Abstract: UV-induced graft polymerization has been widely applied as a simple, useful and versatile approach to improve the surface properties of fibers and polymers. A bis-vinylsulfone reactive dye was continuously photografted onto cotton with one of five vinyl monomers including HEMA, ACMO, AA, VP and DMAPMA. The AA/dye grafting system could synergistically promote the surface photografting, which disclose a novel environmentally friendly coloration method. Moreover, the influence of photografting factors on color yield were investigated., such as UV energy, dye and photoinitiator concentrations, the molar ratio of monomer to dye and pH. Furthermore, while both color fastness to staining and rubbing were good to excellent, color fastness to shade change was moderate indicating negligible photo-degradation of the photo-reactive dye.

Introduction
Cotton is the most widely used textiles in the world as it possesses many useful characteristics such as comfort, excellent softness, good absorbency, color retention, good strength and machine washable. The fiber can be dyed with five major classes of dyes including direct, vat, sulfur, azoic and reactive dyes. Among them, reactive dyes are the major class of cellulosic dyestuff in that they furnish a wide gamut of shades of good light fastness and excellent wash fastness on cotton. Moreover, reactive dyes do not have to be rendered insoluble in water nor highly substantive to the cellulosic fibres. Hence, reactive dyes of comparatively low molecular weight are used to achieve good penetration and levelness within the fibers and they were reacted to form covalent bond with hydroxyl groups of cellulose under alkaline condition. A particular problem with the application of many reactive dyes is the competing reaction of hydroxide ions in the dyebath to produce a hydrolysed, non-reactive form of the dye. Also, large amount of salts are needed to overcome the electrostatic repulsion between cotton fibers and reactive dye, which suppresses negative charge build-up at the fiber surface and promotes increased dye-uptake. But the use of high salt concentration would lead to environmental unfriendliness. Therefore salt-free or low-salt dyeing technology using reactive dyes has become a popular topic. Although cotton can be dyed in pale shade in supercritical carbon dioxide without auxiliaries, it requires non-polar dyes and high pressure equipment. An alternative approach to increase dye uptake and dye fixation is by the modification of...
cellulosic fibers themselves. Surface modification and functionalization of textile materials became a very important technique in textile industry. Recently solvent-assisted chemical modifications introduce cationic groups on cotton\(^4\). But this method would inevitably cause contaminants and residual solvents. Surface grafting process is a promising technology which can graft polymer chains onto textile surfaces without changing bulk properties of the materials. Moreover, the graft polymerization on polymeric fibers can be initiated with the use of ozone, \(\gamma\)-rays, electron beams, plasma, corona discharge, and UV irradiation. Among them, surface graft polymerizations induced by UV irradiation exhibit several advantages such as fast reaction rate, energy saving, simple equipment, easy exploitation, and environmentally friendliness. In this study, a novel coloration approach for cotton is carried out by the photografting of the photo-reactive dye. Binary monomers of one of five vinyl monomers and a bisvinylsulfone reactive dye were grafted onto cotton by UV irradiation, which can be carried out at room temperature without any salt.

**Experimental**

**Materials**

A bisvinylsulfone reactive dye and five water-soluble monomers were used as UV-active binary monomers for cotton coloration. The five water-soluble monomers were used including acrylic acid (AA, Aldrich Chemicals Co.), 2-hydroxyethyl methacrylate (HEMA, Junsei Chemical. Co.), 1-vinyl-2-pyrrolidone (VP, Aldrich Chemicals Co.), 4-acryloylmorpholine (ACMO, Aldrich Chemical Co.) and dimethylaminopropyl methacrylamide (DMAPMA, Aldrich Chemical Co.) were used as comonomers.

**Photografting**

Cotton fabrics were immersed into the grafting formulation containing dye, monomer, PI and Triton X100. Then the wetted fabric was squeezed to a wet pick up of about 90% using a padding mangle. A UV apparatus enclosing D-bulb (a metal 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\(^\circ\)C for 30min and subsequently with running water to remove unreacted materials.

**The evaluation of coloration**

K/S values were calculated from reflectance at \(\lambda_{\text{max}}\) measured with a reflectance spectrophotometer (Gretag Macbeth, Coloreye 3100). The colorfastness to laundering and rubbing of dyed fabrics were carried out with a Launder-O-meter (Atlas, Type LP2) and a crock meter respectively according to ISO 105-CO1 and 105-X12 respectively.
Results and Discussion

Comonomer effect

Under alkaline conditions, some of the hydroxyl groups on the cellulose become ionized to produce cellulosate ion. The vinylsulfone dye reacts with the cellulosic ions by a nucleophilic substitution mechanism to form covalent bonds. However, the dyes can also react with hydroxyl groups of water so that they are no longer able to react with cellulose, resulting in low dye fixation. The effect of individual dye, HEMA/dye, ACMO/dye, ACMO/dye, AA/dye, VP/dye and DMAPMA/dye binary monomers on K/S values was shown in Figure 1.

It can be seen that the K/S value of individual dye as a monomer was low compared with other monomer mixed systems. It may be resulted from that the molecular weight of dye was too high and hence it is difficult to be grafted on cotton directly. In the VP/dye grafting system, the K/S value did not change with increasing VP/dye molar ratio. While the molar ratio of both HEMA/dye and ACMO/dye also did not change surface photografting significantly, the AA/dye and DMAPMA/dye grafting systems synergistically promoted the photografting. Therefore, the optimal molar ratio of AA/dye systems for photografting was chosen to 3:1.
**Photoinitiator concentration**

With increasing PI concentration, K/S increase up to 3% and then leveled off (Figure 2) due to a higher concentration of initiating radicals in the grafting systems. When the concentration is too high, the recombination of the radical may dominate over the grafting reaction. The cleavage-type photoinitiator can strongly absorb in the near UV to the visible region of the spectrum and produce up to four radicals in a stepwise fashion. For cotton, free radicals could be generated by the breakage of C-H bonds rather than O-H bonds, which has the lower bonds dissociation energy.

![Figure 2](image-url)

**Figure 2** Effect of photoinitiator concentration on K/S.

**Dye concentration**

The effect of dye concentration on the color yield was shown in Figure 4. It was observed that the K/S value dramatically increased to dye concentration up to 9% and then leveled off. Under alkaline conditions, the β-sulfatoethyl sulfone of the dye hydrolyzed to form the reactive vinyl sulfone (VS) group which can subsequently form propagating radicals by UV irradiation. But potential dye hydrolysis
can make fiber-unreactive β-hydroxyethyl sulfone (HES). As more of the VS groups are hydrolyzed, the photografting of the dye decreases correspondingly.

![Graph showing the effect of dye concentration on K/S.](image)

**Figure 4** Effect of dye concentration on K/S.

**Fastness properties**

The color fastness of the dyed fabrics with and without UV irradiation to washing and rubbing were shown in Table 1. The shade rating for C.I. Reactive Black 5 was poor but staining fastness was good for both samples. The wet rubbing fastness of the photografted fabrics was better than that of the sample without UV irradiation. Even though the UV treatment changed only outer surface layer of cotton fabric and the dyes were more preferentially deposited at fabric surface, the dyes have strong enough interaction with the fibers to withstand the fastness tests.

<table>
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<tr>
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<th>K/S</th>
<th>Shade</th>
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<th>Rubbing</th>
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**Table 1** Colorfastness to laundering and rubbing of the photografted cotton
Conclusions

AA/dye binary monomers were easily grafted onto cotton by continuous UV irradiation under ambient condition. The color yield for the grafted fabrics increased remarkably due to covalent bonds between the cotton and reactive dyes under optimal photografting condition including comonomer ratio, dye and photoinitiator concentrations. Moreover, the vinyl sulfone dye should be carried out under alkaline condition. Furthermore, the color fastness of washing and rubbing of the photografted cotton fabric were excellent to good.

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References


