Effect of pH on the Rate of Emulsion Polymerization of Styrene Initiated by Potassium Persulfate

A. RAHMAN and C. W. BROWN,* *Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, Lancashire, England*

Synopsis

The influence of pH on the emulsifier property (micellar molecular weight) of sodium dodecyl sulfate has been studied in conjunction with the effect of pH on the rate of emulsion polymerization of styrene initiated by potassium persulfate. The rate of polymerization was found to be pH dependent. The micellar weight of sodium dodecyl sulfate has been determined at various pH values. The micellar weight was found to increase with decrease in pH. On the basis of the result, a suggestion was made that the effect of pH on micellar molecular weight can account for the observed behavior of the rate of polymerization.

INTRODUCTION

The emulsion polymerization of styrene using potassium persulfate as initiator at pH 3–9 has been studied. Thermal decomposition of persulfate anion results in sulfate ion radicals which initiate polymerization.[1-3] In the mechanism, emulsifier largely exists in the form of micelles. As the polymerization proceeds, the radicals initiate the polymerization of the monomer solubilized in the micelles. The pH of the system might influence the rate of polymerization in a variety of ways, e.g., through its effect on initiator decomposition and on the properties of the emulsifier. Therefore, the micellar molecular weight has been examined at the above pH values using light scattering technique at a wavelength 436 nm.

EXPERIMENTAL

Preparation and Purification of Materials

Styrene was obtained from BDH. The inhibitor was washed with dilute sodium hydroxide solution followed by deionized water and distilled under reduced pressure in an atmosphere of nitrogen. The pure styrene was stored at 10°C.

Sodium dodecyl sulfate was obtained from Sigma Chem. Co. (St. Louis, MO). The solution was prepared by dissolving in deionized water. The purity of this emulsifier was specified at 99.9%.

Nitrogen (The British Oxygen Company's "White Spot" nitrogen) was deoxygenated by passing through alkaline sodium dithionite solution containing silver salt as indicator and subsequently through dilute sodium hydroxide, dilute sulfuric acid, and deionized water.

* Deceased.

Method

The basic polymerization technique employed is the same as that used by Longbottom.[4,5] The reaction flask containing the required (100 cm^3) amount of sodium dodecyl sulfate was immersed in a constant-temperature bath at 50 ± 0.1°C, and nitrogen was bubbled through the solution for 1 h. Distilled styrene, 50 g, was added and the mixture was stirred vigorously for 10 min to homogenize the system, after which the stirring was reduced. The pH of the mixture was adjusted to the desired value by the addition of dilute hydrochloric acid and dilute sodium hydroxide solution. The polymerization was started by the addition of potassium persulfate.

The percentage conversion was calculated from the formula

$$\% \text{ conversion} = \frac{RT}{S} - N$$

where R is the weight of residue, T is the total weight of all ingredients (based on 100 parts of monomer), S is the weight of sample taken, and N is the total weight of nonvolatile nonpolymer components (based on 100 parts of monomer). Percentage conversion was plotted against time at each pH, and the rate of polymerization was obtained from the straight-line portion of the graph. The rate of polymerization was plotted against pH and is shown in Figure 1.

The micellar molecular weight of emulsifier at various pH values between 3 and 9 was determined by using Brice–Phonix light scattering photometer 2000
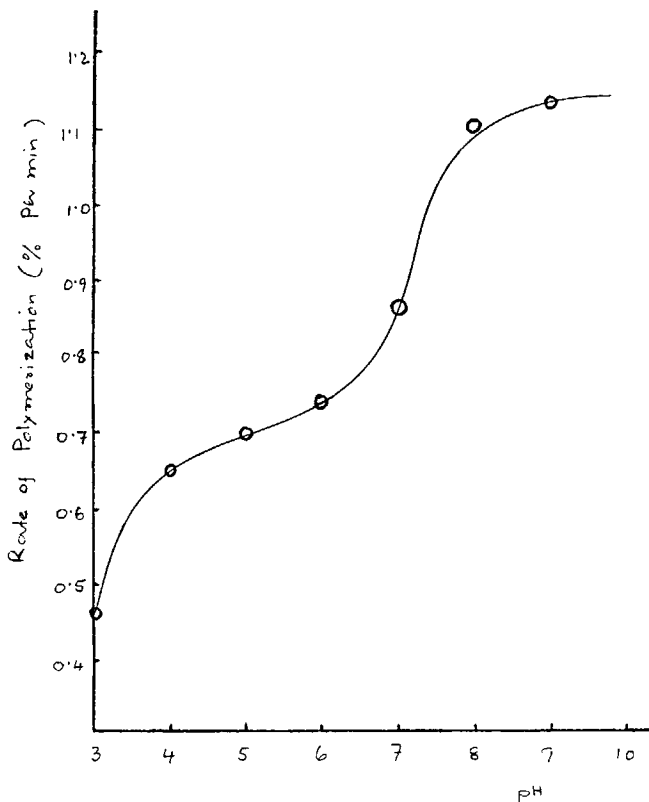

Fig. 1. Rate-pH curve for the emulsion polymerization of styrene.

series. The technique was the same as that used by Debye[6] and Mysels.[7,8] An Algol computer has been devised to manipulate the light scattering data obtained from the photometer. These values were fed into the previously programmed computer. The value of the coefficient l was obtained from the output data. The average micellar weight $\overline{M}_w$ for each pH was calculated from the equation

$$\overline{M}_w = \frac{W}{K^*} \times \frac{1}{l}$$

where

$$K^* = \frac{2\pi n^2 (dn/dc)^2}{(N_A \lambda)^4}$$

$$W = \frac{TD \cdot a \cdot n^2 (R_w/R_c)(r/r')}{1.049\pi h} \frac{1}{(1 - R)^2(1 - 4R^2)}$$

and n, N_A, λ, dn/dc, R_w/R_c, r/r, and R represent the refractive index of the solvent, Avagrodro's number, wavelength of the light used, specific refractive index increment, correction for incomplete compensation for refractive effect in the cell, calibrating factor, and fraction of the primary beam reflected at the exit window of the cell, respectively. TD, a, and h are caliberated constants for
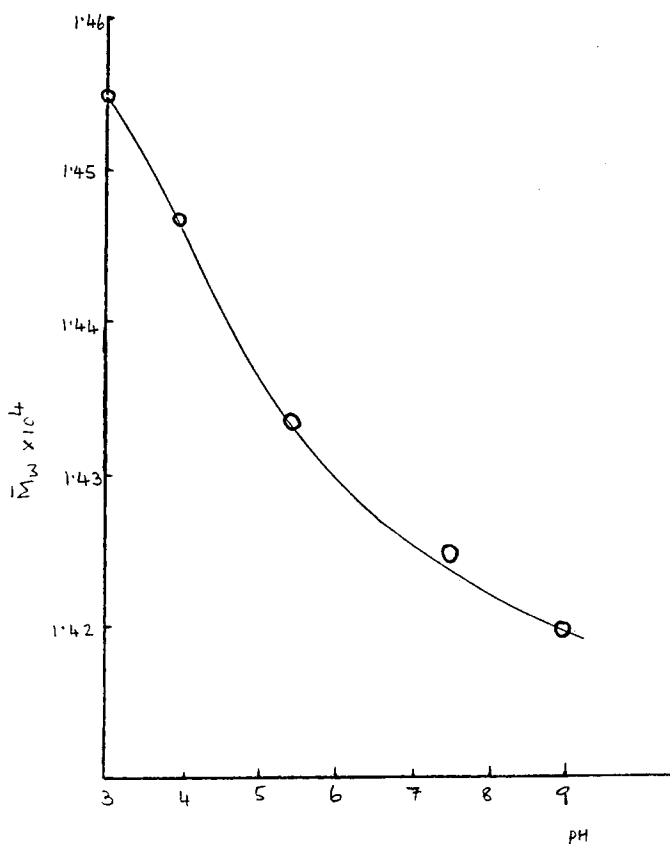

Fig. 2. Plot of micellar molecular weight ($\overline{M}_w$) vs. pH.

the particular photometer used and have values of 0.306, 0.04, and 1.20 at a wavelength of 436 nm. The result of the micellar weight was plotted against pH as shown in Figure 2.

RESULTS AND DISCUSSION

It was observed that the rate of polymerization increases as pH increases; and in the case of micellar weight, an opposite result was obtained. The decrease of micellar molecular weight of sodium dodecyl sulfate in the present study may arise from the charged density at the micelle surface. Micelle formation in aqueous solution of ionic surfactant involves electrical changes. An ionic micelle bears charges on its surface,[9] and these charges may be influenced by additional electrolyte. Hydrogen ions may decrease the electrostatic repulsion of the charged heads by decreasing the charged density on the surface of the micelle. A decrease in the charge density on the micelle surface may increase the micellar size. On the basis of this result when considering the micellar size, it was observed from Figure 2 that lowering of pH has increased the micellar weight. As the micellar size increases at lower pH, the number of micelles decreases. Consequently, any factor that decreases the number of micelles should decrease the rate of polymerization since the latter is dependent on the number of micelles. On the other hand, an opposite results may be obtained from a higher pH. Therefore, the effect of pH on the micellar weight can account for the observed behavior of the rate of polymerization.

References

1. W. V. Smith and H. N. Cambell, *J. Chem. Phys.*, **15**, 338 (1947).
2. P. D. Bartlett and K. Nozaki, *J. Polym. Sci.*, **3**, 216 (1948).
3. P. D. Bartlett and J. D. Cotman, Jr., *J. Am. Chem. Soc.*, **71**, 1414 (1949).
4. J. Bond and H. M. Longbottom, *J. Appl. Polym. Sci.*, **13**, 2333 (1969).
5. C. W. Brown and H. M. Longbottom, *J. Appl. Polym. Sci.*, **14**, 2927 (1970).
6. P. Debye, *J. Phys. Colloid Chem.*, **51**, 18 (1947).
7. K. J. Mysels, *J. Phys. Chem.*, **58**, 303 (1954).
8. K. J. Mysels, *J. Colloid Sci.*, **10**, 507 (1955).
9. K. Shinoda and T. Nakagawer, *Colloidal Surfactants*, Academic, London, 1963.