

Novel Coloration of Cotton Fabrics by UV-induced Photografting of Reactive Black 5 and Acrylic acid

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Abstract— UV-induced surface copolymerization has been widely applied as a simple, useful and versatile approach to improve the surface properties of textiles. C.I. Reactive Black 5 and acrylic acid (AA) were continuously grafted onto cotton by UV irradiation. The photografting may occur by the copolymerization of AA with the vinylsulfone reactive dye which photochemically converted from the bisulfatoethylsulfone reactive group. The graft yield and color yield were influenced by UV energy, the dye and photoinitiator concentrations, a mole ratio of AA to dye, and pH. The coloration of cotton fabrics having a K/S of 7.0 can be obtained under a UV irradiation energy of 15J/cm² by the photografting of an aqueous alkaline formulation of 6% dye concentration containing 3% photoinitiator concentration on the weight of monomers, and a 3:1 mole ratio addition of AA to the dye. Furthermore, the photochemically dyed cotton fabrics showed comparable washing (staining) and rubbing fastness to conventional reactive dyeing method except shade change in the wash fastness and light fastness.

Keywords: cotton, C.I. Reactive Black 5, acrylic acid, photografting, color yield

1. Introduction

Cotton fabrics are the most widely used textile in the world as it possesses many useful characteristics such as comfort, excellent softness, good absorbency, color retention and good strength. Cotton fabrics are dyed with several major classes of dyes including direct, vat, sulfur, azoic and reactive dyes¹⁾. Among them, reactive dyes furnish a wide gamut of shades of good light fastness and excellent wash fastness. Hence, reactive dyes of comparatively a low molecular weight are frequently used for the covalent bond formation with the hydroxyl groups of cellulose to achieve good penetration and levelness within the fibers²⁾. Traditionally, large amount of salts are needed to increase dye-uptake by reducing the electrostatic repulsion between cotton fibers and reactive dyes inevitably causing environmental problems³⁾. Therefore salt-free or low-salt dyeing technology using reactive dyes has become a popular topic. As an example, cotton can be dyed in pale shade in supercritical carbon dioxide fluid without auxiliaries, which requires nonpolar dyes

and high pressure equipment⁴⁾.

An alternative approach to increase dye uptake and dye fixation is the modification of the cellulosic fibers themselves. Surface modification and functionalization of textile materials became a very important technique in textile industry.

Recently solvent-assisted chemical modifications introduced cationic groups on cotton⁵⁾. But these methods would also cause the discharge of contaminants and residual solvents. Surface grafting process can graft polymer chains onto textile surfaces without significantly altering their bulk properties. The graft polymerization on polymeric fibers can be initiated with the use of ozone⁶⁾, γ rays⁷⁾, electron beams⁸⁾, plasma⁹⁾, corona discharge¹⁰⁾, and UV irradiation^{11,12)}. Among them, surface graft polymerizations induced by UV irradiation exhibit several advantages such as fast reaction rate, simple equipment, easy exploitation, low temperature treatment, energy saving and environmentally friendliness. In this study, a novel coloration approach for cotton was carried out by the grafting of C.I. Reactive Black 5 with acrylic acid onto cotton by UV irradiation.

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Moreover, the effects of the photografting conditions on the graft yield and dyeability as well as UV-induced graft copolymerization mechanism were investigated.

Compared with conventional dyeing method, the advantages of UV grafting dyeing include the rapid photografting dyeing without any salt addition at room temperature. Furthermore, both the washing (staining) and rubbing fastness of the dyed cotton fabrics with photografting was as good as conventional dyeing method except the shade change of wash fastness and light fastness. The color yield may be increased with more careful optimization.

2. Experimental

2.1 Materials and chemicals

Plain weave cotton (88.1g/m²) fabrics were used throughout the study. Acrylic acid (AA, Aldrich Chemicals Co.) was used as a water-soluble comonomer. Bis(2,4,6-trimethylbenzoyl) phenyl phosphineoxide (Irgacure 819, Ciba Specialty Chemicals Inc.) was used as a photoinitiator (PI) and Trion X100, a wetting agent, was bought from Yakuri Pure Chemical Co. Ltd (Japan). C.I. Reactive Black 5 (Remazol Black B), supplied by Dystar Textilfarben GmbH & Co., was employed with or without purification. The chemical structures of the photoinitiator and dye are shown in Fig. 1.

2.2 Photografting

Cotton fabrics were immersed into an aqueous grafting formulation containing dye, comonomer, PI and Triton X100. Then the impregnated fabric was squeezed to a wet pick up of about 90% using a padding mangle. A UV apparatus enclosing a D-bulb (a Fe doped mercury lamp) of 80W/cm intensity was used for UV irradiation. UV energy was controlled by adjusting the speed and passing cycles of a conveyor belt. After irradiation, the fabrics were thoroughly extracted first with 2% detergent solution at 60°C for 30min and subsequently with running water to remove the unreacted dye and monomer, PI and soluble homopolymer. Grafting yield (G%) was calculated from the following equation:

$$G\% = (W_2 - W_1) / W_1 * 100$$

where, W₁ is the weight of the original fabric, and W₂ is the weight of UV-irradiated fabric after the extraction.

2.3 Characterization of the photografted cotton surface

400 MHz ¹H NMR (Avance Digital 400, Bruker) using D₂O as a solvent was used to characterize the molecular structures of the C.I. Reactive Black 5 before and after UV irradiation. Elemental analysis (EA 1110, Mccoy Co.) was used to measure

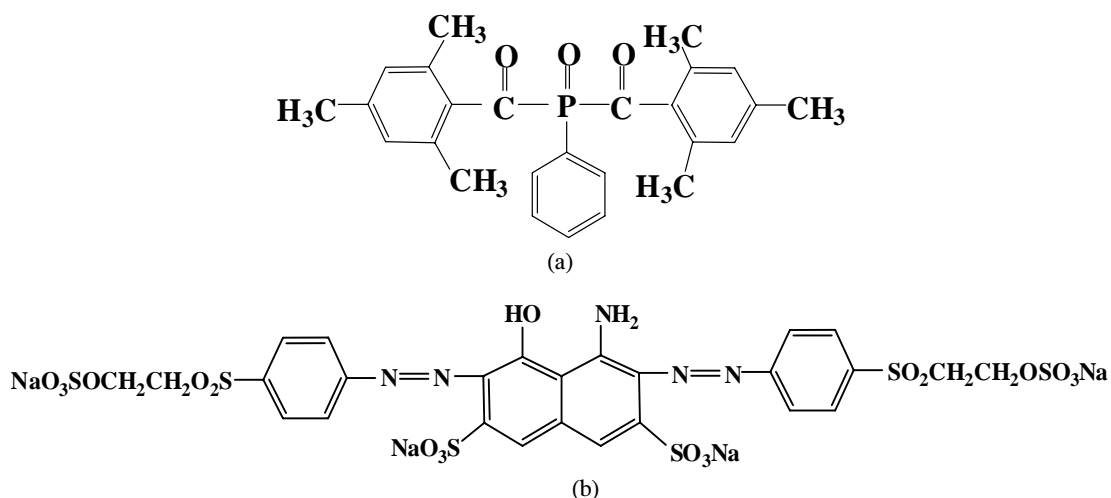


Fig. 1. Molecular structures of (a) Irgacure 819 and (b) C.I. Reactive Black 5.

the contents of sulfur, carbon, hydrogen and nitrogen of the C.I. Reactive Black 5 before and after UV irradiation. A UV/Vis spectrophotometer (Agilent Technologies, US/8453) was used to measure the absorbance of C.I. Reactive Black 5 solutions in the wavelength region between 200 and 800 nm and maximum absorption wavelength (λ_{\max}) was recorded at 600 nm.

2.4 The evaluation of coloration

K/S values were calculated from reflectance at λ_{\max} measured with a reflectance spectrophotometer (Gretag Macbeth, Coloreye 3100). Colour yield was evaluated by Kubelka-Munk equation as the following: $K/S=(1-R)^2/2R$ where K is an absorption coefficient, S is a scattering coefficient, and R is the reflectance at λ_{\max} . The colorfastness test to laundering, rubbing and light irradiation of the dyed fabrics were carried out using a Launder-O-meter (Daelim Engineering, Korea), crock meter (Heungshin Engineering, Korea), and Fade-O-meter (Korea Science, Korea) according to KS K ISO 105-C01, KS K 0650 and KS K 0700 respectively.

3. Results and Discussion

3.1 ^1H NMR analysis

The NMR spectrum of the purified C.I. Reactive Black 5 before UV-irradiation is shown in Fig. 2(a). The benzene protons of the dye (Scheme 1) were indicated at the peaks of 3 and 4, 5, 5', 6, and 6' and the intense peaks of 7 and 8 were attributed to the ethylene protons in sulfatoethylsulfone (SES) groups¹³⁾ of the dye. The weak peaks of *a*, *b* and *c* could be assigned to pristine vinylsulfone (VS) protons¹⁴⁾. After UV irradiation, the proposed photoreaction of C.I. Reactive Black 5 was shown in Scheme 1. With a UV energy of $5\text{J}/\text{cm}^2$ (Fig. 2(b)), the intensity of benzene protons decreased and there appeared some new peaks of 3' and 4', 9 and 9', 10, 11 and 11', 12 and 12', indicating the fragmentation¹⁵⁾ reaction of the dye under UV irradiation as possibly proposed by Scheme 2.

Interestingly, new VS protons are produced by the UV irradiation as shown by the intensified peaks of *a*, *b* and *c*. Also the VS groups are expected to photochemically cyclize¹⁶⁾ [2+2] or

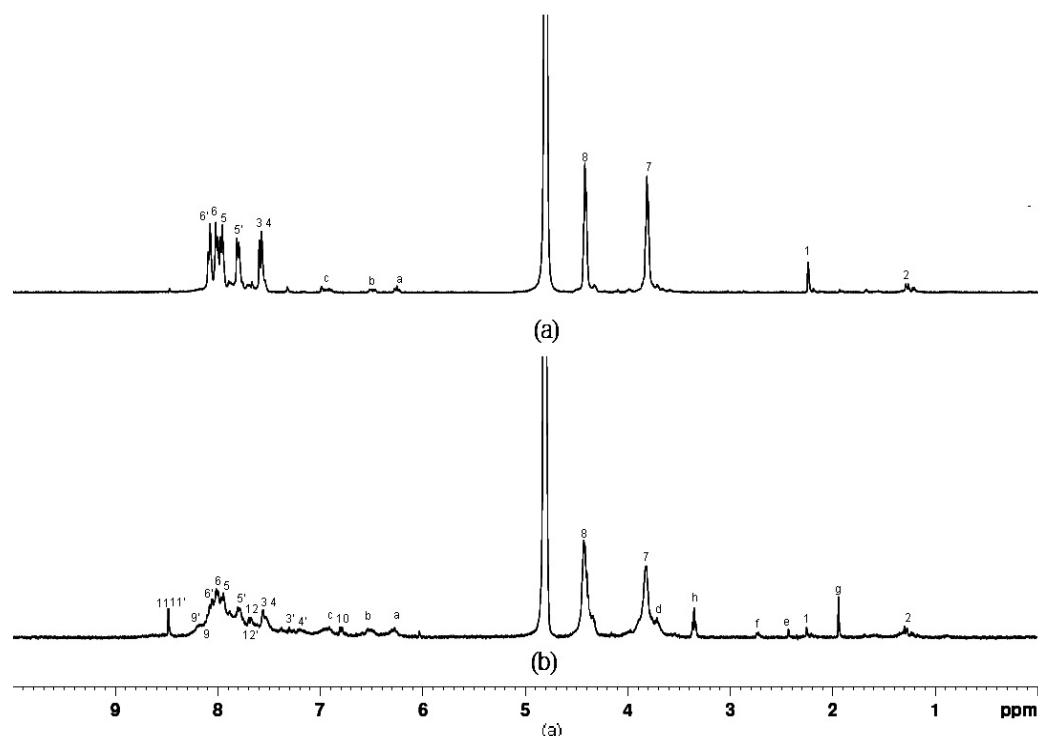
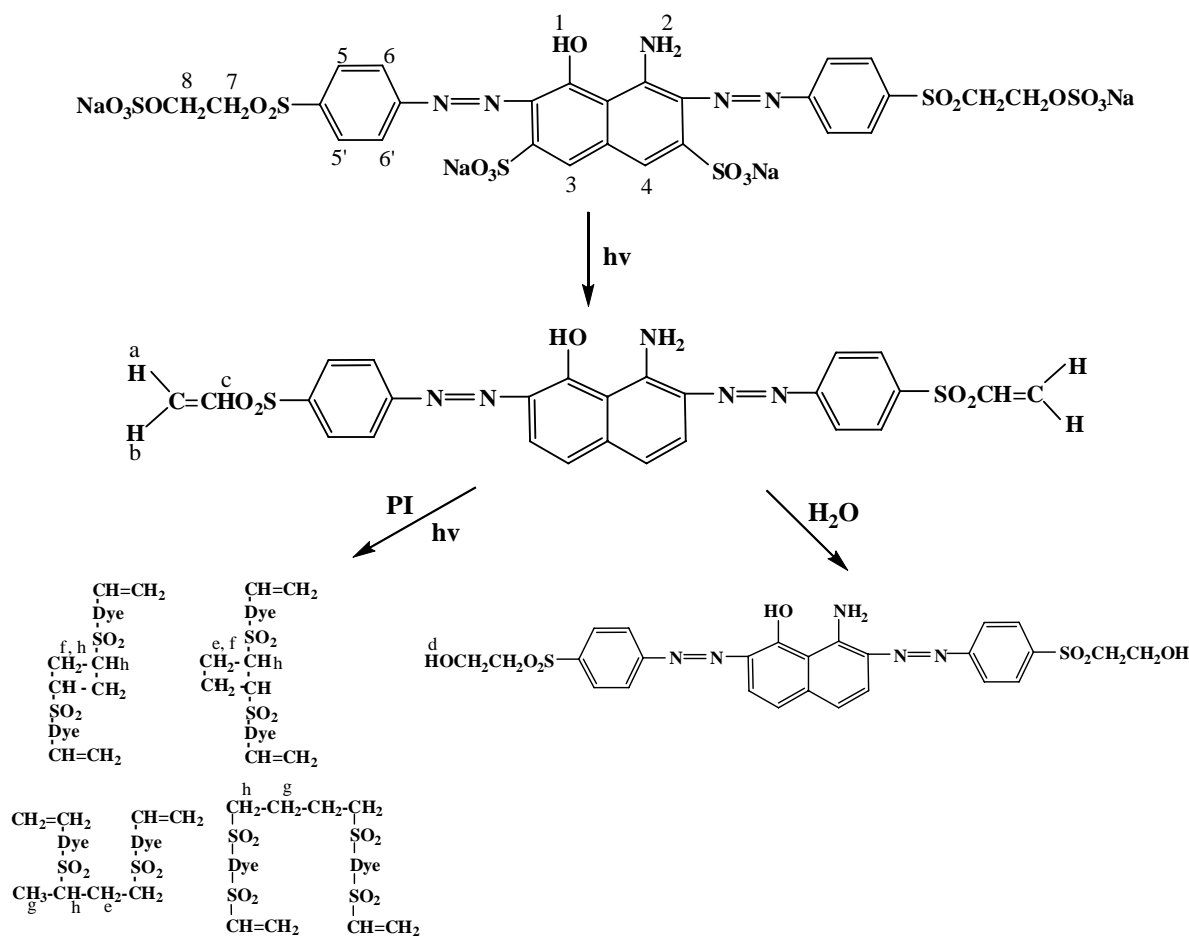


Fig. 2. ^1H NMR spectra of C.I. Reactive Black 5 (a) before and (b) after UV irradiation ($5\text{J}/\text{cm}^2$).

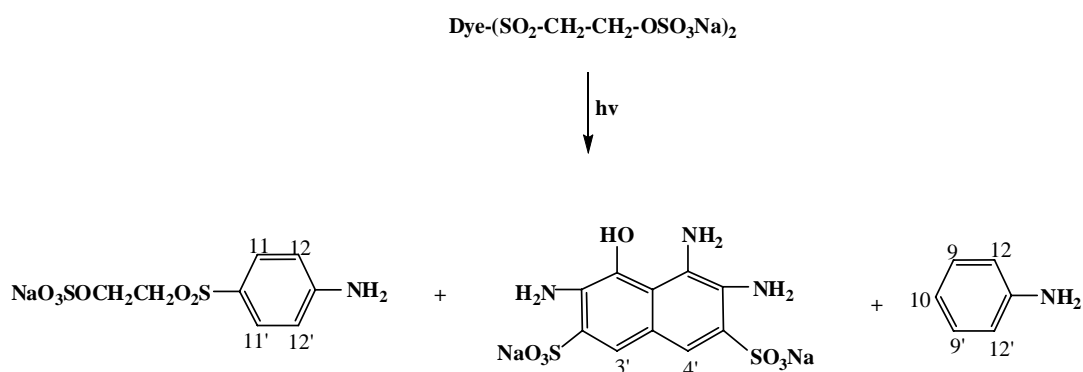
dimerize linearly¹⁷⁻²⁰ into four different forms of polyvinylsulfone(PVS) dyes in a different ratio under UV irradiation as shown in Scheme 1.

Because same methylene protons in a dimer could show different chemical shifts depending on the neighboring magnetic environment, some methine protons at *h* in a dimer structure could be overlapped with the methylene peaks such as

f, *e*, and *h* in another. Moreover, if the sterically less-hindered dimers may be obtained more than the high-hindered dimmers, the calculated protons ratio of *g* to *e* (5.8) and *h* to *f* (5.5) from the Scheme 1 was similar to the peak area ratio of *g* to *e* (5.8) and *h* to *f* (5.7) in Fig. 2(b), indicating the unfavorable influence of the bulky dye residue in the photochemical cyclo- and linear-addition.



Scheme 1. Proposed photoreaction of C.I. Reactive Black 5.



Scheme 2. Proposed photofragmentation of C.I. Reactive Black 5.

The linear dimer of *head-to-head* addition of the vinyl sulfone dye is expected to occur most probably. Furthermore, the hydroxyl in hydroxyethyl sulfone (HES) group appeared at *d* suggesting the facile hydrolysis²¹⁾ of the dyes under UV irradiation. Therefore, the vinyl sulfone formation, dimerization, fragmentation and hydrolysis of the dye under UV light can be evaluated by the ¹H NMR analysis. The changes of four different functional groups depending on the UV energy were summarized in Fig. 3. The VS reactive group which generated from the SES dye under UV light can be converted to PVS photochemically, which would be significantly important for the UV-induced coloration through the copolymerization of the dye and AA comonomers.

3.2 Elemental analysis

The elemental analysis showed that UV irradiation of 5J/cm² induced 58.1%, 34%, 27.1% and 1% decreases in the sulfur, carbon, hydrogen and nitrogen contents of the dye respectively as given in Table 1. It was attributed to the lowest bond energy (89.6kJ/mol) of the six C-S bonds in the dye structure which can be easily cleaved by UV irradiation²²⁾.

After UV irradiation, some of the C-S bonds would be cut off and result in several modified dye structures containing different amount of sulfur atoms. Since the content of sulfur decreased to 6.4% after UV irradiation, the content of the

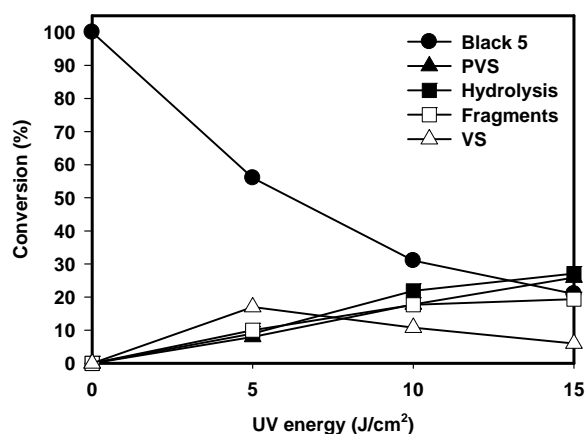


Fig. 3. The photochemical conversion of C.I. Reactive Black 5.

dye with different amount of C-S bond from six to zero may be estimated. The sum of the amount C-S from six to three may correspond to the amount of the SES and VS dyes. And the sum of the amount of C-S from two to zero may be consistent with the amount of the photochemically reacted dye, fragmentation and hydrolysis in Fig. 4. In addition, based on the different amount of C-S links, the amount of carbon and hydrogen elements after UV irradiation can be 17.6% and 2.3% respectively, which is reasonably similar to the elemental analysis data.

3.3 UV-VIS spectra

As shown in Fig. 4, the spectrum of C.I. Reactive Black 5 before UV irradiation exhibited three primary absorption peaks at 600, 312 and 254 nm. The absorption peaks at 312 and 254 nm corresponded to the naphthalene and benzene components. The characteristic absorption peak at 600 nm can be attributed to the bisazo chromophoric group²³⁾. As the UV energy increased, the intensity of the three peaks decreased gradually. But there were no new intermediates or products that would have displayed new absorption features

Table 1. Elemental analysis of C.I. Reactive Black 5

	N (wt%)	C (wt%)	H (wt%)	S (wt%)
Original dye	5.0	26.2	2.6	15.3
UV irradiation (5J/cm ²)	4.9	17.3	1.9	6.4

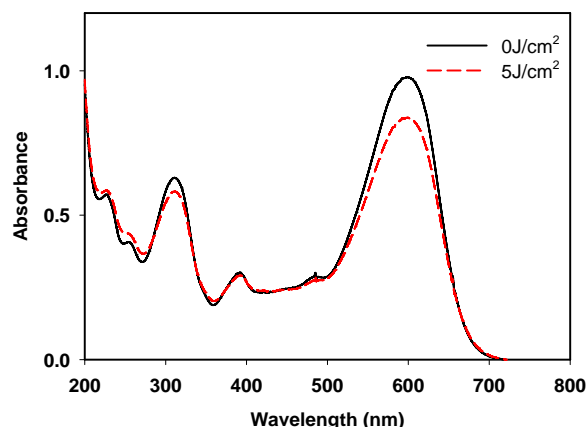


Fig. 4. UV-VIS spectra of C.I. Reactive Black 5 (0.027g dye/L in water).

in the visible and UV region. While UV irradiation can cleave some weak bonds of the dye and induce the dye fragmentation resulting in disappearance of color, the main bisazo structure in the dye was not changed and the amount of the dye degradation was expected to low as shown by the ^1H NMR analysis.

3.4 Effect of comonomer concentration

The dye itself or binary monomers of AA and dye were used to be photografted onto cotton as given in Table 2. The graft yield of the photochemically dyed fabric with the dye alone was immeasurable because the dye was too bulky for the efficient polymerization even though the fabric still showed a K/S of 3.1. While it may be difficult to be grafted on cotton directly, the dye solution containing AA as a comonomer improved the photografting and dyeability. The synergistic effect of binary monomers was a key factor contributing to the facile surface photografting of the dye⁴⁾. For the AA/dye system, the grafting yield increased with the increase in the AA/dye molar ratio until 3:1. The AA component in the binary monomers may accelerate the photopolymerization of the dye. Whereas AA was the most efficient comonomer for the photo-reactive coloration of cotton, excessive AA content can increase the homopolymerization²⁴⁾ as well. Therefore, AA/dye binary system with a mole ratio of 3:1 was chosen for the UV-induced coloration of cotton.

3.5 Effect of photoinitiator concentration

In the photoinduced grafting of the binary AA/dye system, the effect of PI concentration on the photografting of AA/dye onto cotton was shown in Fig. 5. Irgacure 819 is a cleavage-type photoinitiator. It can strongly absorb in the near UV to the visible spectrum and produce up to four radicals in a stepwise fashion, with which results in photobleaching effect. With increasing I819 concentration up to 3%owm, the K/S and grafting yield increased to a maximum and then reduced. The generated radicals by the PI also enhance the

grafting by creating polymer radicals via hydrogen-abstraction reaction of the cotton. When the PI concentration is too high, the self recombination of the radicals or homopolymerization may be facilitated over the grafting reaction. The photografting mechanism^{25,26)} under alkaline condition was suggested in Scheme 3.

3.6 Effect of UV energy

The UV energy effect on the grafting and dyeing results of AA/dye was shown in Fig. 6. The maximum G% and K/S were obtained when the UV energy was $15\text{J}/\text{cm}^2$ because of the additional photoreactivity of acrylic acid compared to the black dye. But when the UV energy is higher than that, the G% decreased unexpectedly. It can be understood that the higher energy caused the photodegradation of the photografted chains on the cotton fabric which corresponded to the UV-VIS spectra and elemental analysis.

Table 2. The effect of acrylic acid addition on K/S and graft yield

AA to dye (mole ratio)	G%	K/S
0	-	3.1
0.5	0.31	4.8
1	0.52	5.5
3	0.71	7.0
5	0.43	6.4
7	0.52	6.0

(UV energy: $15\text{J}/\text{cm}^2$, dye concentration: 6%, PI concentration: 3%, pH 10)

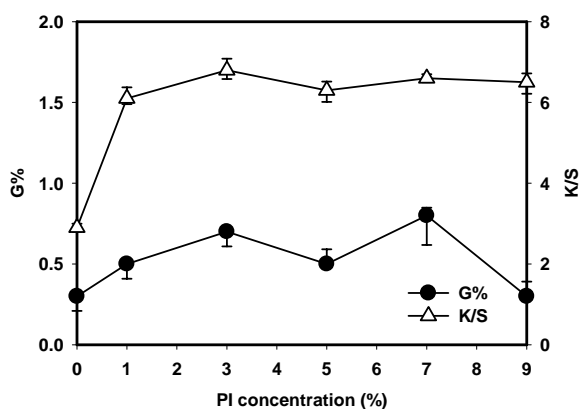
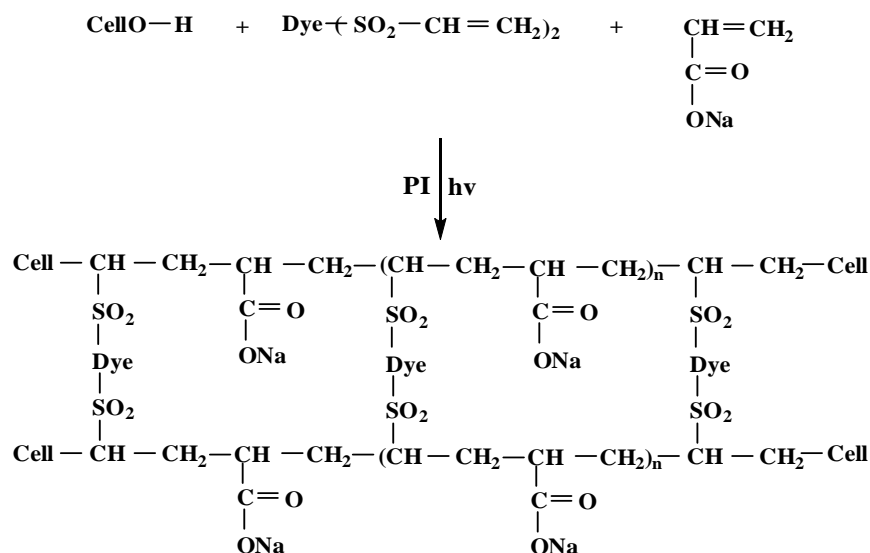


Fig. 5. The effect of PI concentration on G% and K/S (UV energy: $15\text{J}/\text{cm}^2$, dye concentration: 6%, pH 10).



Scheme 3. Photografting mechanism of C.I. Reactive Black 5 and acrylic acid.

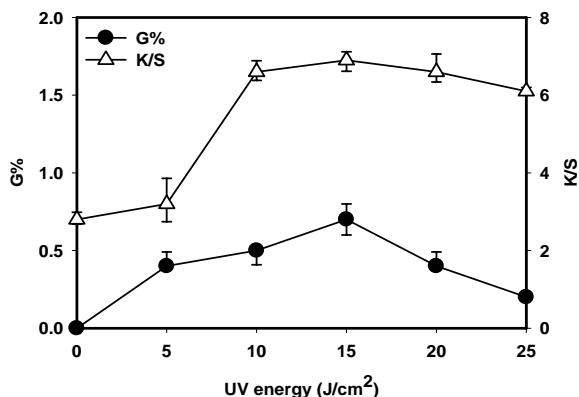


Fig. 6. The effect of UV energy on G% and K/S (PI concentration: 3%, dye concentration: 6%, pH 10).

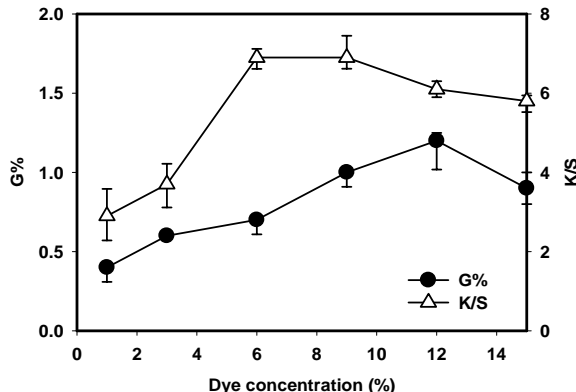


Fig. 7. The effect of dye concentration on G% (UV energy: 15J/cm², PI concentration: 3%, pH 10).

3.7 Effect of dye concentration

The grafting yield and color yield of the dyed cotton at different dye concentration were represented in Fig. 7.

The G% and K/S value increased with dye concentration up to 6% and then decreased with further increase in the dye concentration. While an initial increase in the dye concentration may promote the photografting onto the cotton, the graft copolymerization reaction may be discouraged by the blocking of UV light absorption by the excess dyes with the increased dye concentration.

3.8 Effect of pH

As can be observed in Fig. 8, the highest K/S was obtained at pH 10.

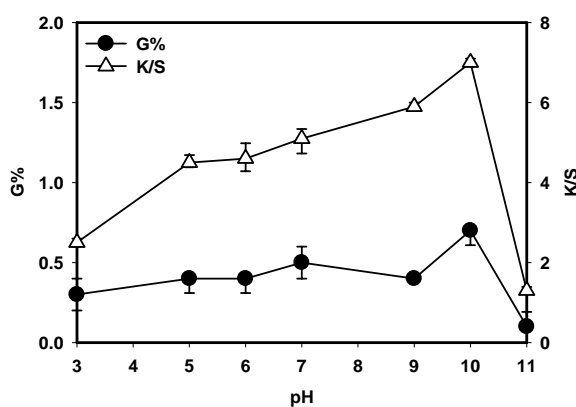


Fig. 8. The effect of pH on G% and K/S (UV energy: 15J/cm², PI concentration: 3%, dye concentration: 6%).

As well as the photo chemical conversion pathway, the β -elimination reaction of SES into the reactive VS form would be expected to occur favorably under the alkaline condition.

Table 3. Colorfastness of the dyed fabrics to laundering, rubbing and light irradiation

	K/S	Laundering							Rubbing		Light
		Shade	Stain						Dry	Wet	
			Wool	Acrylic	PET	Nylon	Cotton	Acetate			
Black ¹	7.0	2-3	4-5	5	4-5	4-5	4-5	4-5	4	4	2
Black ²	4.7	5	4-5	4-5	4-5	4	4-5	4-5	4-5	4-5	3

1 : 6%owb(dye), AA: dye (3:1), 3%owm(PI), 15J/cm², pH 10

2 : 1%owf(dye), 60°C for 60min, pH 10

However at pH 11, the reactivity of the VS group would be much decreased by more facile alkaline hydrolysis to the formation of HES, which greatly decrease the photoreactivity of the dye towards the photografting.

3.9 Color fastness properties

The color fastness of the dyed fabrics with UV irradiation to washing, rubbing and light irradiation were shown in Table 3.

Compared to a standard dyeing method without UV irradiation, the washing (staining) and rubbing fastness of the dyed cotton fabrics with photografting was good or excellent suggesting the polymeric nature of the photografted fabrics.

However both shade changes in the washing and light fastness were not good enough possibly due to the photodegradation of the grafted layer and the extraction of the dye fragments.

The photo-reactive coloration requires additional improvement on the shade change rating in wash and light fastness.

4. Conclusions

Acrylic acid was an efficient comonomer for the photo-reactive coloration of cotton using C.I. Reactive Black 5 as a monomer. The AA/dye binary monomers can be easily grafted onto cotton by continuous UV irradiation under ambient condition without salt. The UV-induced graft copolymerization mechanism was suggested by UV-VIS spectra, elemental analysis and ¹H NMR. The K/S and G% values for the grafted fabrics increased remarkably with UV energy, photoinitiator and dye concentrations at a 3:1

mole ratio of AA to the dye. Furthermore, the washing and rubbing fastness of the UV-dyeing cotton fabric were good except the shade change of wash fastness and light fastness testings.

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