

# Influence of Steric Length in Electrosteric Surfactants on Emulsion Polymerization

CARLA B. DITTMAN-McBAIN and IRJA PIIRMA, *Department of Polymer Science, The University of Akron, Akron, Ohio 44325-3909*

## Synopsis

Four PPG Avanel Series S surfactants (sodium alkyl polyether sulfonates) with varying ethylene oxide content ( $n = 3, 7, 9,$  and  $15$ ) were used to investigate the influence of the steric length in this type of electrosteric stabilizers on emulsion polymerization. The polymerization studies employing potassium persulfate as an initiator with styrene, methyl methacrylate, and vinyl acetate monomers showed no apparent change in particle size, number of particles, and polymerization rate with the changing steric length of the surfactant. Steric influences were observed in the redox-initiated systems of styrene, butyl acrylate, and methyl methacrylate. Increasing the ethylene oxide unit content from three to nine units decreased the rate of polymerization, the particle size and number in the polystyrene latexes. Polymerizations with the acrylates displayed the same trend except that the polymerization rate reached a minimum value at nine ethylene oxide units and increased when the surfactant containing 15 ethylene oxide units was used.

## INTRODUCTION

Relatively few investigators have studied the effect in polymerization of changing the hydrophilic portion of the anionic electrosteric surfactants. A change in the actual structure of the surfactant could possibly reflect a change in the capabilities of the stabilizing substance. The goal of the investigation was to monitor how changes in the structure of the surfactant influences the rate of polymerization, the size and number of the particles using monomers of differing water solubility and employing different types of initiation systems.

In previous investigations researchers have studied the effect of changing the length of the hydrophilic portion of the nonionic surfactants as well as the total weight percent content of the hydrophilic blocks in the case of graft type polymers. Poly(ethylene oxide) (PEO) is a favorite hydrophilic compound to incorporate into surface-active materials. Gritskova and co-workers<sup>1,2</sup> found that increasing the amount of PEO content in the polyethylated polypropylene glycols increased the rate of polymerization and decreased the latex particle size. Chao and Piirma<sup>3</sup> found that increasing PEO content in the alkylphenol poly(ethylene oxide) ethers produced decreasing particle sizes, an increase in the number of particles/cm<sup>-3</sup>, and correspondingly increases in the rate of polymerization. This effect was further studied in graft copolymers of poly(*p*-methylstyrene-*g*-polyoxyethylene) by Lenzotti and Piirma.<sup>4</sup> They found that graft nonionic copolymers followed the same trend that had been established for nonionic block copolymers.

## EXPERIMENTAL

### Materials

Styrene (Aldrich), methyl methacrylate (Fisher), butyl acrylate (Kodak), and vinyl acetate (Eastman) were washed with 5% aq NaOH, water and brine to remove the inhibitor. They were distilled (the first three under vacuum), and stored in the refrigerator at 0°C. Avel S Series surfactants (PPG), S-30, S-70, S-90, and S-150, received as 36% aqueous solutions, were diluted with distilled water to the appropriate concentrations. The Avels are sodium alkyl polyether sulfonates of a chemical structure  $C_{12-15}H_{25-31}(C_2H_4O)_nCH_2CH_2SO_3^-Na^+$ , where  $n$  equals 3, 7, 9, and 15 ethylene oxide units. Impurities of Avel surfactants (data provided by PPG from IR, NMR, and GPC measurements) were 3–5% maximum of alkyl alcohol and 2% max sodium salt. Benzoyl peroxide (Aldrich), ferrous sulfate heptahydrate (Fisher), and 1,4-diisopropylbenzene hydroperoxide (Hercules) were used as supplied. Tetraethylenepentamine (Fisher) was distilled under reduced pressure and stored in the refrigerator before using.

### Procedures

Water, surfactant, initiator, and monomer in the weight ratio of 500 : 25 (or 7) : 0.3–1 : 100 were weighed into 100 cm<sup>3</sup> glass bottles. The amount of the surfactant was based on the amount of monomer. Experiments were also carried out where the surfactant concentrations were on molar basis.<sup>5</sup> A comparison of S-30 and S-150 on that basis was not possible, since S-30 did not yield a stable latex. The higher molar levels of each surfactant showed increases, but appeared to be more structure relationship rather than number of molecules problem.

The bottles were capped with self-sealing butyl rubber lined screw cap. Degassing of the content in bottles was done by bubbling nitrogen through a needle in the cap and another needle was used for an outlet. All bottles were pressurized with nitrogen after degassing. The bottles were rotated end-over-end at 60 rpm in a constant temperature bath. After an induction period of 0.5–2 h, a blue fluorescent tint indicated polymerization had started. Conversion rates were determined by withdrawing latex samples with disposable 25 cm<sup>3</sup> syringes at timed intervals. The latex samples were weighed, coagulated, and dried in an oven in aluminum pans. The pans were reweighed to determine the percent polymer formed after the weights were corrected for other insoluble components present. At the same time the conversion samples were taken, samples also were removed for particle size determination. These were determined by a light scattering method on a Malvern Autosizer 2c.

## RESULTS

### Potassium-Persulfate-Initiated Polymerizations

Potassium persulfate decomposes into two radical anions in the aqueous phase. The effect of a negatively charged primary radical with an anionic electrosteric surfactant was of interest.

TABLE I  
 Styrene Polymerizations at 45 and 55°C Initiated with Persulfate<sup>a</sup>

<i>n</i>	45°C			55°C		
	$R_p \times 10^4$ (M/s) ± 5.5%	$D_z$ (nm) ± 3	$N^b \times 10^{-14}$ (cm <sup>-3</sup> ) ± 0.5	$R_p \times 10^4$ (M/s) ± 6.7%	$D_z$ (nm) ± 3	$N^b \times 10^{-14}$ (cm <sup>-3</sup> ) ± 0.5
3	4.4	65	9.8	13.4	52	18.4
7	5.4	65	9.8	14.4	55	13.2
9	5.2	62	10.5	14.9	54	13.0
15	5.3	64	10.2	14.2	54	13.0

<sup>a</sup>Surfactant: C<sub>12-15</sub>H<sub>15-31</sub>[OC<sub>2</sub>H<sub>4</sub>]<sub>*n*</sub>OCH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>NA, where *n* = 3, 7, 9, 15 ethylene oxide units.

<sup>b</sup>*N* is the number of particles per cm<sup>3</sup> of aqueous solution.

As the data in Table I show, the rates of polymerization of styrene at 45 and 55°C were relatively constant for surfactants containing seven to 15 ethylene oxide units. Raising the temperature to 55°C served to increase the rate of polymerization by approximately a factor of 2.7. Thus, an increase in the surfactant steric length did not have an influence on the number of particles formed. A slightly slower rate was observed at both temperatures for the Avanel surfactant containing only three ethylene oxide units. For all four surfactants, the particle size did not vary with the surfactant steric length, although the size decreased by approximately 10 nm upon an increase by 10°C in the polymerization temperature.

Polymerizations at 45°C using more water-soluble monomers than styrene such as methyl methacrylate and vinyl acetate were also carried out. The data in Table II show that the polymerizations of both of these monomers display the same relative insensitivity to the change in the length of the steric portion of the electrosteric surfactant in the size range as used in these experiments.

### Benzoyl-Peroxide- and Ferrous-Sulfate-Initiated Polymerizations

Styrene polymerizations at 25, 35, and 45°C were initiated with the redox couple benzoyl peroxide and ferrous sulfate. The results are tabulated in Table III, where it can be seen that the rates of polymerization decrease with

 TABLE II  
 Methyl Methacrylate and Vinyl Acetate Polymerizations at 45°C  
 Initiated with Potassium Persulfate

<i>n</i>	MMA			Vinyl Acetate		
	$R_p \times 10^4$ (M/s) ± 6.1%	$D_z$ (nm) ± 3	$N \times 10^{-14}$ (cm <sup>-3</sup> ) ± 0.5	$R_p \times 10^4$ (M/s) ± 8.5%	$D_z$ (nm) ± 3	$N \times 10^{-14}$ (cm <sup>-3</sup> ) ± 0.5
3	11.2	70	6.6	2.0	—	—
7	12.8	72	5.8	3.5	62	9.1
9	12.7	74	6.1	3.3	57	10.9
15	13.0	74	5.7	3.4	64	8.3

TABLE III  
 Styrene Polymerization with Benzoyl Peroxide/Iron(II)

<i>n</i>	Temp <sup>a</sup> (°C) ±0.5	$R_p \times 10^4$ (M/s)	$D_z$ (nm) ±2	$N^b \times 10^{-14}$ (cm <sup>-3</sup> ) ±0.5
3	25	3.4	65	9.2
7	25	2.2	70	7.3
9	25	1.8	69	7.6
15	25	1.0	77	5.5
3	35	6.3	59	13.0
7	35	3.8	65	9.2
9	35	3.2	69	7.3
15	35	2.4	73	6.1
3	45	12.6	57	13.6
7	45	8.1	65	9.1
9	45	6.3	66	8.7
15	45	4.4	70	7.3

<sup>a</sup>Error for all 25°C experiments is ±0.1, for all 35°C experiments ±0.3, and for all 45°C experiments ±0.4.

<sup>b</sup>*N* is the number of particles per cm<sup>3</sup> of aqueous solution.

increasing units of ethylene oxide in the surfactant molecule at all three temperatures. Particle sizes were not observed to vary as noticeably as the rate of polymerization did either with temperature or steric length of the surfactant. Activation energies of 14, 15, 14, and 16 kcal/mol (±1 kcal/mol) were calculated for the reactions with 3, 7, 8, and 15 ethylene oxide units, respectively, in the Avanel surfactant molecules.

Using this peroxide/iron(II) redox initiator in the polymerization of butyl acrylate and methyl methacrylate yielded polymerization rates that decreased with increasing ethylene oxide content from three to nine units. The results in Table IV show that at nine ethylene oxide units a minimum in the rate occurred for both acrylates. A change in ethylene oxide units from nine to 15 caused the rate of polymerization again to increase. The particle size did not vary as much in magnitude as the rate did but followed the same pattern. It was also noted that the number of particles formed were not always proportional to the rate of polymerization as one would expect when the polymerization kinetics follows the Smith-Ewart relationship. Lowering the surfactant

 TABLE IV  
 MMA and Butyl Acrylate Polymerizations at 35°C Initiated with Benzoyl Peroxide/Iron(II)

<i>n</i>	MMA			Butyl acrylate		
	$R_p \times 10^4$ (M/s) ±2.8%	$D_z$ (nm) ±2	$N \times 10^{-14}$ (cm <sup>-3</sup> ) ±0.5	$R_p \times 10^4$ (M/s) ±6.9%	$D_z$ (nm) ±4	$N \times 10^{-14}$ (cm <sup>-3</sup> ) ±0.5
3	12.8	83	4.5	16.1	86	3.8
7	8.2	98	2.1	9.3	96	3.0
9	6.1	95	2.5	4.6	87	3.4
15	10.5	90	2.7	11.5	87	4.0

TABLE V  
 Polymerization Data for Styrene Using 7 phm Surfactant at 35°C with Benzoyl Peroxide/Fe(II)

<i>n</i>	$R_p \times 10^4$ ( <i>M</i> /s) ± 8.0%	$D_n^a$ (nm) ± 5	$N^b \times 10^{-14}$ ( $\text{cm}^{-3}$ ) ± 0.5
3	3.8	37	33.0
7	3.6	63	9.1
9	2.1	77	4.5
15	1.9	66	8.0

<sup>a</sup> $D_n$  determined by electron microscope at approximately 60% conversion.

<sup>b</sup> $N$  is the number of particles per  $\text{cm}^3$  of aqueous solution.

concentration in styrene polymerizations from 25 phm to 7 phm resulted in unstable latexes after approximately 60% conversion. Table V shows the polymerization rates calculated for the stable constant rate regions. Here it was observed that the rate of polymerization decreased with increasing ethylene oxide content, but that the particle sizes showed more of a variation between the four surfactants employed. A maximum was also observed in the particle size for the polymerization with surfactant containing nine ethylene oxide units.

### Emulsion Polymerization with Hydroperoxide and Amine Initiation

Diisopropylbenzene hydroperoxide is more water-soluble than benzoyl peroxide; thus the initial initiation stage should be expected to be faster. The polymerization of styrene at 35°C did show a very short induction time. The data in Table VI show that the polymerization rate decreased from  $(27.5 \pm 0.9) \times 10^{-4} M/s$  for three ethylene oxide units to a minimum of  $(3.8 \pm 0.01) \times 10^{-4} M/s$  for the surfactant with nine ethylene oxide units. The styrene polymerization shows the same trend in the rates of polymerization as the acrylates did in the peroxide/iron(II) systems.

### DISCUSSION

The polymerizations initiated using potassium persulfate did not appear to be influenced by the change in the hydrophilic length in the electrosteric

TABLE VI  
 Emulsion Polymerization of Styrene Initiated with Diisopropylbenzene Hydroperoxide and Tetraethylenepentamine at 35°C

<i>n</i>	$R_p \times 10^4$ ( <i>M</i> /s) ± 7.4%	$D_z$ (nm) ± 2	$N \times 10^{-14}$ ( $\text{cm}^{-3}$ ) ± 0.5
3	27.5	43	38.4
7	16.0	51	20.0
9	3.8	75	5.2
15	6.7	68	8.2

surfactant series. The anionic surfactant in the presence of a radical anion as additional stabilizer seems to function only as an electrostatic stabilizer; the steric stabilizing contribution is negligible. A slight slowing of the rate of polymerization was observed for the shortest steric length, probably due to the higher surface charge density on the particle surfaces present in solution.

The same trend was observed regardless of water solubility of the monomer or the electron density of the polymerizable double bond. The more water-soluble methyl methacrylate monomer displayed faster polymerization rates probably due to the increased concentration of the monomer in the aqueous phase. Vinyl acetate, the most water-soluble monomer polymerized, yielded slower rates than styrene for several reasons. The vinyl acetate derived radical is a very reactive radical which can and does undergo many chain transfer reactions. The chain transfer constant to vinyl acetate monomer is high at  $2 \times 10^{-3}$  at  $60^\circ\text{C}$ .<sup>6</sup> Thus the chain radical can transfer the radical to a single monomeric unit that can easily diffuse out of the polymer particle (desorption) or start another chain within the original particle. There is substantial precedence for the desorption of vinyl acetate derived radicals in emulsion polymerization.<sup>7-9</sup> Vinyl acetate emulsion polymerizations are thought to follow Smith-Ewart Case 1 kinetics where the average number of radicals in a particle ( $\bar{n}$ ) is less than 0.5 under some conditions. Vinyl acetate is also known to accelerate the decomposition of potassium persulfate,<sup>9,10</sup> thus decreasing the amount of initiator present in the reaction medium. Anionic surfactants have been observed to retard vinyl acetate polymerizations, although this effect is usually enhanced by the presence of the unsaturated linkages in the surfactant.<sup>11,12</sup>

### Redox-initiated Polymerizations

The energy of activation calculated for each of the four surfactants employed in this study agree well with previously reported values<sup>13-15</sup> and do not vary significantly with the steric length of the surfactant. This would seem to indicate that there is no change in the overall polymerization steps of the monomer. The rate differences observed are due to either the ability of the surfactant to stabilize the polymerization and/or assist the initiation stage of the polymerization. Overall, the polymerization rates were observed to decrease with increasing ethylene oxide content until a minimum was obtained at nine ethylene oxide units. The surfactant containing 15 ethylene oxide units showed an increase in the polymerization rate except for styrene polymerized with the peroxide/iron(II) redox system. At lower surfactant levels the rates of polymerization do not change much on changing the ethylene oxide content from nine to 15 units; however, the nine-unit ethylene oxide containing surfactant shows a larger particle size which could be an indication of a lesser degree of stability. The lack of significant particle size variations at higher surfactant concentrations could be due to the excess surfactant acting as a post-polymerization stabilizer. Styrene polymerizations showed a direct relationship between the rate of polymerization and the number of particles in the system.

Differences in the water solubility of the acrylate monomers did not change the trend only the individual polymerization rates. It would appear that, with

increasing ethylene oxide length, the hydrophilic portion decreases the effectiveness of the surfactant. This decline in effectiveness continues until a critical ethylene oxide unit length of 15 is reached based on the surfactants used. This trend is also true in the hydroperoxide/amine-initiated styrene polymerization studies.

In either of the redox initiations of monomers, the Avel surfactants containing three ethylene oxide units appear not to hinder the diffusion of the organic soluble component of the initiator into the aqueous phase to the same extent that the longer surfactants did. As the steric barrier grows the diffusion of the initiator is hindered as the equilibrium concentrations change in the total system. It has been shown<sup>16</sup> that an ethylene oxide chain of less than 11 units has a zig-zag conformation. Chains of greater than 11 units have a meandering chain conformation. Meandering chains are contracted in length relative to the zig-zag form: One unit in the zig-zag form is about 3.5 Å whereas the meandering form is only 1.9 Å in length. This contraction may be another contributing factor why the Avel Series S surfactant of 15 ethylene oxide units shows an increase in the rate of polymerization for the monomers polymerized. A contraction in length would allow for more facile diffusion path, even though the steric length of the surfactant has increased.

## CONCLUSIONS

Anionic electrosteric surfactants in the presence of negatively charged initiating moieties stabilize mainly by electrostatic means. Neutral initiating species allow the observation of steric effects of the hydrophilic length. Increasing the hydrophilic length in the electrosteric surfactants hinders the diffusion of the organic soluble component into the aqueous phase. The effectiveness of the electrosteric surfactant appears to be compromised by "intermediate length" steric portions. At shorter steric lengths the surfactant functions more as a pure electrostatic stabilizer and only at some critical longer length does steric stabilization contribute favorably towards the surfactants effectiveness.

The Avel S surfactants were donated by PPG Industries.

## References

1. I. A. Gritskova, S. S. Medvedev, and M. F. Margaritova, *Colloid J. USSR*, **26**, 140 (1967).
2. V. V. Dudkin, I. M. Medvedeva, I. A. Gritskova, S. S. Medvedev, Z. M. Ustinova, and N. M. Fodinian, *Polym. Sci. USSR*, **10** 527 (1968).
3. T. C. Chao, Ph.D. dissertation, University of Akron, 1985.
4. J. Lenzotti, Ph.D. dissertation, University of Akron, 1988.
5. Carla Dittman-McBain, Ph.D. dissertation, University of Akron, 1988.
6. E. S. Huyser, *Free Radical Chain Reactions*, Wiley-Interscience, New York, 1970.
7. I. M. Kolthoff and I. K. Miller, *J. Polym. Sci.*, **15**, 459 (1955).
8. M. S. El-Aasser and J. W. Vanderhoff, Eds., *Emulsion Polymerization of Vinyl Acetate*, Applied Science, London, 1981.
9. C. E. M. Morris and A. G. Parts, *Makromol. Chem.*, **119**, 212 (1968).
10. R. Patsiga, Ph.D. thesis, Syracuse University, 1962.
11. H. K. Stryker, G. J. Mantell and A. F. Helin, *J. Polym. Sci.*, **11**, 1 (1967).

12. S. Okamura and T. Motoyama, *J. Polym. Sci.*, **58**, 221 (1962).
13. S. D. Stavrova, M. F. Margaritova and S. S. Medvedev, *Voysokomol. Soyedin*, **7**, 725 (1965).
14. S. D. Stavrova, M. F. Margaritova, and S. S. Medvedev, *Voysokomol. Soyedin*, **7**, 717 (1965).
15. S. S. Medvedev, *International Symposium on Macromolecular Chemistry*, Pergamon, New York, 1959.
16. N. Schonfeldt, *Surface Active Ethylene Oxide Adducts*, Pergamon, Oxford, 1969.

Received January 8, 1988

Accepted March 15, 1988