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Eco-friendly Dyeing of Poly(trimethylene terephthalate) with Temporarily Solubilized Azo Disperse Dyes Based on Pyridone Derivatives

Hae Kyoung Jang, Song Jun Doh[1], and Jung Jin Lee*

Fiber System Engineering Program, Division of Polymer System Engineering, Dankook University, Yongin 448-701, Korea
[1]Fusion Technology R&D Division, Korea Institute of Industrial Technology, Ansan 426-791, Korea
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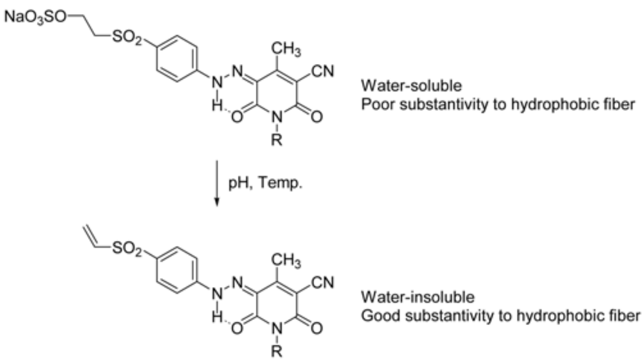
Abstract: Dispersant-free PTT dyeing of temporarily solubilized azo disperse dyes based on pyridone moiety which contain β-sulfatoethylsulfonyl group was investigated. The dyes were successfully applied to PTT without the use of dispersants. The color yields of the dyes on PTT fabric were dependent on dyeing pH as well as dyeing temperature. The optimum results were obtained at pH 5-6 and 110 ^{o}C. The dyes showed alkali-clearing property and exhibited good to excellent fastness on the PTT fabric. The COD levels of the dyeing effluent from the temporarily solubilized disperse dyes were much smaller than those from commercial disperse dye.

Keywords: Temporarily solubilized disperse dye, Dispersant-free dyeing, Alkali-clearing, Dyeing effluent, COD

Introduction

Poly(trimethylene terephthalate), PTT, is a kind of aromatic polyester fibers along with poly(ethylene terephthalate), PET, and poly(butylene terephthalate), PBT. Although PTT was originally developed by Whinfield and Dickson in 1941, it was commercialized in 1990s only after the 1,3-propandiol, the prime material for PTT, could be prepared at a low cost. This fiber has good softness and resilience, easiness of dyeing, great soil resistance and antistaticity [1,2]. Dyeing of hydrophobic fibers such as PTT and PET with disperse dye is usually performed in the presence of dispersant. Dispersants are added to the dyebath in order to increase solubility of disperse dye and to maintain dispersion stability during dyeing procedure. However, they may cause staining of the fabric. They are also discharged as effluents with the residual dyeing liquor, which increases the COD and BOD values of the effluent [3].



Scheme 1. Conversion of β-sulfatoethylsulfone group into vinylsulfone group in the temporarily solubilized azo disperse dyes based on pyridone moiety.

*Corresponding author: jjlee@dankook.ac.kr

In an effort to overcome the environmental problems associated with the use of dispersants, development of temporarily solubilized azo disperse dyes containing β-sulfatoethylsulfonyl group was reported and the feasibility of dispersant-free PET dyeing with the dyes was investigated [4,5]. The terminal sodium sulfate group of the dye confers sufficient water solubility at room temperature so that milling process is not needed during manufacturing of the dyes, and the dyebath can be prepared without the dispersants. During the dyeing procedure, the soluble dye is gradually converted to insoluble form as the β-sulfatoethylsulfonyl group is hydrolyzed into vinylsulfone group through β-elimination reaction (Scheme 1). Then the water-insoluble form of the dye having substantivity to hydrophobic polyester fiber such as PTT and PET can be adsorbed into the fiber.

Our group has reported several works about synthesis of the temporarily solubilized disperse dyes which have various color range and dyeing properties of the dyes on PET and PET/Cotton blend fabric [6-10]. Recently, we investigated dyeing properties of the temporarily solubilized disperse dyes from aminoazobenzene moiety on PTT fabric [11]. PTT fabric was successfully dyed with the dyes without using any dispersant and COD levels of the dyeing effluent were quite smaller when compared with those from commercial dyes. However, PTT dyeing with yellow temporarily solubilized disperse dyes has not been studied yet. While aminoazobenzene dyes can cover orange, red, purple, violet, and blue color, yellow color shade can be produced by the dyes from azopyridone or azoindole derivatives.

In this study, dispersant-free dyeing of the temporarily solubilized azo disperse dyes based on pyridone derivatives on PTT fabric was investigated. Color fastness and alkali-clearing properties of the dyes have also been examined. For the evaluation of eco-friendliness, COD value of the dyeing effluent from the temporarily solubilized dipserse dyes was compared with that from a commercial disperse dye.

Experimental

Materials

Scoured, woven PTT fabric (plain, warp: SDY 75 d/72 f, weft: SDY 75 d/72 f, weight: 116.3 g/m^2) was obtained from Huvis Co. Three yellow temporarily solubilized azo disperse dyes from pyridone derivatives were prepared by previous method [6], and their structures are given in Table 1. A commercial disperse dye was supplied by Kyung-In Synthetic Co. The commercial dye also contains pyridone moiety and shows yellow shade. The commercial and C.I. generic name and structure of the dye are shown in Table 2. All the other reagents used were of laboratory grade.

Dispersant-free Dyeing of PTT

PTT fabrics were dyed in an IR dyeing machine without using any dispersant. The dyebaths were prepared with dyes 1-3 (0.5-3.0 % owf) and buffered as follows: at pH 4 and 5 with sodium acetate (0.05M)/acetic acid; at pH 6, 7, and 8 with sodium dihydrogen phosphate (0.05 M)/disodium hydrogen phosphate; at pH 10 with sodium dihydrogen phosphate (0.05 M)/trisodium phosphate. Liquor-to-goods ratio was 20:1.

Table 1. Temporarily solubilized disperse dyes used in this study

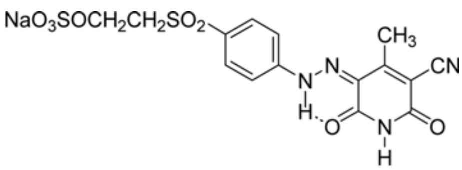
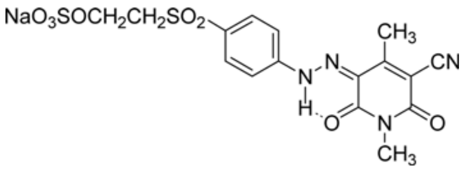
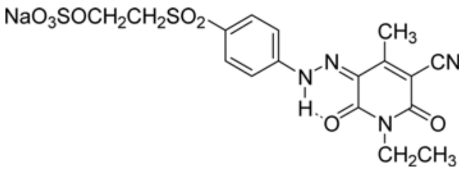
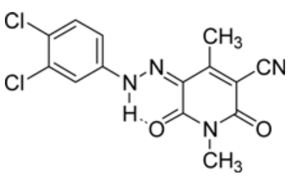
Dye	Structure
Dye 1	
Dye 2	
Dye 3	

Table 2. A commercial disperse dye used in this study

Dye	Commercial name	C.I. generic name	Structure
Dye 4	Synolon yellow K-5GL	C.I. disperse yellow 241	

Dyeing was commenced at 70 ^oC. The dyebath temperature was raised at a rate of 1 ^oC/min to 110-130 ^oC, maintained at these temperatures for 60 min and rapidly cooled to room temperature. The dyed samples were either reduction-cleared (2 g/*l* sodium hydroxide and 2 g/*l* sodium hydrosulfite; 80 ^oC, 10 min), or alkali-cleared (20 g/*l* sodium carbonate; 80 ^oC, 10 min), or not cleared.

Measurement of Color Yield and Fastness

The color parameters of the dyed PTT fabric were determined on a Macbeth coloreye 3100 spectrophotometer under illuminant D65 using 10^o standard observer.

The dyed fabrics (dye concentration: 1 % owf) were subjected to wash (ISO 105-C06/C1S:1994) and light (ISO 105-B02:1994) fastness tests with some samples being heat-set at 130 ^oC for 60 s. The staining of adjacent fabrics was rated according to appropriate grey scale.

COD Analysis of Dyeing Effluent

PTT fabrics was dyed with temporarily solubilized disperse dyes (dyes 1-3) in the absence of dispersants and they were also dyed with a commercial disperse dye (dye 4) containing a dispersant. Before and after dyeing, dyeing liquor of 100 m*l* was collected and than COD_{Mn} values of the dyeing liquor were measured according to the test method in KS M 0111.

Results and Discussion

Dyeing Properties

In dyeing of temporarily solubilized disperse dyes containing β-sulfatoethylsulfonyl group, pH condition and dyeing temperature are important factors as these factors are closely related to the conversion rate of the soluble form into insoluble vinylsulfone form, which was reported in previous studies [4,5]. In the initial stage of dyeing, the dyes are soluble in dyeing liquor but do not have enough substantivity to the hydrophobic PTT fiber yet. During the dyeing procedure, the conversion reaction would gradually occur and then the insoluble dyes can be dyed onto the fiber. Therefore, it is important to investigate the effect of pH condition and dyeing temperature on the color yield of PTT fabric.

Figure 1 shows the color yields of dye 2 on PTT fabric at various pH values and at 110 ^oC. Good color yields were obtained at pH 5 and 6. Final *K/S* values were similar to each other although dyeing rates were different. At pH 4, color yield was much lower than at pH 5 and 6 which is due to the low conversion rate of the soluble dye into the insoluble vinylsulfone form. Although dyeing rate at pH 4 was slow, the color yield increased continuously throughout the whole dyeing procedure, implying that the conversion of dye occurred steadily. The color yields and dyeing rates at pH 7 and 8 were lower than at pH 5 and 6 and poor uptake was

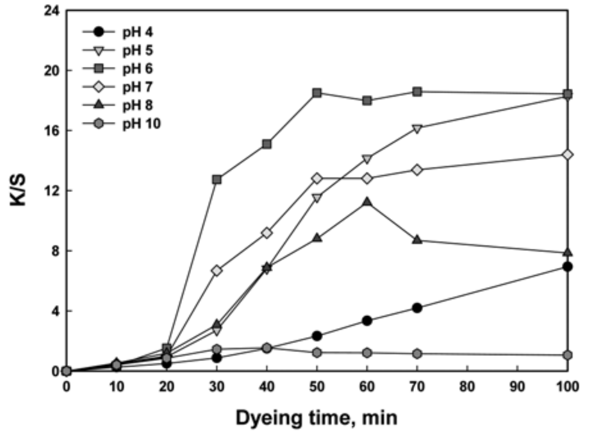
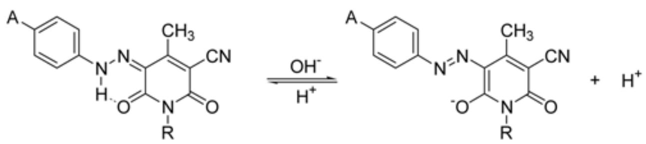


Figure 1. Effect of pH on the color yield of dye 2 on PTT fabric (dye concentration: 1 % owf, dyeing temperature: 110 °C).



Scheme 2. Hydrazone - azo anion equilibrium of azohydroxypyridone dyes.

obtained at pH 10. These results can be explained by the ionization of the hydroxypyridone dye under alkaline conditions. It is well known that hydroxypyridone dye exists predominantly as hydrazone form rather than azo form in the solid state and acidic solutions. In alkaline solutions, however, the hydrazone form of the hydroxypyridone dye is converted to the azo anion form as shown in Scheme 2 [6,12]. Thus, when dyeing is carried out at pH 7, 8, or 10, the hydrazone form of each dye would be ionized and the azo anion form would occur which has a low substantivity to the hydrophobic PTT fabric resulting in unsatisfactory color yields. The ionization of the hydroxypyridone dye could be advantageous in after-treatment step and thus the alkali-clearing property of the dyes may be enhanced.

Figure 2 shows the color yield of dye 2 on PTT fabric at various dyeing temperatures and at pH 5, 6, and 7 while dye concentration was fixed to 1 % owf. High color yield was obtained at 110 °C and the color yield decreased as dyeing temperature increased to 130 °C. It is well known that PTT fiber can be dyed at lower temperatures when compared to PET fiber because PTT fiber has less packed macromolecular structure and lower crystallinity than PET although both fibers have similar chemical structure [13,14]. At each dyeing temperature, color yield at pH 5 and 6 was higher than that at pH 7 which is consistent with the results in Figure 1. Figure 3 shows the build-up of the dyes 1-3 at pH 6 and 110 °C. Dye 1 showed limited build-up at all the dye concentrations when compared to dyes 2 and 3. This can be explained by weak hydrophobic interaction between dye 1

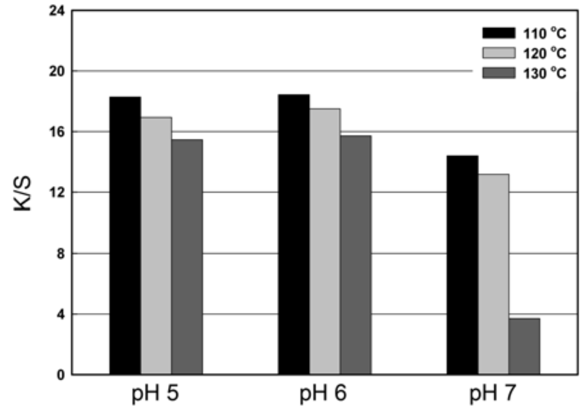


Figure 2. Effect of temperature on the color yield of dye 2 on PTT fabric (dye concentration: 1 % owf).

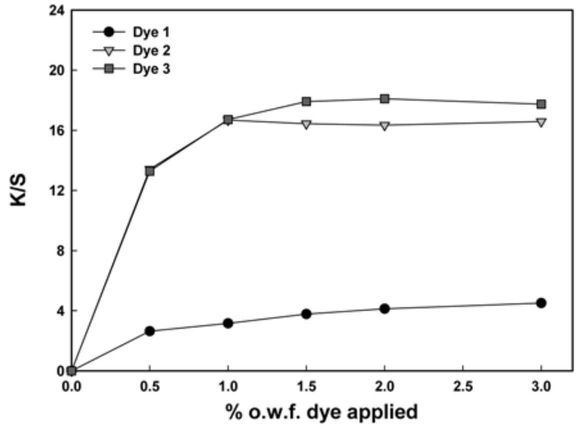


Figure 3. Build-up properties of dyes 1 to 3 on PTT fabric (110 °C, pH 6, liquor ratio 20:1).

and PTT fiber due to the presence of the polar NH group in the pyridine ring. Low uptake of dye 1 on PTT fiber was similar to the previous result that dye 1 exhibited limited exhaustion on hydrophobic PET fiber [6]. Dyes 2 and 3 exhibited moderate build-up on PTT and the color strength of the dyes reached saturation at 1-1.5 % owf.

From the results in Figures 1-3, PTT fabric was successfully dyed with the temporarily solubilized disperse dye without using dispersant. Optimum results were obtained at pH 5-6 and at 110 °C.

Comparison with a Commercial Disperse Dye

For comparison of the temporarily solubilized disperse dyes (dyes 1-3) with the commercial disperse dye, dye 4 were selected as it contains 1,4-dimethyl-2-hydroxy-5-cyano-6-pyridone which is the same coupling component as dye 2. PTT fabrics were dyed with dyes 1-4 under the same dyeing conditions (1 % owf, pH 6, and 110 °C) except that a dispersant was only used for the commercial dye and not for the temporarily solubilized disperse dye. Considering the influence of the dispersants, the fastness properties of the dyed fabric and COD values of dyeing effluent were compared.

Table 3 show CIEL*a*b* values and ISCC-NBS color names of the dyes on PTT fabric. Dyes 1 to 3 exhibited greenish yellow, light yellow and moderate yellow on PTT, respectively. The commercial dye (dye 4) which has the same coupling component as dye 2 showed also light yellow and similar CIEL*a*b* values on PTT fabric.

As previously mentioned, hydroxypyridone azo dyes become ionized in alkaline solutions and the unexhausted dye on the fiber surface can be washed off by alkali-clearing. In order to investigate this, the fastness of alkali-cleared PTT fabric was compared with that of reduction-cleared one. Table 4 shows the wash fastness results for the uncleared, alkali-cleared, and reduction-cleared PTT fabrics, with or without heat setting. When heat setting was not performed, the alkali-cleared samples showed excellent fastness to staining for dyes 1-3 while the uncleared samples showed some staining. Dye 4, the commercial dye showed the similar trend to dyes 1-3 and alkali-cleared sample was better than uncleared one but ratings of staining on acetate and nylon adjacent fabrics for the alkali-cleared sample were just good. For the heat set samples, the fastnesses of the alkali- and reduction-cleared samples for dyes 1-3 were generally similar showing good to excellent ratings although the level of staining decreased slightly when compared to the samples without heat setting. The fastness of reduction-cleared sample for the commercial dye (dye 4) showed very good rating while that of alkali-cleared one was moderate. Table 5 shows the light fastness results and the ratings of the alkali- and reduction-cleared samples for all the dyes were same, showing over 4. The wash and light fastness results demonstrate that an alkali-clearing process can be applied for the pyridone-based temporarily solubilized disperse dyes.

Figure 4 and 5 show COD_{Mn} levels of PTT dyeing liquor before and after dyeing for temporarily solubilized disperse dyes (dyes 1-3) and the commercial dye (dye 4). At the initial dyeing stage, COD level of dyeing liquor for dye 4 (700 mg/*l*) was higher than those for dyes 1-3 (less than 320 mg/*l*) as shown in Figure 4. In case of dyeing effluent, the difference became more significant. Thus, in Figure 5, COD level of dyeing liquor after dyeing for dye 4 (496 mg/*l*) was still high while those for dyes 1-3 (77 to 183 mg/*l*) were much lower than dye 4. Low COD levels of dyeing effluents for the temporarily solubilized disperse dyes are probably due to the fact that no dispersant was used when applying dyes 1-3 to PTT. As most dyes should be adsorbed onto the fiber, dyeing effluent would contain unexhausted dye and small amount of electrolyte which were added to adjust pH of dyeing liquors. Among dyes 1-3, COD level of dye 1 was higher than those of dye 2 and 3, which could be attributed to low exhaustion of dye 1 on PTT as previously mentioned.

Table 3. The color data of dyes 1-4 on PTT fabric

Dye	CIE L*a*b* values			ISCC-NBS color name
	L*	a*	b*	
Dye 1	86.07	-9.73	42.25	Light greenish yellow
Dye 2	83.01	-4.64	49.87	Light yellow
Dye 3	79.85	0.54	47.96	Moderate yellow
Dye 4	82.04	-2.76	50.55	Light yellow

Table 5. Light fastness of dyes 1-4 (1 % owf) on PTT fabric

Dye	Heat setting	
	Alkali clearing	Reduction clearing
Dye 1	over 4	over 4
Dye 2	over 4	over 4
Dye 3	over 4	over 4
Dye 4	over 4	over 4

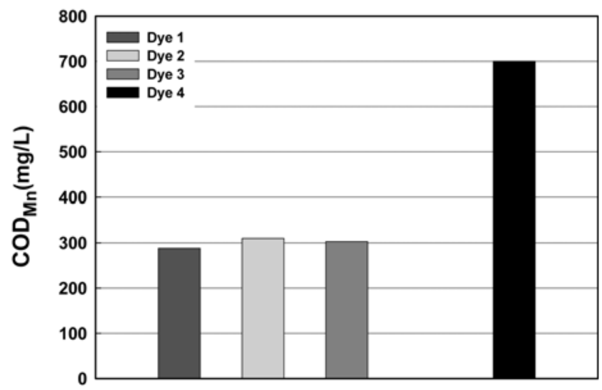


Figure 4. COD_{Mn} levels of PTT dyeing liquor before dyeing.

Table 4. Wash fastness of dyes 1-4 (1 % owf) on PTT fabric with and without heat setting (130 °C, 60 s)

Dye	No heat setting				Heat setting			
	No clearing		Alkali clearing		Alkali clearing		Reduction clearing	
	A[a]	N[a]	A[a]	N[a]	A[a]	N[a]	A[a]	N[a]
Dye 1	4-5	5	5	5	5	5	4-5	4-5
Dye 2	4	4	5	5	4-5	4-5	4	4-5
Dye 3	4	4	5	5	4	4	4-5	4-5
Dye 4	3	3	4	4	3	3	4-5	4-5

[a]A: staining on acetate, N: staining on nylon.

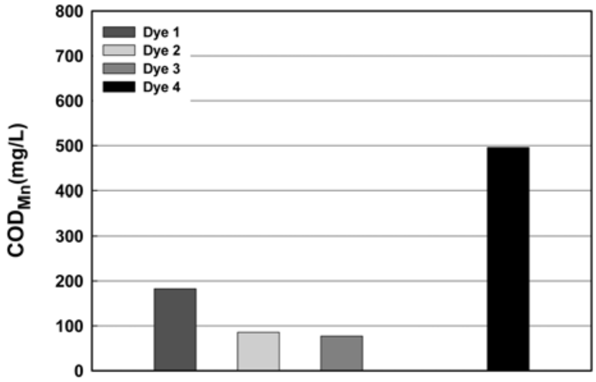


Figure 5. COD$_{Mn}$ levels of PTT dyeing liquor after dyeing.

On the other hand, the commercial dye exhibited high COD levels at the initial and final stage of dyeing. In commercial dyeing of PTT, dispersants are contained in the commercial dye itself to some extent and are added separately to the dyebath in order to stabilize dye dispersion. Most of the dispersants, not being adsorbed to the fiber, would remain in the dyeing liquor after dyeing and increase the COD level.

Conclusion

Dispersant-free PTT dyeing of the temporarily solubilized azo disperse dyes from pyridone derivatives was investigated and color fastness including alkali-clearing property as well as environmental aspects of the dyes were compared with a commercial disperse dye.

PTT fabric was successfully dyed with the dyes without using any dispersant. The color yield on PTT fabric was highly dependent on the dyeing pH and also dependent on dyeing temperature. The optimum result was obtained at pH 5-6 and 110 ^{o}C. Dye 2 and 3 showed moderate build-up on PTT whereas limited exhaustion was observed in the case of dye 1.

Ionization of the hydroxypyridone azo dyes occurs under alkaline conditions and this confers alkali-clearing property which can replace reduction-clearing. Wash and light fastness of PTT dyed with dyes 1-3 from both alkali- and reduction-clearing processes were generally similar and the overall results were good to excellent.

The COD levels of the dyeing effluent from the temporarily solubilized disperse dyes were considerably smaller than those from commercial disperse dye, which is probably attributed to the absence of dispersants for the temporarily solubilized disperse dyes. Considering dispersant-free dyeing as well as alkali-clearing property, the temporary solubilized disperse dyes based on pyridone derivatives could be promising as eco-friendly dyes.

Acknowledgement

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