

Synthesis, Characterization, and Properties of Ethoxylated Azo Dyes

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Abstract: The nonionic surfactant properties of ethoxylated azo dyes, such as cloud point and surface tension have been investigated. The synthesized ethoxylated azo dyes could dye polyester fabric without any special pre-treatment. When the average number of ethylene oxide (EO) in the ethoxylated azo dye reached 6, its fixation could exceed 90 % from the thermosol dyeing process. The average degree of condensation of ethylene glycol in the chain was interrelated with the dyeing results and did not affect on the maximum absorption wavelength (λ_{max}) of the polyoxyethylene dye. When the average length of polyoxyethylene chain decreased, the molecular weight of dyes became smaller and the fixation of dyes was improved.

Keywords: Azo, Surface tension, Cloud point, Thermosol dyeing process, Ethoxylated reaction

Introduction

Disperse dye has very low solubility in H₂O and is suitable for dyeing the hydrophobic synthetic fabrics. They are usually introduced in its finely dispersed form. The results of dyeing with disperse dye depend not only on the physical property of the fabric, thermodynamic and kinetic parameters of the dye used, but also on the characteristics of the dyes in the dyeing media to a large extent. The important physical properties of the dye are solubility, melting point, sublimation point, and crystal form of single dye molecule. The property of disperse dye is also assessed by the processing technology, viz., pre-dispersion, mixing, milling, homogenization, etc[1-3].

Recently, a new kind of disperse dye which has been grafted with polyoxyethylene is developed for dyeing the synthetic fabric directly without any special pre-treatments. Azo disperse dye, anthraquinone disperse dye, phthalocyanine disperse dye, and triphenylmethane disperse dye being grafted into the nonionic polyoxyethylene chain would dye the synthetic fabric effectively[4-8].

The ethoxylated dye is broadly regarded as a kind of bifunctional molecule of dye and nonionic surfactant with a clear cloud point. The dye may be dissolved in water without adding any dispersing agent at room temperature, but very low aqueous solubility above its cloud point is observed. It was reported that the impurity was removed from ethoxylated dyes using its cloud point[9].

The present paper describes the synthesis of the ethoxylated azo dyes, the properties as surfactants, fastness, and their spectral properties. In fact, we also investigated the properties of dye when dyeing polyester fabric in thermosol dyeing process.

Experimental

Ethoxylated azo dye was prepared according to the synthetic

procedure shown in Scheme 1:

Synthesis of Polyoxyethylaniline

N,N-(Dihydroxyethyl)aniline

Aniline (18.6 g, 0.2 mol), acetic acid (14 g), and water (50 ml) were charged into a 200 ml stainless steel autoclave, being saturated with N₂ and kept at room temperature. Ethylene oxide (11 g, 0.4 mol) was added over several hours. After the reaction was kept for 24 h at room temperature, the product solidified on cooling to 0-5 °C, a white crystal was collected by filtration to yield 22 g (73 %), m.p 56-58 °C (lit. m.p. 56-58 °C).

Polyoxyethylaniline

A mixture of *N,N*-(dihydroxyethyl)aniline (18.2 g, 0.1 mol) and NaOH (0.2 g) was put into a 200 ml stainless steel autoclave, being saturated with N₂ and heated up to 125 °C. Then, ethylene oxide was added over about 1 hour. After continuing the reaction for another 3 h at 125 °C, residual EO was removed by vacuum for 30 min. Then it was cooled to room temperature and the intermediate obtained was an amber-colored viscous liquid. The constant average number of EO could be achieved every time by controlling the amount of ethylene oxide in the synthesis.

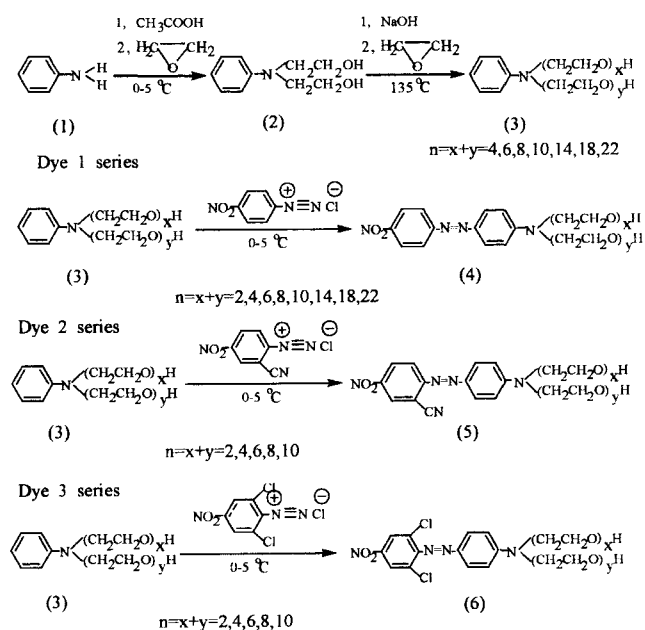
Synthesis of Dyes

Dye 1 Series

p-Nitroaniline (14 g, 0.1 mol), HCl (30 g, 30 %), and water (50 ml) were charged into 500 ml glass flask and cooled to 0-5 °C. NaNO₂ (7.6 g, 0.11 mol) dissolved into water (15 ml) was added dropwise to the p-nitroaniline solution at 5 °C. When addition was completed for diazotization, the mixture was being stirred for 30 min and excess sodium nitrite was consumed by adding sulfamic acid.

In another flask, a certain amount of polyoxyethylaniline

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Scheme 1. Synthesis of ethoxylated azo dyes.

($n=2-22$) with different average length of polyoxyethylene chain was charged. A solution of NaOAc (2.96 g, 36 mmol) in 5 ml H_2O was prepared. The prepared diazonium salt solution was added into the above solution for coupling reaction and the pH 4-5 was maintained by adding a proper amount of NaOAc solution. After addition of diazonium salt solution, the reaction was kept for another hour at 0-5 $^\circ\text{C}$. The mixture was extracted with CHCl_3 and organic layer was separated from the solution. After concentrating the solution, an orange dye was obtained. Dye 1 series consists of dye 102, dye 104, dye 106, dye 108, dye 110, and dye 122 in which 1 represents dye 1 series and 22 represents the number of EO ($n=22$).

Dye 2 Series

A deep red dye 2 series was obtained in the same synthetic manner as described in dye 1 series except that the diazonium salt of 2-cyano-4-nitroaniline was used instead of p-nitroaniline. Dye 2 series includes dye 202, dye 204, dye 206, dye 208 and dye 210 in which 2 represents dye 2 series and 10 represents the average number of EO ($n=10$).

Dye 3 Series

A red dye 3 series was prepared in the same synthetic manner as described in dye 1 series except that the diazonium salt of 2,6-dichloro-4-nitroaniline was used instead of p-nitroaniline. Dye 3 series consists of dye 302, dye 304, dye 306, dye 308, and dye 310 in which 3 represents dye 3 series and 10 represents the average number of EO ($n=10$).

Thermosol Dyeing Process

Preparation of Dyebath

A dyeing solution (2 % by weight) was prepared in water at room temperature without any special pre-treatment and dispersing agent and pH was adjusted to 4.5-5 by adding a proper amount of acetic acid.

Dyeing Procedures

Dyeing was carried out in a Roaches laboratory-dyeing machine. The solution was padded onto a 100 % polyester fabric. Excess dye solution was removed by squeezing to give about 70 %-wet pick up. After being dried at 100 $^\circ\text{C}$ for 20 s, the fabric was thermosoled at 200 $^\circ\text{C}$ for 2 min again. The dyed fabric was rinsed with hot water to remove residual dyes on the surface and the amount of fixed dyes was measured by dissolving dyed and dried fabric in a mixture of phenol and benzene. After extracting the dye with acetone, the fixation of the dyes was calculated by comparing the optical densities of blank sample and dyed sample.

Determination of the Nonionic Surfactant Properties

Cloud Point

A 1 % test solution was prepared by weighing 1 g of dye 1 and 100 ml distilled water in a 150 ml beaker at room temperature. 50 ml of test solution was poured into a 25 by 200-mm test tube of borosilicate glass. While the test solution was being agitated slowly, the test tube was heated on a water bath until the test solution became definitely cloudy. The heater was removed from the water bath and the solution was allowed to cool down slowly until it became clear. This temperature (cloud point) was recorded.

A 1 % test solution of polyoxyethylaniline was prepared by weighing 1 g polyoxyethylaniline and 100 ml of 10 % NaCl solution at room temperature. The procedure was as the same as above.

Surface Tension

The dye solutions were prepared at room temperature and then the surface tension was recorded on Processor tensiometer.

UV-Vis, NMR, and MS Spectroscopy

UV-Vis absorption spectra of dyes were determined on Shimadzu spectrophotometer UV-3100.

NMR and MS spectra were recorded on JEOL FX-90Q spectrometer and HP High performance capillary electrophoresis/Mass detector.

MS spectra:

Drying Gas Flow (l/min) 5.0 Nebulizer Pressure (psig) 30
 Drying Gas Temperature ($^\circ\text{C}$) 350
 Vaporizer Temperature ($^\circ\text{C}$) 350
 Capillary Voltage (V) 4000 Corona Current (μA) 4.0

NMR spectra:

Concentration (M) 0.08 Observed Frequency (MHz) 89.55
 Spectrum Width (Hz) 900 Date Points (k) 8
 Solvent CDCl₃ Repeated Time (s) 8
 Flip Angle 60° Temperature (°C) 45

Results and Discussion**Synthesis of Dyes and Intermediate**

N,N-(Dihydroxyethyl)aniline (2) and polyoxyethylaniline (3) were synthesized according to the reaction routes outlined in Scheme 1. Compound 2 was prepared with aniline, ethylene oxide, and catalytic acetic acid at low temperature. Compound 3 was synthesized with compound 2, ethylene oxide and catalytic NaOH at high temperature. The structure of compound 2 could be identified by ¹H-NMR and APCI/MS spectrum. APCI/MS spectrum of *N,N*-(dihydroxyethyl)aniline shown in Figure 1 has M⁺ at m/e 182 (C₁₀H₁₅N₁O₂ requires 182). Compound 3 could be identified by APCI/MS spectra too (see Figure 1). APCI/MS spectra of compound 2 and compound 3 have shown that compound 2 was pure compound and was different from compound 3. Compound 3 was a mixture compounds with a similar fundamental

structure (aniline structure), but it only differed in the length of polyoxyethylene chain. The average chain length could be fixed by controlling the amount of ethylene oxide during the synthesis and confirmed by the ¹H-NMR spectrum. From ¹H-NMR spectrum of polyoxyethylaniline (n=18), the average chain length could be calculated by counting the relative numbers of hydrogen of ethylene group and hydroxyl group (see Figure 2). We could calculate it to be 17.6 approximately that was close to the desired value.

When the diazonium salts of p-nitroaniline, 2,6-dichloro-4-nitroaniline and 2-cyano-4-nitroaniline were coupled to

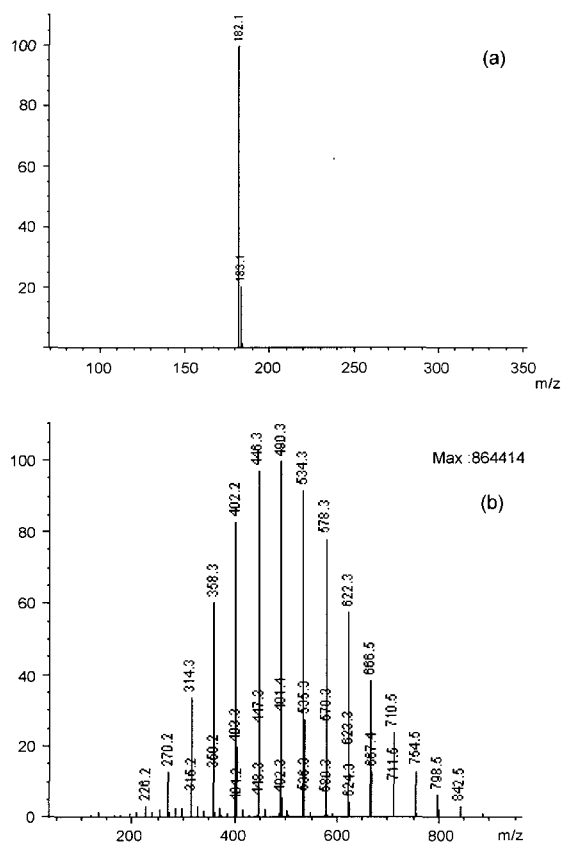


Figure 1. APCI/MS spectra of *N,N*-(dihydroxyethyl)aniline (a) and polyoxyethylaniline (n=10) (b).

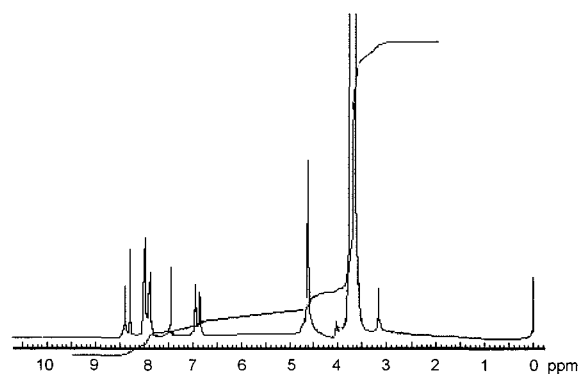


Figure 2. ¹H-NMR spectra of polyoxyethylaniline (n=18).

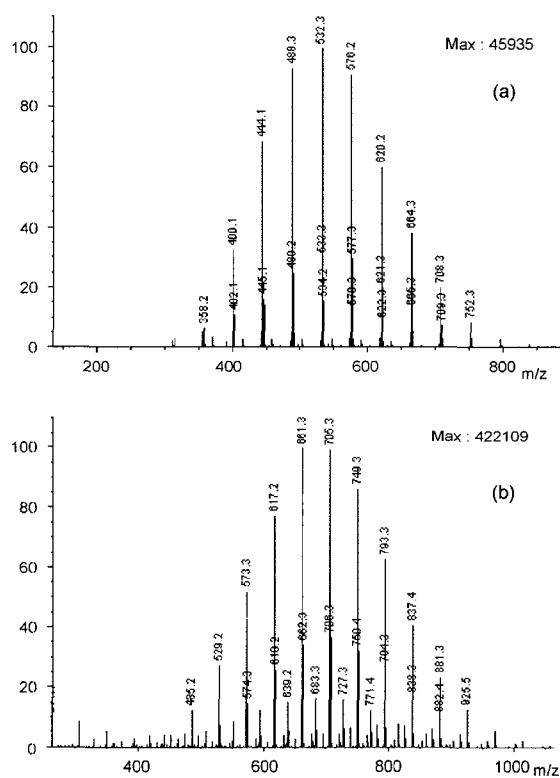


Figure 3. APCI/MS spectra of dye 206 (n=6) and dye 110 (n=10).

polyoxyethylaniline (3) according to Scheme 1, dye 1 series, dye 2 series, and dye 3 series were synthesized successfully. In fact, the diazonium salts were overdosed slightly in the synthesis of dye and worked the coupling component out at the final point of experiment. Then, the reaction mixture was extracted with CHCl_3 and organic layer was separated from the binary solution. Because the diazonium salts were not soluble in CHCl_3 , organic layer just contained ethoxylated dyes and solvent. After distillation of solvent, the dye was obtained with high purity and yield. The structure of ethoxylated azo dyes could be identified by APCI/MS spectra. Spectrum of dye 110 in Figure 3 revealed that the ethoxylated azo dyes were a mixture of dyes whose chain length of polyoxyethylene varied from 6 to 16. Dye 206 was also a mixture of the dyes whose chain length of polyoxyethylene varied from 2 to 11. From the results of APCI/MS spectra, the degree of ethoxylation and distribution of dyes could be clearly observed. Ethoxylated azo dyes and polyoxyethylaniline exhibited similar characteristics on the APCI/MS spectra.

Nonionic Surfactant Properties of Anilinopolyoxyethylene and Dyes

Cloud point is a unique characteristic of nonionic surfactant. Aniline does not have any cloud point at all, unless it is to be grafted with polyoxyethylene chain. Polyoxyethylaniline would exhibit a cloud point clearly because of grafting with

polyoxyethylene chain. The results are shown in Table 1.

Because of being grafted with a certain polyoxyethylene chain, ethoxylated azo dye would show the nonionic surfactant properties too. The cloud points of dye 1 series are shown in Table 2.

From Tables 1 and 2, it is obvious that ethoxylated dyes would give clear cloud points until the average number of EO reached 8. However for polyoxyethylaniline the cloud point could be observed until the average number of EO reached 10. In fact, the test solutions were quite different from each other. Once we could not observe the cloud point of 1% polyoxyethylaniline solution under heating and cooling cycle repeatedly. Comparing with ethoxylated azo dyes, polyoxyethylaniline only had a benzene ring as a lipophilic group and would not show clear cloud point of 1%wt solution unless 10% NaCl solution was mixed. For ethoxylated dyes with an azobenzene as a lipophilic group, it possessed more hydrophobic character and its cloud point appeared when the average number of EO reached 8 under normal condition (1%wt solution).

Surface tension is also a main characteristic of nonionic surfactant. Surface tension and CMC of dye 1 series are shown in Table 3. CMC of dye 1 series at 25 °C decreases as the average number of EO in dye structure increases. The conventional disperse dyes would not give any such characteristics at all.

Table 1. The cloud point of polyoxyethylaniline

The number of EO of polyoxyethylaniline (n)	Cloud point T _{cp} (°C)
2	No cloud point, soluble in water
4	No cloud point, soluble in water
6	No cloud point, soluble in water
8	No cloud point, soluble in water
10	72.5
14	82.0
18	84.0
22	86.0

Test solution: 1 g polyoxyethylaniline in 100 ml of 10% NaCl solution.

Table 2. The cloud point of dye in dye 1 series

	The number of EO (n)	Cloud point T _{cp} (°C)
Dye 102	2	Solidinsoluble in water
Dye 104	4	Macrodispersoid
Dye 106	6	Colloidal solution
Dye 108	8	46.5
Dye 110	10	60.5
Dye 114	14	73.3
Dye 118	18	77.5
Dye 122	22	83.4

Test solution: 1 g dye 1 in 100 ml distilled water.

Absorption Spectral Analysis

The maximum absorption wavelengths (λ_{max}) of ethoxylated

Table 3. The surface tension and CMC of the dye in dye 1 series

	The number of EO (n)	Surface tension (mN/m)	CMC (g/l)
Dye 108	8	53.1	0.0028
Dye 110	10	55.4	0.0015
Dye 114	14	57.3	0.0010
Dye 118	18	57.9	0.0008
Dye 122	22	59.8	0.0006

Table 4. The maximum absorption wavelengths (λ_{max}) of ethoxylated azo dyes

	The number of EO (n)	λ_{max} /nm		The number of EO (n)	λ_{max} /nm
Dye 102	2	473.8	Dye 110	10	478.4
Dye 104	4	477.4	Dye 114	14	482.0
Dye 106	6	477.4	Dye 118	18	481.4
Dye 108	8	479.4	Dye 122	22	480.2
Dye 202	2	525.4	Dye 208	8	527.4
Dye 204	4	528.0	Dye 210	10	527.0
Dye 206	6	527.8	Dye 302	2	436.2
Dye 304	4	435.6	Dye 308	8	437.4
Dye 306	6	437.2	Dye 310	10	437.6

azo dyes were determined and summarized in Table 4. From these results, it can be concluded that the number of EO has little effect on λ_{\max} of the dye.

Dyeing Properties

Ethoxylated azo dyes, possessing the properties of nonionic surfactant could be used for dyeing polyester fabric. Without special pre-treatment, for example, pre-dispersion, mixing, milling, and homogenization, the dyebath could be prepared by dissolving ethoxylated dyes into water at room temperature.

Table 5. The dyeing properties of ethoxylated dyes

	The number of EO (n)	Fixation (%)		The number of EO (n)	Fixation (%)
Dye 108	8	81.4	Dye 118	18	33.9
Dye 110	10	67.8	Dye 122	22	33.2
Dye 206	6	96.0	Dye 210	10	81.2
Dye 208	8	85.8	Dye 306	6	93.7
Dye 308	8	86.0	Dye 310	10	86.5

Table 6. Fastness of polyester fabric dyed with ethoxylated dyes

Dye	Light fastness (grade)	Washing fastness (grade)	Sublimation fastness (grade)			
			180 °C		210 °C	
			cc	cs	cc	cs
106	4-5	5	3-4	3-4	3-4	3-4
108	4-5	5	4-5	4-5	4	4
110	4-5	5	4-5	4-5	4-5	4-5
206	5	5	4-5	4-5	3-4	3-4
208	5-6	5	5	5	4-5	4-5
210	5	5	5	4-5	4-5	4-5
306	5-6	5	4	4	3-4	3-4
308	5	5	4-5	4-5	4	4
310	5-6	5	5	4-5	4-5	4-5

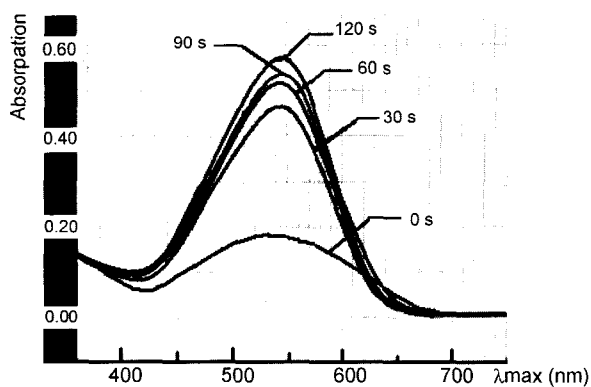


Figure 4. K/S spectrum of dye 110 in the thermosol dyeing process (T=200 °C).

Dyeing results obtained from the thermosol dyeing process are shown in Tables 5 and 6.

From Table 5, it could be seen that the dyeing behaviors in the thermosol process have strong relation with the average

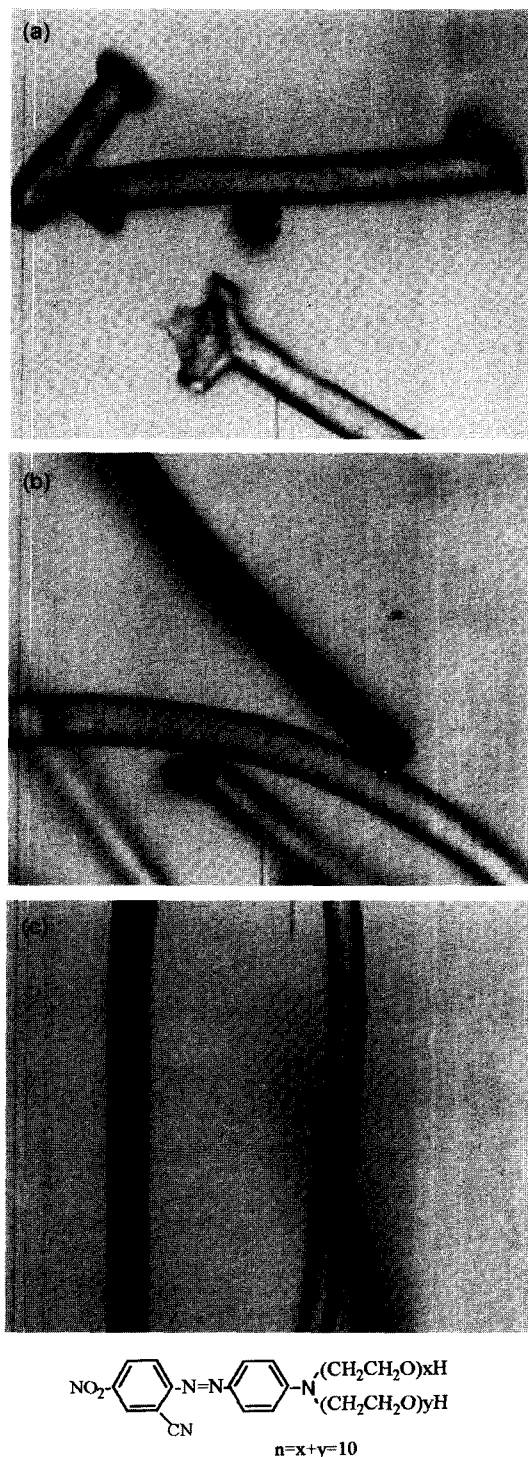


Figure 5. The optical micrographs of dye 110 in the thermosol dyeing process (a: 200 °C 0s, b: 200 °C 60s, and c: 200 °C 120s).

number of EO in polyoxyethylene chain. If the average number of EO in ethoxylated dyes reached 6, fixation of dyes with polyoxyethylene group could exceed 90 %. When the average length of polyoxyethylene chain increased, the fixation of dyes decreased accordingly. In fact, the molecular weight of dyes would become larger as the average length of polyoxyethylene chain increased and the dyes were difficult to be dispersed into the middle part of fiber. So the fixation of the dyes decreased.

Figures 4 and 5 illustrate dyeing property using dye 110 for polyester. When we kept the dyeing condition as described in dyeing procedure at 200 °C for 2 min, the absorption intensity of polyester fabric increased at the maximum absorption wavelength (λ_{\max}) and the color became deeper. From the optical micrographs (see Figure 5), it was obvious that the dye was dispersed from surface of polyester fabric into the middle part as dyeing time increased from 0 to 120 seconds. In blank fabric, its color did not change during the thermosol process.

Fastness data, such as light, sublimation, and washing fastnesses were obtained on the basis of ISO105/BS 1006: 1992 B02 and ISO 195/P01-1978 and shown in Table 6. From Table 6, no difference regarding the light and washing fastness improvement was observed in this work. Comparing the sublimation fastness of the dyes, a slight increase (0.5 grade) was observed. When the length of polyoxyethylene chain increased, the molecular weight could become larger and was more difficult to be migrated into the middle part of the dyed fiber than the dye with small molecular weight after thermosol dyeing process. Therefore sublimation fastness was slightly improved in this case. In fact, the polyoxyethylene chain was grafted on the side position and did not change the chromophoric system and seldom affected on light fastness.

Conclusions

The azo disperse dyes grafted with polyoxyethylene chain exhibited nonionic surfactant properties, such as cloud point

and surface tension. The conventional disperse dye did not exhibit any characteristic as indicated above. As the average number of EO increases, the solubility of ethoxylated azo dyes would increase, but the maximum absorption wavelengths (λ_{\max}) were not changed. Without any special treatment, the dyebath of ethoxylated dyes could be prepared and polyester fiber can be dyed in the thermosol dyeing process. It was shown that the fixation value of ethoxylated azo dyes decreased gradually as the average number of EO increased in the thermosol dyeing process. If the average number of EO in the ethoxylated azo dye reached 6, its fixation could exceed 90 % with the thermosol dyeing process. In fact, the molecular weight of dyes would increase with the average length of polyoxyethylene chain, and it was more difficult for the synthesized dyes to penetrate into the middle part of fiber.

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