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Preparation of a water soluble polyester surfactant and its use in the emulsion polymerization of styrene

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Summary

The synthesis procedure of Chen and Liu (1) was used to prepare a polyester surfactant from dimethyl 5-sulfoisophthalate, sodium salt, polyoxyethylene (MW 200) and phthalic anhydride by a two step esterification process. The surfactant has the unique structural features of multiple ionic groups and polyoxyethylene chains for hydrophilicity and aromatic ester linkages for hydrophobicity. The polyester surfactant exhibited a CMC of 0.25% (w/v) and a surface tension lowering of 23 dynes/cm. The use of the surfactant as stabilizer for the emulsion polymerization of styrene produced some unusual results. While the rate of polymerization was independent of surfactant concentration, the number of particles increased as $N \propto [S]^{0.91}$. The molecular weight of polystyrene produced was low and found not to be a function of surfactant concentration. The structural features of the surfactant suggest that a depletion stabilization mechanism might be operative in this system.

Introduction

Polyester surfactants prepared by the condensation of different dicarboxylic acids or anhydrides and polyoxyethylene are used in a variety of industrial applications. Chen and Liu (1) synthesized a novel series of water soluble polyester surfactants by a two step condensation of dimethyl 5-sulfoisophthalate, sodium salt, polyoxyethylene and phthalic anhydride. Six polyesters were prepared with polyoxyethylene ranging in molecular weight from 106 to 1000. These materials showed excellent surfact activity and were investigated for applications in the textile industry such as dye solubilization and dye dispersibility at elevated temperatures.

Typically, polymeric surfactants useful for stabilizing emulsion polymerization systems are of the block or graft type with hydrophobic moieties capable of anchoring the surfactant at the particle and stabilizing moieties which extend into the dispersion medium. Although polyester surfactants are of significant importance in dispersion related industries, the mechanism by which these materials stabilize dispersions and the kinetics of emulsion polymerization using polyester surfactants as emulsifiers has not been thoroughly investigated.

The purpose of this study was to prepare a water soluble polyester surfactant using the procedure outlined by Chen and Liu (1), and to use this material as the sole stabilizer in the emulsion polymerization of styrene to examine reaction kinetics, latex particle size and number and molecular weight of polymer as a function of surfactant concentration. From these results an effort was made to deduce the mechanism of particle stabilization.

Experimental

The reaction scheme and the synthesis procedure for the preparation of the water soluble polyester surfactant are outlined in the article by Chen and Liu (1). The first step of the synthesis involved the reaction of one mole of dimethyl 5-sulfoisophthalate, sodium salt with two moles of polyoxyethylene (MW 200) in the presence of titanium isopropoxide, a catalyst, at 180-200°C under nitrogen, to form a trimer. Polyesterification occurred during Step 2 by the reaction of one mole of phthalic anhydride with the trimer formed in Step 1. Because phthalic anhydride sublimes when heated below its melting point, the reaction of phthalic anhydride was allowed to proceed for several hours at 180-200°C in the presence of a small amount of 1-methyl-2-pyrrolidinone, a solvent for the reaction ingredients. Vacuum was applied to the system and the temperature raised to 240-250°C. The 1-methyl-2-pyrrolidinone, rapidly distilled off under these conditions and the reaction proceeded as a melt polymerization. The extent of reaction was monitored by the removal of methanol during the first step and water during the second step of the synthesis. The viscous, brown polymer was retrieved while hot and used without further purification.

Emulsion polymerizations were carried out in 2 ounce glass reaction bottles fitted with perforated screw caps which were lined with self-sealing butyl rubber gaskets. The polymerization recipe is given in Table I.

Table I

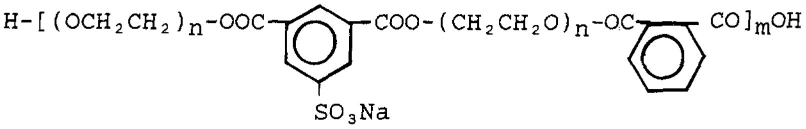
Emulsion Polymerization Recipe

Ingredient	Amount (g/100g monomer)
Water	800
Surfactant	Variable
$K_2S_2O_8$	1
Styrene	100

The polymerization temperature was 50°C. Reaction bottles were purged with nitrogen for 15 minutes after the addition of styrene, clamped into a thermostatted water bath and rotated end-over-end at 38 rpm. Percent conversion was determined by a total solids method. Latex particle size, D_Z, was determined by light scattering using a Malvern Autosizer IIc. Number of particles per cm of aqueous phase was calculated from D_Z.

Results and Discussion

The structure of the prepared water soluble polyester surfactant is shown below:



The structure was confirmed by FTIR and NMR analyses. In the FTIR spectrum characteristic absorption bands corresponding to O-H, C-H (methylene), C-H (aromatic) and C=O stretching frequencies occur at 3400, 2900, 3000, and 1700 cm^{-1}, respectively. The absorption bands in the NMR spectrum coincided with those in the literature spectrum (1).

Surface tension measurements were carried out on aqueous solutions of the polyester surfactant. The surfactant exhibited a CMC of 0.25% (w/v) and a surface tension lowering of 23 dynes/cm.

Emulsion polymerizations of styrene were studied using the recipe in Table I and surfactant concentrations of 5, 10, 15, 17.5, 20, 30, 40, 50, and 60g/100g monomer. Utilizing a surfactant concentration of 5g/100g monomer, the latex coagulated at approximately 20% conversion. Partial coagulation of the latices occurred after 20% conversion when surfactant concentrations of 10, 15, and 17.5g/100g monomer were employed. Stable latices were obtained with surfactant concentrations of 20 - 60g/100g monomer. The rates of polymerization, final average particle sizes, and number of particles per cm aqueous phase for these polymerizations are listed in Table II. While increasing surfactant concentration decreased particle size and increased particle number, it had virtually no effect on the rate of polymerization. A natural log plot of N vs. surfactant concentration is shown in Figure 1. From the slope of this plot the relationship N [S] is implied. The molecular weight of polystyrene was also determined as a function of surfactant concentration by GPC. The results are listed in Table II. Polystyrene molecular weight was not a function of surfactant concentration. In addition, the molecular weights were low for emulsion polymerization. These results suggest that chain transfer was occurring during polymerization. Although chain transfer to surfactant could not be determined from an NMR analysis of polystyrene, it is probable that chain transfer occurred but the generated surfactant radicals retarded or inhibited polymerization.

That the rate of polymerization did not increase as the number of particles increased by three-fold over the concentration range studied is unusual for emulsion polymerization. Polymerization occurs within the polymer particles; therefore, increasing the number of sites where polymerization can take place generally increases the rate of polymerization.

Table II

Kinetic Data for Styrene Emulsion Polymerizations at Different Surfactant Concentrations

Surfactant Conc. (g/100g monomer)	(% aq.phase)	R_px10^4 (mol/Ls)	D_z * (nm)	Nx10^{-14}/cm^3)**	M_nx10^{-5}
20	2.5	2.52	76	3.8	6.39
30	3.75	2.79	70	5.0	10.0
40	5.0	2.72	62	6.4	7.37
50	6.25	2.75	60	8.1	3.00
60	7.5	2.81	52	10.5	4.19

*D_z from light scattering measurements
**D_z rather than D_v used for the calculation of N

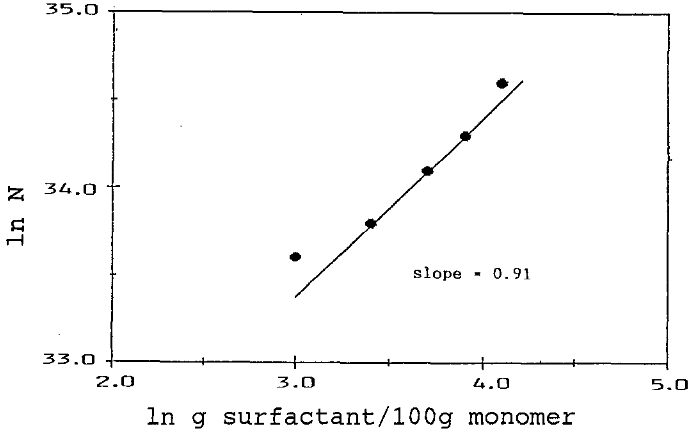


Figure 1. Natural Log Plot of Number of Particles vs. Surfactant Concentration

The unique feature of this system is the surfactant employed. Inherent in the structure are multiple ionic groups and polyoxyethylene chains for hydrophilicity and aromatic ester linkages for hydrophobicity. Based solely on chemical structure this surfactant might not be expected to stabilize emulsion polymerization because it lacks hydrophobic moieties of sufficient length to anchor the stabilizing moieties to the particle surface. In addition, the hydrophobic aromatic groups are positioned along the polymer chain between hydrophilic segments of considerable size which would tend to shield them from any interaction with the particle surface.

These structural features suggest that the polyester surfactant might prefer to remain in the aqueous phase rather than associate with the particles. In this case stabilization would occur by a depletion stabilization mechanism. Depletion stabilization is the method whereby particles in a colloidal dispersion are stabilized by the presence of free polymer in solution (2). Contributing to stabilization, if depletion stabilization were operative in this system, would be the electrostatic repulsion between the charged initiator end groups on the particle surface and the ionic sulfonate groups of the surfactant molecules in the aqueous phase.

However, depletion stabilization is a phenomenon that is not well understood and it has not been applied to emulsion polymerization. The kinetic dependencies observed seem to indicate that the colloidal properties of the latices are independent of kinetic variables. The approximate 1:1 dependence of number of particles on surfactant concentration suggests that N is controlled by stability and colloidal properties. Rate of polymerization is a kinetic parameter and is affected by such factors as the number of radicals per particle, the concentration of monomer in the particles and chain transfer. Whether the unusual kinetic dependencies observed for this polymerization system are direct consequences or characteristic of depletion stabilization cannot be concluded based on this preliminary study.

Finally, polystyrene latices prepared with 20, 30, 40, 50 and 60g surfactant/100g monomer exhibited excellent freeze-thaw and storage stability.

References

1. Chen, K. M.; Liu, H. J., J. Appl. Polym. Sci., 34,1879 (1987)
2. Napper, D. H., "Polymeric Stabilization of Colloidal Dispersions", Academic Press, 1983

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