♣ Synthesis and Surface Activity of Maleic Anhydride-Polyethylene Glycol-Phthalic Anhydride Polymeric Surfactants

K.M. Chen and **C.C. Tsai**
Department of Textiles, National Taiwan Institute of Technology, 43, Keelung Road, Section 4, Taipei, Taiwan

A novel series of polymeric surfactants has been synthesized by the reaction of maleic anhydride (MA), polyethylene glycol (PEG) and phthalic anhydride (PA). The unique structural features of these surfactants have been confirmed by IR, NMR and elemental analysis. These polymeric surfactants have been found to exhibit excellent surface active properties including surface tension, low-foaming, solubilization, and dispersant properties in disperse dye systems.

Because of their amphipathic molecular structure consisting of a hydrophobic portion together with a polar or an ionic portion, many water-soluble polymers have been found to exhibit surface activity similar to traditional surfactants, and are used as surfactants for many purposes (1). For example, the lignosulfonates exhibit dispersant properties in disperse or vat dye systems (2); the polysorbates exhibit excellent emulsifying properties for oil-in-water systems (3,4), and the polyoxyethylene-polyoxypropylene-polyoxyethylene block copolymers, known by their generic name as poloxamers, exhibit properties of demulsification, dispersion and emulsion stabilization (5).
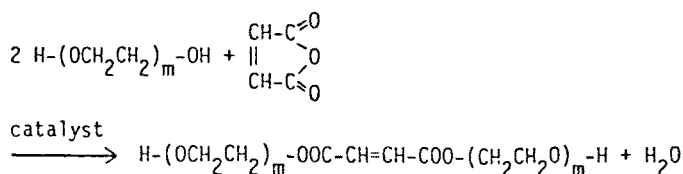
Water-soluble polyesters, prepared from dicarboxylic acid and diol, have been used mainly in the paint industry (6). However, only limited information is available in regard to the water-soluble polyesters used as surfactants

through these polymers which have an amphipathic molecular structure similar to the traditional surfactants. In our previous studies, the water-soluble polyesters prepared by the polymerization of 5-sulfoisophthalic acid dimethyl ester sodium salt (SIPM), PA and PEG have been found to exhibit excellent surface active properties (7,8). In the present study, a novel series of water-soluble polyesters are prepared by the reaction of MA, PA and PEG, and the surface active properties including surface tension, foaming, solubilization and dispersant characteristics for disperse dyes are studied.
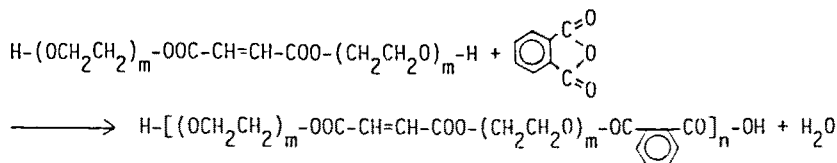
EXPERIMENTAL

Materials. MA, PA, sodium hydrogen sulfite, titanium isopropoxide, and PEG, molecular weight from 400 (PEG 400) to 2,000 (PEG 2,000), purchased from Hayashi Pure Chemical Co. (Osaka, Japan), were all reagent grade and used without further purification. Naphthalene sulfonate condensate supplied by C. L. Chemical Co. (Changhwa, Taiwan) was extracted with ethyl ether for eight hr and recrystallized twice from ether-methanol. All the other reagents were analytical grade and used without further purification. Three disperse dyes used were Dispersol Red B-2B (C. I. Disperse Red 60), Dispersol Blue BR (C. I. Disperse Blue 56) and Dispersol Yellow B-6G (C. I. Disperse Yellow 218). These dyes supplied by I. C. I. Co. (Manchester, England) were recrystallized three times
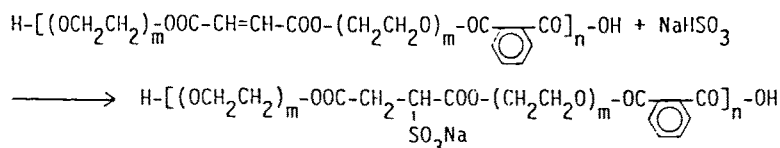
Step 1

$$2\ H\text{-}(OCH_2CH_2)_m\text{-}OH\ +\ \begin{array}{c} CH\text{-}C{\nwarrow}^{O} \\ \| \quad\quad\ {>}O \\ CH\text{-}C{\swarrow}_{O} \end{array}$$

$$\xrightarrow{\text{catalyst}}\ H\text{-}(OCH_2CH_2)_m\text{-}OOC\text{-}CH{=}CH\text{-}COO\text{-}(CH_2CH_2O)_m\text{-}H\ +\ H_2O$$

Step 2

$$H\text{-}(OCH_2CH_2)_m\text{-}OOC\text{-}CH{=}CH\text{-}COO\text{-}(CH_2CH_2O)_m\text{-}H\ +\ \text{[phthalic anhydride]}$$

$$\longrightarrow\ H\text{-}[(OCH_2CH_2)_m\text{-}OOC\text{-}CH{=}CH\text{-}COO\text{-}(CH_2CH_2O)_m\text{-}OC{-}\bigcirc\!\!-CO]_n\text{-}OH\ +\ H_2O$$

Step 3

$$H\text{-}[(OCH_2CH_2)_m\text{-}OOC\text{-}CH{=}CH\text{-}COO\text{-}(CH_2CH_2O)_m\text{-}OC{-}\bigcirc\!\!-CO]_n\text{-}OH\ +\ NaHSO_3$$

$$\longrightarrow\ H\text{-}[(OCH_2CH_2)_m\text{-}OOC\text{-}CH_2\text{-}\underset{\underset{SO_3Na}{|}}{CH}\text{-}COO\text{-}(CH_2CH_2O)_m\text{-}OC{-}\bigcirc\!\!-CO]_n\text{-}OH$$

SCHEME 1. Synthesis of MA-PEG-PA polymeric surfactants.

from ethanol, and their purities were confirmed by thin layer chromatography (TLC).

Synthesis of polymeric surfactants. The surfactants were prepared through three steps and can be represented as shown in Scheme 1. The first step is reacting MA with PEG by the presence of catalyst (titanium isopropoxide) at 180-200 C; the second step is reacting the products obtained in the first step with PA at 240-250 C, and the third step is to introduce the sulfonate group by reacting the products with sodium hydrogen sulfite at 120 C. Because the reactions of the first two steps are reversible, the water must be removed from the system continuously to maintain the reaction in a forward direction. The following example shows a typical recipe for preparing a polymeric surfactant which involves MA, PA and PEG 400.

A reaction mixture containing 57 g (0.5 mol) of MA, 400 g (1 mol) of PEG 400 and one g of catalyst was stirred mechanically and heated to 180-200 C under a nitrogen atmosphere. The temperature was held there under vacuum until nine ml (ca. 0.5 mol) of water was trapped. Next, 74 g (0.5 mol) of PA was added and the mixture was reheated to 240-250 C under vacuum. The reaction was followed until another nine ml (ca. 0.5 mol) of water was trapped (ca. 3 hr). Then the product was cooled to 120 C and 62 g (ca. 0.5 mol) of sodium hydrogen sulfite was added. After stirring for two hr at the same temperature, the product was cooled under nitrogen atmosphere.

The purification of products was carried out by ultrafiltration with a Spectra/Por MWCO 1000 and 5000 membrance (nominal cutoff MW = 1000, 5000). The purity of purified products was confirmed by TLC, using chloroform/toluene/methanol (13/1/1) as eluting solvent.

Analyses. The acid value and hydroxyl value were determined by usual methods, and from these values the molecular weight of polymeric surfactants was calculated (9). The sulfonate group (SO₃) content was determined by the method described in JIS (Japan Industrial Standards), K 3366. The elemental analyses were performed by Perkin-Elmer 240 C elemental analyzer. Infrared (IR) spectra were obtained with a Japan Spectroscopic FT/IR-3 spectrophotometer, and nuclear magnetic resonance (NMR) spectra were obtained with a Varian EM 360 L NMR spectrophotometer.

The analyses of final products are shown in Table 1. The molecular weight of PEG used in this study varies from 400 (PEG 400) to 2000 (PEG 2000), and the molecular weight of the products are controlled between 3000 to 9000. The acid value, hydroxyl value and sulfonate group content are found to decrease with the increase of the ethylene oxide chain length of PEG. All four polymeric surfactants are water soluble; compounds I and II are light brown liquids and compounds III and IV are brown solids.

The elemental analyses of products also are shown in Table 1. It was observed that the elemental analysis of all surfactants for C and H was within 2.5% of the calculated value. The structure of surfactants also was confirmed by IR analysis which displayed bands at 3400 (O-H, intermolecular hydrogen bond), 2900 (C-H, methylene), 1730 (C=O), 1600, 1470 (C=C, ring stretch), 1290 (C-O-C, asymmetric), 1250 (C-O-C, symmetric), 1120, 1030, 950 (-SO₃), and 740, 850 cm⁻¹ (C-H, out of plane) in all four surfactants. The proton NMR spectra of products gave further support to the assigned structure which gave signals at δ 3.6 (-CH₂-O-), 4.1 (-CH₂-OOC-), 4.4 (-CH-SO₃-), and 7.5, 7.7 ppm (-OOC——COO-).
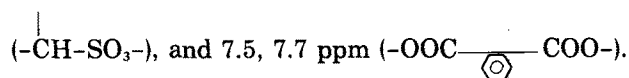
Measurements. Surface tension was determined at room temperature with a Fisher Du Nouy type interfacial tensiometer. Foaming properties were determined by the Ross-Miles method using a foam accumulate measuring system, while the foam production was measured by the height of the foam initially produced and the foam stability was measured by the height after three min. Solubilization was measured by a usual method that shakes a 50-ml solution containing 40 mg of purified disperse dye and various concentrations of polymeric surfactants for 48 hr at 30 C. The insoluble dyes were removed using a glass filter, and solubilized dyes were extracted from the filtrate by toluene and their concentrations determined spectrophotometrically (10). Dispersant properties were determined by the following method. A 100-ml solution containing 0.1 g commercial disperse dye and 0.1g dispersing agent was adjusted to pH 5.0 by adding an appropriate amount of acetic acid. Then the solution was heated to 130 C by a computer-controlled dyeing system for one hr. After this treatment, the solution was cooled to 90-95 C and vacuum filtered immediately by using a Buchner funnel, through Toyo No. 5A filter paper. The filtrate was diluted by acetone and the concentration was determined spectrophotometrically. The dispersibility was calculated as follows (11):

$$\text{Dispersibility} (\%) = \frac{\text{dye concentration of filtrate}}{\text{dye concentration of original solution}}$$

TABLE 1

Analyses of MA-PEG-PA Polymeric Surfactants

Compound	Mol wt of PEG used	Acid value	OH value	Mol wt	Sulfate group content (%)	Elemental analyses			
						(%)		H (%)	
						Found	Calcd.	Found	Calcd.
I	400	14.1	21.8	3125	6.7	51.07	51.26	7.39	7.22
II	600	13.4	14.6	4007	5.6	51.67	52.12	7.88	7.71
III	1000	10.6	12.1	4943	4.1	52.31	52.95	8.20	8.18
IV	2000	5.8	7.2	8631	2.2	53.77	53.69	8.75	8.60

RESULTS AND DISCUSSION

Surface tension. The surface activity of polymeric surfactants prepared in this study is shown in Figure 1. The surface tension of the solutions is reduced by addition of the polymeric surfactants, due to the polymers which have an amphipathic molecular structure similar to the traditional surfactants. However, an abrupt inflection point in the curves, which corresponds to the critical micelle concentration (CMC) in the cases of traditional surfactants, was not observed. No such CMC phenomenon has been reported in the cases of other polymeric surfactants (12,13). Increases in the length of the polyoxyethylene chain result in a decreased surface activity. This, as would be expected, is due to the increase in hydrophilicity of surfactants decreasing the concentration of surfactants at the surface.

Foaming properties. The low-foaming tendency of surfactants is an important property in some recent applications, such as dyeing auxiliaries in the modern textile-dyeing industry. The relative low-foaming properties of polymeric surfactants are shown in Table 2. These four
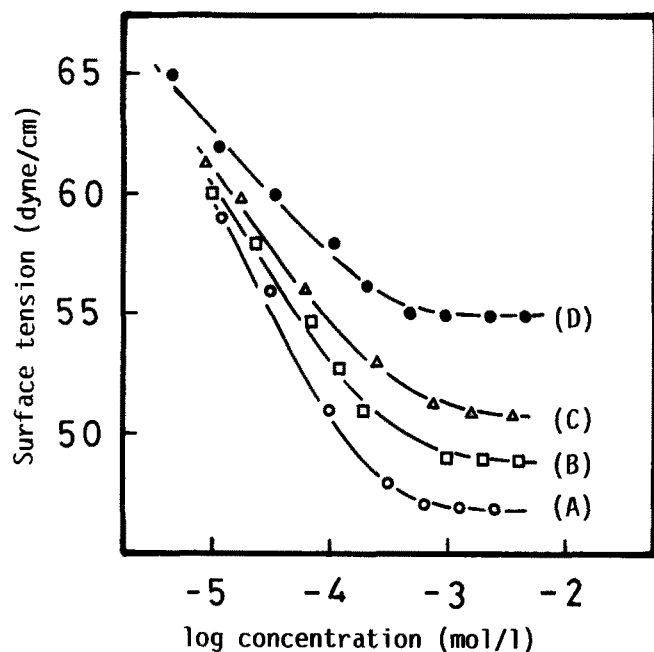
surfactants present not only the low-foaming production measured by the height of the foam initially produced, but also low-foaming stability, the height after three min. These low-foaming effects probably are due to (a) the presence of multihydrophilic groups causing a considerable increase in the area per molecule producing less cohesive forces at the surface; (b) the multianionic hydrophilic groups (SO_3Na) increasing the electrostatic repulsion among surfactant molecules counteracting the interchain cohesive forces, and (c) the polymeric surfactants which are believed to coil in the aqueous phase decreasing the cohesive force due to intra- and intermolecular bonding (7).

Solubilization. Solubilization is one of the important properties of surfactants. In general, solubilization occurred only above the CMC; above this, the amount of insoluble substance solubilized in the case of traditional surfactants increases with the surfactant concentration. Therefore, in general, solubilization would be used for establishing the CMC of surfactants (14). However, the solubilization is different in the case of the polymeric surfactants prepared in this study. Figure 2 shows the solubilization of polymeric surfactants for three purified disperse dyes. It is obvious that a linear relationship is

FIG. 1. Plots of surface tension vs log molar concentration for polymeric surfactants at 25 C. (A), compound I; (B), compound II; (C), compound III, and (D), compound IV.

TABLE 2

Foaming Properties of Polymeric Surfactants

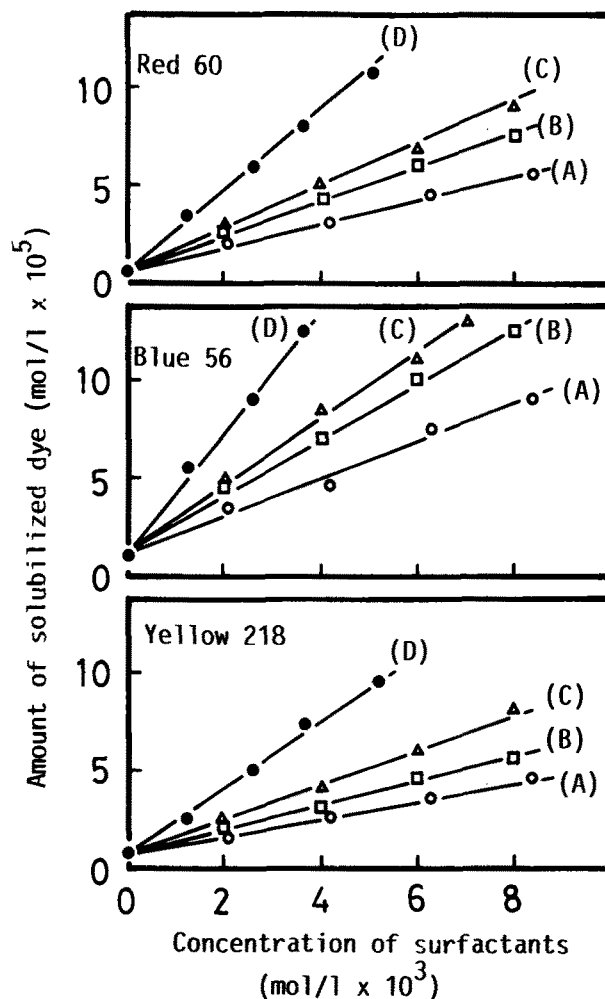| | Foam height (mm) | | | |
| | 30°C | | 85°C | |
Compound	Initial	3 min	Initial	3 min
I	15	0	18	0
II	15	2	18	1
III	16	2	18	2
IV	18	2	20	2

FIG. 2. Plots of amount of disperse dye solubilized as a function of concentration of surfactants. (A), compound I; (B), compound II; (C), compound III, and (D), compound IV.

obtained for the solubilization of all three disperse dyes and concentration of polymeric surfactants. It is generally accepted that at lower concentrations these surfactants form nonmicellar aggregates having the ability to solubilize disperse dyes. The solubilizing capacity of polymeric surfactants is observed to increase gradually as the hydrophilicity of the surfactant increases. It is believed that the solubilizate of disperse dyes contains hydrogen-bonding amino or carbonyl groups and can associate with the polyoxyethylene chains of surfactants. At longer polyoxyethylene chain lengths micellization no longer occurs and the surfactant becomes too soluble. However, the solubilizing capacity is observed less for less hydrophobic dye such as C. I. Disperse Yellow 218 than more hydrophobic dyes such as C. I. Disperse Red 60 and Blue 56, indicating that the solubilization also would be influenced by the interaction between the hydrophobic portions of dyes and surfactants (8).

Dispersant properties. Because the purified disperse dyes are almost insoluble in water, some surfactants (namely the dispersing agent) are incorporated during production of the final dye powder or liquid, to prevent any aggregation or precipitation of dye particles during application (15,16). However, in some practical dyeing processes, such as dyeing of polyester fibers at high temperature, the reaggregation of dye particles will occur at elevated temperatures when the heat stability of the dispersant system is insufficient. To prevent this, an additional dispersing agent, having high stability, may be introduced into the dye bath initially or during the course of dyeing (2, 16-18). In our previous studies, the water soluble polyester surfactants have been shown effective due to their high heat stability in disperse dye systems (7,8). The heat stability of polymeric surfactants prepared in this study also is determined at elevated temperature in three disperse dye systems, as shown in Table 3. It is obvious that in all three disperse dye systems, the heat stability is improved by the addition of polymeric surfactants. These improvements are similar to the results of the surfactants prepared in our previous studies (7) and better than the traditional dispersing agent (naphthalene sulfonate condensate). For the same disperse dye, the length of polyoxyethylene chain of surfactants has only a slight influence on heat stability; however, the heat stability is much lower for less hydrophobic dyes such as C. I. Disperse Yellow 218 than more hydrophobic dyes such as C. I. Disperse Red 60 and Blue 56. This effect is consistent with the results of solubilization shown previously and may be responsible for the difference in interaction between dispersing agents and dyes (8).

The high heat stability of polymeric surfactants probably is due to their unique structural feature: (a) high molecular weight; (b) aromatic structure and ester linkage of the hydrophobic portion, and (c) multiple ionic groups and polyoxyethylene chains of the hydrophilic portion. The high molecular weight, aromatic structure and ester linkage of the surfactant favor its adsorption onto the surface of dye particles. The multisulfonate groups on the adsorbed dispersing molecules produce strong electrostatic repulsion, and hence stabilize the dispersion (17). On the other hand, the nonionic portion also leads to stabilization of the dispersion, presumably because of their high hydrated polyoxyethylene chain extending into

TABLE 3

Dispersant Properties of Polymeric Surfactants

Compound	Dispersibility (%)		
	Red 60	Blue 56	Yellow 218
I	68.4	75.2	18.5
II	66.5	68.4	24.8
III	61.5	71.0	28.1
IV	59.6	69.5	22.1
Naphthalene sulfonate condensate	26.8	52.3	16.6
Blank	25.6	32.7	15.5

the solution in the form of coils that present an excellent steric barrier to aggregation (17,19). In both cases, the hydrophobic groups come into contact with the particle surface, leaving the hydrophilic groups directed toward the aqueous phase and producing a solvation protection for dye particles. At an elevated temperature, the desorption of the novel dispersing agent from dye particles is minimized due to strong association between the dispersing agent and dye particles, thus resulting in high stability of these dispersant systems.

REFERENCES

1. Hancock, R.I., *Surfactants*, edited by Th. F. Tadros, Academic Press, New York, 1984, pp. 287-321.
2. Lin, S.Y., *Text. Chem. Colorist 13*:261 (1981).
3. Atlwood, D., and A.T. Florence, *Surfactant Systems*, Chapmon and Hall, London, 1983, p. 469.
4. Boyd, J., C. Parkinson and P. Sherman, *J. Colloid Interface Sci. 41*:359 (1972).
5. Schmolka, J.R., *J. Am. Oil Chem. Soc. 54*:110 (1977).
6. Mitsuwa, T., *Chemistry of Synthetic Resin*, Gihoto, Tokyo, 1983, p. 292.
7. Chen, K.M., and H.J. Liu, *J. Appl. Polym. Sci. 34*:1879 (1987).
8. Chen, K.M., *J. Chinese Inst. Chem. Eng. 10*:579 (1987).
9. Sorenson, W.R., and T.W. Champbell, *Preparative Methods of Polymer Chemistry*, Wiley-Interscience, New York, 1968, pp. 50-51.
10. Steinhardt, J., N. Stocker, D. Carroll and K.S. Birdi, *Biochem. 13*:4461 (1974).
11. Abe, N., *Dyeing Ind. 27*:331 (1979).
12. Moriya, M., A. Nishimura, K. Hosoda, M. Takai and H. Hidaka, *J. Am. Oil Chem. Soc. 63*:263 (1986).
13. Saden, A. Al., A.T. Florence, T.L. Whateley, F. PUisieux and C. Vaution, *J. Colloid Interface Sci. 86*:51 (1982).
14. Kitahara, A., S. Hayano and I. Hara, *Analysis and Testing of Surfactants*, Kodansha, Tokyo, 1982, pp. 52-54.
15. Bird, C.L., *J. Soc. Dyers Colour 70*:68 (1954).
16. Kuroiwa, S., *Sen-i Gakkaishi 36*:27 (1980).
17. Jones, F., *J. Soc. Dyers Colour 100*:66 (1984).
18. Chen, K.M., *New Fibers 6*:7 (1985).
19. Finch, C.A., in *Chemistry and Technology of Water-Soluble Polymers*, edited by C.A. Finch,Plenum Press, New York, 1981, pp. 233-234.