

# Preparation and Properties of Water-Soluble Polyester Surfactants. II. Preparation and Surface Activity of Silicone-Modified Polyester Surfactants

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**ABSTRACT:** We prepared a novel series of water-soluble silicone-modified polyesters [poly(ethylene glycol) (PEG)-silicone polyesters] by reacting organopolysiloxane with a hydroxy-terminated polyester. The polyesters were obtained by the polymerization of maleic anhydride and PEGs (molecular weights = 2000, 4000, 6000, 8000, and 10000). These water-soluble PEG-silicone polyesters can be used as auxiliaries in dyeing process because they exhibit good surface activities such as surface tension, low foaming, and wetting power. The presence of these surfactants also re-

tarded the rate of nylon dyeing with acid dyes. The retarding effect and low-foaming property of these novel PEG-silicone polyesters make it possible for these surfactants to be used as leveling agents for modern nylon dyeing with acid dyes. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3005–3012, 2002

**Key words:** dyes/pigments; polyesters; polysiloxanes; surfactants

## INTRODUCTION

In textile dyeing, surfactants, or so-called leveling agents, are applied to improve the dyeing properties of natural and synthetic fibers. When fibers are dyed with ionic dyes, leveling agents are generally acted either by being fiber affinitive, thus leveling up surface irregularities or competing with the dye for available sites, or by being dye affinitive, thus lowering the rate of diffusion of the dye-surfactant complex.<sup>1,2</sup>

In modern textile dyeing, there has been increased speed in dyeing bath circulation due to advancements in dyeing machine design. This has made the low-foaming tendency of leveling agents an indispensable property. However, traditional surfactants that have been used as leveling agents in previous studies were almost all insufficient in low-foaming property demand.<sup>3–5</sup>

Various modified polyesters, wherein the polyester is copolymerized with a material reactive with the polyester, are known and have been proposed for certain interesting applications. For example, products of some silicone-modified polyesters that exhibit resin-like characteristics have been employed for coating applications.<sup>6</sup> However, almost all of these silicone-

modified polyesters are solvent soluble and can be used only in nonaqueous conditions or require the help of an emulsifier to form the emulsion in aqueous solution.

In our previous studies, water-soluble polyesters prepared by the reaction of dimethyl 5-sulfoisophthalate sodium salt (SIPM) and poly(ethylene glycol) (PEG) exhibited excellent surface-active properties similar to traditional surfactants.<sup>7–9</sup>

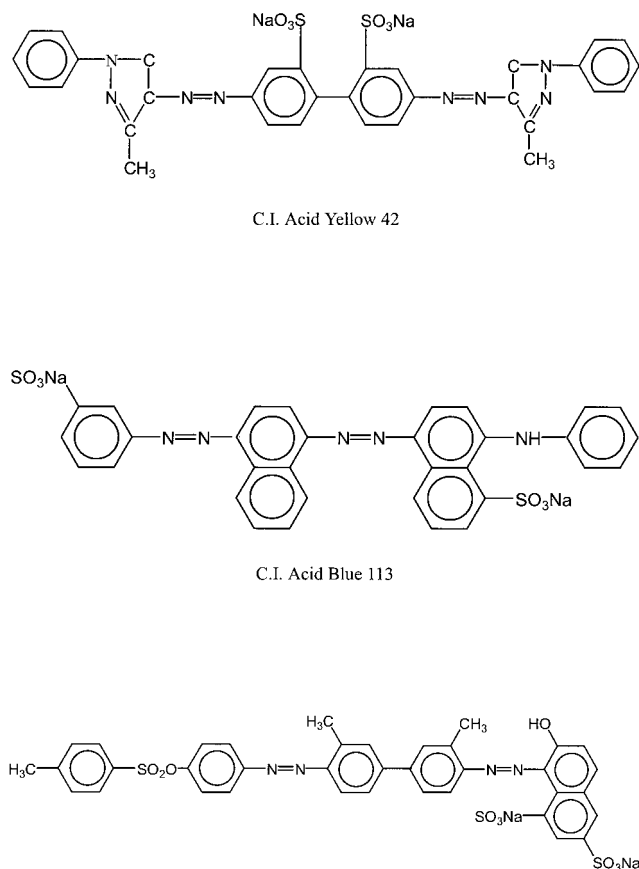
In this study, a novel series of water-soluble silicone-modified polyesters were prepared by the reaction of a hydroxyl-terminated polyester and an organopolysiloxane. The polyesters used in this study were prepared by the polymerization of maleic anhydride (MA) and PEG. We investigated the surface-active properties of silicone-modified polyesters, including surface tension, foaming, and wetting, and the influence on the dyeing of nylon with acid dyes.

## EXPERIMENTAL

### Materials

Commercial-grade silanol chainstopped polydimethylsiloxane [molecular weight (*MW*) = 3400] was supplied by Dow Corning (USA). Reagent-grade titanium isopropoxide, sodium hydrogen sulfite, MA, and PEG (*MWs* = 2000–10,000), were purchased from Hayashi Pure Chemical Co. (Japan) and used without further purification. Three acid dyes were used: Everacid Mill

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**Figure 1** Structures of the acid dyes used in this study.

Yellow MR (C.I. Acid Yellow 42), Everacid Mill Cyanine 5R (C.I. Acid Blue 113), and Everacid Mill Red RS (C.I. Acid Red 114). These dyes were supplied by Everlight Co. The structure for each dye is shown in Figure 1. Scoured nylon taffeta fabric was used throughout the experiment.

### Preparation of silicone-modified polyesters

Figure 2 illustrates that the silicone-modified polyesters were prepared with three steps. In the first step, the water-soluble polyesters were prepared by the polymerization of 2 mol of PEG and 1 mol of MA in the presence of a catalyst (titanium isopropoxide) at 200–220°C. In the second step, 2 mol of the polyesters that were obtained from the first step were reacted with 1 mol of silanol chainstopped polysiloxane in the presence of the same catalyst at 125–130°C for 3–5 h. In the third step, 1 mol of the product from the second step and 2 mol of sodium hydrogen sulfite were mixed and stirred mechanically at 90–100°C for 8–13 h.

### Analysis

The acid value and hydroxyl values were determined by standard methods described elsewhere, and from

these values, the MW of polyesters was calculated.<sup>10</sup> The structure of the final products was confirmed by elemental analysis.

### Measurements

Surface tension was determined at room temperature with a Japan Kaimenkaguka CBVP-A3 surface tensiometer. Foaming properties were determined by the Ross–Miles method. Foam production was measured as the height of the foam initially produced, and foam stability was measured as the height after 3 min.

*Contact angle*, which describes the angle formed between the planes tangent to the surfaces of the solid and the liquid at the wetting perimeter,<sup>11</sup> was measured with a Face CA-5 contact angle meter. An acrylic plastic sheet and unscoured cotton fabric were used.

Dispersant properties of silicone-modified polyesters for disperse dyes were determined by the measurement of the particle size of the dye–surfactant particle in aqueous solution. A 100-mL solution containing 20 mg of commercial disperse dye and 50 mg of surfactant was adjusted to pH 4.5 by the addition of an appropriate amount of acetic acid. Then the solution was heated to 130°C by a computer-controlled dyeing system and maintained at this temperature for 1 h. After this, the solution was cooled to room temperature (25°C), and the dye–surfactant particle size in the solution was determined by a light-scattering method with a Malvern 4700.<sup>12</sup>

A rapid laboratory dyeing machine was used for the nylon dyeing with acid dyes. The dyeing solution contained 1% on the weight of the fabric (owf) dye and 0.5 g/L surfactant; the liquor ratio was 40:1. The solution was at pH 4.5 and at temperatures of 70, 75, 80, 85, 90, and 95°C. We expressed the amount of dye adsorbed on the fabric as a K/S value by measuring the reflectance at the wavelength of maximum dye absorption with an ACS spectrophotometer.<sup>13</sup> (The K/S values are the indirect measurement of dye depth based on reflectance values for color depth of fabric.) After the dyeing process, we evaluated the softness of each nylon fabric sample by measuring the distance at the bending point of a moving fabric with a Cantilever bending tester.<sup>14</sup>

## RESULTS AND DISCUSSION

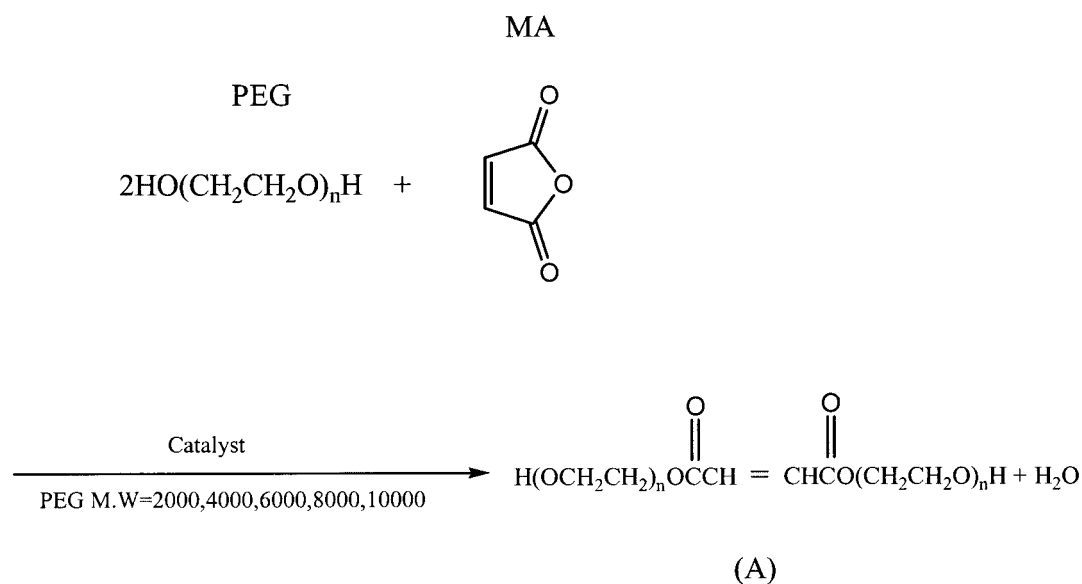
### Preparation

Table I shows the results of the elemental analysis of the final silicone-modified polyesters containing different lengths of a polyoxyethylene chain.

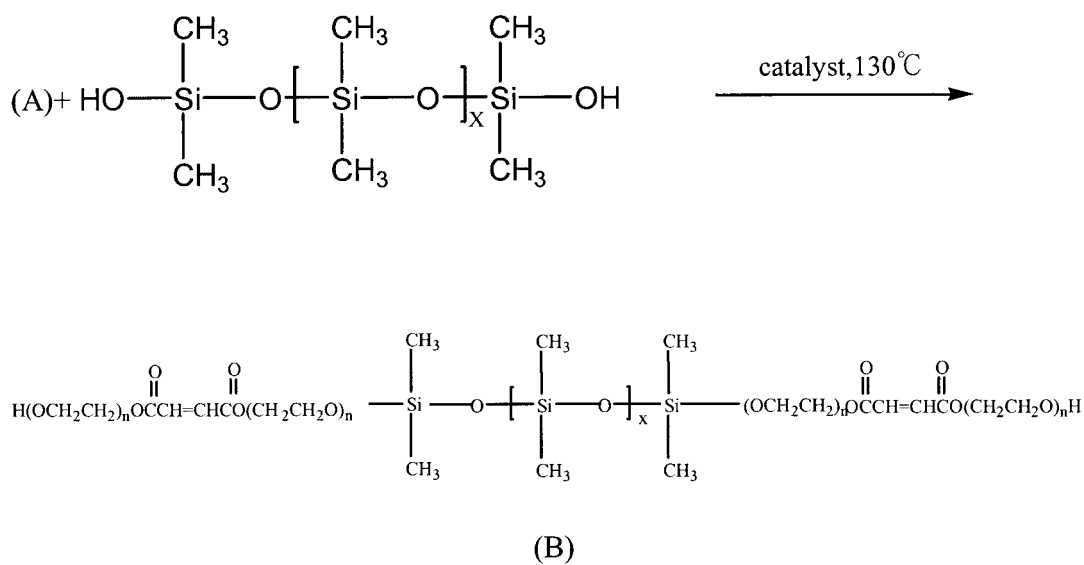
### Surface tension

Surface tension is one of the most important surface properties of a surfactant solution. The PEG–silicone

Step1 :



Step2 :



Step 3 :

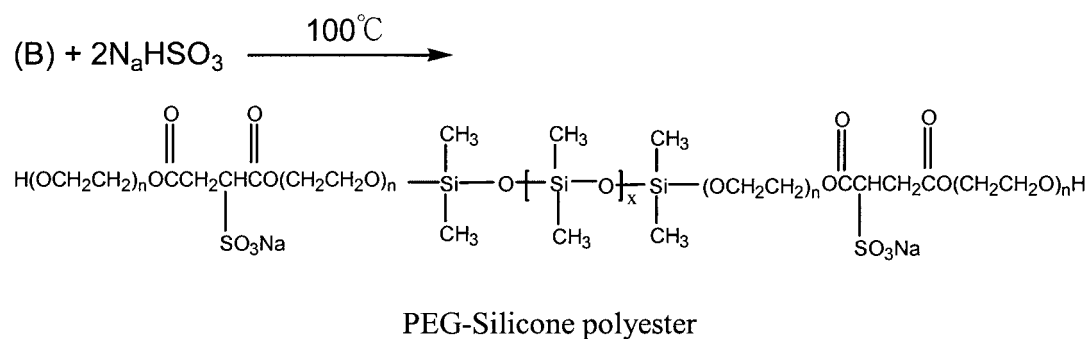


Figure 2 Preparation of silicone-modified polyesters.

**TABLE I**  
Analysis of Silicone-Modified Polyesters

Compound	Mw	Elemental analysis (%)			
		C		H	
		Found	Calcd.	Found	Calcd.
PEG 2000-silicone	9,466	41.20	38.83	8.96	8.55
PEG 4000-silicone	18,324	48.80	45.20	8.95	8.77
PEG 6000-silicone	25,640	49.56	47.90	8.83	8.86
PEG 8000-silicone	34,632	50.58	49.39	8.92	8.91
PEG 10,000-silicone	42,328	51.62	50.33	8.91	8.94

polyesters prepared in this study possessed complex amphipathic structures contributed by the polydimethylsiloxane group. As shown in Figure 3, a decrease in the surface tension of the aqueous solution was observed when the concentration of the PEG-silicone polyesters in the solution was increased. In addition, the surface activity was sensitive to the length of the polyoxyethylene chain presented in these polyesters. An increase in the chain length resulted in a decrease in the surface activity. These results may be attributed to the fact that an increase of the hydrophilic portion of the PEG-silicone polyester resulted in a decrease in its concentration at the surface. It is interesting that the observed reduction in the surface tension by PEG-silicone polyesters was larger than that of the polyester surfactants reported previously.<sup>7,8</sup>

### Foaming properties

A low-foaming tendency of surfactants is an important property required in some applications, such as in

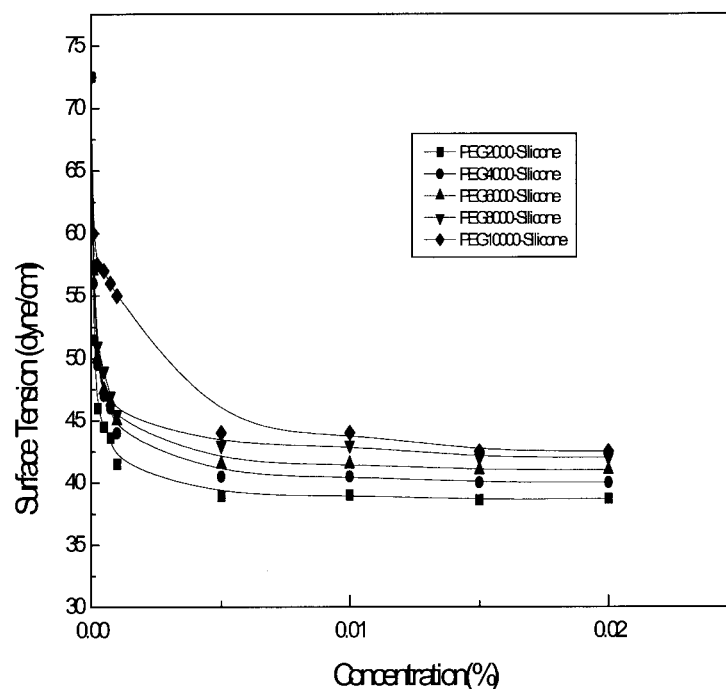
**TABLE II**  
Foaming Properties of Silicone-Modified Polyesters

Compound	Foam height (mm)	
	Initial	After 3 min
PEG 2000-silicone	3.5	2.0
PEG 4000-silicone	7.0	3.2
PEG 6000-silicone	7.2	4.0
PEG 8000-silicone	11.6	4.8
PEG 10,000-silicone	14.0	5.0

the use of surfactants as dyeing auxiliaries in the modern textile industry. In some cases, most of the silicone-containing surfactants have been shown to be excellent defoamers in antifoam applications.<sup>15</sup> As shown in Table II, all of the PEG-silicone polyesters showed excellent low-foaming properties and low-foam stability. These excellent low-foaming properties were probably due to the presence of multihydrophilic groups, which caused a considerable increase in the area per molecule and produced less cohesive forces at the surface. Water-soluble polymers, which are believed to coil in the aqueous phase to decrease the cohesive force, are the result of intramolecular and intermolecular bonding.<sup>7</sup>

### Wetting power

Wetting power is another important property of dyeing auxiliaries. In the dyeing process, good wetting power of dyeing auxiliaries may accelerate the diffusion or penetration of dyes into the fibers and may



**Figure 3** Plots of surface tension against concentration of silicone-modified polyesters.

**TABLE III**  
**Contact Angles of Solution and Softening Properties of**  
**Silicone-Modified Polyesters**

Compound	Contact angle (°)		Softening properties (mm) for nylon fabric
	Acrylic plastic	Cotton fabric	
H <sub>2</sub> O	74	124	51
PEG 2000-silicone	70	119	42
PEG 4000-silicone	70	117	45
PEG 6000-silicone	69	116	47
PEG 8000-silicone	68	116	47
PEG 10,000-silicone	68	114	48

improve with leveling. The silicone additives induce better or similar wetting effects than conventional surfactants.<sup>16</sup> The outward measure of the degree of wetting is the contact angle, the angle formed between planes tangential to the surfaces of the solid and the liquid at the wetting perimeter.<sup>15</sup>

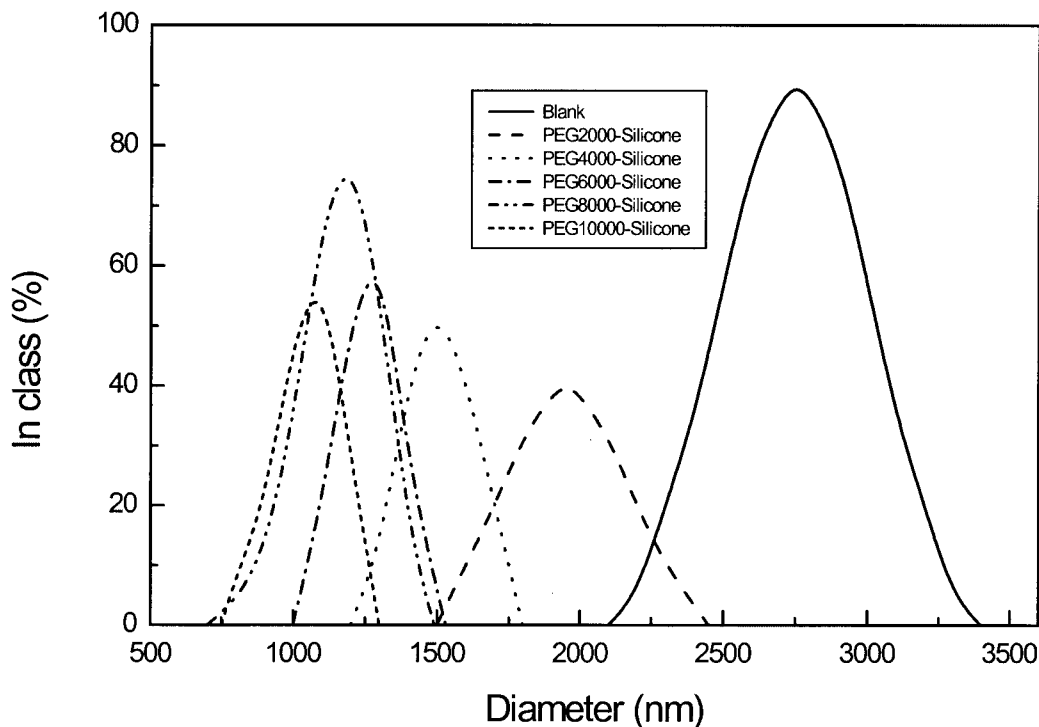
Table III shows the contact angles formed between the aqueous solutions of the PEG-silicone polyester and the surface of an acrylic plastic sheet or cotton fabric. These angles were smaller than those found with water, indicating that solutions of all the five products possessed the power to wet acrylic plastic and the fabric, although the extent of such wetting power was not greatly enhanced.

### Disperse stability

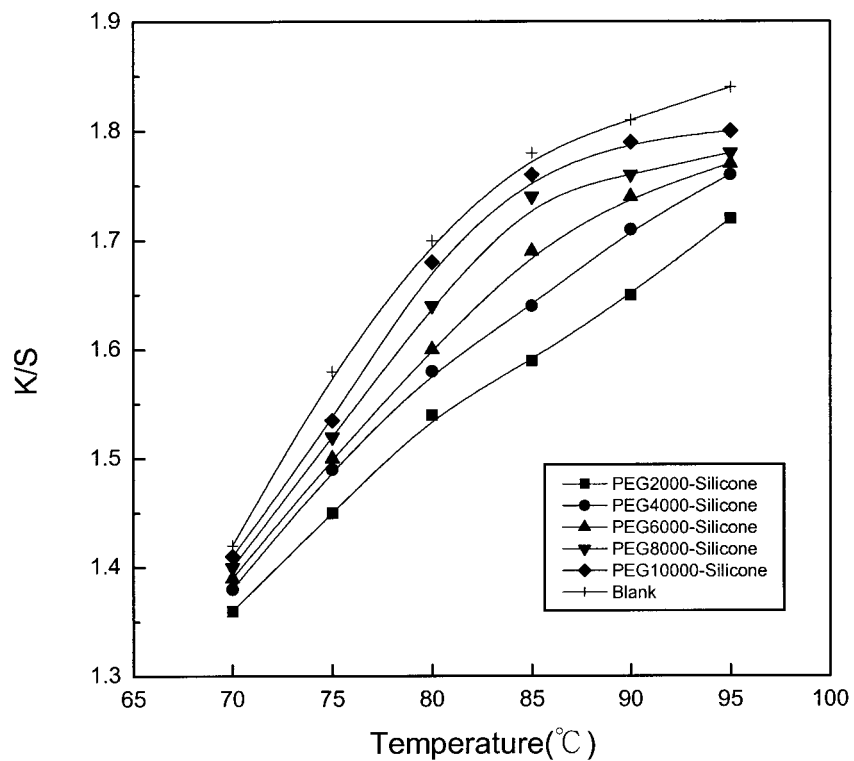
Reaggregation of disperse dye particles often occurs when a low-heat-stable dispersant is used in dyeing

polyester fabrics with disperse dye at an elevated temperature.<sup>17,18</sup> The use of deemulsifier commercial silicone auxiliaries, which are often hydrophobic in character, will accelerate the formation of reaggregated disperse dye particles. The formation of such aggregated dye particles is not desirable for the dyeing of polyester fabrics because the aggregation of the dye particles can cause unlevelled or specked dyeing products and can result in a dyeing product with poor tintorial value.

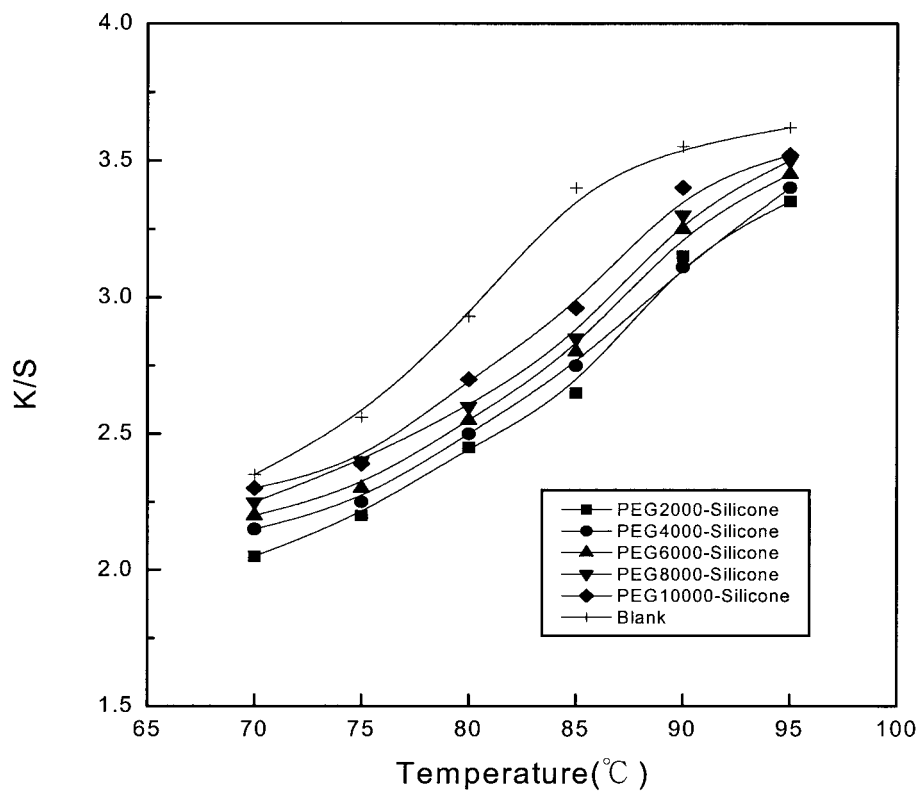
The water-soluble silicone-modified polyesters prepared in this study had heat stability to properly be employed for the prevention of the reaggregation of dye particles in dyeing system. The average diameters of disperse dye in the presence of PEG-silicone polyesters are shown in Figure 4. It is clear that the dispersions in the presence of auxiliaries consisted of particles whose average diameter was smaller than when the dyes were present alone. These results indicated that unlike the conventional silicone auxiliaries, the water-soluble PEG-silicone polyester did not cause reaggregation of disperse dye particles and was applicable in the high-temperature dyeing process. The ability to prevent the aggregation of dye particles of silicone-modified polyester auxiliaries was probably caused by their multihydrophobic and hydrophilic amphipathic structure. In the disperse dye solution, the hydrophobic groups would surround the surface of dye particles, whereas the hydrophilic group would be exposed in the aqueous phase. The formation of such solvated disperse dye particles could prevent reaggregation from occurring.



**Figure 4** Average diameter of disperse dye systems in the presence of silicone-modified polyester.

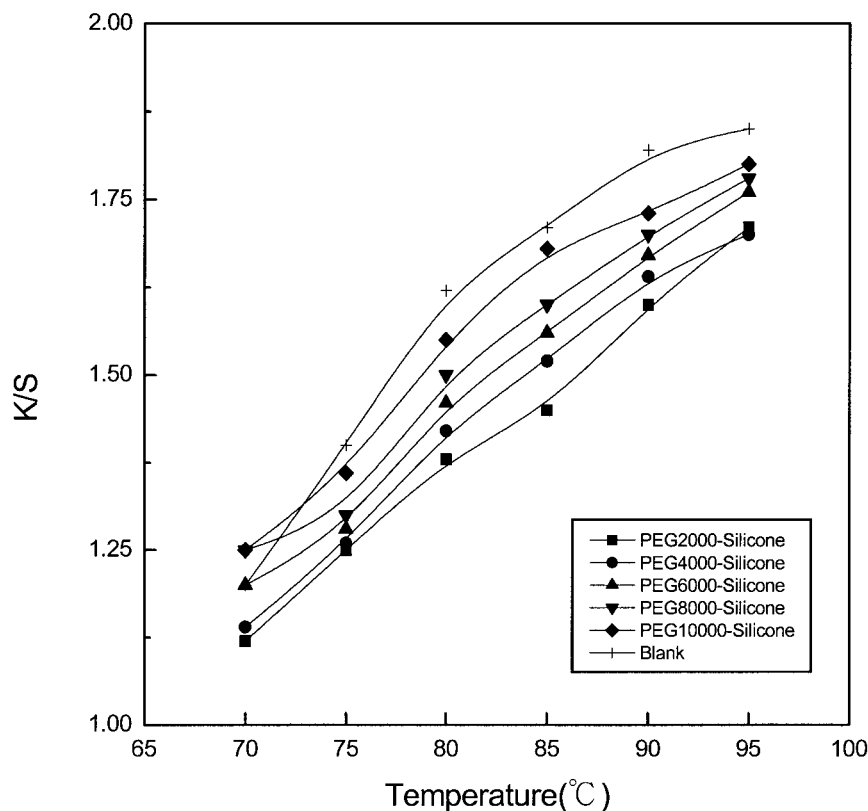


(a)



(b)

**Figure 5** Rates of dyeing with (a) C.I. Acid Yellow 42, (b) C.I. Acid Blue 113, and (c) C.I. Acid Red 114 expressed in terms of color yield (K/S).



(c)

Figure 5 (Continued from the previous page)

### Softening properties

The softening properties of the PEG–silicone polyester on nylon fabrics were also studied, and the results are shown in Table III. Table III shows that the softness increased with a decrease in the ethylene oxide (EO) moles of the water-soluble PEG–silicone polyester. The improvement in fabric softness could make an important contribution to the prevention of creases or scars that are created in the fabrics during the dyeing process.

### Influence of silicone-modified polyester in nylon dyeing

During the nylon dyeing process, protonation of the amino groups of the fiber by the acid in the dyeing bath creates positive sites on the fiber, and the acid dye anions are adsorbed and bound to these positive sites. The electrostatic bond thus formed is fairly strong so that any initial unevenness of dyeing is difficult to correct, especially where fiber irregularities exist. In such cases, leveling agents are used to retard the first strike of exhaustion on fibers but not to decrease it too much.

The rates of nylon dyeing with the three acid dyes in the presence of the PEG–silicone polyesters are shown

in Figure 5. This figure shows that the presence of the surfactants retarded the dyeing rates, indicating that the formation of dye–surfactant complexes in the dye bath had an important influence on the dyeing rate. The PEG–silicone polyesters would enhance the dyeing rate in an acid dyeing system if they could form dye–surfactant complexes that have a lower solubility than the dye itself. In contrary, the results observed in Figure 5 can be explained by the fact that our surfactant molecules contained hydrophilic polyoxyethylene chains. These hydrophilic chains facilitated the formation of soluble dye–surfactant complexes and reduced the dyeing rate. Decreasing the number of polyoxyethylene units in the surfactant molecule improves the retarding effect, probably because of the increase in the surfactant's hydrophobic qualities, which favors complex formation. Slower dyeing is generally accepted to favor good leveling.

### CONCLUSIONS

A novel series of silicone-modified polyesters with water-soluble properties were prepared by the reaction of organopolysiloxane and hydroxy-terminated

polyesters. The polyesters used in this study were prepared by the polymerization of MA and PEG. These novel compounds were found to exhibit good surface activities, including surface tension, foaming, and wetting power.

The presence of these surfactants was found to retard the rate of nylon dyeing with the acid dyes. This could be due to the hydrophilic polyoxyethylene chains in the surfactant molecules, which help the formation of dye-surfactant complexes with greater solubility than the dye itself, decrease the dye's substantivity for the fiber, and lower the rate of the dyeing. Because slower dyeing is generally accepted to favor good leveling, the retarding effect and low-foaming properties make these new compounds suitable for use as leveling agents for nylon dyeing with acid dyes.

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