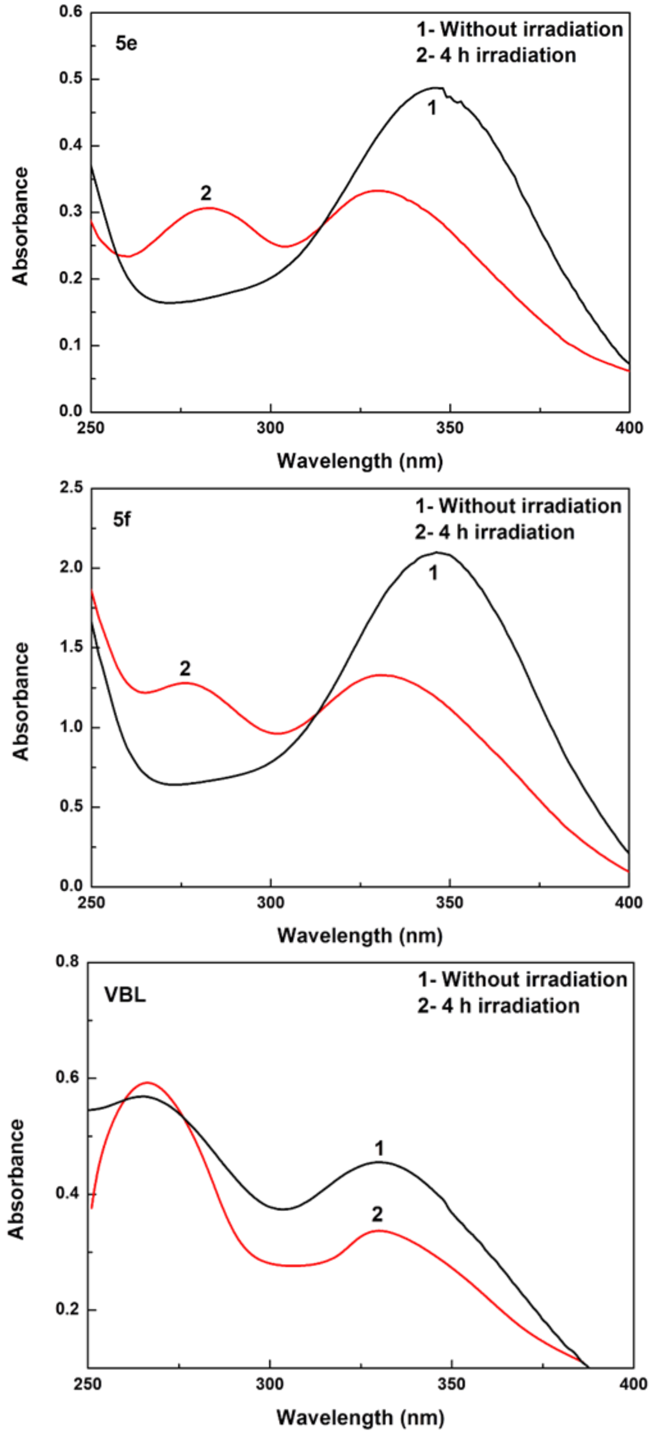


Fig. 3. UV absorption spectra of PFWAs and FWA in aqueous solution

Because the PFWAs and FWA were synthesized based on the 4,4'-diamino-stilbene-2,2'-disulfonic acid-triazine structure, their UV absorption spectra in aqueous solution were similar. Before illumination, the PFWAs only had the trans-isomers and their maximum absorption peaks were located between 328 nm and 346 nm. At the same time, FWA had both trans-isomer and cis-isomer, and the proportion of cis-isomer was larger, which affected the degree and intensity of spectral peaks compared to the trans-isomer. With illumination for 4 h, the absorption intensity of trans-isomers in PFWAs and FWA decreased, and the maximum absorption wavelength showed a blue-shift because it accepted the energy from the natural light, whereas the intensity of cis-isomers increased distinctly. This phenomenon indicated that they had undergone a cis-trans isomerization under the illumination. The absorbance and content of FWA decreased markedly in comparison with the slight decline in absorbance and trans-isomer content of PFWAs, which further indicated that PFWAs had a better light stability and inhibited the transformation from hyper-fluorescence trans-isomers to non-fluorescence cis-isomers. In addition, the concentration of trans- (C_T) and cis- (C_c) in the solution can be expressed through the following Eqs. 3 and 4, and the results are shown in Table 3,

$$C_T = \frac{[A_T(A'_C - A_C)]}{[A_T A'_C - A_C A'_T]} \times 100\% \tag{3}$$

$$C_C = 1 - C_T \tag{4}$$

where, A_T and A_c denote the absorption of the cis- and trans- isomers before light irradiation in the solution (the dimension is 1), respectively, A_T' and A_c' are the respective absorptions after irradiation (the dimension is 1), and C_C and C_T are the percent concentrations of the cis- and trans-isomers in the solution, respectively.

Table 3. Concentration of Trans-(C_t) and Cis-(C_c) in the Solution

Compounds	Before Illumination				Illumination 4 h				C_T (%)	C_C (%)
	Cis-isomers		Trans-isomers		Cis-isomers		Trans-isomers			
	λ/nm	*A*	*λ*/nm	*A*	*λ*/nm	*A*	λ/nm	*A*		
5a	-	-	327	0.1866	271	0.1862	325	0.1763	70.82	29.18
5b	-	-	343	0.9568	278	0.8356	346	0.7762	82.14	17.86
5c	-	-	346	0.3733	275	0.2649	330	0.2676	83.94	16.06
5d	-	-	345	0.6429	278	0.4652	329	0.4894	89.33	10.67
5e	-	-	345	0.4867	281	0.3047	329	0.3307	71.58	28.42
5f	-	-	346	2.0974	278	1.2747	331	1.8276	88.54	11.46
FWA	265	0.5011	332	0.4559	269	0.5905	329	0.2993	34.18	65.82

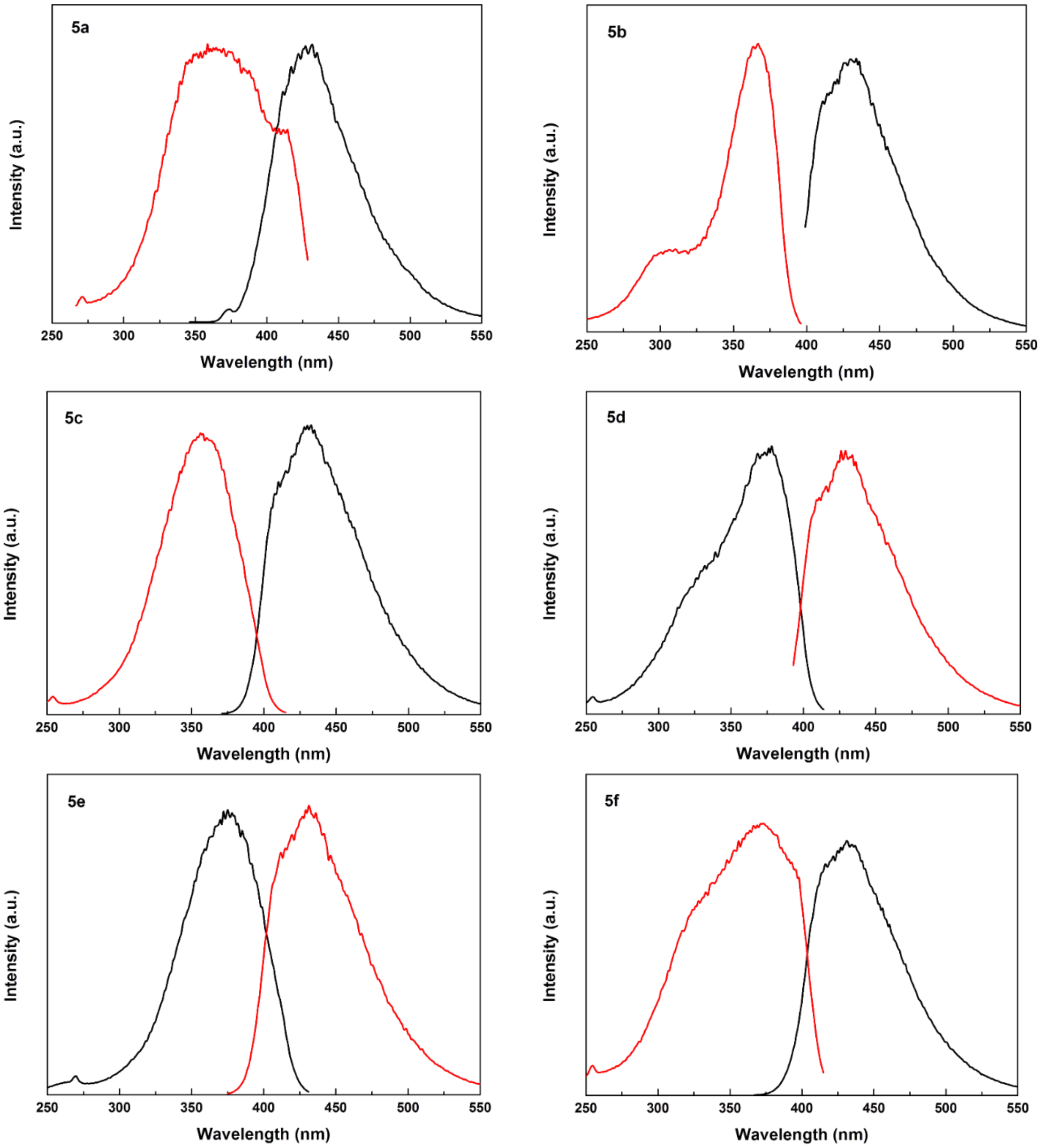
The C_T of PFWAs was much higher than the C_T of FWA in aqueous solution. This finding also implies that the PFWAs were sensitive to light. Under the illumination, the double bond of the vinyl group of FWA obtains energy from the UV light, and then the trans-isomers will transform into cis-isomers (trans (E) →cis (Z)), which resulted in non-fluorescent radiation transitions ($S_1^* \rightarrow S_0$). Therefore, the effectiveness of FWA was reduced, which led to the weakness of light stability. However, when the macromolecules of polyethylene glycol and polyvinyl alcohol were attached to the fluorescent monomer, the steric hindrance of the isomerization was greatly increased, which greatly improved the stability of the fluorescent monomer and reduced the trans-cis-type conversion. Therefore, the fluorescence intensity was remarkably improved.

Photoluminescence Behavior

The fluorescence measurement of compounds 5a through 5f and FWA was performed using a concentration of 5×10^{-6} g·mL^{-1} in deionized water in a quartz cell (size was 12.5×12.5×45 (mm). The optical length was 10 mm and the detected wavelength was 200 to 2500 nm.) at room temperature. An increment of 3 nm was used for recording all of the spectra.

Property of the fluorescence spectra and stokes shift (Δδ)

The fluorescence spectra of 5a through 5f and FWA are shown in Fig. 4. As shown in Fig. 4, 5a through f and FWA all had similar curve shapes, and the emission spectra and excitation spectra presented a good mirror relationship. The max excitation and emission wavelength of the FWA and the 5a through 5f were 356 nm/434 nm, 365 nm/427 nm, 366 nm/429 nm, 357 nm/431 nm, 378 nm/430 nm, 371 nm/432 nm, and 371 nm/431 nm (excitation/emission).



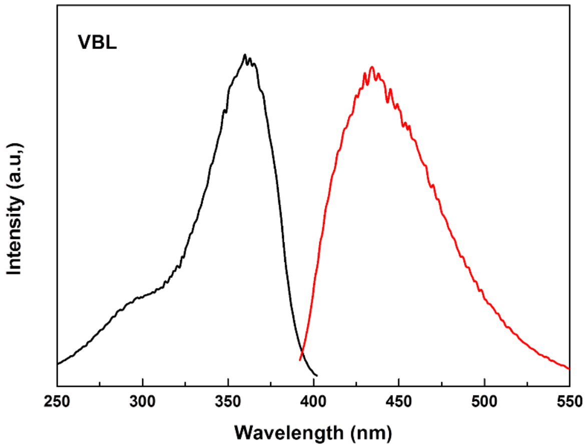


Fig. 4. Fluorescence excitation and emission spectra of PFWAs and FWA in aqueous solution

Table 4 shows the corresponding fluorescence spectral data. In the table, Δ*δ* is the Stokes shift, which means the size of the space molecule transition position during the electronic transition in the chromophore group. In addition to 5c (Δ*δ* = 4784), the Stokes shift of 5a through 5b and 5d through 5f (Δ*δ* = 4292, 3972, 3482, 3643, and 3734) were lower than that of FWA (Δδ = 4530),which illustrated that PFWAs had little change of steric configuration, and lost less energy than those of FWA in the transition process of S_0 to S_1. Δ*δ* can be calculated by Eq. 5,

$$\Delta\delta = \frac{(\lambda_F - \lambda_A)\times 10^7}{\lambda_F \lambda_A} \tag{5}$$

where, λ_A and λ_F are the maximum absorption wavelength (nm) and fluorescent emission wavelength (nm).

Table 4. Fluorescence Characteristics of PFWAS and FWA in Water Solution

Compounds	λ_A (nm)	λ_F (nm)	I_F ($\times 10^5$)	$\Delta\delta$ (cm^{-1})
5a	363	430	3.4	4292
5b	368	431	14.7	3972
5c	358	432	29	4784
5d	374	430	45	3482
5e	374	433	28.5	3643
5f	372	432	46.5	3734
FWA	362	433	41.3	4530

Influence of concentration on fluorescence property

The fluorescence intensity changes of 5c and 5f with variation of the concentration are presented in Fig. 5. For compound 5c, when the concentration increased from 1 × 10^{-6} to 1 × 10^{-5} g·mL^{-1}, the fluorescence intensity increased. If the concentration was over 5 × 10^{-5} g·mL^{-1}, the fluorescence was quenched. However, for compound 5f, the fluorescence quenching concentration was as high as 5 × 10^{-5} g·mL^{-1}. This indicated that the fluorescence monomer attached to PVA had a higher quenching concentration than the fluorescence monomer of PEG and had a wider use.

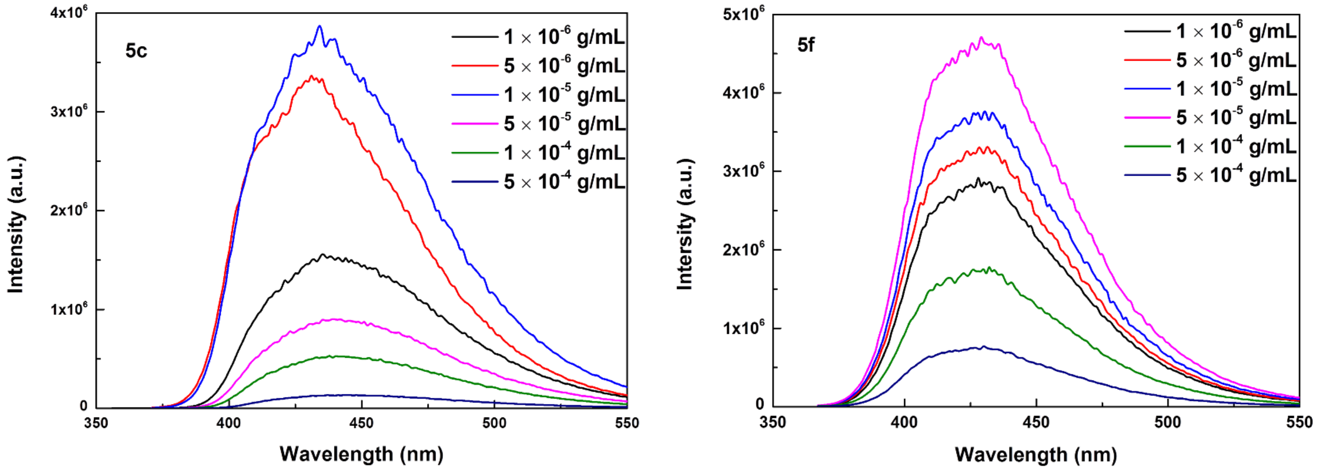


Fig. 5. Fluorescence emission spectra of 5c and 5f with different concentration

UV Accelerated Aging Test

The level of anti-UV aging of paper is usually represented by the post color number (PC), which describes the relative quantities of the chromogenic substances during the process of the UV accelerated aging test. A higher PC value indicates that more chromogenic substances are contained in the paper. The PC value was calculated using Eqs. 6 and 7,

$$PC = \left[\left(\frac{k}{s}\right)_t - \left(\frac{k}{s}\right)_o\right] \times 100 \qquad (6)$$

$$\frac{k}{s} = \frac{(1-R_\infty)^2}{2R_\infty} \qquad (7)$$

where k and $\boldsymbol{s}$ denote the UV absorbance and scattering coefficients, respectively, R_∞ represents the whiteness (ISO%) measured at 457 nm (R_{457}), and the subscripts o and t denote the initial and final UV aging, respectively.

The surface-sized paper sheets with concentration 0.8 wt.% of 5a through f, FWA, and blank paper sheet were conducted in the contrast test. During the 26-h UV accelerated aging test, the brightness of paper sheets and the PC value were measured and the results are shown in Fig. 6 and 7 (The coating weight of 5b through 5f and FWA was 0.4 g·m^{-2}).

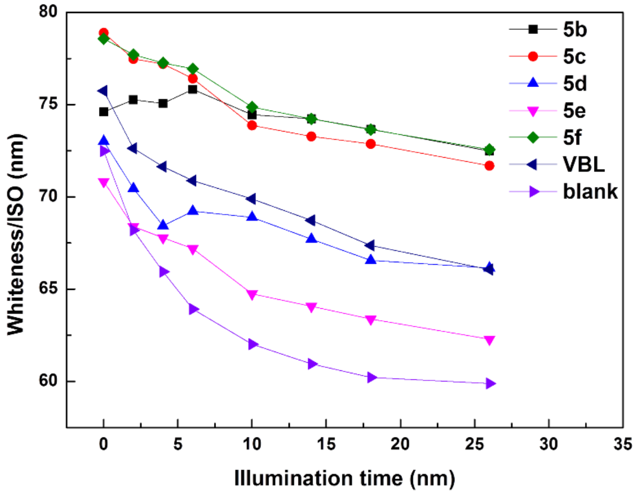


Fig. 6. The change of whiteness of paper sheets with UV irradiation time

As is shown in Fig. 6, after 26 h of the UV aging test, the brightness of all samples had a certain decline. The blank pattern whiteness decreased from 72.49 ISO% to 59.89 ISO% (about 12.6 ISO%), which demonstrated that the anti-aging effect of blank pattern is the worst. The whiteness of the FWA pattern decreased clearly among them (from 75.75 ISO% to 66.06 ISO%), which decreased 9.69 ISO%. The whiteness values of surface-sized paper sheets with 5c (78.89 ISO%) were slightly higher than those of FWA. The performance was further improved with 5b (74.61 ISO%), 5d (73.01 ISO%), and 5f (78.58 ISO%). Based on the above results, it was concluded that the performance of 5f on the whiteness of paper sheets was the best. However, the sample with 5e had the lowest initial paper sheet whiteness (70.83 ISO%), which was due to the poor solubility in water, and resulted in too low effective monomer content.

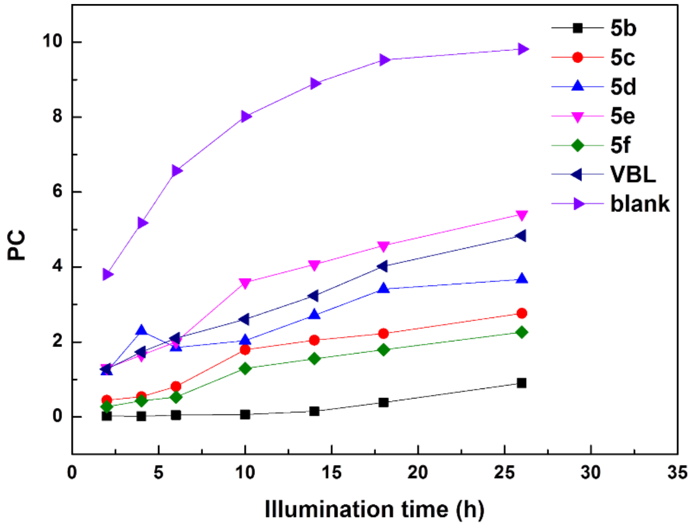


Fig. 7. The change of PC value of paper sheets with differing UV irradiation time

The PC value in Fig. 7 also indicated the same result. After the 26-h UV aging test, the PC value of the surface sized paper sheets with 0.8 wt.% FWA, 5c, and 5f was 4.837, 2.764, and 2.263, respectively. In addition, the PC value of blank paper sheet was 9.818, which proved that the introduction of polymer macromolecules improved the yellowing inhibition effect of the fluorescent monomer.

Surface-sizing Experiment

For printing paper, surface strength and smoothness are important indicators. Figures 8 and 9 show the surface-sized paper sheets with varying concentrations of PFWAs and FWA solution.

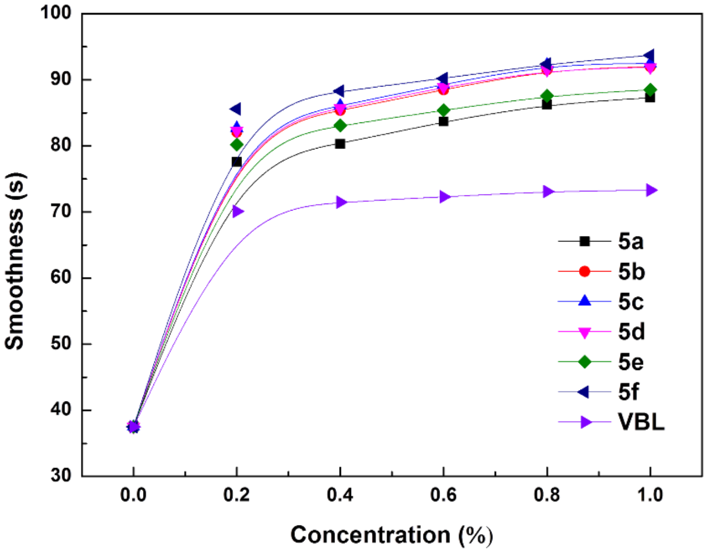


Fig. 8. The smoothness curve of surface-sized paper sheets (concentrations are 0.0 wt.%, 0.2 wt.%, 0.4 wt.%, 0.6 wt.%, 0.8 wt.%, and 1.0 wt.%, respectively)

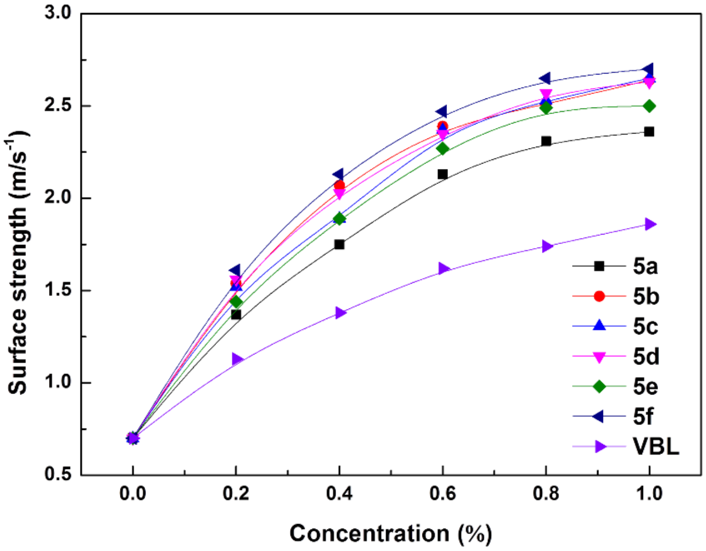


Fig. 9. Surface strength curve of surface-sized paper sheets (concentrations are 0.0 wt.%, 0.2 wt.%, 0.4 wt.%, 0.6 wt.%, 0.8 wt.%, and 1.0 wt.%, respectively)

As shown in Figs. 8 and 9, the paper-sizing PFWAs had higher surface strength and smoothness than sizing FWA, but they were all better than blank paper. Compared with blank paper sheet, whose surface strength and smoothness were 0.70 m·s^{-1} and 37.5 s, the surface strength of surface-sized paper sheets with 0.2 wt.%, 0.4 wt.%, 0.6 wt.%, 0.8 wt.%, and 1.0 wt.% of FWA solutions increased by 0.43 m·s^{-1}, 0.69 m·s^{-1}, 0.92 m·s^{-1}, 1.04 m·s^{-1}, and 1.16 m·s^{-1}, respectively. With the same concentrations of 5c and 5f solutions, they increased by 0.82 m·s^{-1}, 1.28 m·s^{-1}, 1.67 m·s^{-1}, 1.83 m·s^{-1}, and 1.95 m·s^{-1}, and 0.91 m·s^{-1}, 1.43 m·s^{-1}, 1.77 m·s^{-1}, 1.95 m·s^{-1}, and 2.0 m·s^{-1}. Therefore, with the increased concentration of PFWAs and FWA, the surface strength and smoothness of surface-sized paper sheets were raised, and those of paper sheet-sized PFWAs were better than sized FWA, which indicated that PFWAs had a better film-forming property than

FWA. Comparing 5c and 5f, it was found that the surface strength and smoothness of surface-sized 5f were higher than sized 5c, which was because PVA is a good film-forming material. All of the above indicate that PFWAs can be applied in the paper industry as a surface-sizing agent (Wang *et al.* 2014) (The coating weights of PFWAs and FWA are 0.1 $g \cdot m^{-2}$, 0.2 $g \cdot m^{-2}$, 0.3 $g \cdot m^{-2}$, 0.4 $g \cdot m^{-2}$, and 0.5 $g \cdot m^{-2}$ while the dosages of PFWAs are 0.2 wt.%, 0.4 wt.%, 0.6 wt.%, 0.8 wt.%, and 1.0 wt.%).

CONCLUSIONS

In this paper, a series of multifunctional water-soluble polymeric fluorescent whitening agents (PFWAs, 5a through 5f) based on 4,4'-diamino-stilbene-2,2'-disulfonic acid-triazine structure were successfully synthesized by a three-step synthetic route.

1. The water solubility of the fluorescent whitening agent modified with PEG and PVA was not only greatly improved, but also exhibited excellent luminescent properties.
2. According to the UV spectra and the fluorescence spectra, PFWAs showed excellent light stability. Their Stokes shift was markedly less than that of FWA, which indicated that the PFWAs had little change in steric hindrance. The UV accelerated aging test indicated that the PFWAs had a beneficial effect on the increase of the papers' initial brightness and on the yellowing inhibition, which resulted from the steric hindrance of PEG and PVA.
3. The surface-sizing experiment showed that the PFWAs were applied to enhance the surface strength and smoothness of paper, which was due to the good adhesive property and film-forming of PEG and PVA.

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