

Preparation and Properties of Water-Soluble Polyester Surfactants. I. Preparation and Surface Activity of Poly(Ethylene Glycol)-Dimethyl 5-Sulfo-Isophthalate Sodium Salt Polyester Surfactants

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Received 29 October 2001; accepted 8 January 2002

ABSTRACT: The reaction of poly(ethylene glycol) (PEG, number-average molecular weight $M_n = 400$ –2000) and dimethyl 5-sulfoisophthalate sodium salt (SIPM) synthesized a series of anionic polymeric surfactants having a range of molecular weights. ¹H-NMR, FTIR, and elemental analysis were employed to characterize the structures of these compounds. Also, the influences of the PEG segment lengths of PEG/SIPM copolymers on the surface tension, foaming

properties, wetting power, and dispersant properties were investigated. The experimental results indicated that the solution that contained the PEG/SIPM copolymer surfactants exhibited excellent surface-active properties. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2727–2731, 2002

Key words: water-soluble polymers; polyesters; surfactants

INTRODUCTION

In the past 20 years, polymeric surface-active materials have gained enormous popularity in a variety of applications and research fields. The most obvious and best known is the stabilization of dispersions. However, polymeric surfactants appear in a multitude of other research areas and applications acquiring numerous different names. In addition to being called polymeric surface-active agents or surfactants, these amphiphathic materials, when used as dispersion stabilizers, are also known as emulsifiers, detergents, or dispersants. Obviously, the name polymeric surfactant does not fully indicate the broad capabilities of these materials in a multitude of applications. In modern textile dyeing processes, a dyeing auxiliary with a structural moiety of poly(ethylene oxide) (PEO) is used because the oxygen atom binds readily to dyes via hydrogen bonding. With an increase in temperature and dyeing time, dyes are dissociated slowly and absorbed by polyester textiles to achieve dispersibility.^{1–3} However, the traditional surfactant is limited in its practical use. Thus, a variety of surface-active agents must be added to improve its effect.

In our previous investigations, we reported that water-soluble polyesters, prepared by the reaction of dicar-

boxylic anhydride and poly(ethylene glycol) (PEG), exhibit excellent surface-active properties which are similar to those of other traditional surfactants.^{4–6} Here, a novel series of water-soluble polyester surfactants is synthesized. The surface-active properties examined in this investigation include surface tension, foaming, wetting power, and dispersant properties.

EXPERIMENTAL

Materials

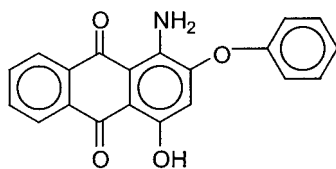
PEG, with number-average molecular weights (M_n) that ranged from 400 to 2000, were purchased from Hanawa (Japan). The samples were thoroughly dried at 100°C at < 10 mmHg pressure for 10 h and were used without further purification. Commercial grade dimethyl 5-sulfoisophthalate sodium salt (SIPM) was purchased from Sanyo Chemistry (Japan). All other reagents were of analytical grade and used without further subsequent purification. Three disperse dyes used were Dispersol Red B-2B (C.I. Disperse Red 60), Dispersol Blue B-R (C.I. Disperse Blue 56), and Dispersol Yellow B-6G (C.I. Disperse Yellow 218). These dyes were supplied by BASF Co. (Germany). The structure for each dye is shown in Figure 1. Finally, scoured polyester fabric from one preparation batch was employed in all experiments.

Preparation of PEG-SIPM polyesters

Figure 2 illustrates that the PEG-SIPM polyesters were prepared in three steps. In Step 1, 1 mol PEG and 0.5 mol

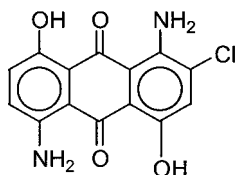
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(1) Dispersol Red B-2B



(C.I. Disperse Red 60)

(2) Dispersol Blue B-R



(C.I. Disperse Blue 56)

Figure 1 Structure of disperse dyes used in the present study.

SIPM were mixed evenly and polymerized with 1 g catalyst of titanium isopropyl oxide at 200–220°C for 2 h. In Step 2, 0.5 mol SIPM was added and stirred evenly at 250°C for 4 h. In Step 3, the reaction temperature was cooled to room temperature. Finally, the reaction solution was adjusted to pH 7 by means of adding NaOH solution to yield water-soluble polyesters. This raw product was then dissolved in ethanol. The undissolved impurities were separated by filtration, and the ethanol and water were removed from the filtrate with a rotary evaporator. The solvent was evaporated from the purified polyesters at reduced pressure and the final product was dried in a vacuum desiccator.

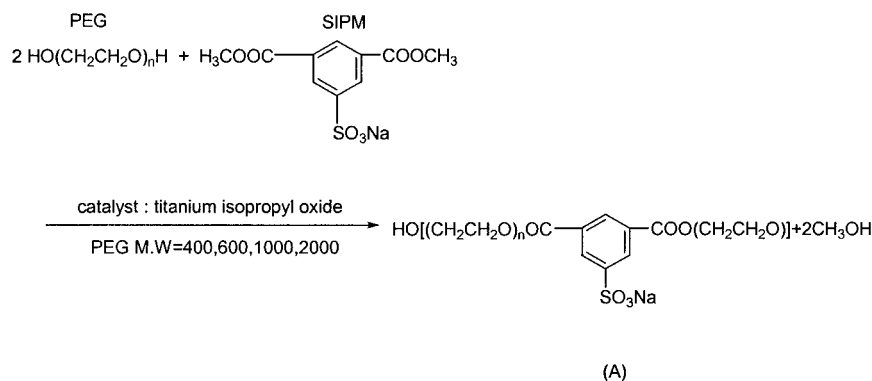
Analysis

Standard methods were employed to determine the acid and hydroxyl values which provided the molecular weight of the polyesters obtained in the first step. Infrared (IR) and nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were obtained with a FTIR-3 spectrophotometer and a Varian 360 L NMR, respectively.

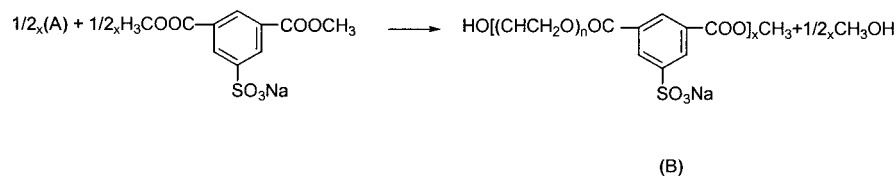
Physical measurements

A Japan Kaimenagaku CBVP-A3 surface tension meter was employed to determine surface tension at

step 1:



step 2:



step 3:

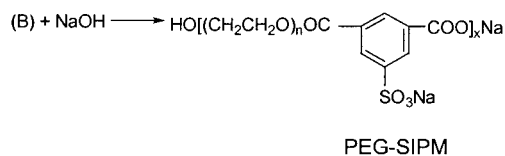
**Figure 2** Preparation of PEG-SIPM polyesters.

TABLE I
Analysis of Anionic Derivatives of PEG-SIPM Polyesters

Compound	Yield (%)	Elemental analysis (%)			
		C		H	
		Obs.	Calc.	Obs.	Calc.
PEG400-SIPM	95.1	45.16	47.5	6.24	6.35
PEG600-SIPM	99.24	47.24	47.6	7.23	6.90
PEG1000-SIPM	99.3	49.27	49.6	7.92	7.72
PEG2000-SIPM	97.6	49.79	51.0	8.42	8.27

room temperature. Foaming properties were determined by the Ross-Miles method. The measured height of the foam that was produced in initial foam production, and the height of the foam after 3 min, determined foam stability. In determining contact angle, a syringe that contained a 0.2 wt % solution of PEG-SIPM polyester deposited several drops of this solution on the surface of an acrylic plastic sheet and an unscoured cotton fabric stretched as surface of the solid.

RESULTS AND DISCUSSION

Preparation of anionic derivatives

Table I lists the elemental analysis results of the PEG-SIPM polyesters that contained polyoxyethylene chain lengths. A typical IR spectrum of the synthesized PEG-SIPM polyesters (Fig. 3) displayed bands at 2830 cm^{-1} ($-\text{CH}_2$), $3221\text{--}3628\text{ cm}^{-1}$ ($\text{R}-\text{OH}$), $1044\text{--}1099\text{ cm}^{-1}$ ($-\text{S}=\text{O}$), and $1553\text{--}1718\text{ cm}^{-1}$ ($-\text{C}=\text{O}$). These bands were characteristic of the desired compound. Compound structure was further supported by the $^1\text{H-NMR}$ spectrum, as illustrated for Compound

PEG400-SIPM in Figure 4. Figure 4 shows signals at δ 8.4 ppm ($-\text{SO}_3\text{Na}$), δ 4.63 ppm ($-\text{OH}$), and δ 3.2–3.8 ppm ($-\text{CH}_2\text{CH}_2\text{O}-$). Also, Table II lists the HLB values.^{7,8} HLB value is a measure of the hydrophilic/hydrophobic ratio of a given surfactant, and the value frequently is used to determine the emulsification power of surfactants. This table shows an increase in the length of polyoxyethylene chain of nonionic segment increased the HLB value (i.e., the PEG2000-SIPM has significantly greater hydrophilicity).

Surface tension

Surface tension of a surfactant solution is one of its most significant properties. Water-soluble polyesters prepared in this study are observably of an amphiphatic structure similar to those of traditional surfactants. The aromatic residues are the hydrophobic segment; however, the sulfonate group (anionic), the carboxylic group (anionic), and the polyoxyethylene chain (nonionic) are hydrophilic segments. Figure 5 shows that adding surfactants reduced the surface tensions of the solutions relatively (i.e., the amphiphatic structure causes surfactant molecules to concentrate at the surface and reduces surface tension). An increase in the length of polyoxyethylene chain of the nonionic segment clearly reduced surface activity. This phenomenon is due to the increase of hydrophilicity of surfactants and makes the concentration of the surfactants at the surface of solution decrease.

The surface tension of the solutions is reduced by addition of the surfactants. However, an abrupt inflection in the curves, which corresponds to the critical micelle concentration (CMC) in the case of traditional surfactants, was not observed, due to the monomolecular micelles.

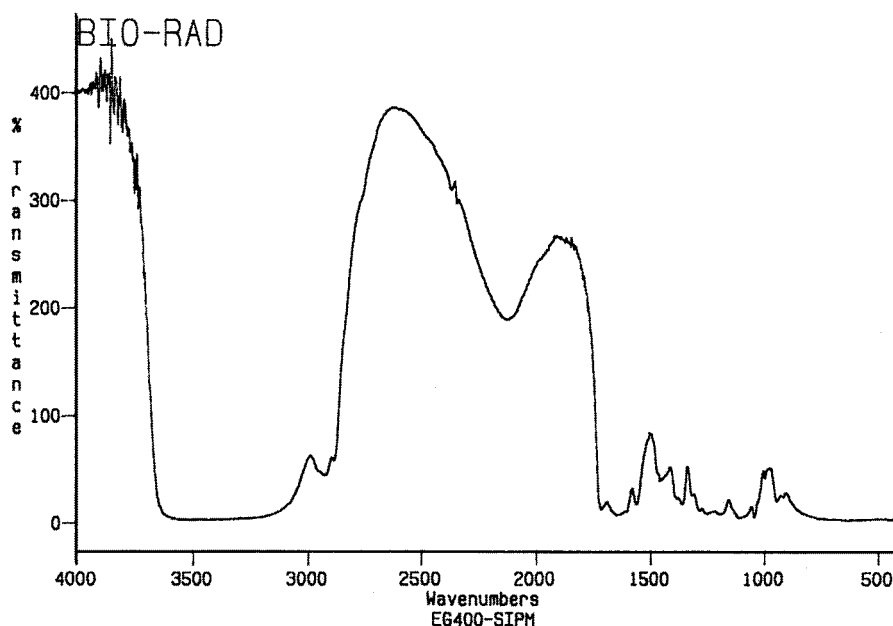


Figure 3 FTIR spectra of PEG400-SIPM polyester.

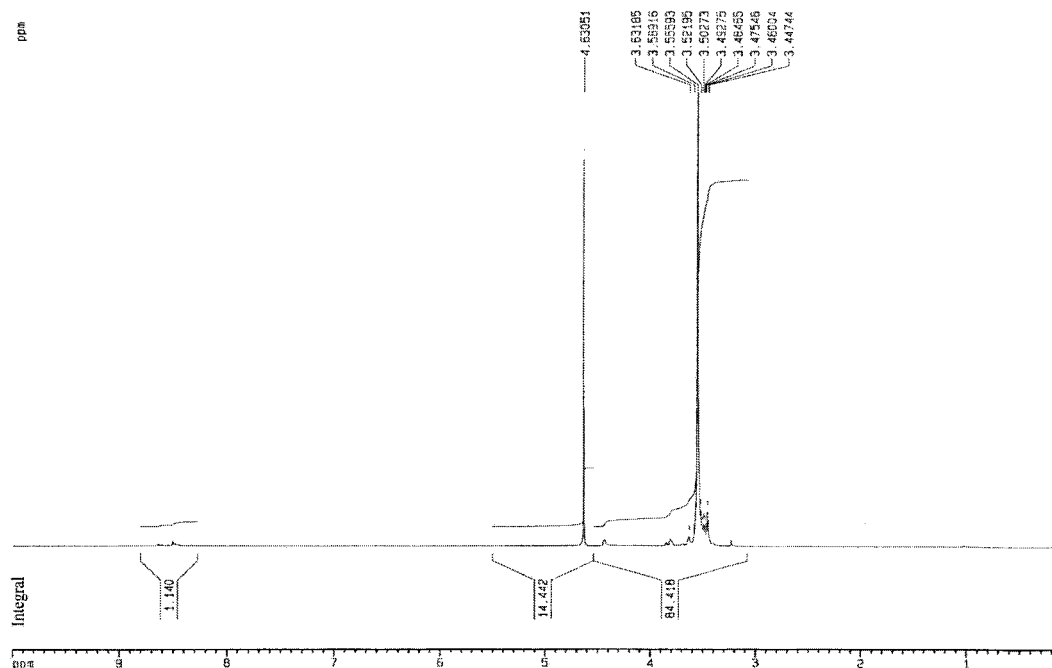


Figure 4 $^1\text{H-NMR}$ spectra of PEG400-SIPM polyester.

Foaming properties

Table III shows the foaming properties of the PEG-SIPM polyesters. The initial foam height was low in all cases, giving an indication of the suitability for use where low-foaming properties are required. The compounds can also lower the stability of the existing foams, as indicated by the decrease in foam height measured after 3 min from initial foam formation. These low-foaming effects are probably due to (1) the presence of multihydrophilic groups causing a considerable increase in the area per molecule and producing less cohesive forces at the surface; (2) the multianionic hydrophilic repulsion among surfactant molecules counteracting the interchain cohesive force; and (3) the water-soluble polyesters which are believed to coil in the aqueous phase decreasing the cohesive force due to intramolecular and intermolecular bonds.

Wetting power

Wetting power is another significant property of dyeing auxiliaries. In the dyeing process, the wetting power of auxiliaries may accelerate the diffusion or penetration of dyes into the fibers, as well as improve leveling. The outward measurement of the degree of

wetting is the contact angle formed between phases tangential to the surfaces of the solid and the liquid at the wetting perimeter. Table IV shows the contact angle found between solutions of the PEG-SIPM polyesters and acrylic films and cotton fabrics.

Dispersant properties

Disperse dyeing of polyester fabric is usually carried out in the presence of dispersants. Notably they are added to increase dispersion stability, as well as the leveling and fastness properties of the dyes. Purified disperse dyes are hydrophobic and almost completely insoluble in water. Their low aqueous stability is attributed to hydrophobic bonding, which causes aggregation and precipitation when the concentration is increased. Generally, several surfactants are incorpo-

TABLE II
HLB Values of PEG-SIPM Polyesters

Compound	Griffin method	Davies method
PEG400-SIPM	14	69.42
PEG600-SIPM	15	70.74
PEG1000-SIPM	17	73.71
PEG2000-SIPM	18	81.30

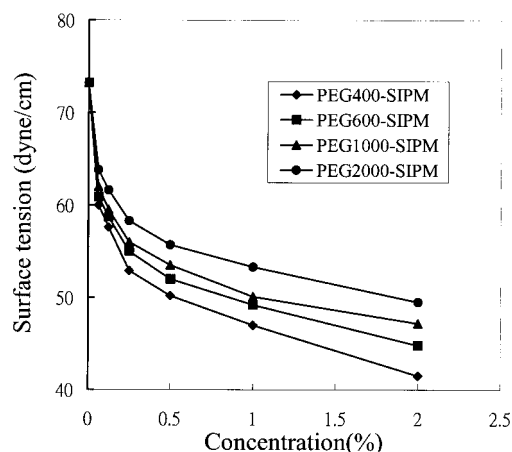


Figure 5 The surface tension of PEG-SIPM polyesters.

TABLE III
Foaming Properties of Anionic Derivatires
of PEG-SIPM Polycsters

Compounds	Foam height (mm)	
	Initial	After 3 min
PEG400-SIPM	15	0
PEG600-SIPM	20	0
PEG1000-SIPM	25	5
PEG2000-SIPM	25	5

rated during production of the final product. This function prevents aggregation and precipitation of dye particles during application.⁹ However, in some practical dyeing processes, such as for polyester fibers dyed at high temperatures, reaggregation of dyed particles will occur. Furthermore, this also occurs at elevated temperatures when the heat stability of the dispersant system is insufficient. To prevent this phenomenon, an additional dispersing agent, that has high heat stability, can be introduced into the dye either initially or during the course of dyeing.¹⁰⁻¹² Water-soluble polyester surfactants prepared here in three dispersed dye systems are suitable for these uses and have stability at elevated temperatures as well (Table V). Clearly, in all three dispersed dye systems, the heat stability was improved by adding water-soluble polyester surfactants. Moreover, the proposed systems are far superior to the traditional dispersing agent (i.e., naphthalene sulfonate condensate). Also, due to the corresponding increase of hydrophilic seg-

TABLE V
Dispersant Properties of Self-Sequestering Surfactants

Compound	Dispersibility(%)		
	Red 60	Blue 56	Yellow 218
Blank	57.9	57.7	26.7
Naphthalene sulfonate condensate	26.8	52.3	16.6
PEG400-SIPM	51.5	43.4	27.7
PEG600-SIPM	56.6	47.3	33.6
PEG1000-SIPM	63.5	64.0	85.4
PEG2000-SIPM	65.2	73.0	90.1

TABLE IV
Contact Angles of Solution of PEG-SIPM Polyesters

Compound	Acrylic film (degree)	Cotton fabric (degree)
H ₂ O	84	152
PEG400-SIPM	63	127
PEG600-SIPM	66	134
PEG1000-SIPM	70	138
PEG2000-SIPM	78	142

ments, the heat stability increased with an increase in the length of polyoxyethylene chain of the water-soluble polyester. This dissolves the partial reaggregates of dye particles. Therefore, the dye particles are not reaggregated readily and have excellent dispersion.

CONCLUSION

In this study, water-soluble polyesters PEG-SIPM with excellent hydrophilic properties were synthesized. These polyesters can be dissolved easily in water to form transparent solutions and reduce surface tension. Moreover, the surface activity decreases with an increase in the polyoxyethylene segment length. These water-soluble polyester surfactants exhibit excellent surface-active properties including surface tension, low-foaming, wetting power, and dispersant properties within disperse dyes.

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