

Synthesis of a New, Yellow Crosslinking Polyvinylamine Dye and Its Crosslinking/Dyeing Process through a Crosslinker

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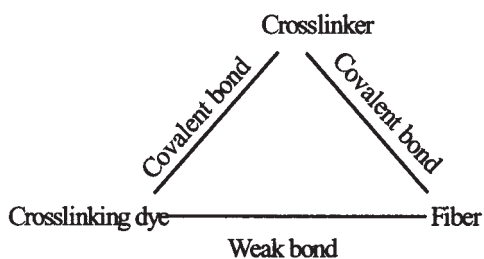
ABSTRACT: A new, yellow crosslinking polyvinylamine dye was synthesized by the reaction of 2,4-dinitrochlorobenzene with polyvinylamine prepared from Hofmann degradation of polyacrylamide. It was crosslinked and dyed to cotton and silk by a crosslinker synthesized from 1,3,5-trichloro-*s*-triazine and sodium 2-(*p*-aminophenylsulfonyl)ethyl sulfate. The crosslinking/dyeing conditions of the yellow polyvinylamine dye, such as pH, cure temperature, and concentration of the crosslinker were investigated. The fixations of the polymeric dye by the crosslinker on cotton

and silk were greater than 99%. The crosslinking covalent dye–fiber bond was proved indirectly by the comparison of IR spectra of the undyed fiber, the dyed fiber, and the crosslinked one, and also by the fact that no dye was stripped off from the crosslinked and dyed sample by extraction with DMF/water (1 : 1). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1568–1573, 2006

Key words: polyvinylamine; crosslinking polymeric dye; crosslinker; covalent dye–fiber bond

INTRODUCTION

Reactive dyes form the covalent bond with fiber, which results in its excellent fastness and large production. However, the serious hydrolysis of the reactive groups in application and storage causes about 20–50% reactive dyes wastage¹; hence, this demands new dyes with high fixation to avoid the environmental and inhibitory cost problems of reactive dyes. Under this background, crosslinking dyes such as Basazol,² Indosol,³ and alkylamine dyes⁴ with excellent fixation, without aforementioned shortcomings, have been developed. In general, crosslinking dyes have one or more suitable nucleophilic crosslinkable groups, such as amino, sulfydryl, hydroxyl groups, etc. As well known, cellulose and protein fibers have abundant similar groups. Therefore, nucleophilic reaction will take place easily on them in the presence of a crosslinker. Crosslinking dyes permanently bonded to the fiber may be represented as follows:



Polyvinylamine (PVAm) as a water-soluble polymer has been widely applied in catalysis,⁵ chelation,⁶ biomedical research,⁷ treatment of waste water,⁸ paper making,⁹ and the recovery of oil¹⁰, and so on. It is abundant in primary amino groups, which can be crosslinked readily by the crosslinker through nucleophilic reaction. If only one amino group in the PVAm chain is crosslinked to the fiber by the crosslinker, the whole PVAm molecule can be crosslinked to the fiber with covalent bond. Therefore, it may be predicted that the polymeric dye with PVAm as the backbone will be a kind of promising crosslinking dye with good crosslinking/dyeing properties.

The formation of crosslinking dye–fiber bond is accomplished actually by crosslinkers. In general, crosslinkers have two or more functional groups that make them react with both the crosslinking dye and the fiber. A number of readily available crosslinkers include aldehydes, multifunctional epoxides, isocyanates, acrylamides, and various reactive polymers, etc.¹¹ However there are a lot of environmental, operational, and economical problems against their use because of some drawbacks such as water insolubility, the release of toxicants, e.g. formaldehyde, isocyanates, etc. Therefore, it is necessary to synthesize new ones to overcome these problems. Among many reactive groups, sulfonyl ethyl sulfate group and 1,3,5-trichloro-*s*-triazine have been widely used in reactive dyes as the common, cheap, nontoxic, and excellent reactive groups, and they can also be employed as reactive groups of crosslinkers. Furthermore, the sulfonyl ethyl sulfate can endow the crosslinker with water solubility.

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In this study, a yellow crosslinking polyvinylamine dye (PVAmY) was prepared by the reaction of PVAm and 2,4-dinitrochlorobenzene, and a crosslinker (CDST) was synthesized via the reaction of 1,3,5-trichloro-*s*-triazine with sodium 2-(*p*-aminophenylsulfonyl)ethyl sulfate. PVAmY was crosslinked and dyed to cotton and silk by CDST. The covalent bond formed between PVAmY and fiber through CDST was proved.

EXPERIMENTAL

Reagents and instruments

PVAm with 80% amination degree was prepared from Hofmann degradation of polyacrylamide, according to our previous paper.¹² And other chemicals were analytical grade reagents.

HP1100 system of HPLC/MS, FT/IR-430 Spectrophotometer, and HP-8453 UV-Visible Spectrometer were used to confirm the structures of PVAmY and CDST.

Preparation of PVAmY

A 500-mL three-necked flask was charged with PVAm HCl (38.9 g, 0.40 mol amino group), Na₂CO₃ (24.4 g, 0.23 mol), and 250 mL water. The mixture was heated to 60°C. Then 2,4-dinitrochlorobenzene (12.2 g, 0.06 mol) was added, the temperature was raised to 80°C, and kept at 80°C until the reaction was over, and the reaction termination was monitored by TLC (Silica GF254, benzene:dioxane:acetic acid = 90:25:4, v/v). The resultant dye solution was poured into 1 L of methanol, and a yellow precipitate was obtained. The product was dried to constant weight (33.3 g; 97.1%).

Synthesis of CDST

1,3,5-Trichloro-*s*-triazine (19.4 g, 0.105 mol), broken ice (75 g), and 75 mL of water were mixed in a 500-mL flask and stirred fiercely for 30 min. Then a neutral solution of sodium 2-(*p*-aminophenylsulfonyl)ethyl sulfate (30.3 g, 0.100 mol) was added. The mixture was stirred under cooling while the pH was controlled at 7 or below with a 20% aqueous sodium carbonate solution. The reaction was monitored by Erich agent. When the reaction was over, the reaction mixture was salted out with a 20% aqueous sodium chloride solution. After the salt being removed by washing with 10% aqueous sodium chloride solution, the product yielded was 42.1 g (93.4%).

Crosslinking dyeing process

Dyeing of PVAmY on cotton and silk was carried out by use of a "two-dip-two-nip" operation at room tem-

perature. The fiber was dipped in the dye bath containing 7% (w/w) PVAmY at a liquor-to-goods ratio of 20:1 for 3 min and nipped with 70% wet pick up. After the dyed fiber had been dried at the room temperature, it was dipped into the crosslinking bath for another 3 min and nipped once with 70% wet pick up. Then the fiber was heated in an oven for 10 min, and then soaped using 2 g/L anionic detergent (sodium dodecyl benzene sulfonate; 10 min, 100°C), washed, and air dried. Finally, the soaped fiber was treated with DMF/water (1 : 1) at the boil.

Crosslinking/dyeing of polypropylene was carried out by the same process.

Measurement of dye fixation

The fixation of PVAmY was calculated first by determining the reflectance (*R*) of the dyed samples at the wavelength of maximum absorption on a Pye-Unicam SP8400 Spectrophotometer. The color yield (*K/S*) was calculated according to the Kubelka-Munk equation (eq. (1)). *K/S* values were measured twice: before soaping process [(*K/S*)_b] and after soaping treatment [(*K/S*)_a]. Percent fixation of the dye was calculated as follows (eq. (2)).

$$K/S = (1 - R)^2/2R \quad (1)$$

$$\text{Dye fixation (\%)} = [(K/S)_a/(K/S)_b] \times 100 \quad (2)$$

Fastness testing

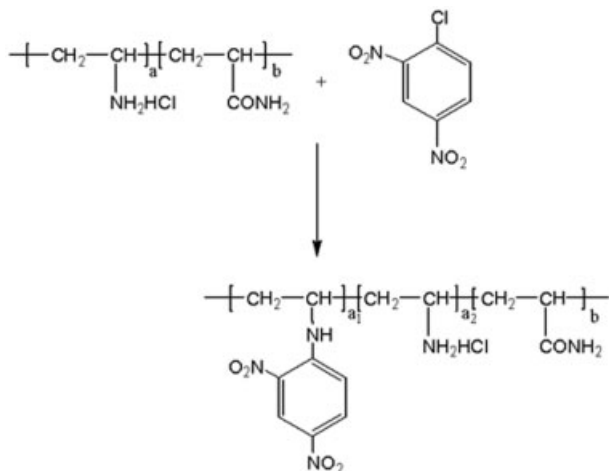
The color fastness of the dyed fabrics was tested according to Chinese Criteria methods including fastness to light [GB/T8427-87], washing [GB/T 3921-97], and rubbing [GB/T 3 920-97]. The light fastness was carried on a Light and Weather-Fastness Tester Heraeus 150S. The rubbing fastness was tested on a Circular Rub Fastness Tester YG571B. The washing fastness was tested in a standard bath. Finally, all the samples were evaluated to give their grade using the Standard Gray Scales.

RESULTS AND DISCUSSION

Structure confirmation of PVAmY and CDST

PVAmY was prepared as shown in Scheme 1.

PVAmY was characterized by TLC, UV-visible, and IR. TLC is the effective method to monitor the reaction. It was observed from TLC that, during the reaction, the *R_f* of PVAmY was 0 and the *R_f* of 2,4-dinitrochlorobenzene was 0.71. The hydrolysate of 2,4-dinitrochlorobenzene (*R_f* = 0.86) was not found by TLC. When the reaction was over, the disappearance of 2,4-dinitrochlorobenzene and the appearance of the yellow spot (*R_f* = 0) in the reaction mixture revealed



Scheme 1 Preparation of PVAmY.

that the reaction really took place, and the yellow resultant product was PVAmY. The absorbance curves of PVAmY and 2,4-dinitrochlorobenzene are shown in Figure 1, and the λ_{\max} of PVAmY and 2,4-dinitrochlorobenzene are 355 and 240 nm, respectively. The difference between them was caused by the red shift of absorption due to the increase of electron density of the phenyl ring after the substitution of Cl by NH. This difference also demonstrated that PVAmY was formed. IR spectra also exhibits the typical absorptions of PVAmY, i.e., $\nu_{\text{N-H}}$ at 3440 cm^{-1} assigned to NH_2 , the typical bands of $\nu_{\text{C=O}}$ at 1672 cm^{-1} of the amide residue after Hofmann degradation, and at 1515 and 1330 cm^{-1} due to NO_2 .

The synthesis of CDST is represented in Scheme 2.

IR spectrum of CDST exhibits the typical bands of $\nu_{\text{C=N}}$ at 1550 and 1510 cm^{-1} in the *s*-triazine ring, the stretching bands of $\nu_{\text{C=C}}$ for phenyl group at 1603 and 1550 cm^{-1} , and the band of $\nu_{\text{S=O}}$ for sulfonic group at 1241 cm^{-1} . MS (APCI) spectrum of CDST gives a correct quasimolecular ion peak (M-Na) at m/z 426.9. These data confirmed the structure of CDST.

The crosslinking dye-fiber bond

PVAmY was attached to the fiber by hydrogen bond and van der Waal's force before crosslinking/dyeing.

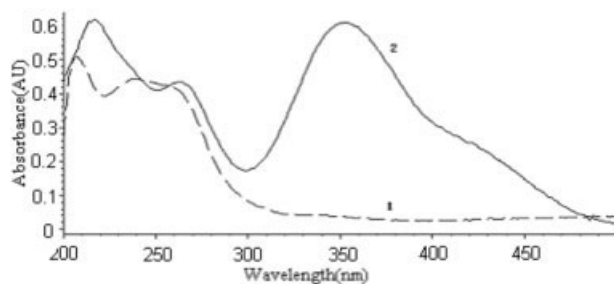
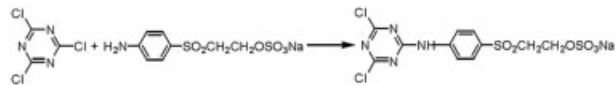


Figure 1 Absorption curves of 2,4-dinitrochlorobenzene (1) and PVAmY (2).



Scheme 2 Preparation of CDST.

However, these weak bonds were not strong enough to fix the dye to fiber, which is revealed by Table I. The fixations were only 42.7% and 27.6% on cotton and silk without crosslinker; whereas, when the concentration of CDST was 5% (w/w), the fixations on both fibers were over 99%. Moreover, the crosslinked and dyed fiber was soaped with a mild detergent at 100°C for 10 min, and no dye was stripped off after subsequent treatment with DMF/water (1:1) at the boil.

Furthermore, the IR spectra in Figure 2 show that there is a weak peak at about 1600 cm^{-1} in spectra B (dyed cotton) compared with that of A (cotton), which is the typical band of the ring of phenyl in the dye; and spectra C (the crosslinked cotton with CDST) also exhibits a weak peak at 1580 cm^{-1} , which may be attributed to the addition of the typical bands of PVAmY and CDST. Their weakness might result from the small amount of the dye molecules and the crosslinker compared with the glucose residue in cellulose. Because of the same reason, the peaks of the covalent bonds between CDST and PVAmY or cotton could not be observed in the spectra. The IR comparison of silk is shown in Figure 3. The difference between D (silk) and E (dyed silk) can not be observed because of the small amount of dye on silk, but there is an obvious difference in F (crosslinked and dyed silk) compared with D and E, that is, in D and E, the peak at 1520 cm^{-1} is weaker than that at 1600 cm^{-1} , but in F, the former peak is stronger than the latter one. The change of the absorption intensity between before crosslinking/dyeing and after crosslinking/dyeing indicated the existence of CDST on silk. In a word, although the spectra could not prove the covalent bond among them obviously, the existence of CDST on fiber and no dye washing off after DMF/water extraction still can indirectly give the proof of the covalent bond formed between the PAVmY and fiber after crosslinking/dyeing process.

Effect of concentrations of CDST on fixation

The effect of the concentration of CDST on cotton and silk was investigated (Table I). It demonstrated that

TABLE I
Effect of Concentrations of CDST on Fixation
Crosslinking Bath, pH 8.0

Conc. % (w/w)		0	1	3	5	7
Fixation (%)	Cotton	42.7	84.6	97.4	99.2	99.3
	Silk	27.6	87.3	97.9	99.3	99.5

The fabric was cured at 60°C for 10min.

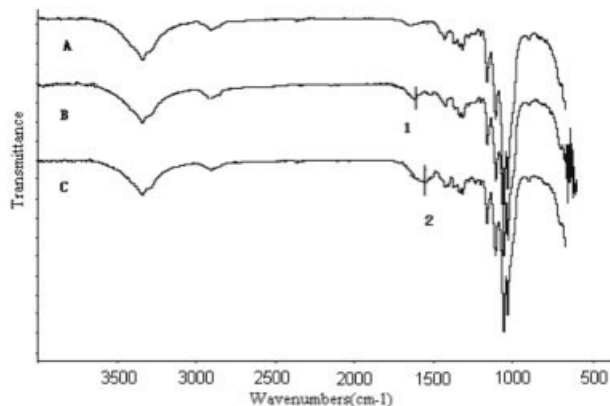


Figure 2 IR spectra of cotton (A), the dyed cotton (B), and the crosslinked and dyed cotton (C). Peak 1: 1600 cm^{-1} , peak 2: 1580 cm^{-1} .

the concentration of CDST had a great effect on the fixation, as expected. High, stable fixation was obtained when the concentration was more than 5%; and with the decrease of the concentration, the fixation also decreased. When the concentration was less than 5%, the amount of CDST molecules was not enough to complete the crosslinking reaction between PVAmY and the fiber; therefore, the fixation was lower. While at concentration over 5%, the amount of CDST molecules is enough to fully complete the crosslinking reaction, so high stable fixation was obtained. In addition, it can be seen that the fixation on cotton was greater than that on silk in the absence of the crosslinker. The main reason would be that hydrogen bond between cotton and PVAmY is stronger than that between silk and PVAmY, because cotton has more hydroxyl groups which can easily form hydrogen bond with amino groups of PVAmY.

Effect of cure temperature on fixation

The results of the dye fixation with varying cure temperatures are shown in Figure 4. This figure shows

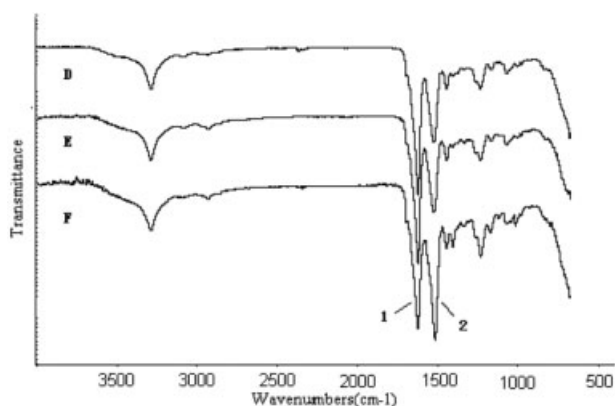


Figure 3 IR spectra of silk (D), the dyed silk (E), and the crosslinked and dyed silk (F). Peak 1: 1600 cm^{-1} , peak 2: 1520 cm^{-1} .

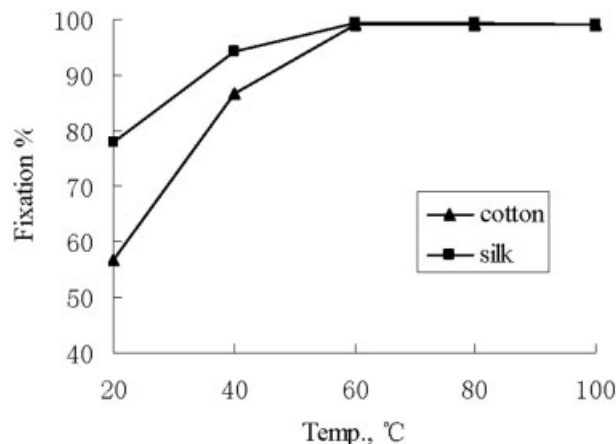


Figure 4 Effect of the cure temperature on fixation. Crosslinking bath containing 5% CDST, pH = 8.0. The fabric was cured for 10 min.

that the plot reaches a plateau over a fixation value of 99% when the cure temperature reaches 60°C . This might be attributed to the reactivity of CDST, because the reaction temperatures of both the sulfonylethyl sulfate group and the second chloride of 1,3,5-trichloro-*s*-triazine with hydroxyl group is about 60°C . When the cured temperature was above 60°C , both the groups would react fully, and even a part of the third chloride group of 1,3,5-trichloro-*s*-triazine would be activated to react with dye and fiber, thereby higher fixation was obtained.

On the contrary, at lower temperature, the crosslinker might react with the amino groups in the dye, but could not react with the hydroxyl groups in fiber successfully, which resulted in lower fixation. It was verified by the crosslinking/dyeing comparison between cotton and polypropylene fiber, as listed in Table II. Polypropylene fiber has no nucleophilic group; therefore, it can not be crosslinked by the crosslinker. Table II shows that dye fixations on both fibers are similar at 20 and 40°C , but the fixation on cotton is much greater than that on polypropylene at 60°C , which indicated that, at lower temperature, the reactions on cotton and polypropylene were similar; that is, by and large, the crosslinker could not react with the fiber at those temperatures. When the cured temperature was above 60°C , the fixation on cotton

TABLE II
Crosslinking Dyeing Comparison on Polypropylene and Cotton

Cured temp ($^{\circ}\text{C}$)	20	40	60	80
Cotton (F%)	56.7	86.7	99.2	99.1
Polypropylene (F%)	55.8	79.3	82.5	81.8

Crosslinking bath containing 5% CDST, pH, 8.0; the fabric was cured for 10min.

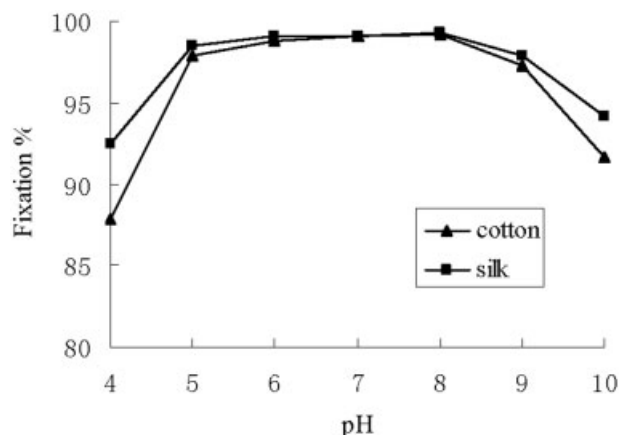


Figure 5 Effect of pH on fixation. Crosslinking bath containing 5% CDST. The fabric was cured at 60°C for 10 min.

was obviously greater than that on polypropylene, which revealed that the crosslinking reaction took place between fiber and CDST at that temperature. Although the crosslinking reaction did not occur between CDST and polypropylene fiber, the dye fixation was also far greater than that (15.3%) without CDST. This might owe to the crosslinking reaction of PVAmY itself through CDST to form a netlike structure. When the net is strong enough, it can resist washing and extracting with DMF/water. In addition, it can be seen that the fixation on silk is greater than that on cotton at both lower temperatures and concentrations. This difference results from the different composites of the fibers. As well known, cotton is a cellulose fiber containing abundant hydroxyl groups, and silk is a protein fiber with plenty of sulfydryl and amino groups. The nucleophilic reactivity of sulfydryl and amino groups is much greater than that of hydroxyl groups, so under even lower temperatures and concentrations, the possibility of the crosslinking reaction between silk and the crosslinker is greater than that between cotton and the crosslinker.

Effect of pH of crosslinker bath on fixation

Figure 5 shows the effect of pH values of CDST on fixation. It was found that the fixation was high and stable at neutral conditions; however, the fixation was slightly decreased at acidic and basic conditions. The main reason involved is that some amino groups of PVAm could form ammonium groups under acidic conditions, and as these ammonium groups were not nucleophilic groups any longer, the nucleophilic reaction could not take place between the ammonium groups and the crosslinker, thus the amount of the crosslinkable amino groups was reduced, which resulted in lower fixation. Under alkaline conditions, the hydrolysis of the sulfonyl ethyl sulfate group and the *s*-triazine of CDST were accelerated owing to the rea-

son that the nucleophilic reactivity of hydroxide ions was far greater than that of hydroxyl groups. As the result of the hydrolysis, the *s*-triazine lost reactivity because of the increase of electron density of *s*-triazine ring after chloride being replaced by hydroxyl group, and the reactivity of sulfonyl ethyl sulfate group vanished after a β elimination and an addition reactions.¹³ Therefore, the amount of crosslinkable crosslinker was reduced too. Consequently the dye fixation was lower than 99%.

Fastness properties

The fastness to light, washing, and rubbing for the crosslinked and dyed fabrics are listed in Table III. The rubbing fastness of crosslinking/dyeing is as good as that of the conventional reactive dyeing, while the washing fastness achieved by PVAmY and CDST is obviously better than that produced by the conventional dyeing, and the light fastness of the crosslinking method is somewhat worse than the reactive dyeing.

CONCLUSIONS

To improve the fixation, we designed and prepared a crosslinking polymeric dye PVAmY by the reaction of PVAm with 2,4-dinitrochlorobenzene, and a crosslinker CDST via the reaction of 1,3,5-trichloro-*s*-triazine and sodium 2-(*p*-aminophenylsulfonyl)ethyl sulfate. And the yields were 97.1% and 93.4% respectively.

PVAmY was crosslinked and dyed to cotton and silk by CDST. The optimum dye fixation of 99.2% and 99.3% on cotton and silk respectively, was obtained from a crosslinking bath set at pH = 8.0, concentration 5% (w/w), and cure temperature at 60°C. The wash and rub fastnesses of the crosslinked and dyed samples were found to be excellent.

The formation of the covalent bond is the core of the crosslinking/dyeing. The dyed-cured fiber fastness to DMF/water (1:1) extraction and the IR spectra of fiber, dyed fiber, and crosslinked and dyed fiber indirectly indicated that the covalent bond formed between PVAmY and the fiber through CDST. This reveals that PVAm is a kind of attractive crosslinkable backbone, as expected, and CDST is an effective, water-soluble, nontoxic crosslinker and synthesized readily.

TABLE III
Fastness Properties of the Crosslinking Dyed Fibers of PVAmY and CDST

Fiber	Light fastness	Wash fastness		Rub fastness	
		Change	Stain	Dry	Wet
Cotton (grade)	4	5	5	4	3-4
Silk (grade)	4	4-5	5	4	4

The 99% fixation of PVAmY is far greater than that of conventional reactive dyes (50–80%). These results indicate that the crosslinking/dyeing is a promising dyeing that can save costs, processing time, energy, and water consumption. It may be predicted that the crosslinking/dyeing will change a lot the coloration technology, including both the traditional and the rising color fields.

References

1. Lewis, D. M.; Sen, I. *Gakaishi* 1997, 53, 357.
2. Luzeln, G. *JSDC* 1966, 82, 293.
3. Egger, W. B.; Kissling, B.; Rohindon, T. *ADR* 1982, 7, 55.
4. Lei, X. P.; Lewis, D. M.; Shen, X. M. *Dyes Pigments* 1996, 30, 271.
5. Prabhakaran, P. V.; Venkatachalam, S.; Ninan, K. N. *Eur Polym J* 1999, 35, 1743.
6. Kobayashi, S.; Suh, K. D.; Shirokura, Y. *Macromolecules* 1989, 22, 2363.
7. Qiu, Y.; Zhang, T.; Ruegsegger, M.; Marchant, R. E. *Macromolecules* 1995, 31, 165.
8. Dubins, P. L. U.S. Pat 4,217,214 (1980).
9. Wu, Z.; Chen, S.; Tanaka, H. *J Appl Polym Sci* 1997, 65, 2159.
10. Ta-Wang, L.; Vllayendran, B. R. *Eur Pat* 295,614 (1988).
11. Hinton, E. H. *Text Res J* 1974, 44, 233.
12. Hu, Z. Y.; Zhang, Y. F.; Yang, J. Z.; Chen, Y. *J Appl Polym Sci* 2003, 89, 3889.
13. Datyner, A.; Rys, P.; Zollinger, H. *Helv Chim Acta* 1966, 49, 749.