

A novel polymeric fluorescent brightener agent based on 4,4'-diamino-stilbene-2,2'-disulfonic acid-triazine structure: synthesis, characterization, photo-property, and performance on paper as light stabilizer, fluorescent brightener, and surface-sizing agent

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Abstract In this work, a novel polymeric fluorescent brightener agent based on 4,4'-diamino-stilbene-2,2'-disulfonic acid-triazine structure has been synthesized by radical polymerization. The structure of 4,4'-diamino-stilbene-2,2'-disulfonic acid -based polymeric fluorescent brightener agent was characterized by Fourier-transform-infrared spectroscopy, ¹HNMR, and gel permeation chromatography. Photo-property was measured and analyzed by the ultraviolet–vis spectra and fluorescence spectra. The performance on paper was evaluated by determining the surface strength and smoothness, the brightness degree, and the post color number value of paper. Results showed that 4,4'-diamino-stilbene-2,2'-disulfonic acid-based polymeric fluorescent brightener agent had a better light stability in water solution than that of 4,4'-diamino-stilbene-2,2'-disulfonic acid-based fluorescent monomer as light

stabilizer. Through the surface-sizing experiment and ultraviolet aging experiment, the 4,4'-diamino-stilbene-2,2'-disulfonic acid-based polymeric fluorescent brightener agent not only enhanced the surface strength and smoothness of paper as a surface-sizing agent, but also had a better effect on anti-ultraviolet aging than that of 4,4'-diamino-stilbene-2,2'-disulfonic acid-based fluorescent monomer as a light stabilizer and fluorescent brightener agent.

Keywords Fluorescent brightener agent · Polymerization · Photo-property · Photoisomerization · Surface strength

Introduction

With the limit of forest resources all over the world, high-yield pulp (HYP), containing attractive features, such as high bulk, high opacity, high stiffness, good printability et al., has been gaining increasing interests in the manufacturing of uncoated and coated fine paper and paperboards. However, the main drawback of HYP is the color reversion, since it contains much more lignin [1–4]. The special chemical structure of lignin is easily influenced by a certain external environment, for instance, temperature, light, and the presence of metal cations. Among them, the light is the main factor. When the long term exposed under the sunshine, the structure of lignin can easily generate chromophores or auxochromes, losing the brightness of paper to make it yellowing. It leads to the weakness of light stability, especially the brightness stability of HYP, which greatly hindered its application in some high-value paper. According to the research about the light-induced yellowing mechanism of HYP, different proposed yellowing inhibition methods were studied, such as chemical modification of lignin, exploring a new bleaching process of

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high-yield pulp and adding chemical auxiliaries. From the perspective of cost and effect of light stability, adding chemical auxiliaries (ultraviolet absorbers, radical scavenger, and fluorescent brighteners, et al.) is considered as the most feasible method to exhibit the yellowing of HYP.

The fluorescent brightener agents (FBAs) could be primarily applied to paper to enhance their whiteness and brightness characteristics, because it increases the ultraviolet-blocking properties by absorbing light in the near ultraviolet region and re-emitting at a longer wavelength in the blue and visible regions [4–7]. As an important class of fluorescent brightener agents, 4,4'-diamino-stilbene-2,2'-disulfonic acid (DSD), which includes great conjugated system containing double carbon bonds, is widely used for whitening paper [8–10]. However, there still exist some deficiencies. DSD-based FBAs on paper tended to have a poor light fastness resulting from the *trans-cis* photoisomerization during the irradiation, and, consequently, had negative effects on the visual quality and value of paper. In addition, the solutions of the DSD-based FBAs in water have no adhesive property and film-forming property. Therefore, the practical applications of them are limited. To overcome the shortcomings mentioned above, the synthesis of a high-performance fluorescent brightener agent has become an intriguing topic. Zhang et al. prepared many kinds of triazine–stilbene fluorescent brightener agents which include different substitutes in the triazine rings [11–16]. Konstantinova et al. prepared polymeric fluorescent brightener agent based on the DSD acid-triazine structure [17–19]. Grabachev and Konstantinova et al. prepared polymeric fluorescent brightener by fixing DSD acid-triazine monomer on the long chain of styrene or acrylonitrile [20–23]. However, the triazine–stilbene fluorescent brightener agent and the synthetic polymeric fluorescent brightener agent had poor water solubility and single function, which also restrict the practical applications of them. Therefore, the synthesis of water-soluble, multifunctional and polymeric fluorescent brightener agent remains a great challenge.

Herein, to endow DSD-based FBAs with useful properties, a novel polymeric fluorescent brightener agent based on DSD acid-triazine structure (PFBD) was synthesized by copolymerization. As a cationic monomer, DSD acid-triazine fluorescent monomer (FBD) can provide improvements in adhesion on the surface of paper on account of its positive charge and high polarity, and acrylamide (AM) plays an important role in the copolymerization as a bridge. The novel synthetic method for the preparation of PFBD makes the water-insoluble DSD acid-triazine fluorescent monomer turn into a multifunctional polymer with water-soluble and adhesive property. Results showed that PFBD not only has higher hydrophilicity, light stability and brightness than those of FBD as light stabilizer, and

fluorescent brightener agent, but also enhances the surface strength and smoothness of paper as a surface-sizing agent.

Experiment

Materials

DSD acid, allyl chloride, and cyanuric chloride as cross-linker in industrial grade were purchased from Hebei Chemical Reagent Co. Ltd, Hebei, China. Analytical grade of benzoyl peroxide (BPO) (Tianli Chemical Reagent Co. Ltd, Tianjin, China) was used as an initiator without further purification. 2-aminoethanol, 2-methoxyethanol, *N*-methylpiperazine, *N,N*-dimethylformamide (DMF), acrylic amide, acetone, toluene, anhydrous ethanol, and sodium hydroxide in analytical grade were purchased from Tianjin Chemical Reagent Co. Ltd, Tianjin, China. Poplar chemi-mechanical pulp (CMP) was purchased from Yueyang Paper Co. Ltd, Hunan, China.

Characterization

Fourier-transform-infrared (FT-IR) spectroscopy was acquired on the VECTOR-22 FT-IR spectrometer (Bruker Corporation, Germany) with KBr pellets. ¹H NMR spectra was recorded by Bruker Advance III HD 400 MHz NMR spectrometer (Bruker Corporation, Germany), DMSO-*d*₆ as a solvent, and tetramethylsilane (TMS) as an internal standard. UV spectra were measured using the Cary 100UV-Visible Spectrophotometer (Agilent, USA). Fluorescence spectra were measured on a Fluorolog spectrofluorometer (HORIBA, France). The brightness was recorded on ZB-A colorimeter (Hangzhou Zhibang Instrument Co. Ltd, China). The morphology of handsheets was observed by the S4800 Scanning Electron Microscope (SEM) images (Rigaku, Japan). The molecular weight of the PFBDs was determined by the GPC-MALLS (Wyatt Technology Corporation). The dilute solution of PFBD was made by adding PFBD (0.01 mg) into DMF (0.1 mL). After a night, the solution was filtered by semi-permeable membrane, whose aperture is 0.45 μm, and then injected the GPC-MALLS to measure. The mobile phase is DMF (HPLC grade), the flow rate is 0.5 mL/min, and the temperature is 25 °C.

Synthesis

Synthesis of FBD

Cyanuric chloride (0.0166 mol) in acetone (5 mL) was added to the mixture solution of DSD (0.0083 mol) in alkali solution (50 mL) at 0 °C; while maintaining pH at

5–6 with NaOH (10 %), the reaction mixture was stirred at 0–5 °C for 3 h. The temperature was then increased to 35–40 °C, and 2-aminoethanol (0.0166 mol) was added and stirred for 2 h at pH 7–8. The mixture solution of *N*-methylpiperazine (0.012 mol) in 2-methoxyethanol (5 mL) was added to the reaction flask. The reaction mixture was heated to 100–110 °C and stirred for 5 h while maintaining pH at 11 with NaOH (10 %). After washed and filtered with acetone, the precipitate was obtained. Under the protection of nitrogen, the solution of allyl chloride (0.006 mol) in DMF (5 mL) was added into the mixture solution of precipitate (0.003 mol) in DMF (5 mL) at 60 °C for 6 h. At the end of the reaction, the mixture was cooled to room temperature and precipitated with acetone. Then, the product was repeatedly washed with acetone, filtered, and dried in vacuum drying oven overnight at 40 °C. The FBD was obtained, and the synthetic course is shown in Fig. 1. ¹HNMR: (400 MHz, DMSO, 40 °C): 7.92 (CH=CH of DSD acid), 7.29 (ArH), 7.11 (ArH), 6.89 (ArH), 7.56 (ArH), 6.23 (CH=CH of allyl chloride), 4.3 (NH), 3.45–3.45 (H of piperazine), and 3.25 (CH₃ of quaternary ammonium salt). I.R. (KBr): 3413 cm⁻¹ (NH

stretch), 3113, 3089 cm⁻¹ (C=CH stretch), 2981 cm⁻¹ (CH₃ stretch), 2964 cm⁻¹ (CH₂ stretch), 2843 cm⁻¹ (CH stretch), 1633 cm⁻¹ (the characteristic absorption peak of quaternary ammonium salt), 1618 cm⁻¹ (C=C stretch), 1528, 1502, 1455, and 1430 cm⁻¹ (Ar stretch), 1362 cm⁻¹ (CH₃ bend), and 545 cm⁻¹ (N–C stretch).

Synthesis of PFBD

DMF (20 mL) was added into a 250 mL round-bottom flask with a stirring bar, thermometer, and a reflux condenser. Under the protection of nitrogen, the solutions of BPO (0.0004 mol) in DMF (5 mL) and FBD (0.0002 mol) in DMF (5 mL) were added simultaneously. In 30 min, the solution of FBD in DMF was added completely, while half of the solution of BPO in DMF was added into the reaction flask. Then, the solution of acrylic amide (0.141 mol) in DMF (10 mL) and the remaining solution of BPO in DMF were added dropwise into the reaction flask at 80 °C for 8–10 h. At the end of the reaction, the resulting product was dissolved in toluene and then precipitated in anhydrous ethanol. At last, the precipitate was repeatedly washed with

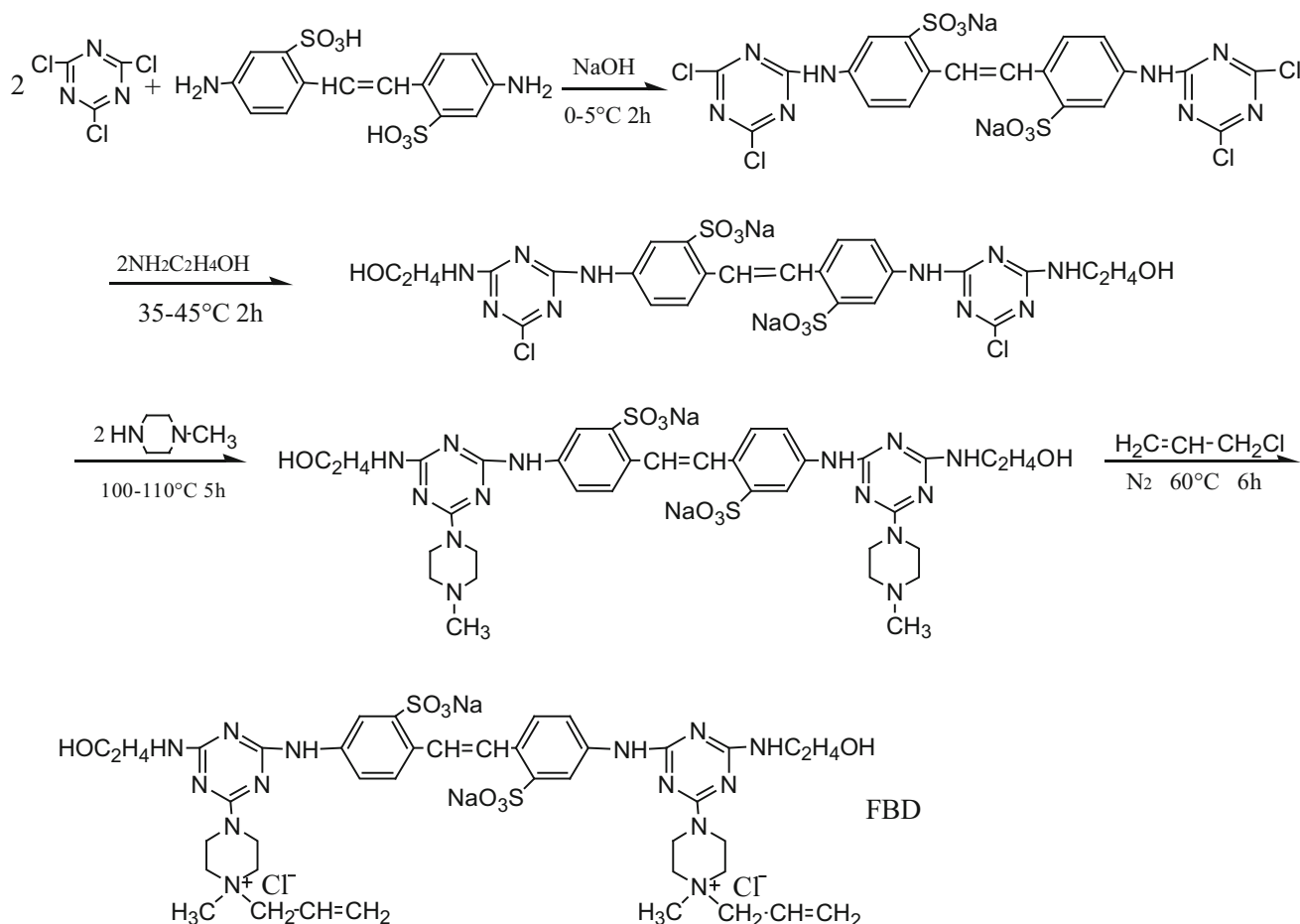


Fig. 1 Schematic diagram of synthetic route of FBD (DSD acid-triazine fluorescent monomer)

anhydrous ethanol and dried in vacuum drying oven overnight at 40 °C. The PFBD was obtained, and the synthetic course is shown in Fig. 2. ¹HNMR: (400 MHz, DMSO, 40 °C): 7.90 (CH=CH of DSD acid), 7.52–6.18 (ArH), 6.0 (H₂NC=O), 4.0 (NH), 3.5–3.47 (H of piperazine), and 1.04–2.89 (CH–CH₂ of the main chain). I.R. (KBr): 3440 and 3353 cm⁻¹ (NH₂ stretch), 3300 cm⁻¹ (NH stretch), 2981 cm⁻¹ (CH₃ stretch), 2925 cm⁻¹ (CH₂ stretch), 2853 cm⁻¹ (CH stretch), 1670 cm⁻¹ (O=C stretch), 1630 cm⁻¹ (the characteristic absorption peak of quaternary ammonium salt), 1618, 1539, 1449, and 1430 cm⁻¹ (Ar stretch), 1360 cm⁻¹ (CH₃ bend), and 542 cm⁻¹ (N–C stretch). The elemental analysis data: *W_C* % = 43.36, *W_H* % = 6.56, *W_N* % = 18.43, and *W_S* % = 0.071. The yield is 43.5 %.

Performance on paper

Preparation of the hand sheets for test

With the deionized water, the pulp was prepared to 10 % concentration (on dry pulp), and then 1 % H₂O₂, 0.05 % ethylenediaminetetraacetic acid (EDTA), and 0.5 % Na₂SiO₃·9H₂O (on dry pulp) were added to adjust pH at 9–10. After maintaining in hot water (70 °C) for 90 min, the pulp was washed to neutral with deionized water. The hand sheets (100 g m⁻²) were made with the pulp and cut into pieces (68 mm × 73 mm). The papermaking method mentioned above is based on the national standard in China [24]. In

addition, a surface-sizing agent was prepared by adding PFBD (the synthesized compounds) into the deionized water. The hand sheets were coated on the coating machine (ST-1-260, Shaanxi University of Science and Technology, China) with the sizing materials. In the opaque background, the paper samples were dried at room temperature [25, 26].

The surface-sizing experiment

PFBD were added into deionized water at concentrations 0.2, 0.4, 0.6, and 0.8 wt%. The papers were coated with the solutions in 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, China) and electronic smoothness tester (Changchun Instrument Co. Ltd, China). According to the national standard method, all the quality indicators of the patterns are measured [26].

The UV-accelerated-aging test

The brightness of the hand sheets was measured by the ZB-A colorimeter (Hangzhou Zhibang Instrument Co. Ltd, China) at R457 nm. In addition, the brightness numerical value was the average value of 5 times determination.

Paper anti-UV-aging testing was carried out using a ZN-100N UV (Xi'an Tong Sheng Instrument Manufacturing Co. Ltd, China) light resistant climate chamber (tube of UV-340). In addition, the test conditions were as follows: 25 °C,

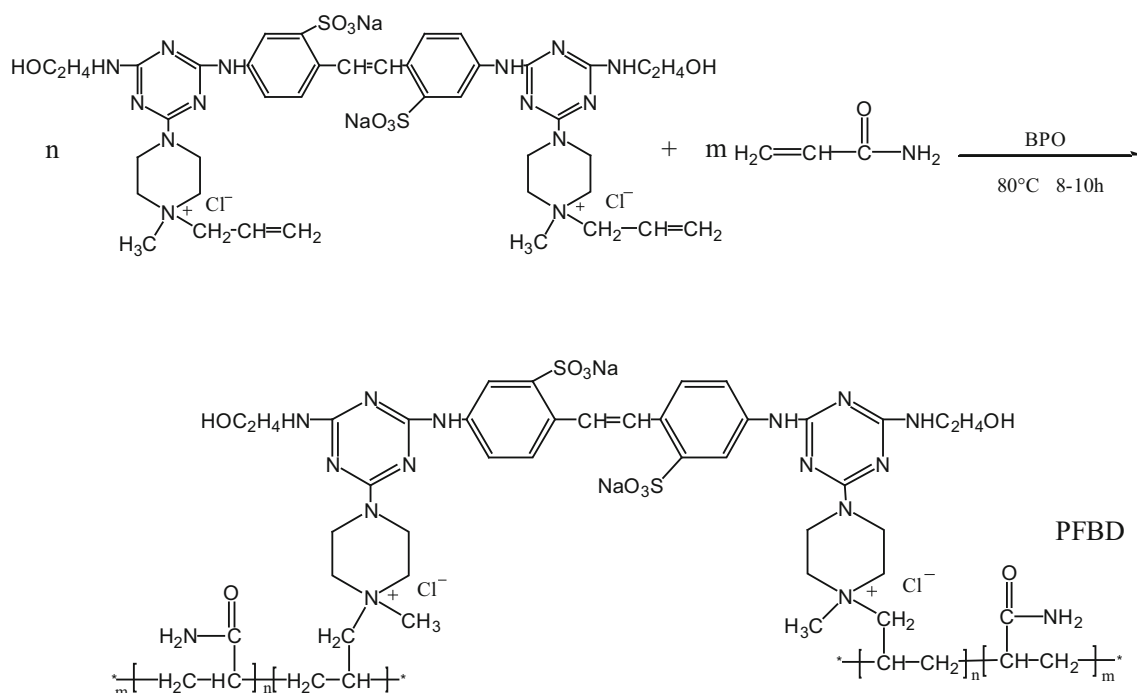


Fig. 2 Schematic diagram of synthetic route of PFBD (polymeric fluorescent brightener agent based on DSD acid-triazine structure)

wavelength of the UV lamp was 340 nm, output power was 5.3 mW cm^{-2} , radiation for 48 h, and the distance between the samples and the lamp was 30 cm. The whiteness of the samples was determined at the set interval time [27].

Results and discussion

Determination of the molecular weight of the polymer

The GPC curve of PFBD was shown in Fig. 3, the LS and DRI of which mean the light-scattering spectra and the corresponding differential spectra, respectively. The weight average molecular weight (M_w g/mol) is 5.853×10^5 , the number-average molecular weight (M_n g/mol) is 4.580×10^5 , and the molecular weight distribution index (M_w/M_n) is 1.278. A single peak indicates that there is little impurity in PFBD and the molecular weight distribution index is small, which proves that the size of PFBD distributed uniformly. The average molecular weight of synthetic PFBD is about 387,000.

The analysis of photo-property

Property of the UV absorption and fluorescence emission

The property of the UV absorption and fluorescence emission of FBD and PFBD in aqueous and ethanol solution, containing the maximum absorption wavelength (λ_A), fluorescent emission wavelength (λ_F), the Stokes' shift ($\Delta\sigma$), fluorescence quantum yield (Φ_F), and fluorescence energy yield (E_F), was shown in Tables 1 and 2. In addition, the absorption and fluorescence spectra of them were illustrated in Fig. 4.

As shown in Fig. 4, the FBD and PFBD have similar curve shapes, and the absorption spectra and the

fluorescence spectra present a good mirror relationship. As the existence of double bond of vinyl group, both FBD and PFBD have *cis* isomer and *trans* isomer. The *trans* isomer owns the fluorescence property, while the *cis* isomer does not have it, since the coplanarity of it is destroyed, which would not emit fluorescent. Therefore, *trans* isomer is the fluorescence active component. In addition, the fluorescence active component occupies a small proportion in the structure of PFBC, so the UV absorption and fluorescence intensity of PFBC is lower than that of FBC.

In aqueous solution, FBD and PFBD only exist *trans* isomer, and the maximum absorption wavelength (λ_A) and fluorescent emission wavelength (λ_F) of them are, respectively, 375, 366, 448, and 446 nm, as shown in Table 1. Compared with FBD, λ_A and λ_F of PFBD were blue-shifted 9 and 2 nm, which because the fluorophore was firmly fixed on the macromolecular chain via covalent bond by polymerization, making reduce of deactivation in transition process, and stability was improved significantly. In ethanol solution, FBD and PFBD have similar property, as shown in Table 2.

The fluorescence energy yield (E_F), fluorescence quantum yield (Φ_F), and Stokes' shift ($\Delta\sigma$)

Fluorescence energy yield (E_F) was used to represent the property of fluorescence absorption and emission, as calculated in Eq (1) [28]. The bigger the value of E_F is, the lower the energy losses in the electron transition process are. Fluorescence quantum yield (Φ_F) could directly reflect the whitening ability of FBAs, by comparing with fluorescence spectra of quinine sulfate ($\Phi_0 = 0.55$), as calculated in Eq (2) [29]. As shown in Table 1, the values of Φ_F and E_F of PFBD are 0.382 and 0.309, respectively, which is higher than those of FBD, indicating that the ability of fluorescence emission of PFBD is better than that of FBD.

The Stokes' shift ($\Delta\sigma$) indicates the difference in the properties and structure of the fluorophores between the ground state S_0 and the first excited state S_1 , as calculated in Eq (3). The Stokes' shift of PFBD ($\Delta\sigma = 5279.3$) is lower than that of FBD ($\Delta\sigma = 5927.2$), illustrating that PFBD has a little change of steric hindrance, losses lower energy than those of FBC in the transition process of S_0 to S_1 , as shown in Table 1 [30, 31]:

$$E_F = \frac{\lambda_A}{\lambda_F} \times \Phi_F \quad (1)$$

$$\Phi_F = \Phi_0 \times \frac{S_1 \times A_0 \times n_1^2}{S_0 \times A_1 \times n_0^2} \quad (2)$$

$$\Delta\sigma = \left(\frac{1}{\lambda_A} - \frac{1}{\lambda_F} \right) \times 10^7 \quad (3)$$

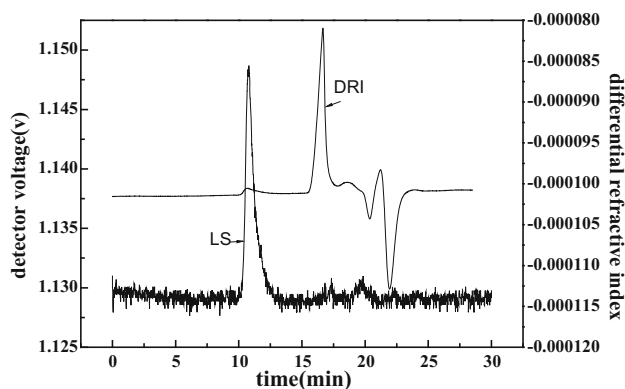


Fig. 3 GPC curve of PFBD (polymeric fluorescent brightener agent based on DSD acid-triazine structure). LS the light-scattering spectra, DRI the corresponding differential spectra

Table 1 Characteristics of *cis* and *trans* isomers of FBD and PFBD in aqueous solution

	<i>Cis</i> isomers, λ_A (nm)	<i>Trans</i> isomers, λ_A (nm)	λ_F (nm)	$\Delta\sigma$ (cm ⁻¹)	Φ_F	E_F
FBD	–	375	448	5927.2	0.226	0.179
PFBD	–	366	446	5279.3	0.382	0.309

FBD: DSD acid-triazine fluorescent monomer, PFBD polymeric fluorescent brightener agent based on DSD acid-triazine structure

Table 2 Characteristics of *cis* and *trans* isomers of FBD and PFBD in ethanol solution

	<i>Cis</i> isomers λ_A (nm)	<i>Trans</i> isomers λ_A (nm)	λ_F (nm)	$\Delta\sigma$ (cm ⁻¹)	Φ_F	E_F
FBD	–	353	432	5020.9	0.261	0.215
PFBD	–	373	443	4823.9	0.471	0.388

FBD: DSD acid-triazine fluorescent monomer, PFBD polymeric fluorescent brightener agent based on DSD acid-triazine structure

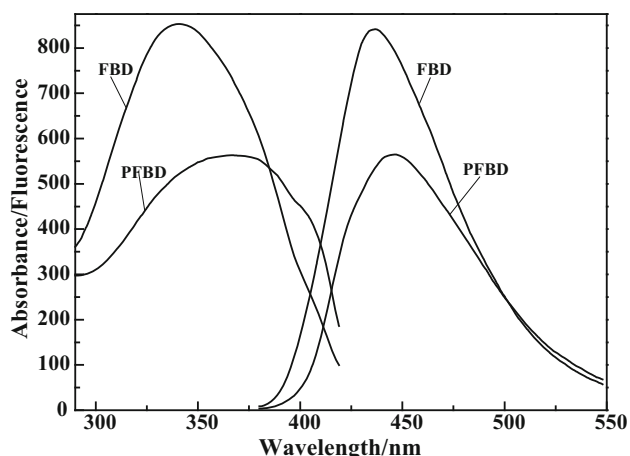


Fig. 4 Absorption and fluorescence spectra of FBD (DSD acid-triazine fluorescent monomer) and PFBD (polymeric fluorescent brightener agent based on DSD acid-triazine structure) in aqueous solution

where λ_A and λ_F are the maximum absorption wavelength and fluorescent emission wavelength, respectively; Φ_F and Φ_0 are the fluorescence quantum yield of substance to be examined and certified reference material; S_1 and S_0 are the fluorescence integral area of substance to be examined and certified reference material; A_1 and A_0 are the absorbance of substance to be examined and certified reference material; and n_1 and n_0 are the refractive index of substance to be examined and certified reference material in aqueous solution; The certified reference material is quinine sulfate.

Light stability and cis–trans isomerization

Before illumination, both FBD and PFBD only had *trans* isomers in aqueous and ethanol solution, as shown in Figs. 5 and 6, and Tables 1 and 2. With illumination for 3 h, the maximum absorbance of *trans* isomers of FBD and

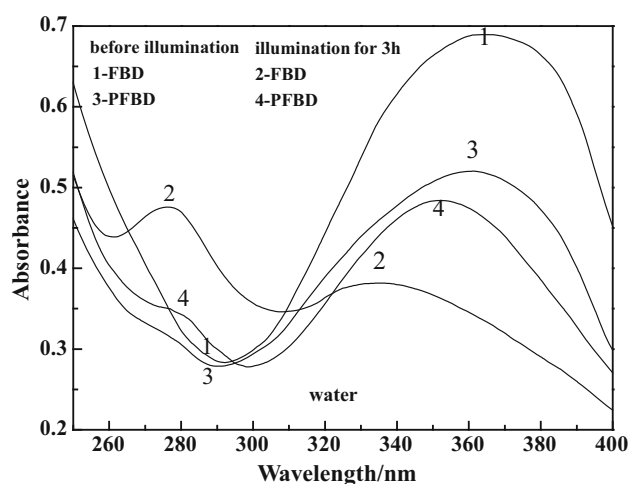


Fig. 5 UV absorption spectra of FBD (DSD acid-triazine fluorescent monomer) and PFBD (polymeric fluorescent brightener agent based on DSD acid-triazine structure) in aqueous solution

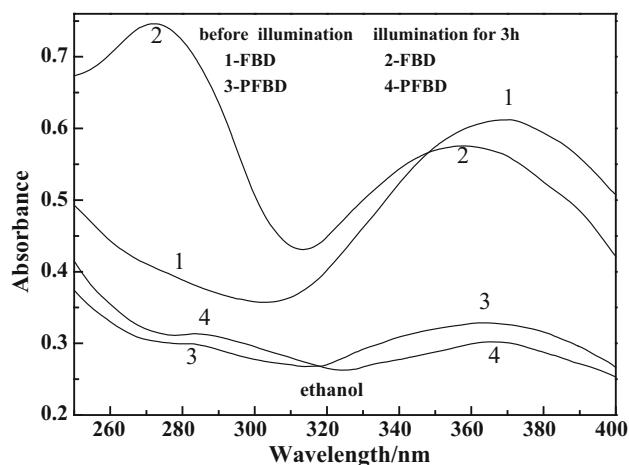


Fig. 6 UV absorption spectra of FBD (DSD acid-triazine fluorescent monomer) and PFBD (polymeric fluorescent brightener agent based on DSD acid-triazine structure) in ethanol solution

Table 3 Concentration of *trans* and *cis* forms of FBD and PFBD for illumination 3 h

	Water (%)		Ethanol (%)	
	C_T	C_C	C_T	C_C
FBD	43.4	56.6	69.7	30.3
PFBD	63.8	36.2	85.6	14.4

FBD: DSD acid-triazine fluorescent monomer, PFBD polymeric fluorescent brightener agent based on DSD acid-triazine structure

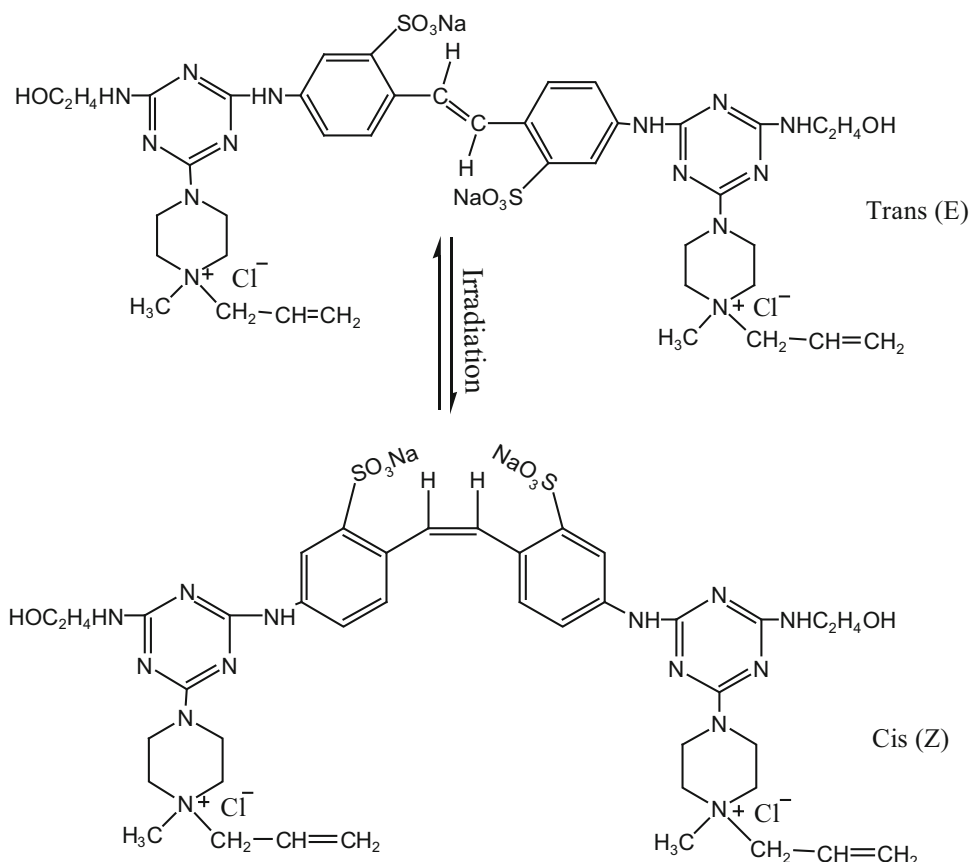
PFBD decreased and the maximum absorption wavelength has blue-shift. While the maximum absorbance of *cis* isomers of them increase and the maximum absorption wavelength had red shift. Compared with slight decline of absorbance and content of *trans* isomer of PFBD, the absorbance and content of FBD decreased seriously, which further indicate that PFBD had a better light stability, inhibiting the transformation from hyper-fluorescence *trans* isomers to non-fluorescence *cis* isomers. In addition, the concentration of *cis* isomers (C_C) and *trans* isomers (C_T) was shown in Table 3 [32].

C_T of PFBD is much higher than C_C of PFBD in aqueous and ethanol solution. In aqueous solution, C_C of FBD is slight higher than C_T of FBD, while C_T of FBD is dominant in ethanol solution. It also illustrate that the FBD is the light

sensitive material. Under the illumination, the double bond of vinyl group of FBD occurs rotation, and easily appears conformation transition from *trans* isomers to *cis* isomer [*trans* (*E*) → *cis* (*Z*)], resulting in non-fluorescent radiation transitions ($S_1^* \rightarrow S_0$). Therefore, the effectiveness of FBD reduces, leading to the weakness of light stability. The photochemical process of FBs molecular isomerization is shown in Fig. 7. However, the active fluorescent compound of PFBD is firmly fixed on the macromolecular chain via chemical bond, making the structure more stable, so the photoinduced isomerization was well inhibited.

Effect of solvent polarity on fluorescence properties

As shown in Tables 1 and 2, the polarity of the solvent directly influences the physical and chemical properties of the fluorescent substance [33]. With the decrease of solvent polarity, Φ_F and E_F increase greatly, but the $\Delta\sigma$ declines. Besides, the absorption and fluorescence wavelength is also affected by the polarity of the solvent. In aqueous and ethanol solutions, the maximum absorption and fluorescence wavelength of PFBC are, respectively, 366, 446, 373, and 443 nm. Compared with PFBC in aqueous solution, the maximum absorption wavelength has 7 nm red shift, and the maximum fluorescence wavelength has 3 nm blue shift.

Fig. 7 Photochemical process of FBs (fluorescent brighteners) molecular isomerization

The SEM images of paper sheet treated with PFBD

The SEM images (Fig. 8) demonstrate a representative overview of blank paper sheet (the paper coated with the aqueous solution of FBD) and paper sheet treated with PFBD. As revealed in Fig. 8, the fiber of blank paper sheet combines more loosely, leading to a lower smoothness of the paper. When adding the 0.8 wt% PFBD solution on the paper sheet, the surface of paper sheet was covered a layer of film formed by PFBC solution. Therefore, the fiber of the paper sheet treated with PFBD combines more closely, and the smoothness of paper becomes better (the coating weights of PFBD are 0.4 g m⁻², while the dosages of PFBD are 0.8 wt%).

The surface strength and smoothness of paper sheets treated with PFBD

The surface strength and smoothness are important indicators for the print paper. As shown in Figs. 9 and 10, the paper sheets treated with different concentrations of PFBD have a better surface strength and smoothness than those of the blank paper. Compared with blank paper sheet, whose surface strength and smoothness are 0.69 m s⁻¹ and 37.6 s, the surface strength of paper sheets treated with 0.2, 0.4, 0.6, and 0.8 wt% of PFBD, respectively, increase by 0.76,

1.15, 1.51, and 1.84 m s⁻¹. Meanwhile, the smoothness of surface-sized paper sheets, respectively, boosts by 45.5, 50.9, 54.1, and 56.7 s. Therefore, with the increase concentration of PFBD, the surface strength and smoothness of paper sheets are heightened, which indicates that PFBD has good film-forming property, which can be applied in the paper industry as a surface-sizing agent [34, 35] (the coating weights of PFBD are 0.1, 0.2, 0.3, and 0.4 g m⁻², while the dosages of PFBD are 0.2, 0.4, 0.6, and 0.8 wt%).

Changes of brightness of surface-sized paper sheets with UV-aging time

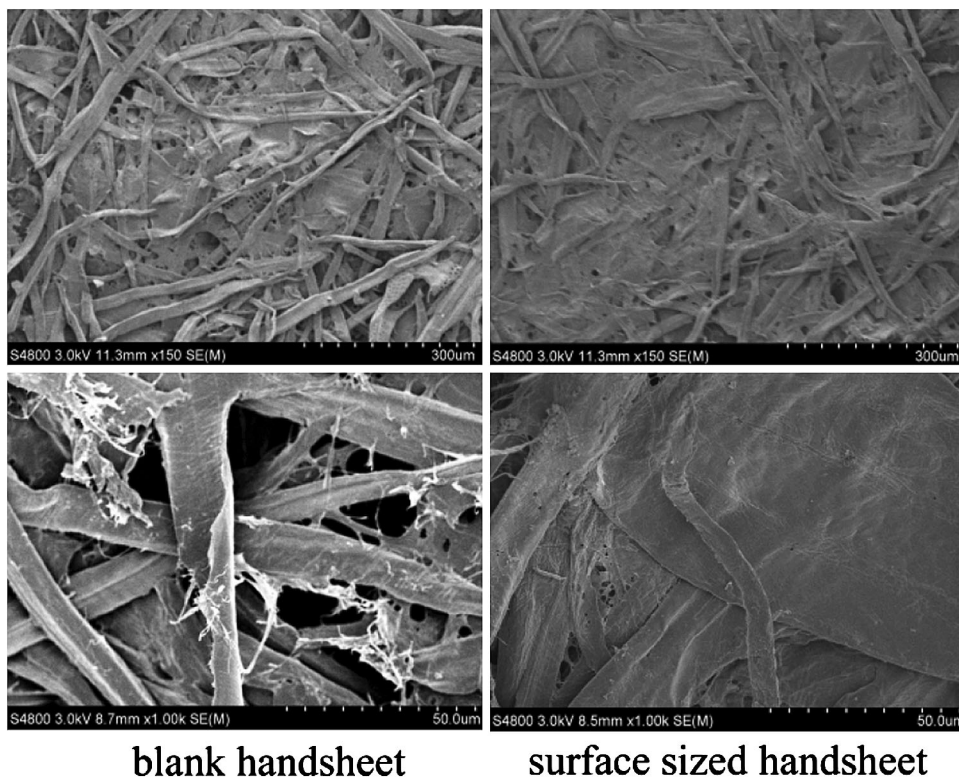
The post color number (PC) is usually used to represent the level of anti-UV-aging of paper, which can reflect the relative quantities of the chromogenic substances during the process of the UV-accelerated-aging test. The PC value was calculated using the following Kubelka–Munk formulas (4) and (5):

$$PC = \left[\left(\frac{k}{s} \right)_t - \left(\frac{k}{s} \right)_o \right] \times 100 \tag{4}$$

$$\frac{k}{s} = \frac{(1 - R_\infty)^2}{2R_\infty} \tag{5}$$

where *k* and *s* denote the light absorption and scattering coefficients, respectively; *R*_∞ represents the whiteness

Fig. 8 Scanning electron microscope (SEM) images of surfaces of paper sheet and surface-sized paper sheet. Scale bars: S4800 3.0 kV 8.5 mm × 1.00 k SE (M)



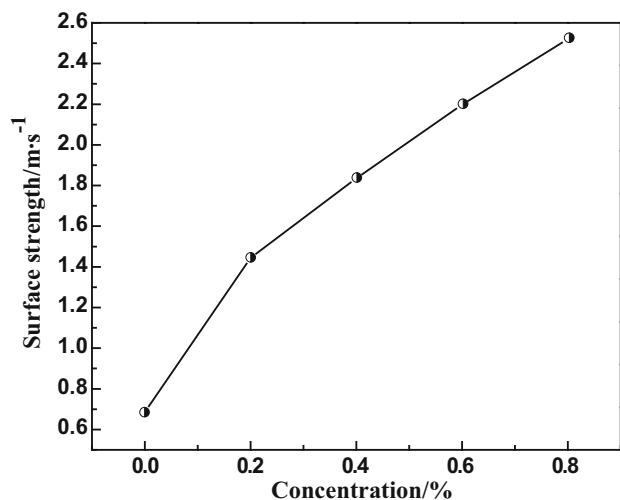


Fig. 9 Surface strength curve of surface-sized paper sheets (concentrations are 0, 0.2, 0.4, 0.6, 0.8 wt%, respectively)

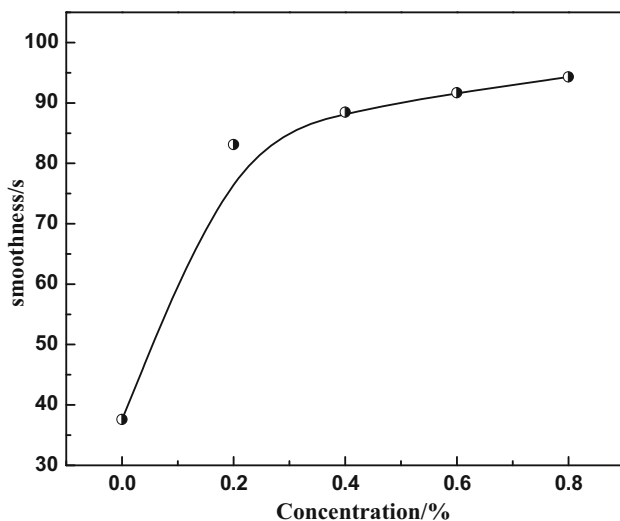


Fig. 10 Smoothness curve of surface-sized paper sheets (concentrations are 0, 0.2, 0.4, 0.6, and 0.8 wt%, respectively)

measured in R457; and the subscripts *o* and *t* denote the initial and final UV agings, respectively.

The surface-sized paper sheets with 0.8 wt% FBC and PFBC were conducted in the contrast test, among which 0.8 wt% FBC was obtained by adding FBC into the gelatinized starch solution, increasing the viscosity of FBC, and 0.8 wt% PFBC is the aqueous solution of PFBD, deriving from the good hydrophilicity and viscosity of it. During the 48 h UV-accelerated-aging test, the brightness of paper sheets and the PC value were measured, and the results were shown in Figs. 11 and 12 (the coating weight of FBD and PFBD is 0.4 g m^{-2} , while the dosage of the products is 0.8 wt%).

After 48 h UV-aging test, the brightness of the blank paper sheet and the surface-sized paper sheets with FBD

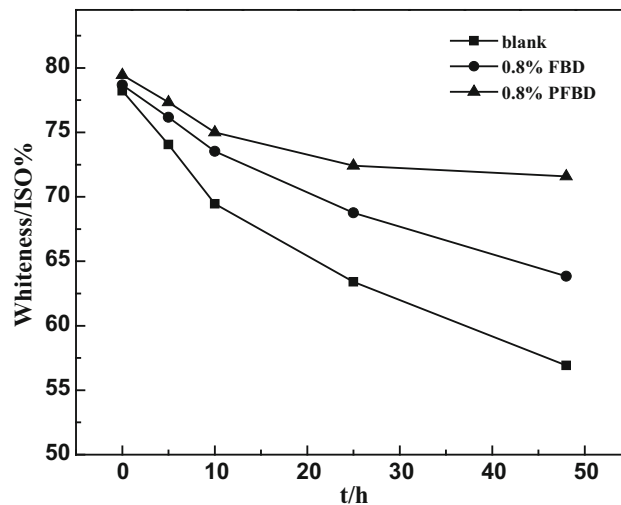


Fig. 11 Change of brightness of paper sheets with UV (ultraviolet) irradiation time

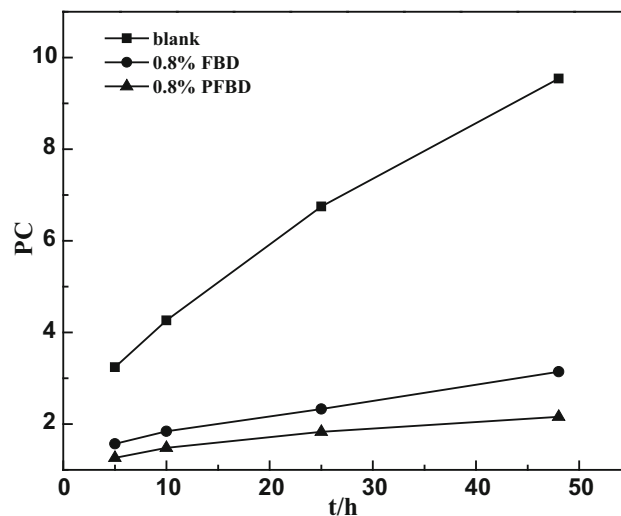


Fig. 12 Change of PC (the post color number) value of paper sheets with irradiation time

and PFBD are, respectively, 56.91 ISO %, 67.84 ISO %, and 71.58 ISO %, and the brightness of paper sheets, respectively, decreases by 21.32 ISO %, 10.85 ISO %, and 7.87 ISO % compared with those of the initial brightness. In addition, the PC value of the blank paper sheet and the surface-sized paper sheets with by FBD and PFBD are, respectively, 9.84, 3.06, and 2.66. Obviously, the paper containing PFBD showed a better effect on the anti-UV aging than that of FBD, which may be due to a better water solubility the PFBD is, and good film-forming property the PFBD owns. PFBD has good water solubility with positive charge, which could enhance the combination with paper fiber. Besides, PFBD solution with cohesiveness could form a layer of thin film when it is coated on the surface of

paper sheet. Therefore, the PFBD has a positive impact on the anti-UV aging as fluorescent brightener.

Conclusion

A novel polymeric fluorescent brightener agent based on DSD acid-triazine structure from radical polymerization has been successfully prepared and characterized for physicochemical properties. The structure of PFBD was confirmed by the FT-IR, ¹HNMR, and GPC. According to the UV and fluorescent spectra, PFBD not only has good stability in water, but also exhibits excellent luminescent properties. The Stokes' shift of it is less than that of FBD, which indicates that PFBD as a light stabilizer has a little change of steric hindrance, losses lower energy, and owns a better photostability than those of FBD. The surface-sizing experiment indicates that PFBD can be applied to enhance the surface strength and smoothness of paper as a kind of a surface-sizing agent, which is due to its good film-forming property. In addition, the UV-aging experiment further proves that PFBD has a better effect on the anti-UV aging as a fluorescent brightener agent.

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