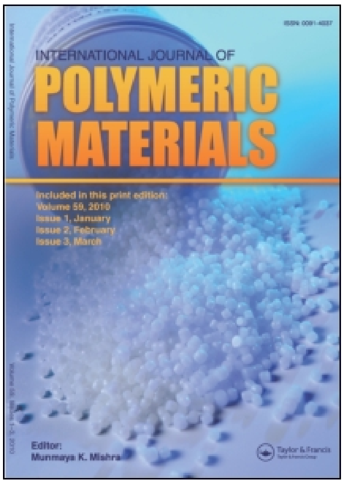

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

The Synthesis and Study on Optical Characteristics of the Asymmetrical Polymerizable Fluorescent Brighteners

Jing Liu[a][b]; Guang-hua Zhang[a]
[a] Key Laboratory of Auxiliary Chemist & Technology for Chemical Industry, Ministry of Education, Shaanxi University of Science & Technology, Xi'an Shaanxi, P. R. China [b] College of Chemistry and Engineering, Xianyang Normal University, Xianyang Shaanxi, P. R. China

To cite this Article Liu, Jing and Zhang, Guang-hua(2011) 'The Synthesis and Study on Optical Characteristics of the Asymmetrical Polymerizable Fluorescent Brighteners', International Journal of Polymeric Materials, 60: 2, 199 — 211
To link to this Article: DOI: 10.1080/00914037.2010.504170
URL: http://dx.doi.org/10.1080/00914037.2010.504170

International Journal of Polymeric Materials, 60:199–211, 2011
Copyright © Shanghai University of Science and Technology
ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914037.2010.504170

The Synthesis and Study on Optical Characteristics of the Asymmetrical Polymerizable Fluorescent Brighteners

Jing Liu[1,2] and Guang-hua Zhang[1]

[1]Key Laboratory of Auxiliary Chemist & Technology for Chemical Industry,
Ministry of Education, Shaanxi University of Science & Technology,
Xi'an Shaanxi, P. R. China
[2]College of Chemistry and Engineering, Xianyang Normal University, Xianyang
Shaanxi, P. R. China

A novel type of asymmetrical polymerizable fluorescent brighteners was synthesized using 4-nitro-4-aminostilbene-2,2′-disulfonic acid (ANSD) and cyanuric chloride as raw materials, through reduction reaction of sodium hydrosulfide and condensation reaction of variant amine compounds replacing the chlorine of triazine rings, containing another dibasic triazine compound grafted polyaminamide. The ultraviolet absorption and fluorescence emission properties, photoinduced isomerization phenomena and application properties of the asymmetrical polymerizable fluorescent brighteners, asymmetrical and symmetrical fluorescent brighteners in aqueous solutions, tetrahydrofuran(THF) N,N-dimethyl formamide (DMF) were particularly investigated. The fluorescence quantum yield was determined using quinine sulfate in 0.5 mol/l $H_2SO_4(\Phi_F = 0.55)$ as the fluorescence standard. The effect of concentration and polarity of solvents on fluorescence properties was observed. Results show that the ultraviolet absorption and dyeing properties as well as light stability of the prepared asymmetrical polymerizable fluorescent brighteners increased obviously compared with asymmetrical and symmetrical FBs with the phenomena of photoinduced isomerization decreasing. It was found that the polarity of the solvents influences the quantum yield of

---

Received 26 March 2010; accepted 2 June 2010.
This work was supported by the Natural Science Foundation of Shaanxi Province (2009JM2010) and the Shaanxi Educational Committee (09JK801), as well as the Ministry of Education open fund, item (ZK200801).

Address correspondence to Jing Liu, Key Laboratory of Auxiliary Chemist & Technology for Chemical Industry, Ministry of Education, Shaanxi University of Science & Technology, Xi'an Shaanxi, P. R. China. E-mail: liujing163@163.com

fluorescence and has only a small effect upon the positions of the absorption and fluorescence maxima of FBs. Meanwhile, concentration of trans- and cis-isomers depends on the nature of the substituents.

Keywords asymmetrical, fluorescence quantum yield, photoinduced isomerization, polyaminamide, polymerizable fluorescent brighteners, symmetrical

INTRODUCTION

Triazine-aminostilbene fluorescent brighteners (referred to as FBs) are an important class of structurally complex, colorless, fluorescent dyes. They can absorb light in the near ultraviolet region of the spectrum (about 330–380 nm) and re-emission of the visible region of the spectrum (about 400–450 nm) as violet-blue fluorescence under sunlight. When fluorescent brighteners are applied, the violet-blue fluorescence complements the yellowness and adds a bluish hue to the materials, and increases the intensity of the reflected light, which increases the whiteness and brightness notably [1]. Thus, they can be widely used in the paper manufacture, textile, paint and detergent and so on [2].

However, these FBs have low photoresistance and poor water-solubility in solution. If the concentration is too high, the fluorescence should quench when fluorescence quantum yields decrease [3], thereby reducing the whitening effect. In particular, special attention has been paid to the preparation and properties of asymmetrical fluorescent brighteners at home and abroad [4], so as to play a synergistic role in enhancing the whitening effect of fiber and water-soluble properties by attempting to increase the type of substituents on the triazine ring and making use of the mutual reinforcing adduct of their different photochemical and photophysical properties. Cao [5] synthesized two new style asymmetrical FBs through four-step condensation reactions of cyanuric chloride with two amino compounds, replacing 4,4′-aminostilbene-2,2′-disulfonic acid with 4-nitro-4′-aminostilbene-2,2′-disulfonic acid. Joon-Kyun Lee synthesized nine asymmetrical fluorescent brighteners with the same method [6]. It was found that, compared with symmetrical FBs, the ultraviolet absorption and dyeing properties of asymmetrical FBs increased, but the fluorescence emission performance was lower. The asymmetrical FBs had obvious photoinduced isomerization phenomena and poor light stability, simultaneously. In this sense the asymmetrical polymeric fluorescent brightener has turned out to be photostabile fluorophores of very high potential. In this article, we make use of 4-nitro-4′-aminostilbene-2,2′-disulfonic acid (ANSD acid) and cyanuric chloride as main raw materials, variant amine compounds as substituents. After condensation stepwise reaction of the replacement of chlorine of triazine rings and the 4-nitro group fluorescent compound being reduced to an amino-group by using sodium bisulfide as a reductant, new style symmetrical and asymmetrical FBs were synthesized containing asymmetrical PFBs through chlorine of reductive 4-amino-group fluorescent compound condensation reaction with polyaminamide. Their basic photophysical characteristics and photochemical trans–cis photoisomerization as well as paper-coating applications were presented.

EXPERIMENTAL

Materials

All chemicals such as cyanuric chloride (CC), 4-nitro-4′-aminostilbene-2, 2′-disulfonic acid (ANSD), ethylenediamine, diethanolamine, diethylene triamine, and so on, were used as purchased from commercial sources from Xi'an, and were of industrial or analytical grade and used without further purification.

Synthesis of Asymmetrical Fluorescent Brighteners

In a flask equipped with a stirrer, 8.3 mmol of 2,4,6-trichloro-1,3,5-triazine (CC,1) dispersed in 20 ml acetone solution was reacted with 8.3 mmol of p-aminobenzene sulfonic acid (2) at 0–5°C for 2 h, maintaining pH 5–6 by the addition of 10% aqueous sodium hydroxide, the single substitution product (2) was obtained. Then 8.3 mmol of 4-nitro-4′-aminostilbene-2,2′-disulfonic acid (ANSD) was added dropwise at 45–50°C, pH 6–7 and stirring continued for a further 3 h. After this second condensation stage, the temperature was increased to 100–110°C for 5 h, and 12.5 mmol of diethanolamine was added at pH 8.0. The temperature was down and maintained at 90–95°C for 3 h, 1.5 times of sodium bisulfide was added at pH 9.0–9.5 without separation, 4′-nitro group of compounds (5) being reduced to amino group afford disodium 4′-amino-4-(2-p-aminobenzene sulfonic acid-4-diethanolamine-1,3,5-triazin-6-yl) aminostilbene-2,2′-disulfonic acid (6). After cooling to ambient temperature, the reduction production was isolated by the addition of sodium chloride; the precipitated product was filtered, washed with acetone and dried under vacuum at 40°C [7].

Reduction production (6) was dissolved in 20 ml acetone and to the solution was added solution of 8.3 mmol the single substitution product (3) at 50–60°C. After stirring for 3 h, while maintaining pH 6, the liquid was heated to 90–95°C, 12.5 mmol amine derivative (RH) was added separately and the mixture was stirred for 3 h at pH 8. After cooling to ambient temperature, disodium 4′-(2-p-aminobenzene sulfonic acid-4-substituted-1,3,5-triazin-6-yl)amino-4-(2-p-aminobenzene sulfonic acid-4-diethanolamine-1,3,5-triazin-6-yl)-2,2′-disulfonate (FBs1–FBs3) were isolated by the addition of sodium chloride; the precipitated product was filtered and washed with absolute ethanol, frozen

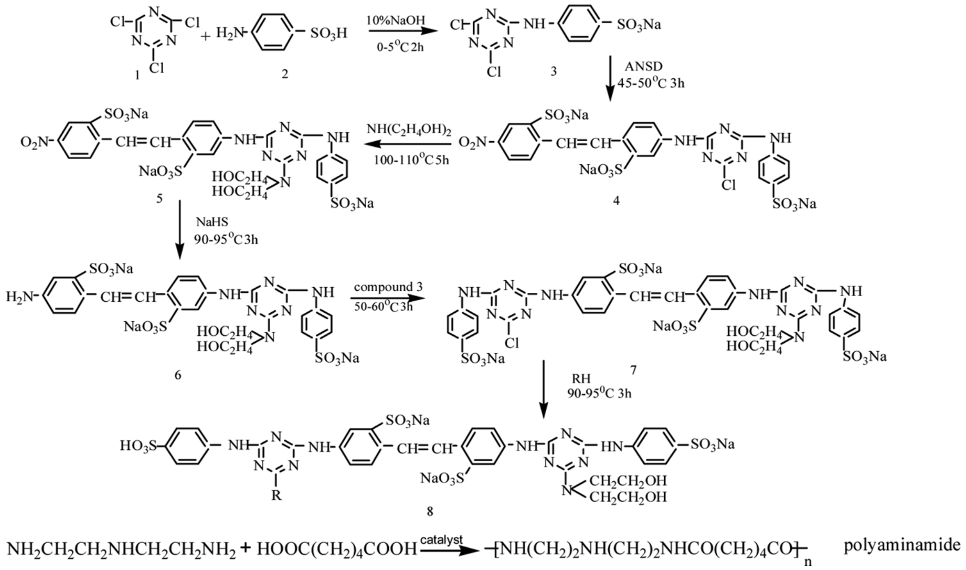

Figure 1: The synthetic route of the asymmetrical fluorescent brighteners.

and dried at −54°C, 0.038 bar on a LABCONCO Freezone 4.5 freezing dryer, kept in reserve and ground to powder in a desiccator. In addition, the synthesis method of polyaminamide was prepared using diethylene triamine and adipic acid as materials. Figure 1 shows the synthetic pathway of the asymmetrical FBs, and the structure of substituents R are shown in Table 1. Relevant characterization data are shown in Tables 2–4.

Methods

FTIR spectra were measured on a Shimadzu IRPRESTIGE-21 infrared spectrometer using KBr coating. UV-vis spectrophotometric investigations of the prepared products of the symmetrical fluorescent brightener (FBs1), asymmetrical fluorescent brightener (FBs2) and the asymmetrical polymerizable fluorescent brightener (FBs3) using aqueous, dimethyl formamide(DMF) and tetrahydrofuran (THF) at a concentration of $2 \times 10^{-5}\,g \cdot ml^{-1}$ were performed on a Jena SPECORD50 spectrophotometer with 260–400 nm wavelength. Fluorescence measurements of inaqueous DMF and THF at a

Table 1: The structure of substituents R of FBs.

FBs	1	2	3
-R	-N(C_2H_4OH)$_2$	-N(CH_2CH_3)$_2$	polyaminamide

Table 2: Absorption and fluorescence characteristics of cis and trans isomers of FBs in aqueous solution.

	Cis-isomers			Trans-isomers							
FBs	λ_A/ nm	A	C_C/ %	λ_A/ nm	A	C_T/ %	λ_F/ nm	I_F	$\Delta\nu$/ cm^{-1}	Φ_F	E_F
FBs1	289	0.8048	42.0	354	0.7508	58.0	445	499.87	5777	0.234	0.186
FBs2	294	0.7117	44.5	352	0.7633	55.5	442	475.81	5785	0.228	0.182
FBs3	—	—	11.7	347	0.7784	88.3	423	585.64	5178	0.261	0.214

Table 3: Absorption and fluorescence characteristics of cis and trans isomers of FBs in DMF.

	Cis		Trans					
FBs	λ_A/nm	C_C/%	λ_A/nm	C_T/%	λ_F/nm	$\Delta\nu$/cm^{-1}	Φ_F	E_F
FBs1	293	45.7	358	54.3	447	4803	0.257	0.216
FBs2	296	43.3	355	56.7	445	4850	0.239	0.197
FBs3	—	13.1	349	86.9	426	4617	0.298	0.249

Table 4: Absorption and fluorescence characteristics of cis and trans isomers of FBs in THF.

	Cis		Trans					
FBs	λ_A/nm	C_C/%	λ_A/nm	C_T/%	λ_F/nm	$\Delta\nu$/cm^{-1}	Φ_F	E_F
FBs1	294	47.9	360	52.1	448	4706	0.265	0.219
FBs2	297	46.7	356	53.3	446	4606	0.244	0.202
FBs3	—	22.3	350	77.7	427	4514	0.317	0.266

concentration of $8 \times 10^{-7}\,g \cdot ml^{-1}$ of FBs1–FBs3 were recorded on a Shimadzu RF5301PC spectrofluorometer at room temperature. The fluorescence quantum yield was determined on the basis of the absorption and fluorescence spectra. Quinine sulfate in $0.5\,mol \cdot l^{-1}$ $H_2SO_4(\Phi_F = 0.55)$ was used as fluorescence standard [8]. Relevant characterization data are shown in Tables 2–4. Photochemical trans-cis isomerization was studied in solution above and exposure of the solution to monochromatic light at 366 nm for 3 h as well as heated at different temperatures. The course of isomerization was followed spectrometrically and its rate as well as final products in the equilibrium was monitored by TLC using chloroform:methanol:25 vol. % NH_3 (11:5:1) as an eluent on silica gel plates. The effect on fluorescence quenching was studied by monitoring at fluorescence intensity at different concentrations of the asymmetrical polymerizable fluorescent brightener (FBs3).

Applied Experiment of Paper Coating

According to Li [9], the FBs2 and FBs3 were added at a mass fraction of 0.2, 0.3, 0.4, 0.6, 0.8 and 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4% into coating, respectively. $120\,g\cdot m^{-2}$ coated paper were cut into 20×30 cm and then coated and dried. After that, the whiteness was tested after 1 day at room temperature and light respectively on a Hangzhou ZB-A Chromometer. Finally, the light stability was particularly studied.

RESULTS AND DISCUSSION

FTIR Characteristics

Figure 2 shows the region 3800–600 cm^{-1} of the infrared spectra of the asymmetrical polymerizable fluorescent brightener (FBs3).

It has been seen that strong and broad absorption peaks between 3300–3450 cm^{-1} are associated with stretching vibration peaks –OH and –NH. Alcohol –OH bond stretching vibration should be 3650–3590 cm^{-1} area, but because of the association between hydroxyl groups, O–H peak shifts to a lower wave number 3425 cm^{-1}. A wide peak of 1050 cm^{-1} is the stretching peak of C–OH on the primary alcohol, and 1610, 1583, 1480 and 1470 cm^{-1} were the stretching vibration peaks of the benzene skeleton. The peak at 792 cm^{-1} is characteristic for the deformation vibration of the aromatic benzene ring. The imide groups (C=O and N-C=O) of the FBs3 gave crucial peak at 1680 and 1340 cm^{-1}, which indicates that the prepared product is the FBs3 target product [10]. Relevant characterization data of symmetrical fluorescent brightener (FBs1) and asymmetrical fluorescent brightener (FBs2) are shown in Table 5.

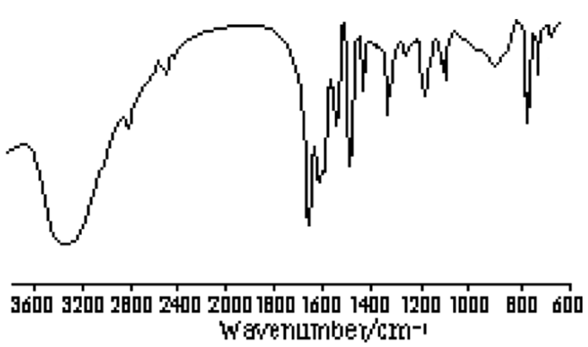

Figure 2: IR spectra of the asymmetrical polymeric fluorescent brightener.

Table 5: IR data of the fluorescent brighteners.

	IR (KBr/cm^{-1})								
FBs	$\nu_{OH}+\nu_{NH}$	$\nu_{C=N}$	$\nu_{C\text{-}OH}$	ν_{SO_2}	$\nu_{C=O}$	$\nu_{Ar\text{-}C}$	$\delta_{CH\text{-}Ar}$	$\nu_{N\text{-}C=O}$	**Yield / %**
1	3440	1615	1060	1140	—	1600,1583, 1480,1460	771	—	87
2	3414	1630	1045	1138	—	1614,1500, 1452	790	—	80
3	3425	1616	1050	1166	1680	1610,1583, 1480,1470	792	1340	76

Spectral Characteristics of the FBs

Tables 2–4 show the basic photophysical characteristics of FBs1–FBs3, obtained from the measurement of the FBs dissolved in aqueous solution DMF and THF. It shows that the UV-vis and fluorescence characteristics of cis and trans isomers of FBs1–FBs3 were presented, including the values of the ground state position of the absorption maxima (λ_A) and absorbances for trans and cis forms A, the values of fluorescent maxima (λ_F), Stokes shift($\Delta\nu$), quantum yield of fluorescence (Φ_F) and the energy yield (E_F).

The FBs1, FBs2 and FBs3 have similar curve profiles as the result of their common matrix structure. And the UV spectrum and fluorescence spectrum show a good symmetry relationship of image, which both indicate that molecules' conformation changed little from the ground state to the excited state.

UV Spectrum and Fluorescence Spectrum

Table 5 shows FBs1 and FBs2 have visible cis- and trans-isomers that have different maximum absorption wavelength in aqueous solution. The maximum absorption wavelength of cis-isomers is in the region 289–294 nm, trans-isomers at 352–354 nm. On light, FBs pass from the ground singled state to the first excited state $S_0 \rightarrow S_1^*$. Fluorescence emission is at 380–550 nm with a well-pronounced maxima at 442–445 nm. Whereas FBs3 only have trans-isomers, absorption maxima and fluorescent maxima wavelength, absorbance is 347, 423 nm and 0.7784, respectively. Compared with monomer FBs1 and FBs2, there is a slight maximum hypsochromic shift of 5–7 nm and fluorescence spectroscopy of 19–22 nm of FBs3. And the maxima absorbance increases by 1.3% compared with asymmetrical fluorescent brightener (FBs1), increases by 2.8% compared with asymmetrical fluorescent brightener (FBs2), and so does the fluorescence emission property.

It is obvious that ultraviolet absorption and fluorescence emission properties of asymmetrical fluorescent brightener, in particular asymmetrical polymerizable fluorescent brightener(FBs3), have been improved markedly. This is because of more substituents in the triazine ring; their respective photophysical and photochemistry can have an additive synergistic effect and promote each other. Meanwhile, chromogen of FBs is well fixed with covalent bonds in macromolecular chains, inactivation function being reduced in the course of $S_1^* \rightarrow S_0$, so chromogen stability augments.

Quantum Fluorescent Yield (Φ_F), Stokes Shift ($\Delta\nu$) and Energy Yield of Fluorescence (E_F)

The quantum fluorescent yield (Φ_F) and energy yield of fluorescence (E_F) are commonly used for characterization of ultraviolet absorption and fluorescence properties of FBs. The greater the value, the stronger fluorescence intensity, which directly expresses the stronger whitening capacity and the smaller energy loss in the transition process. Table 3 shows that FBs1–FBs3 quantum fluorescence yield (Φ_F) is at the range from 0.228 to 0.261, energy yield of fluorescence (E_F) from 0.182 to 0.214 in aqueous solution at the excitation wavelength, respectively. FBs2 < FBs1 < FBs3 indicates that structural asymmetry can decrease fluorescence quantum yield (Φ_F) and energy yield of fluorescence (E_F), yet polymerizable fluorescent brightener covalent bonds between chromogen and macromolecule chains enhance their photochemical stability and fluorescence quantum yield, and so does the energy yield of fluorescence (E_F). Fluorescence quantum yield (Φ_F) and fluorescence energy yield (E_F) are calculated from the following Eqs. (1) and (2) [11]:

$$\Phi_\mathrm{F} = \Phi_{s\tan dard} \times \frac{\mathrm{S}_\mathrm{sample} \times A_{s\tan dard} \times n^2_\mathrm{sample}}{S_{s\tan dard} \times A_{sample\times} \times n^2_\mathrm{standard}} \tag{1}$$

$$E_F = \Phi_F \times \frac{\lambda_A}{\lambda_F} \tag{2}$$

where, Φ_F and Φ_standard represent the quantum fluorescence yield of the sample and standard, respectively. S_sample and S_standard represent the area of fluorescent emission band for sample and standard, respectively. A_sample and A_standard represent the UV/vis absorbances of sample and standard, respectively. n_sample and n_standard the solvent refractive index of the sample and and standard, respectively. The standard in this paper is Quinine sulfate ($\Phi_\mathrm{standard} = \Phi_\mathrm{Quinine\ sulfate} = 0.55$).

Stokes shift ($\Delta\nu$) is a parameter which indicates notable steric changes of FBs between the ground state S_0 and the first excited state S_1^*. The Stokes shift ($\Delta\nu$) was found by Eq. (3):

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

The greater the value of Stokes shift ($\Delta\nu$), the more of the energy losses during the transition into the excited state. The calculated values of Stokes shift of

FBs1–FBs3 in aqueous solution are between 5178–5785 cm^{-1}. The relationship of $\Delta\nu$ (FBs2 > FBs1 > FBs3) indicates that the wavelength difference between the maximum absorption and the maximum fluorescence emission of asymmetrical structure monomer is the largest, and elements coplanar effect makes even worst in transition process with the increase in the number of substituents on the triazine ring.

The quantum yield of fluorescence (Φ_F) and the energy yield (E_F) of the asymmetrical polymerizable fluorescent brightener (FBs3) are the highest of small molecular symmetry FBs1 and asymmetry fluorescent brighteners FBs2; yet the Stokes shift ($\Delta\nu$) is the lowest. It is revealed that the inactivation function of the polymerizable fluorescent brightener is tiny, and fluorescence intensity is high in the process of $S_1^* \rightarrow S_0$. It is probably because the trans-activity fluorescent monomers are firmly fixed to the macromolecular chains that the steric change is smaller, the role of inactivation decreases, quantum yield of fluorescence (Φ_F) and fluorescence energy yield (E_F) rise in the process of energy transition. Comparing with small molecular symmetrical fluorescent brighteners (FBs1) and asymmetric fluorescent brighteners (FBs2), the asymmetric polymerizable fluorescent brighteners (FBs3) have stronger fluorescence emission properties.

Influence of Solvent Polarity on the Absorption and Fluorescence Properties

As seen from the data listed in Tables 2–4 the optical characteristics of the FBs1–FBs3 are determined by solvent polarity. The quantum fluorescence yield (Φ_F) of FBs1–FBs3 in DMF are between 0.257–0.298 and 0.265–0.317 in THF; the energy yield (E_F) 0.216–0.249 and 0.219–0.266, respectively; while the Stokes shift ($\Delta\nu$) decreases compared with aqueous solution. This reveals that the quantum yield of fluorescence increases with decrease in the solvent polarity, whereas the photoisomerization yield decreases. Meanwhile the maximum absorption wavelength λ_A in DMF are between 349–358 nm and 350–360 nm in THF; fluorescence emission wavelength λ_F 426–447 and 427–448 nm, respectively, being red-shift slightly comparing with the aqueous solution. It can be seen that the decrease in the solvents have only a small red shift effect upon the positions of the absorption and fluorescence maxima of the FBs1–FBs3.

Photoisomerization Effect

Figures 3 and 4 show the effect on fluorescent spectra of light and heating, respectively.

After light irradiation with 366 nm wavelength for 3 h, the maximum absorption wavelength of trans-isomer fluorescent brightener takes on blue-shift, but cis-isomer red-shift. FBs3 gets to cis- trans isomers of the two

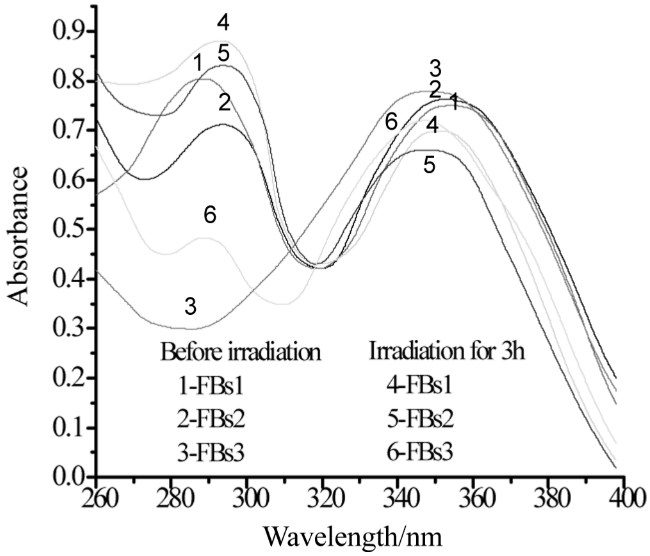

Figure 3: Effect on light irradiation of FBs in aqueous solution.

UV absorption peaks from only an absorption peak of the initial trans-isomer, and trans-isomer absorbance decreases slightly. After light radiation, the absorbance of fluorescent monomer FBs1, FBs2 decreases rapidly in trans-isomer, with a sharp increase in cis-isomer. Similarly, fluorescence intensity of FBs3, FBs1 and FBs2 decreases when heated, but the optical

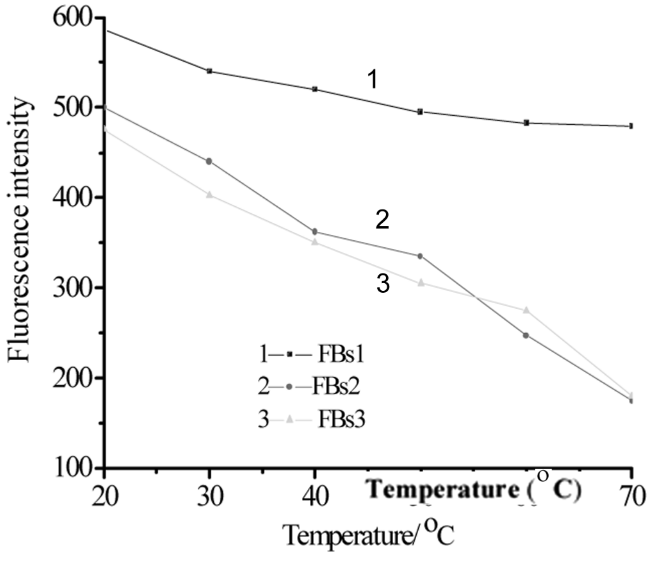

Figure 4: Effect on heating of FBs.

properties of the former decreases much slower than the latter significantly, which shows that light resistance and heat resistance of the asymmetrical polymerizable fluorescent brightener is superior to that of symmetrical and asymmetrical fluorescent brighteners. The obtained percent content of the isomers of FBs studied in solution after irradiation to light was estimated according to Eqs. (4) and (5) [4]:

$$C_T = \frac{A_T(A'_C - A_C)}{A'_C A_T - A_C A'_T} \times 100\% \tag{4}$$

$$C_C = 100 - C_T\% \tag{5}$$

where, A_C and A_T are the absorption of the cis- and trans- isomers before light irradiation the solution, respectively; A_C and A_T are the respective absorption after irradiation. C_C and C_T are the percent concentrations of the cis- and trans-isomers in the solution, respectively.

Table 3 presents the results for C_T and C_C of the two isomers for the FBs1–FBs3. In equilibrium in aqueous solution the concentration of trans-isomers prevails C_T is 88.3% for FBs 3, increasing about 30% compared with FBs–FBs2. In DMF and THF solution, the trends are similar to this in aqueous solution.

Influence of Concentration on Fluorescence Properties

The changes in fluorescence intensity of FBs3 with variation of the concentration are presented in Figure 5.

When the concentration increases from 1×10^{-6} to $5 \times 10^{-4}\,\mathrm{g \cdot ml^{-1}}$, the fluorescence intensity increases. If the concentration is over $1 \times 10^{-3}\,\mathrm{g \cdot ml^{-1}}$, the fluorescence is quenched. Meanwhile, it is evident that the fluorescence emmission wavelength is red-shifted between high concentration of 5×10^{-3} and $1 \times 10^{-2}\,\mathrm{g \cdot ml^{-1}}$. This may be due to polyaminamide into the fluorescent molecule, so that the gathering possibility each other reduces. Yet, when FBs1 and FBs2 are about the concentration of $8 \times 10^{-4}\,\mathrm{g \cdot ml^{-1}}$, the obvious fluorescence quenching occurs, indicating that asymmetrical polymerizable fluorescent brightener has a wider use.

Paper Coating Applied Experiments

It can be shown from Figure 6 that the paper coating whiteness increase obviously with the increasing of FBs3 and FBs2 concentration, when the concentration of FBs2 and FBs3 is over 0.4% and 0.6% respectively, the paper coating whiteness increases slowly and become decreased. At the same concentration, whitening properties of FBs3 is slightly lower than the fluorescence

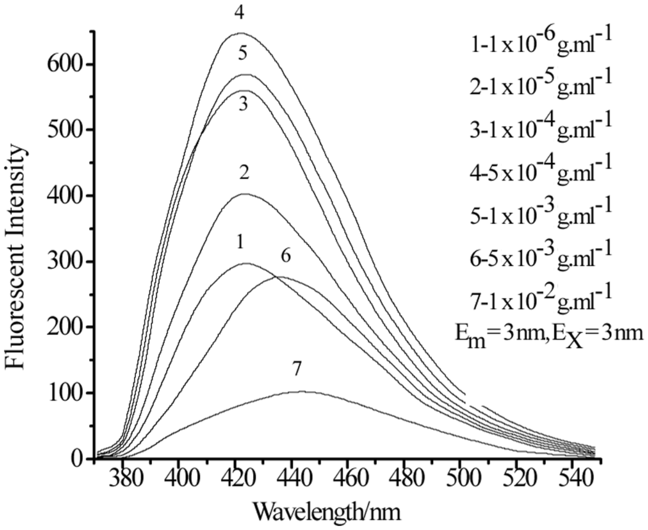

Figure 5: Effect on concentration of FBs3.

monomer, because its content of active component of FBs3 is less than fluorescent monomer FBs2. But after sunlight radiation for 1 day, whiteness of the coating paper with FBs3 changes lightly, while whiteness decreases significantly with FBs2 and is far lower than the former. Application tests demonstrates that covalent bonds between chromogen and macromolecule chains modified by polyamide monomer enhance greatly their photochemical stability [12], inhibit the light-induced effect, and increase conspicuously their whitening performance and fluorescence quantum yield.

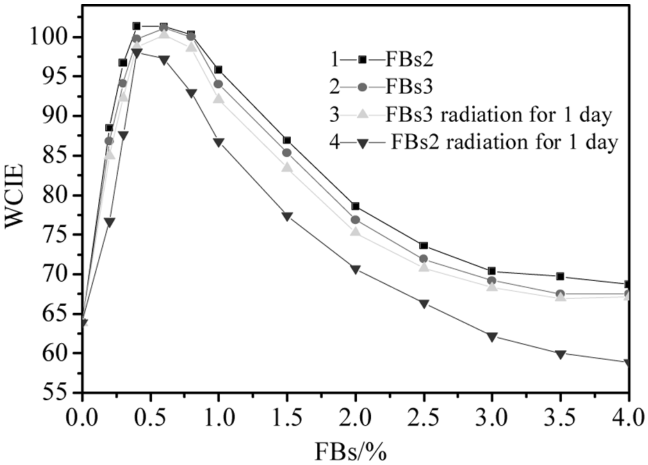

Figure 6: Effect on paper coating whiteness of FBs concentration.

CONCLUSION

A new asymmetrical polymerizable fluorescent brightener grafted polyaminamide is synthesized by condensation and reduction reaction. The ultraviolet absorption and dyeing properties as well as stability increase obviously compared with asymmetrical and symmetrical FBs, the photoisomerization phenomenon is reduced, fluorescence quantum yield and water-solubility are improved significantly, and it's widely used.

The optical properties of asymmetrical polymerizable fluorescent brightener are affected by concentration and the nature of the solvents. With the decrease in solvent polarity, the quantum yield of fluorescence increases significantly, and the maximum absorption and fluorescence emission wavelength have only a small red-shift effect, respectively. The fluorescence intensity can increase with an increase in the concentration, when it is over $1 \times 10^{-3}\,\mathrm{g \cdot ml^{-1}}$, the fluorescence will be quenched. Meanwhile, the type of substituents in the triazine ring does not visibly affect the absorption-fluorescence assignments, and the concentration of trans- and cis-isomers depends on the nature of the substituents.

REFERENCES

[1] Veleva, S., Valcheva, E., Valchev, I., and Radeva, G. *J. Reaction Kinetics and Catalysis Letters* **72**, 355 (2001).

[2] Grabchev, I. *J. Dyes and Pigm.* **29**, 155 (1995).

[3] Konstantinova, T. N., Konstantinov, H. I., and Betcheva, R. I. *J. Dyes and Pigm.* **43**, 197 (1999).

[4] Grabchev, I., and Philipova, T. *J. Die Angewandte Makromolekulare Chemie* **263**, 1 (1998).

[5] Cao, C. B., Han, H. B., Ji, C. N., Wei, D. F., and Li, T. Z. *J. Modern Chemical Industry* **25**, 38 (2005).

[6] Lee, J. K., Um, S. I., Kang, Y. H., and Beak, D. J. *J. Dyes and Pigments* **64**, 25 (2005).

[7] Grabchev, I., and Philipova, T. *J. Dyes and Pigments* **44**, 175 (2000).

[8] Wei, Y. J., Li, N., and Qin, S. J. *J. Spectroscopy and Spectral Analysis* **24**, 647 (2004).

[9] Li, N., Zhang, G. H., and Liu, J. *J. China Pulp and Paper* **27**, 28 (2008).

[10] Grabtchev, I. *J. Dyes and Pigments* **25**, 249 (1994).

[11] Grabchev, I., Chovelon, J. M., and Petkov, C. *J. Spectrochimica Acta Part A* **69**, 100 (2008).

[12] Dave, D. A. *J. Man-Made Textiles in India* **2**, 48 (1992).