

New Photochemical Approach to Cellulose Fabric and Photoinitiator System

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ABSTRACT: The surface modifications of cellulose substrate based on the photo-induced reaction are closely related with the radicals introduced on the surface of cellulose substrates by light irradiation. We have evaluated the ability of radical formation in lyocell fabric and two water-soluble photoinitiator systems by using photoluminescence analyses. Namely, the relative quantum yields of fluorescence and phosphorescence were estimated by the integrated emission intensity under the same values of light absorbance and the identical measuring conditions. First of all the [2-(acryloyloxyethyl)(4-benzoylbenzyl)dimethylammonium bromide (PIA) system had larger UV absorbance values below 287 nm than [3-(3,4-dimethyl-9-oxo-9h-thioxanthene-2-yloxy)-2-hydroxypropyl]trimethylammonium chloride (PIB) system at the same concentration. The relative quantum yields of fluorescence and phosphorescence emission in PIA system were smaller than those in PIB system even if the two systems had the same values of light absorbance. Therefore it

was found that the PIA system was more easily transitioned to the triplet-state and the transitioned molecules reacted with the cellulose substrates more effectively. The modified cellulose fabric with 2-(dimethylamino)ethyl chloride hydrochloride (AM1) and PI system had only a little different UV absorbance and photoluminescence properties from the untreated fabric system. However, the fabric modified with 2-(4-chlorophenyl)-ethylamine (AM2) and PI system showed relatively big differences. The UV absorbance values were increased and the relative quantum yields of photoluminescence were decreased remarkably. We have acquired that the tertiary amine treated cellulose fabric were very effective in photo-induced modification of cellulose. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 352–359, 2007

Key words: photochemistry; fluorescence; luminescence; cellulose; photoinitiator

INTRODUCTION

In the dyeing and finishing processes of textile materials, many research groups have developed special mechanisms and application fields by means of photo-induced reactions. This reaction involves surface modifications after irradiation of UV light, electron beam, excimer laser, X-ray, and γ -ray.^{1–4} There are also two types of application methods. One is the surface treatment of textile substrates by radiation without any additional photosensitive material and the other is the surface grafting, crosslinking, coating and laminating with these materials in radical initiating system or ionic initiating system.^{5–9} Through above any photo-active process, they have acquired much information about photo-degradation effect, antistatic effect, shrink/crease resist effect, flame resist effect, dyeability improvement, pigment dyeing, printing etc.^{10–17}

Photosensitive materials applied to polymer industry have been studied in a variety of fields including reactivity evaluation of these materials, development of advanced materials, and characterizing of reaction

products.¹⁸ In textile applications, first of all, the choosing water-soluble photoinitiator is essential for adapting to textile substrates and mainly benzophenone derivatives and thioxanthone derivatives have been employed.^{14,19} Also after initiating of photoinitiator, mono (or multi) functional acrylate, acrylic acid, allyl, thiol, or epoxy monomer (oligomer) have applied to the grafting, crosslinking, and polymerizing of almost every textile substrates.^{20,21}

In addition, some special chemists concerned with photochemical characterizing of photo-induced reaction have achieved in-depth studies about water-soluble photoinitiator on the basis of fluorescence and phosphorescence analyses.²² The reaction mechanisms of these initiators and some substrates were almost established recently.²³

The spectroscopic analyses of cellulose substrates have been made in mechanical pulp sheet during various irradiation.²⁴ The effects of chemical treatment and photosensitive dye were evaluated by photoluminescence in other cellulose paper, film, and powder.²⁵

However until now, most of the researchers studying the photo-induced reaction of textiles have only concerned with the characterizing of reaction products and any cellulose fabric has not been used in photoluminescence analysis. Therefore it is necessary to

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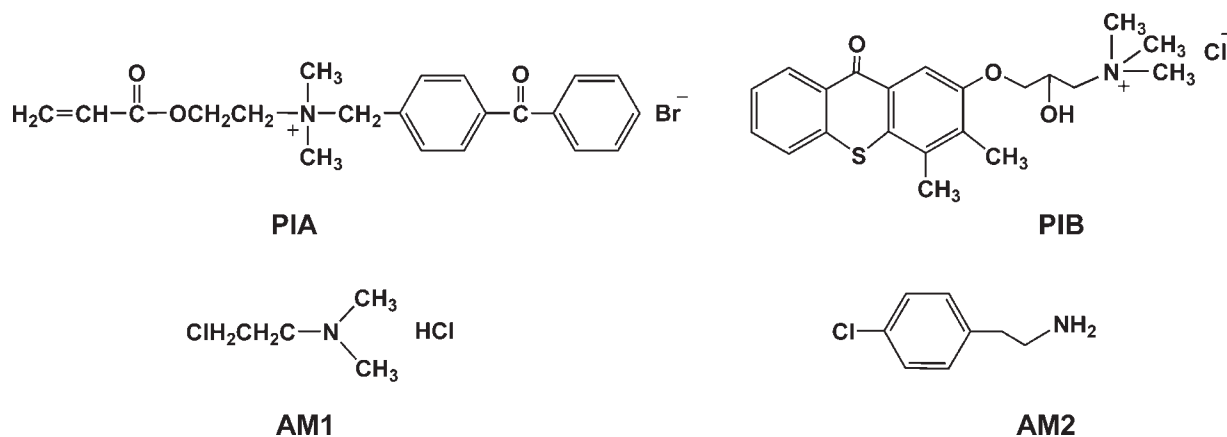


Figure 1 Water-soluble photoinitiators and modifiers.

examine photo-induced reactivity of textiles, more quantitatively, using photoluminescence. In this study, we present spectroscopic analyses of the cellulose fabric containing water-soluble photoinitiators and evaluate the photo reactivity by using UV absorbance and photoluminescence spectra.

EXPERIMENTAL

Materials

The commercial lyocell scoured fabric was used in all experiments. The water-soluble photoinitiators, [2-(acryloyloxy)ethyl](4-benzoylbenzyl)dimethylammonium bromide (PIA) and [3-(3,4-dimethyl-9-oxo-9H-thioxanthene-2-yloxy)-2-hydroxypropyl]trimethylammonium chloride (PIB) were laboratory grade obtained from Aldrich Chemical. Also 2-(dimethylamino)ethyl chloride hydrochloride (AM1), 2-(4-chlorophenyl)-ethylamine (AM2) and sodium carbonate from Aldrich were applied to the modification of cellulose fabric (Fig. 1).

Preparation of modified cellulose fabric

The cellulose fabrics were independently padded and squeezed twice. First the fabrics padded in 8 wt % aqueous ammonium salts or amine solution at room temperature were squeezed to about 90~100% pick-up. Next the fabrics padded in 12 wt % sodium carbonate aqueous solution were squeezed to about 90~100% pick-up. After the fabrics have been cured in 95°C heating chamber for 10 min, they were washed with distilled water and neutralized with dilute acetic acid. Then they were dried at ambient conditions.

Spectroscopic measurements

UV absorbance measurement

The UV absorption spectra of the aqueous photoinitiator solutions were recorded at 200~500 nm by Shi-

madzu UV-1601 spectrophotometer (Japan). The UV absorbance values of the fabrics containing 200~220% solutions were measured after padding the fabrics ($4 \times 2.5 \text{ cm}^2$) in 10 mL solutions (liquid ratio 41 : 1) for a certain period. At this time, the fabric padded in distilled water was used for the reference sample.

Fluorescence and phosphorescence emission measurement

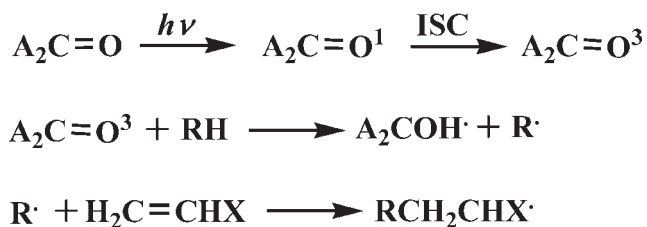
The photoluminescence spectra were obtained by HITACHI F-4500 fluorescence spectrometer (Japan). The fabrics ($2 \times 1.5 \text{ cm}^2$) padded in 5 mL aqueous photoinitiator solutions (liquid ratio 67 : 1) for 24 h were controlled to 150% pick-up and then the four-layered fabrics were placed between two-quartz plates. Fluorescence emission spectra were recorded in a 45° arrangement in a solid sample holder when excited at the wavelength of the maximum UV absorbance (258 nm) and at the wavelength of the other absorbance peak (287 nm). Each measurement was repeated four times and the mean emission curve was selected respectively. Room-temperature phosphorescence emission spectra were measured at the same wavelength with four-layered fabrics which were vacuum dried at 40°C for 8 h after padding in the PI solutions.

Photoluminescence quantum yield determination

The relative quantum yield (ϕ) of photoluminescence in optically thin film or solution system can be estimated on the basis of the following equation.^{26,27}

$$\phi_2 = \phi_1 \left(\frac{I_2}{I_1} \right) \left(\frac{E_1}{E_2} \right) \left(\frac{A_1}{A_2} \right) \left(\frac{n_2}{n_1} \right)^2$$

where I is the integrated emission intensity, E is the monochromatic excitation intensity, A is the fraction of the excitation light absorbed by the sample, n is the index of refraction, and the 1 and 2 subscripts denote different two samples. The excitation intensity at arbitrary exciting wavelength should be corrected by



Scheme 1 Photo-induced PIA reaction with cellulose substrate.

using quantum counter or using standard samples whose exciting spectra and the quantum yield are well-known. In this paper, we would only try to compare the relative photoluminescence quantum yields of some different unknown samples relatively. Therefore, the E_1 and E_2 terms could be eliminated when recorded with the identical instrument under the same measuring conditions.

And the fraction of excitation light can be approximated by the light absorbance in optically thin film or solution systems. The fabrics containing PI aqueous solutions were not optically thin. Also the light absorbance and the integrated emission intensity are not increased linearly to PI concentration at relatively higher concentrations. We have tried to evaluate the relative quantum yields of the different samples when the UV absorbance values at exciting wavelength were equal.

Moreover the refractive indices for corresponding two samples are assumed to be closed and these terms are negligible. Consequently it was found that the relative quantum yields were directly proportional to the integrated emission intensity under above circumstances.

The cellulose fabrics did not have uniform thickness and the control of solution pick-up was very difficult, so the emission spectra had showed some variations. To minimize these experimental errors, we have applied optically thick, four-layered, fabrics like the photoluminescence measurements of pulp paper.^{24,25}

RESULTS AND DISCUSSION

Reaction mechanisms of cellulose substrate and photoinitiator

Two groups of initiators are available in the photo-induced reactions of polymers. One is initiated

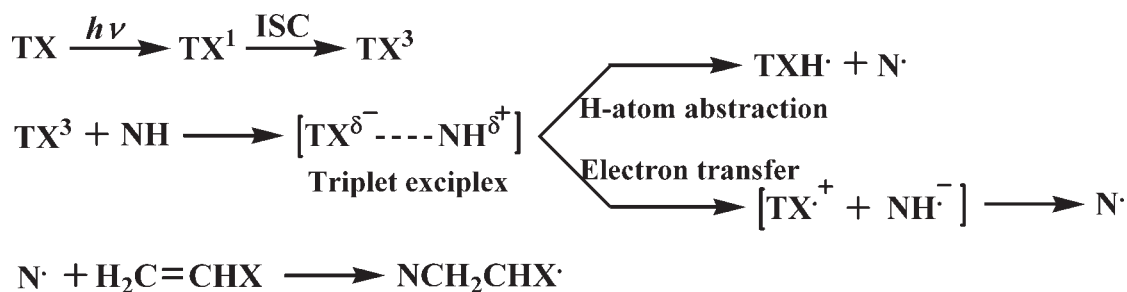
according to the free radical chain process and the other is based on the ionic mechanism, usually ring opening reactions of epoxy resins. Also there are photo-fragmenting initiators (Type I photoinitiators) and hydrogen-atom abstracting initiators (Type II photoinitiators) in the former group.²³

We have applied Type II photoinitiators, especially water-soluble initiators in commercial, to cellulose fabrics and the reaction mechanisms of PIA and PIB initiators are as follows. When the benzophenone derivative, PIA, absorbs light, it can be excited to a singlet-state and transited to a triplet-state after passing through the intersystem-crossing (Scheme 1). It abstracts hydrogen atoms from cellulose molecules of the substrate surface and forms ketyl radicals and alkyl radicals. The surface alkyl radicals react with unsaturated monomers (oligomers), therefore the modification of the substrate surface can be progressed. The thioxanthone derivative, PIB, goes through the similar processes (Scheme 2). Because of the lowest excited triplet state ($\pi\pi^*$), PIB has a low affinity for intermolecular hydrogen atom abstraction in comparison with PIA which has the $n\pi^*$ triplet state. If there is a amine cosynergist for effective photo-curing, PIB forms an intermediate excited electron transfer complex (exciplex). Then the alkylamino radicals are generated by the hydrogen atom abstraction process or the electron transfer process.

It could be found that the two relationships influence the photo-induced reactivity of cellulose fabric and photoinitiator system by the above reaction mechanisms. The first is the relationship between the fluorescence emission intensity and the degree of intersystem-crossing and the second is the relationship between the phosphorescence emission intensity and the amount of radical formation.

UV absorption property

The UV absorption spectra of the aqueous PIA and PIB solutions between 200~500 nm are shown in Figure 2. The PIA solutions had an absorbance peak at 256 nm and the PIB solutions had a shoulder at 256 nm, peaks at 273 nm and 403 nm. The absorbance values of the two PI solutions at 256 nm were linear to



Scheme 2 Photo-induced PIB reaction in the presence of amine cosynergist.

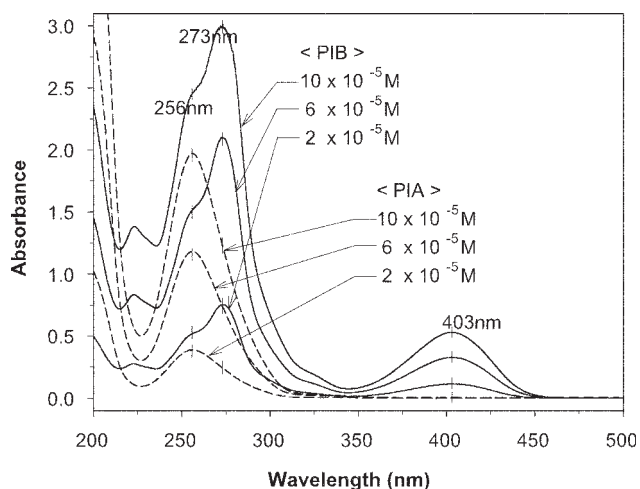


Figure 2 UV absorption spectra of the aqueous photoinitiator solutions.

the concentration in the range of $1 \times 10^{-5} M$ to $1 \times 10^{-4} M$. And PIB solutions had a larger absorbance values than PIA solutions.

However, the absorption spectra of the fabrics padded in PI solutions for 24 h have been somewhat changed (Fig. 3). The absorbance peaks were shifted a little to 258 nm in PIA type and shifted to 258 nm, 287 nm, and 406 nm in PIB type. The PIB absorbance values below 320 nm were decreased remarkably in comparison with those in solution states. Therefore, the fabrics padded in PIA solutions showed much larger absorbance values than those in PIB solutions contrary to the results in solution states.

Because the linearity between the UV absorbance values of the fabrics and the PI concentrations did not exist, we have selected the concentrations of the two aqueous photoinitiator solutions, which have the

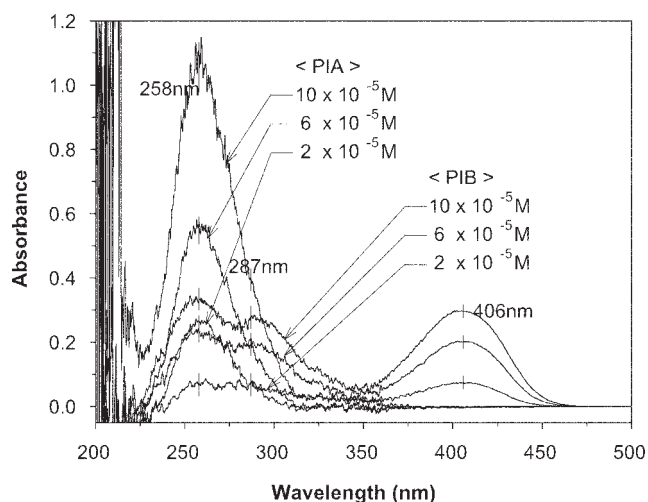


Figure 3 UV absorption spectra of the fabrics padded in PI solutions for 24 h.

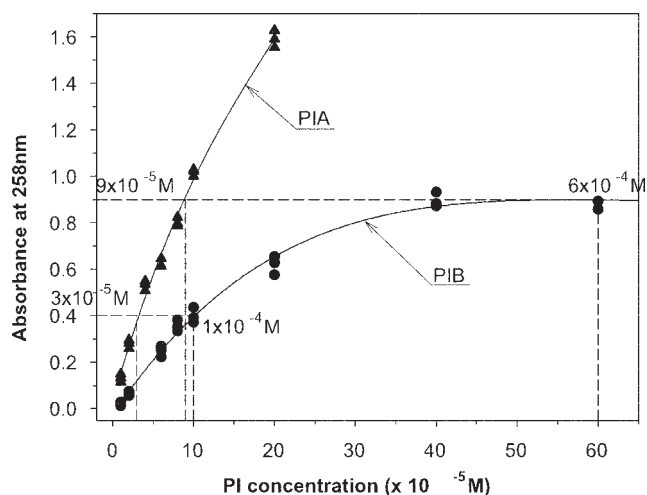


Figure 4 Relationship between the UV absorbance values of the fabrics padded in PI solutions and PI concentrations (padded for 24 h, excited at 258 nm).

same absorbance values (Fig. 4). The solutions which have the same absorbance values, 0.4 and 0.9 at 258 nm, 0.3 and 0.8 at 287 nm, were used in this study.

On the other hand the longer the fabrics were padded, the larger the UV absorbance values were. And the absorbance values became nearly constant after padding for 24 h.

Fluorescence emission property

As mentioned above, photoluminescence measurements were applied to the fabrics having matching absorbance values. When excited at 258 nm, the emission spectra of the fabrics padded in $3 \times 10^{-5} M$ PIA solution were compared with those in $1 \times 10^{-4} M$ PIB solution and those in $9 \times 10^{-5} M$ PIA solution were

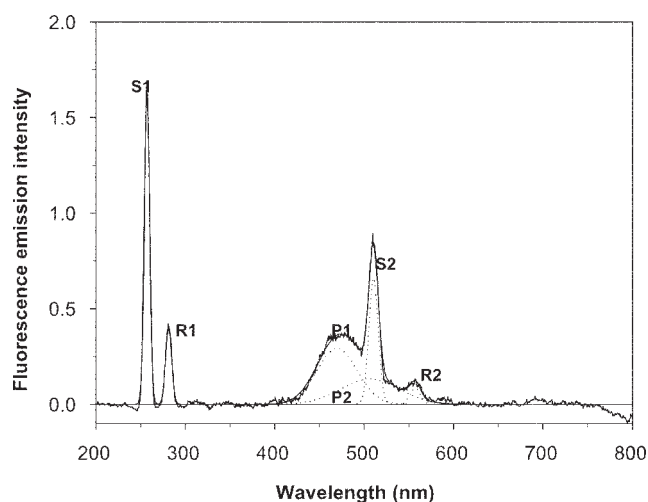


Figure 5 Fluorescence emission spectrum of PIA solution ($3 \times 10^{-5} M$, excited at 258 nm).

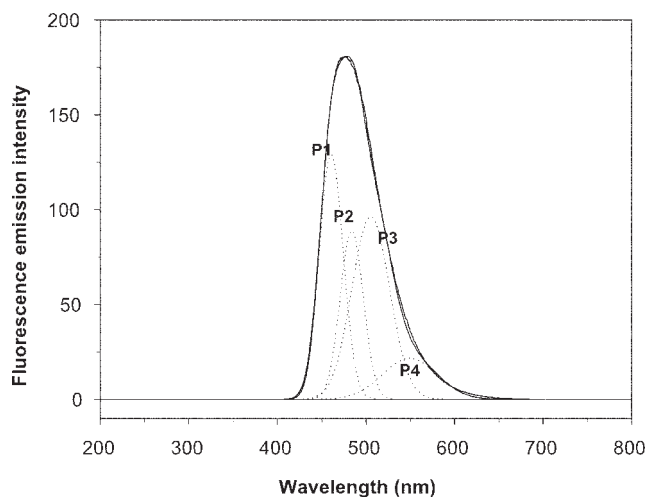


Figure 6 Fluorescence emission spectrum of PIB solution ($1 \times 10^{-4} M$, excited at 258 nm).

compared with those in $6 \times 10^{-4} M$ PIB solution. Also excited at 287 nm, the emission properties of the fabrics padded in $8.5 \times 10^{-5} M$ PIA solution were evaluated with those in $1 \times 10^{-4} M$ PIB solution and those in $2.5 \times 10^{-4} M$ PIA solution were evaluated with those in $6 \times 10^{-4} M$ PIB solution relatively.

The fluorescence emission spectra are shown in Figures 5–9. The fluorescence emission peaks by PI in aqueous solutions were observed and curve-fitted by P1–P4 peaks (Figs. 5 and 6). Also the scattering peaks (S1, S2) and the Ramann lines by solvent (R1, R2) were observed, especially remarkable in PIA solutions having lower fluorescence peak intensity. But the individual fluorescence emission peaks divided by accurate curve-fitting have not the special characteristics of fluorescence emission.

The intensity of scattering peak of the fabric padded in distilled water became larger than those of the solu-

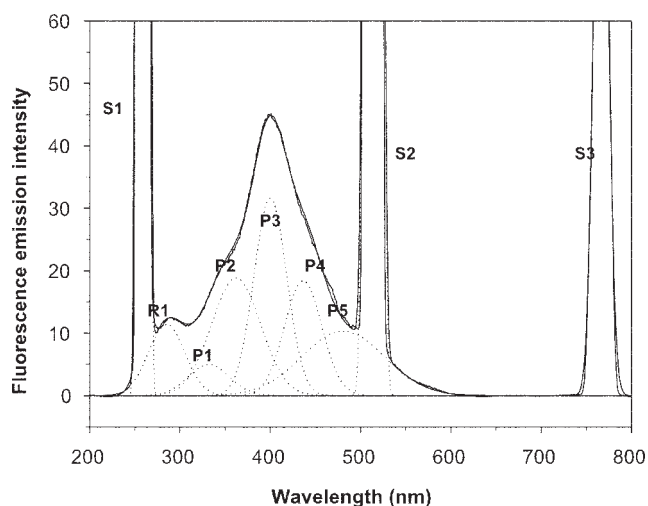


Figure 7 Fluorescence emission spectrum of the cellulose fabric padded in distilled water (excited at 258 nm).

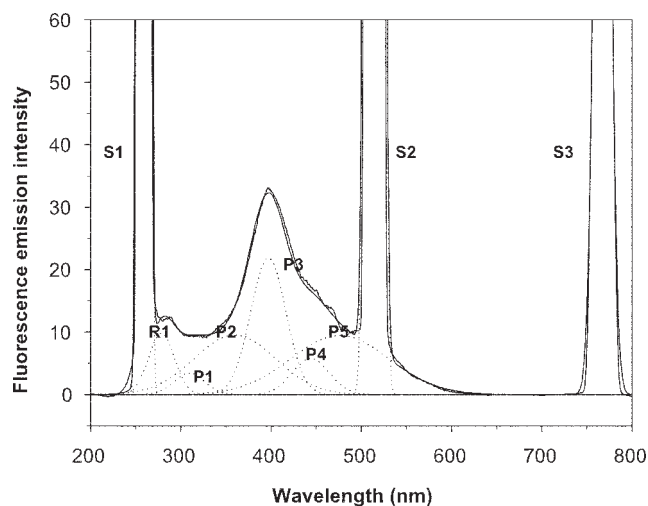


Figure 8 Fluorescence emission spectrum of the fabric padded in PIA solution ($3 \times 10^{-5} M$, excited at 258 nm).

tions and fluorescence was emitted by cellulose (Fig. 7). The fabrics padded in PIA and PIB solutions had the overlapped emission spectra of the PI solutions with the cellulose emission spectrum (Figs. 8 and 9). The large scattering peaks and the Ramann lines appeared and fluorescence was emitted by cellulose and the photoinitiators. However, the intensity and the wavelength at the maximum emission were very different from those of the solutions.

It was already well acquired that the relative fluorescence quantum yields were proportional to the integrated emission intensity values which were calculated by the total sum of the area P1–P5 peak. The integrated emission intensity values of fluorescence (I_f) and the wavelength at maximum emission ($Em\lambda_{max}$) are shown in Table I. The emission peaks of PI solutions appeared at around 475 nm similarly. The I_f values of PIA solutions were much smaller than those

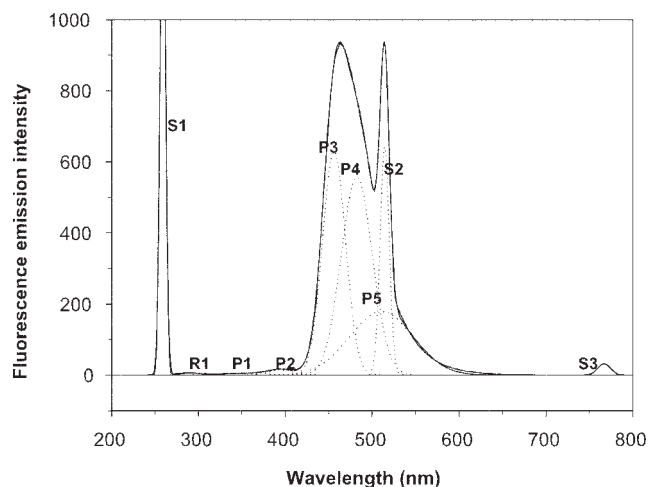


Figure 9 Fluorescence emission spectrum of the fabric padded in PIB solution ($1 \times 10^{-4} M$, excited at 258 nm).

TABLE I
Fluorescence Emission Property of the PI Solutions and the Padded Cellulose Fabrics

Samples	Excited at 258 nm						Excited at 287 nm					
	Em λ_{\max} I_f		Abs. 0.4		Abs. 0.9		Em λ_{\max} I_f		Abs. 0.3		Abs. 0.8	
			Em λ_{\max}	I_f	Em λ_{\max}	I_f			Em λ_{\max}	I_f	Em λ_{\max}	I_f
Solutions												
Distilled water	476.0	398					474.8	268				
PIA solutions			474.8	27	476.6	9			474.2	354	476.0	98
PIB solutions			478.4	14,136	476.0	184			476.6	9912	476.0	167
Fabrics												
Padded in distilled water	398.6	5141					348.8	2,736				
Padded in PIA solutions			397.4	3874	397.4	3477			451.4	2,293	452.6	1,516
Padded in PIB solutions			463.4	63,098	468.2	29,812			463.4	73,794	468.8	38,910

of PIB solutions at the same exciting wavelength and the absorbance values. Therefore it was found that the PIA solutions were transitioned to the triplet-state more easily than PIB solutions after absorbing the same quantity of lights.

When the fabrics padded in PIA solutions were excited at 258 nm, the $Em\lambda_{\max}$ values were about 400 nm corresponding to that of the fabric padded in distilled water. However, excited at 287 nm, the emission intensity at 350 nm caused by cellulose became small and those at about 450 nm caused by photoinitiator became maximum values. The fabrics padded in PIB solutions had very large fluorescence emission peaks at around 465 nm. The I_f values of the fabrics padded in PIA solutions were much smaller than those in PIB solutions. Therefore, it was also acquired that the cellulose fabrics containing PIA solutions were more photo-active than those containing PIB solutions when excited at 258 nm and 287 nm.

The fabrics having larger absorbance values (0.9 and 0.8) had smaller I_f values than those having lower absorbance values (0.4 and 0.3) under the same PI type and exciting wavelength. According to the above relative quantum yields equation, the quantum yield was smaller when the absorbance was larger and the I_f values was smaller, in spite of the nonlinearity of the absorbance and the fluorescence intensity values to concentrations.

Phosphorescence emission property

The PI molecules in triplet-state would induce the photochemical reaction with cellulose molecules or be transitioned to the ground state with emitting phosphorescence.

The phosphorescence emission spectra are shown in Figures 10 and 11. The scattering peaks were observed and the phosphorescence emission peaks

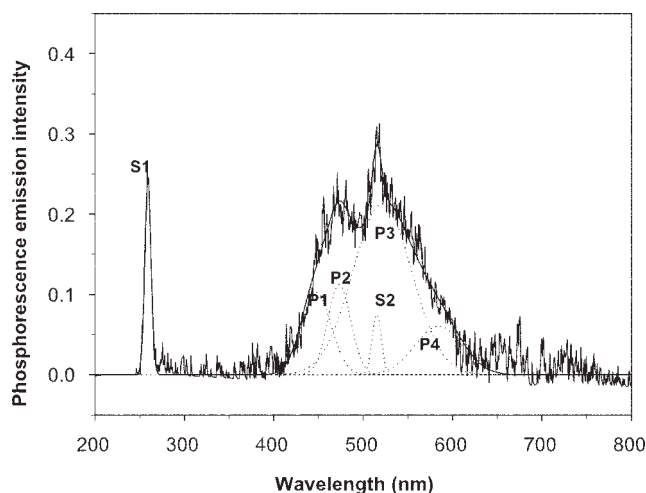


Figure 10 Phosphorescence emission spectrum of the fabric padded in PIA solution ($3 \times 10^{-5} M$, excited at 258 nm).

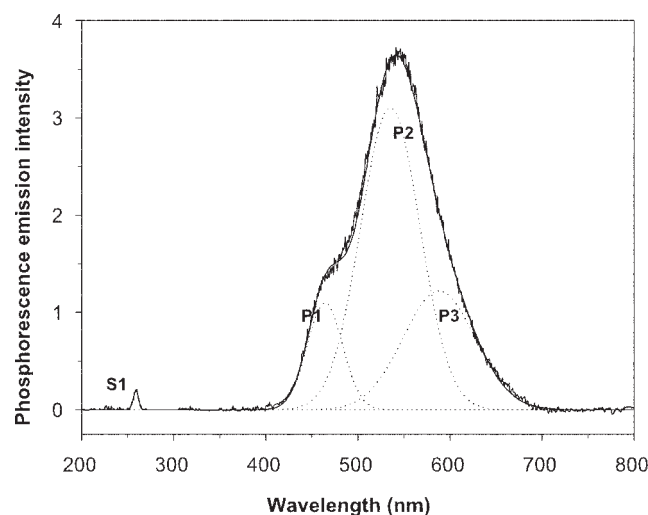


Figure 11 Phosphorescence emission spectrum of the fabric padded in PIB solution ($1 \times 10^{-4} M$, excited at 258 nm).

TABLE II
Room-Temperature Phosphorescence Emission Property of the Vacuum-Dried Fabrics After Padding in the PI Solutions

Samples	Excited at 258 nm						Excited at 287 nm					
	Em λ_{\max} I_p		Abs. 0.4		Abs. 0.9		Em λ_{\max} I_p		Abs. 0.3		Abs. 0.8	
			Em λ_{\max}	I_p	Em λ_{\max}	I_p			Em λ_{\max}	I_p	Em λ_{\max}	I_p
Padded in distilled water	486.2	33					481.4	30				
Padded in PIA solutions			474.1	30	457.3	10			485.0	31	482.6	15
Padded in PIB solutions			541.5	424	540.3	1082			543.9	700	540.3	1657

were fitted. And the integrated emission intensity values of phosphorescence (I_p) were indicated in Table II. The I_p values of the fabrics padded in PIA solutions were much smaller than those in PIB solutions. It was suggested that the fabrics padded in PIA solutions were more easily transitioned to the triplet-state, in addition, the transitioned molecules reacted with the cellulose substrates more effectively.

The I_p values of the fabrics padded in PIA solutions were smaller when the absorbance values were larger, so the relative quantum yields became smaller. But in PIB system, we could not find out any relation between the relative quantum yields and the absorbance values because of the nonlinearity of the absorbance and the phosphorescence intensity values to PI concentrations.

Modified cellulose effects on photoluminescence

It is well known that the reaction efficiency in the photo-induced reaction systems with the hydrogen-atom abstracting photoinitiator is related with the carbon-hydrogen bond strength of the substrates donating the hydrogen atom and the reactions are more effective with the amine cosynergists. The reaction efficiency is enhanced by the decrease of the ionizing potential and the increase of the electron donating ability of the amine.

We have tried to improve the ability of radical formation in cellulose fabric by treatment of ammonium salts (AM1) and tertiary amine (AM2), then evaluated the photoluminescence properties (Table III). The fabrics padded in PIA solution ($2 \times 10^{-5} M$) and PIB solution ($6 \times 10^{-5} M$) were used and the exciting wave-

length was 258 nm. The absorbance values were somewhat increased after AM1 treatment, on the other hand much increased after AM2 treatment. The fabrics treated with AM1 had a little larger or smaller I values of fluorescence and phosphorescence emission than those of the untreated fabric. However, the fabrics treated with AM2 had much smaller I values. Therefore, it was found that the cellulose fabrics modified with tertiary amine have much smaller photoluminescence quantum yields even if they absorb the same quantity of light. And they were more effective in the radical formation on the surface of the cellulose substrates.

CONCLUSIONS

The cellulose fabrics containing photoinitiator aqueous solutions had different UV absorbance and photoluminescence properties from the PI solutions. Namely, the cellulose fabric and benzophenone-derivative photoinitiator (PIA) systems had much larger absorbance values below 287 nm than thioxanthone-derivative photoinitiator (PIB) systems at the same concentration. And the former systems were more easily transitioned to the triplet-state and could produce many radicals on cellulose substrates than the latter systems. The modified cellulose fabrics, especially tertiary amine (AM2) treated fabrics, exhibited lower quantum yields of photoluminescence than the untreated fabric in spite of their large absorbance values. Therefore, it was found that this study can offer more quantitative methods to select suitable conditions in various photo-induced modifications of textiles by using a photoluminescence analyses.

TABLE III
Fluorescence and Phosphorescence Properties of the Modified Cellulose Fabrics

Samples	Untreated fabric			AM1 treated fabric			AM2 treated fabric		
	Abs.	I_f	I_p	Abs.	I_f	I_p	Abs.	I_f	I_p
Padded in PIA solutions	0.22	5811	50	0.35	6247	46	0.60	5017	29
Padded in PIB solutions	0.24	83,768	1807	0.27	81,334	2007	0.44	63,587	1929

References

1. Shao, J.; Hawkyard, C. J.; Carr, C. M. *J Soc Dyers Color* 1997, 113, 126.
2. Warburton, C. E., Jr. *J Appl Polym Sci* 1991, 42, 207.
3. Yip, J.; Chan, K.; Sin, K. M.; Lau, K. S. *Color Technol* 2002, 118, 31.
4. Millington, K. R. *J Soc Dyers Color* 2000, 116, 266.
5. Shao, J.; Liu, J.; Carr, C. M. *Color Technol* 2001, 117, 270.
6. Xin, J. H.; Zhu, R.; Hua, J.; Shen, J. *Color Technol* 2002, 118, 169.
7. Shin, H.; Ueda, M.; Burkinshaw, S. M. *Dyes Pigm* 1999, 41, 11.
8. Jang, J.; Ko, S. W.; Carr, C. M. *Color Technol* 2001, 117, 139.
9. Bellobono, I. R.; Selli, E.; Righetto, L. *J Photochem Photobiol A* 1992, 65, 431.
10. Uchida, E.; Uyama, Y.; Ikada, Y. *Textile Res J* 1991, 61, 483.
11. Reinhardt, R. M.; Arthur, J. C., Jr. *Textile Res J* 1980, 50, 261.
12. Dodd, K. J.; Carr, C. M.; Byrne, K. *J Textile Inst* 1993, 84, 619.
13. Dodd, K. J.; Carr, C. M. *Textile Res J* 1998, 68, 10.
14. Jang, J.; Carr, C. M. *J Textile Inst* 1999, 90, 412.
15. Reddy, P. R. S.; Agathian, G.; Kumar, A. *Radiat Phys Chem* 2005, 72, 511.
16. Ciba-Geigy Corporation, Tarrytown, N. Y. U.S. Pat. 5,597,388.
17. Li, S.; Boyter, H.; Stewart, N. *AATCC Review* 2004, 4, 44.
18. Ranby, B. *Polym Eng Sci* 1998, 38, 1229.
19. Liska, R. *J Polym Sci A: Polym Chem* 2002, 40, 1504.
20. Lecamp, L.; Houllier, F.; Youssef, B.; Bunel, C. *Polym* 2001, 42, 2727.
21. Takahashi, E.; Sanda, F.; Endo, T. *J Appl Polym Sci* 2004, 91, 589.
22. Catalina, F.; Corrales, T.; Peinado, C.; Allen, N. S.; Green, W. A.; Timms, A. *Eur Polym Mater* 1993, 29, 125.
23. Allen, N. S. *J Photochem Photobiol A* 1996, 100, 101.
24. Olmstead, J. A.; Gray, D. G. *J Pulp Paper Sci* 1997, 23, J571.
25. Olmstead, J. A.; Gray, D. G. *J Photochem Photobiol A* 1993, 73, 59.
26. Zhang, X.; Shetty, A. S.; Jenekhe, S. A. *Macromolecules* 1999, 32, 7429.
27. Isak, S. J.; Eyring, E. M.; Spikes, J. D.; Meekins, P. A. *J Photochem Photobiol A* 2000, 134, 77.