# Study on the Leveling Properties of Derivatives of Polyethylene Glycol for Supermilling Acid Dyes on Wool Fabrics

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**ABSTRACT:** The feasibility of the derivatives of polyethylene glycol as leveling agents in the dyeing process of wool was studied. The interaction between the polymers and dyes affected not only the dyeing rate of supermilling acid dyes on wool but also the absorption spectrum of the dyes. The presence of the polymers improved leveling properties. The dyeing rate was slower in the presence of the polymer than without the polymer. The lower the concentration of dyes, the greater the effect of the polymers in the dyeing process was. The color fastnesses to rubbing, washing, and perspiration of the dyed wool fabrics with the polymer were good.
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**Key words:** acid dyes; exhaustion; fastness; leveling properties; polyethylene glycol; wool

## INTRODUCTION

It is commonly known that supermilling acid dyes are used to dye wool fabric under neutral or slightly acidic conditions. These dyes have greater affinity for wool and do not migrate and level as well as leveling and milling dyes. Therefore, the leveling property of wool fabrics dyed with these dyes is an important problem, especially for dark colors, such as blue, black, and so forth. Some leveling agents, as Albegal B and Albegal Set (Ciba), have been applied for wool dyeing. But these leveling agents are expensive. For dyeing factories, it is significant to develop some inexpensive polymer materials as leveling agents and new dyeing methods. Some research on the level-dyeing property and the diffusion of acid dyes into wool fibers has already been carried out. The leveling agents and the pretreatment with low temperature plasma are used in dyeing wool.[1,2] Actually, the dyeing process of wool with acid dyes is a complex interaction of molecules among surfactants, dyes, and fibers. The leveling property of small molecule surfactants is poor. They can decrease the equilibrium exhaustion of acid dyes.[3,4] The effluent pollution from the dyeing bath containing dyes is increased. In recent reports, new polymers can also be used as leveling agents.[5,6] The derivative of polyethylene glycol is water soluble and easy to synthesize. It contains a large amount of hydrophilic groups, so the derivative of polyethylene glycol can be used for phase-transfer catalysis in the multi-phase reaction. The derivative of the proper structure and molecular weight of polyethylene glycol may impart good leveling properties to wool fabrics dyed with supermilling acid dyes.

In this article, different structure polymers of polyethylene glycol as leveling agents are studied. The leveling property of the polymers and the dyeing rate are investigated.

## EXPERIMENTAL

### Materials

The different structure polymers of polyethylene glycol A4,B4 as leveling agents were obtained from Shanghai Handa Chemical Company. The polymer A4 was a 20% aqueous solution of polyethylene glycol maleate. The molecular weight of polymer A4 was 20,000. Polymer B4 was a 20% aqueous solution of a copolymer of polyethylene glycol diacrylate and methacryloyloxyethyl trimethylammonium chloride. The molecular weight of copolymer B4 was 180,000. The acid dyes, Everlight Blue *N*-AFN, were obtained from Taiwan Everlight Company.

Wool fabrics were obtained from Beijing Wool Textile Company. They were treated for 0.5h at 50°C in the presence of 1.0% Detergent 209, and then washed. Detergent 209 was obtained from Shanghai Handa Chemical Company.

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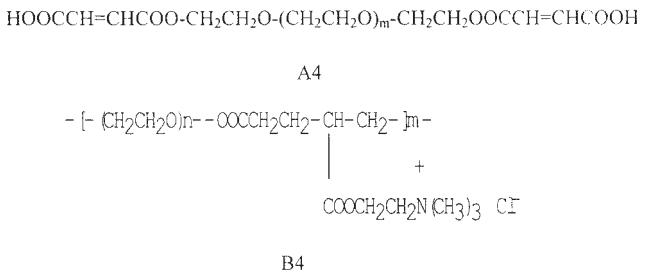


**Scheme 1**

## Dyeing

The dyeing solution was prepared by mixing different concentrations (0.5%, 2%, 5%, and so forth on weight of solution (ows)) of the polymers and certain concentrations of dyes. Wool fabrics were dyed in an IR dyeing machine (PYROTEC-2000), the liquor ratio being 15 : 1 and the dyeing solution pH value (5.5 ~ 6) being maintained by an acetic acid/sodium acetate buffer solution. Fabrics were immersed in the dye bath at 40°C, and the temperature was increased to100°C at a rate of 1°C/min. Dyeing was carried out at this temperature for 60 min. After dyeing, all the dyed samples were squeezed to recover residual liquor and rinsed with water until the rinsing water was clear. The rinsing water was added into the residual liquor to measure the absorbance.

### Exhaustion measurement

The exhaustion of the dyes on the fabric was calculated by measuring the absorbance of the residual dye bath liquor. The percentage of dye bath exhaustion (E%) was calculated according to eq. (1):

$$E(\%) = [1 - (C_2/C_1)]*100 \quad (1)$$

where $C_1$ and $C_2$ are the concentrations of the dyes in the dye bath before and after dyeing, respectively.

Absorption spectra of the dyes were measured with a UV-2102 PCS.

### Color measurement

Color measurement was determined using a Gretag-Macbeth Color-Eye 7000A instrument. The Kubelka-Munk equation (eq. (2), where $R$ is reflectance) was used to determine the $K/S$ values of the dyed wool fabric at $\lambda_{max}$ for the dyes (630nm).

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

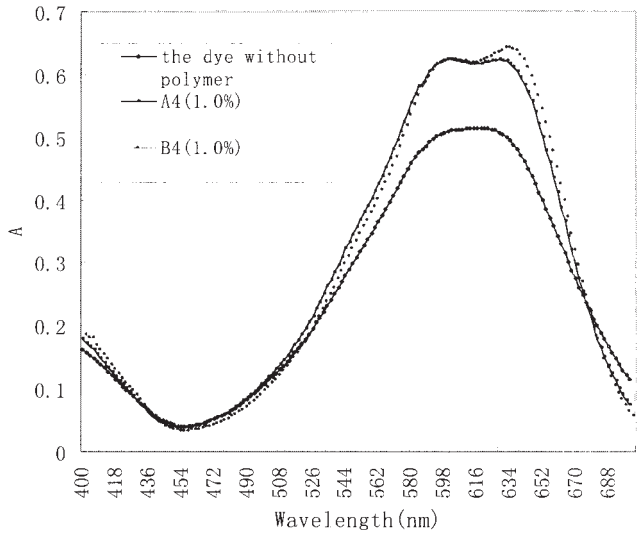


**Figure 1** The absorption spectra of the mixture solutions of the dyes with the polymers.

### Fastness testing

Color fastness was determined according to the respective international standards: fastness to washing, ISO 105-C04 (1989); fastness to perspiration, ISO 105-E04(1994); and fastness to rubbing, ISO 105-X12(1993).

## RESULTS AND DISCUSSION

### Absorption spectrum of the mixture solution of the dyes with the polymers

Polymers A4 and B4 are derivatives of polyethylene glycol. The chemical structure of A4 is shown in Scheme 1. A4 contains the hydrophilic nonionic polyethylene glycol group and anionic (carboxy end group)–COOH. Polymer B4 is a copolymer of polyethylene glycol diacrylate and methacryloyloxyethyl tri-

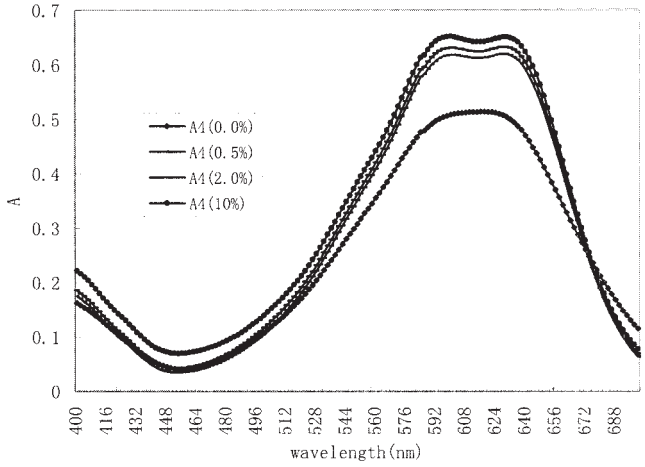


**Figure 2** The absorption spectra of the dyes with different concentrations of A4.

**TABLE I**
**The Maximum Absorption Wave Length and Absorbance (A) of the Mixture Solutions of the Dyes with Different Concentrations of Polymer A4**

| | The first peak | | The second peak | |
|---|---|---|---|---|
| A4 (g/l) | $\lambda_{max}$(nm) | A | $\lambda_{max}$(nm) | A |
| 0 | 618 | 0.5138 | - | - |
| 0.5 | 628 | 0.6192 | 600 | 0.6178 |
| 2 | 629 | 0.6323 | 600 | 0.6307 |
| 5 | 629 | 0.6351 | 599 | 0.6341 |
| 10 | 630 | 0.6505 | 599 | 0.6518 |

methylammonium chloride. It contains hydrophilic nonionic and cationic groups. The chemical structure of B4 is shown in Scheme 1.

Because the molecular weight of the polyethylene glycol used is very high (PEG 20,000), polymers and dyes interact with hydrogen bonds and ionic bonds in the dyeing solution. Interaction between polymers and dyes not only affected the exhaustion rate of the acid dyes in dyeing but also affected the absorption spectrum of the dyes. Figures 1 and 2 are the absorption spectra of the mixture solution of the dyes with the polymers. The concentration of the dye Everlight Blue *N*-AFN is 0.08 g/L. Figure 1 shows that the maximum absorption wave length ($\lambda_{max}$) of Everlight Blue *N*-AFN was 618 nm. The absorption spectra of the mixture solutions of the dyes with polymers A4 and B4 (1.0% ows) had been changed. The maximum absorption wave length ($\lambda_{max}$) of the mixture solution of the dyes with A4 moved from 618nm to 629nm, and the maximum absorbance (A) increased from 0.5138 to 0.6227. The maximum absorption wave length ($\lambda_{max}$) of the mixture solution of dyes with B4 moved from 618 nm to 632 nm, and the maximum absorbance (A) increased from 0.5138 to 0.6417. The absorption band of the dyes had been changed, from one peak to two peaks. It shows that the dyes and the polymers formed

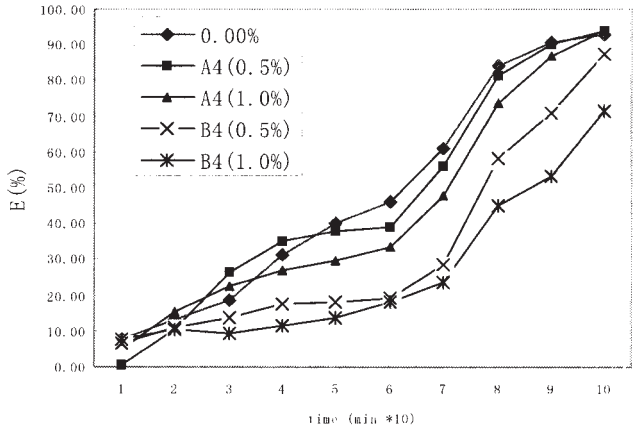


**Figure 3** Effects of different structures of polymers.

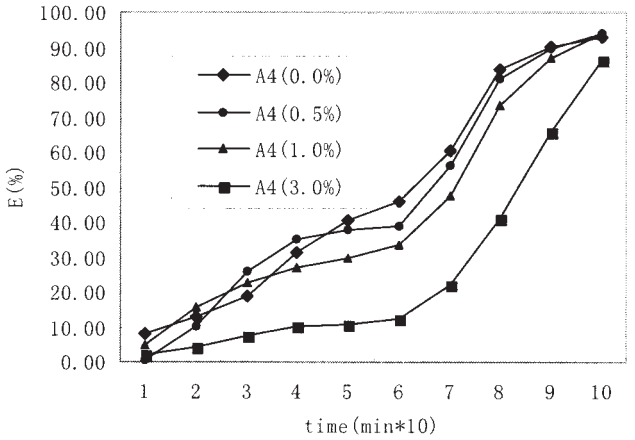


**Figure 4** Effects of the concentration of A4.

complexes. The molecules of the dyes were covered with the polymer molecules. Figure 2 shows that the higher the concentration of polymer A4, the longer the maximum absorption wave length was and the higher the maximum absorbance (A) was. The changes of the maximum absorption wave length and the maximum absorbance (A) are shown in Table I. With raising the concentration of polymer A4, the size of the complex was increased. The complex between the dyes and polymer A4 took longer to diffuse into the fiber, so this affected the absorption and diffusion of the dyes on wool.

### Effects of the concentration of the polymers on the dyeing rate

After scouring, the wool fabric was dyed with Everlight Blue *N*-AFN in different concentrations of polymers A4 and B4, respectively. The exhaustion of the dyes on wool at different times is shown in Figure 3. Figure 3 shows that polymers A4 and B4 obviously affected the exhaustion of the dyes on wool fabrics. The dyeing rate was slower in the presence of the polymers than without the polymers. The polymers

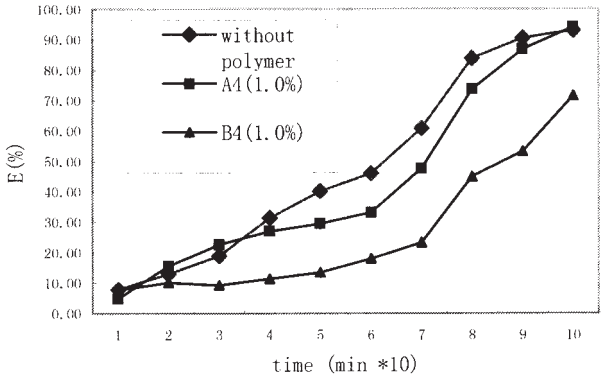


**Figure 5** Exhaustion of the dyes (0.5% owf).

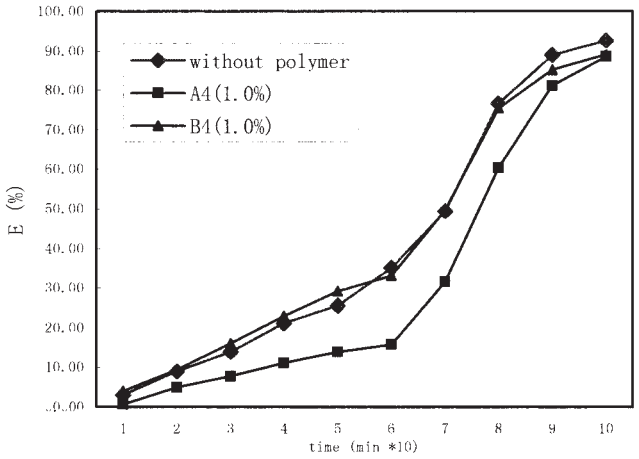


**Figure 6** Exhaustion of the dyes (1.0% owf).

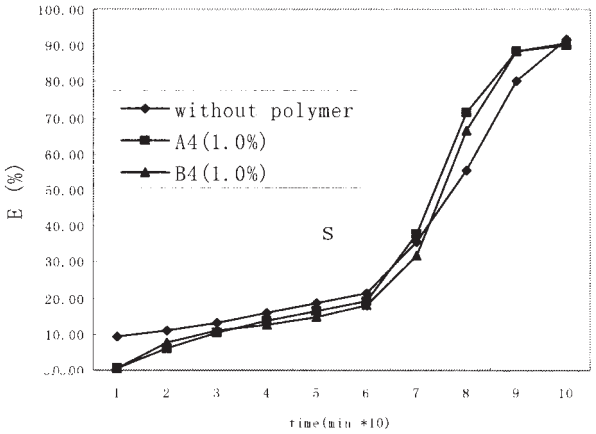


**Figure 8** Exhaustion of the dyes (5.0% owf).

improved leveling properties. The final exhaustion of the dyes with A4 was the same as without polymers. But the final exhaustion of the dyes with B4 was slightly lower than without polymers. This shows that the complex of the dyes and polymer B4 is more stable than that of the dyes and A4. Because B4 contains cationic groups and acid dyes contain anionic groups, they become a complex of anionic dyes by ionic bond in the dyeing solution to slow down the dyeing rate.

The exhaustion of the dyes (1.0% on weight of fabric (owf)) on wool with different concentrations of A4 at different times is shown in Figure 4. It can be seen that the higher the concentration of polymer A4, the lower the exhaustion of dyes in the dyeing process was. However, the final exhaustion of the dyes with different concentrations of A4 was almost the same as without polymer A4. A4 had excellent leveling properties.

In the presence of certain concentrations of the polymers, the different concentrations of dyes in the dyeing solution have different effects. The exhaustion rate of the dyes on wool with different concentrations of Everlight Blue *N*-AFN is shown in Figures 5, 6, 7, and 8, respectively. The results show that the lower the concentration of dyes was, the greater the effect of the polymers on the wool dyeing process. When the concentration of dyes was low, the dyeing rate was obviously slower in the presence of polymers than without the polymers. The presence of the polymer significantly improved the leveling properties of the dyed wool fabrics.

The *K/S* values of the dyed samples (Everlight Blue *N*-AFN, 2% owf, dyeing time 100 min) without the polymers and with polymers A4 and B4 (1% ows, respectively) are listed in Table II. It can be seen that the *K/S* values of the three dyed samples have no significant difference.

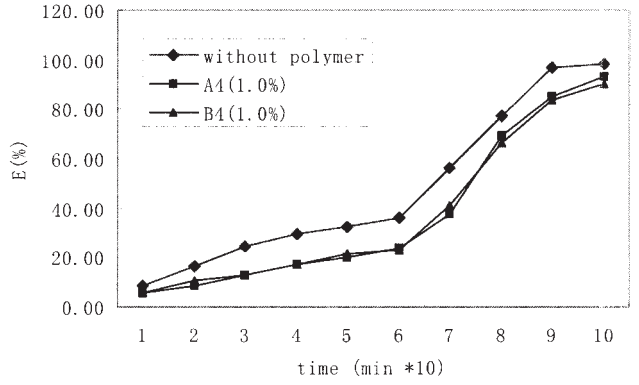


**Figure 7** Exhaustion of the dyes (2.0% owf).

### Fastness properties

The results of fastness tests for the dye Everlight Blue *N*-AFN on wool (2% owf, dyeing time 100 min) with polymers A4 and B4 (1% ows, respectively) and without polymers are summarized in Table III. The results indicate that the fastness to rubbing, washing, and perspiration of the dyed wool fabrics was good.

## CONCLUSIONS

1. Derivatives of polyethylene glycol could be used in combination with acid dyes in the dye bath. Interaction of the polymers and the dyes not only affected the rate of exhaustion of the dyes in the dyeing process but also affected the absorption spectrum of the dyes.

**TABLE II**
***K/S* Values of the Dyed Samples Without Polymers and With Polymers A4 and B4**

| | Without polymers | Polymer A4 | Polymer B4 |
|---|---|---|---|
| *K/S* | 14.437 | 14.362 | 14.285 |

**TABLE III**
**Fastness Properties of Everlight Blue N-AFN on wool**

| | Fastness to rubbing | | Fastness to wash | | Fastness to perspiration | |
|---|---|---|---|---|---|---|
| Dyed sample | Dry | Wet | SC | SW | SC | SW |
| Without polymer | 3–4 | 3 | 5 | 5 | 5 | 5 |
| A4 | 3–4 | 4 | 5 | 3–4 | 4–5 | 4 |
| B4 | 3–4 | 3–4 | 5 | 3–4 | 4 | 3–4 |

SC = staining on cotton; SW = staining on wool.

2. Polymers A4 and B4 affected the exhaustion of the dyes on wool. The dyeing rate was slower in the presence of the polymers than without the polymers. The final exhaustion of the dyes with A4 was almost the same as without the polymers. But the final exhaustion of the dyes with B4 was slightly lower than without the polymers.
3. The lower the concentration of dye was, the greater the effect of the polymers in the dyeing process. Leveling properties of the polymers were good. The fastness to rubbing, washing, and perspiration of the dyed wool fabrics with polymers was good.

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