

Effect of emulsifiers on emulsion copolymerization of styrene and *n*-butyl acrylate

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SUMMARY

The emulsion copolymerization of styrene and *n*-butyl acrylate was conducted at 70°C using anionic or nonionic emulsifiers, or a mixture of both at different concentrations. The effect of the emulsifiers on the overall conversion was examined. The latex morphology with special attention to average particle diameter and particle diameter distribution was also studied. The latexes were characterized by LASER light scattering (LLS) and transmission electron microscopy (TEM).

INTRODUCTION

The emulsification of monomer and the stabilization of the resultant polymer particles are essential characteristics of emulsion polymerization(1).

The chemical and physical nature of the surfaces of latex particles is important in determining stability, performance, and potential for interfacial chemical reactions(2).

The most common surface groups in conventional latex formulations are adsorbed emulsifiers and initiator fragments attached to the ends of polymers. Anionic emulsifiers are the most common stabilizers, but cationic, ampholytic, and nonionic systems are also employed. Combinations of ionic and nonionic emulsifiers are frequently used(2,3).

Nonionic emulsifiers have found application in emulsion polymerization systems in those instances where it is desired to produce a latex whose colloidal properties are relatively insensitive to changes of pH over quite wide ranges of acidic and alkaline conditions(4).

Mixtures of anionic and nonionic emulsifiers increase the stability of the latex to coagulation by electrolyte addition, despite an increase in its average particle size. This is the result of electrostatic stabilization by adsorbed ionic emulsifier, supplemented by steric stabilization by the adsorbed nonionic emulsifier which effectively decreases the van der Waals attractive forces between the latex particles and thus increases their stability(1).

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Several studies have been made on the mechanism and kinetics of emulsion polymerization with ionic emulsifiers but little work has been done on the emulsion copolymerization of styrene and n-butyl acrylate with mixtures of anionic and nonionic emulsifiers.

In a previous paper(5) some topics involving the ideal time of reaction, the effect of temperature, initiator concentration and comonomer composition on the emulsion copolymerization of styrene and n-butyl acrylate were discussed.

The aim of this study was to verify the effect of mixed emulsifiers on overall conversion and latex morphology in the emulsion copolymerization of styrene and n-butyl acrylate.

EXPERIMENTAL PROCEDURES

Materials

The monomers, styrene (STY) and n-butyl acrylate (BuA), from Rohm and Haas, commercial products, were vacuum distilled after the removal of inhibitor and then stored at -5°C under nitrogen. Reagent grade ammonium persulfate (AP), sodium hydrogen phosphate (SHF), isopropanol, hydrochloric acid, lauryl sodium sulfate (LSS) and Disponil B2 (DB2) (a mixture of etoxylated fatty alcohols with approximately 20 ethylene oxide units per molecule) from Henkel, were used without further purification. Water, distilled and deaerated by purging with N₂ freed from O₂, was employed for the preparation of the polymerization recipes and all standard solutions.

Polymerization

Copolymerizations were carried out in 300 ml Erlenmeyer flasks at 70°C in a thermostatted bath (SHAKER).

Known amounts of emulsifiers, water and electrolyte were placed in the flasks and the mixture was deaerated with N₂ freed from O₂ for a 10 min period. Calculated amounts of monomers and initiator in water solution were added. The system was maintained in the bath for 150 min.

The copolymers were coagulated by adding to the latex, drop by drop and with agitation, isopropanol. The copolymers were then filtered off, washed exhaustively with water and dried to constant weight. The overall conversion was determined by gravimetric analysis.

Characterization of the latexes

The average particle diameter was determined by transmission electron microscopy, TEM (JEOL, MODEL JEM-100B), with magnifications generally ranging from 15000 to 100000X.

The measurements were obtained by projection of the film on a micrometer.

The samples were prepared by diluting the latexes in a 2% solution of the emulsifier.

The copper grids were prepared by depositing a thin film of collodium and then a thin film of carbon. To the grid was added a drop of the polymeric solution and after 1

minute, the excess was removed with filter paper. For each sample four different regions, were photographed, using appropriate magnification. Using a micrometer, the diameters of all possible particles were measured.

For particle diameter distribution analysis, a Nicomp Model 270, Submicron Particle Sizer of Pacific Scientific Hiac/Royco Instruments Division LASER Light Scattering Instrument was used. The samples were prepared under the same condition described above. The final solution should be translucent. The apparatus was regulated in the range of 50-3000 nm. The analysis time was of 5-16 min. The counter average velocity was around 300 khz.

Critical Micellar Concentration

The conditions for this study were based on data from the literature(6).

The surface tension measurements were carried out using a "Du Nöuy" tensiometer by Kruss; the measuring ring was of platinum. As the surface tension is affected by temperature (7), all the measurements were taken at 27°C.

RESULTS AND DISCUSSION

Critical Micellar Concentration

It is known that the chemical structure of the surface-active substance affects micelle formation(4).

The results are plotted in Figure 1. The critical micellar concentrations of emulsifiers, indicated by the deviation in the law of variation of surface tension with the emulsifier concentrations, were determined to be approximately: 0.04g/100g water to "LSS" and 0.03g/100g water to "DB2".

As expected it was observed that the surface tension of LSS was higher than that of DB2. It is known that micelle formation results from an equilibrium between the repulsive forces of the polar parts and the attractive forces of the hydrophobic parts of an emulsifier. For the nonionic emulsifier, the intermolecular repulsive force between the polar particles are weaker than those in the ionic system and consequently, the C.M.C. of a nonionic emulsifier is lower and its dependence on the ionic forces of the medium is small (9).

Effect of Anionic Emulsifier on the Copolymerization

According to the Smith-Ewart theory for emulsion polymerization of a water-insoluble monomer, the polymerization rate is proportional to the number of particles, determined by the emulsifier concentration. However, in the case of polar monomers, despite their relatively low water solubility, a deviation from the classical Smith-Ewart theory was observed, caused by the homogeneous nucleation that does not depend on the initial micelle number (10). For this reason, in this study the proportion of styrene in the feed was much higher than that of n-butyl acrylate and, to decrease the water solubility of this monomer, sodium hydrogen phosphate was added to the system.

Figure 2 shows a pronounced effect of the anionic emulsifier (LSS) on the overall conversion of the copolymerization. As expected, it was observed that the

overall conversion increases as the emulsifier content

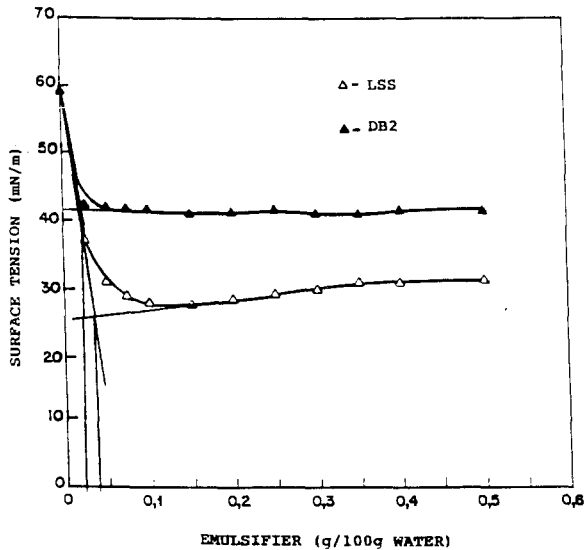


Figure 1: Surface tension vs emulsifier concentration (8)
 AP = $2.5 \times 10^{-5} \text{ M}$
 Temperature = 27°C

increases. At low emulsifier concentration (0.05g/100g water), a low overall conversion (37.1%) was obtained. A possible explanation for this fact is that the emulsifier concentration is very close to its C.M.C., leading to the formation of a low number of micelles in the medium.

The latex morphology was strongly influenced by the emulsifier concentration. As can be seen in Table 1, the average particle diameter decreased as the emulsifier content increased.

A monomodal distribution of particle size as observed by LASER light scattering. Figure 3 shows a micrograph of a monodisperse latex obtained with lauryl sodium sulfate. This distribution may be an indication that in the copolymerization, all particles were formed during a small time interval (11).
Effect of Nonionic Emulsifier on the copolymerization

This study was performed using Disponil B2 in a concentration range higher than that used for the anionic emulsifier. A high instability in the medium was observed.

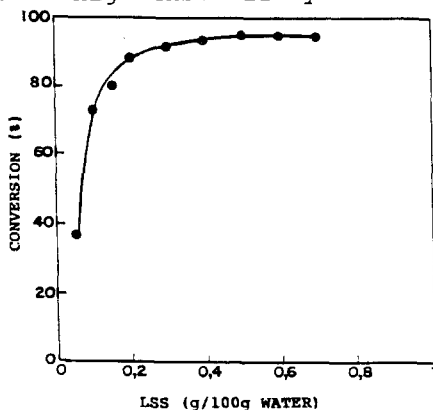


Figure 2: Overall conversion vs emulsifier concentration. Effect of the anionic emulsifier on the copolymerization (8).
 BuA = $3.1 \times 10^{-2} \text{ mol}$,
 STY = $2.2 \times 10^{-1} \text{ mol}$,
 AP = $1.0 \times 10^{-4} \text{ mol}$,
 SHF = $1.7 \times 10^{-4} \text{ mol}$,
 Water = 200g, T = 70°C ,
 Time = 150 min

Table 1: Average particle diameter vs emulsifier concentration.
Effect of the anionic emulsifier on the latex morphology (8).

EMULSIFIER (g/100g water)	AVERAGE PARTICLE DIAMETER (nm)	
	LSS	TEM
0.05	171	166
0.10	122	123
0.15	105	92
0.20	102	90
0.30	94	80
0.40	83	75
0.50	80	67
0.60	76	65
0.70	69	70

BuA = 3.1×10^{-2} mol, STY = 2.2×10^{-1} mol, AP = 1.0×10^{-4} mol,
SHF = 1.7×10^{-4} mol, Water = 200g, T = 70°C, Time = 150 min.

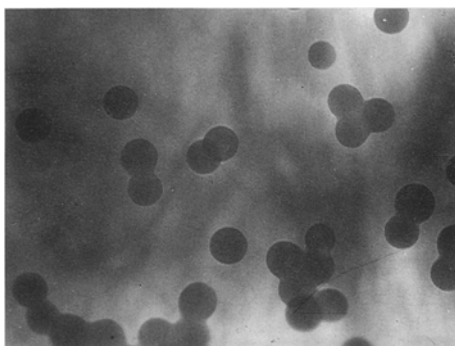


Figure 3: Electron micrograph of latex particles (sample 1) (8)
LSS = 0.05g/100g Water
APD = 166 nm
Magnification = 40.000 X

Figure 4 shows the effect of DB2 on the overall conversion of the copolymerization, and, as can be seen, even in this concentration range, the copolymerizations have attained values of maximum conversion lower than those obtained using anionic emulsifier.

It is known that an emulsifier causes several effects in emulsion polymerization systems, for example, the stabilization of the monomer in emulsion(1). However, in this work this effect was not seen when the nonionic emulsifier was employed. This can be attributed to the differences between the emulsifiers (molecular weight and the characteristics of hydrophilic part). It was also observed that the emulsion instability was influenced by the variation of temperature. At room temperature it was formed a stable emulsion but when the temperature was raised to 70°C it was observed in the system a separation into two phases.

It is known that the solubility of nonionic emulsifiers decreases as the temperature increases. The explanation for this is that the association between the ether linkages and water is partially destroyed as the temperature increases(4). The temperature at which this phenomenon occurs (cloud point) for a ethoxylated emulsifier depends on its degree of ethoxylation(9).

The average particle diameter was determined by TEM (Figure 5) and LLS, and the results are shown in Table 2. It can be seen that for this emulsifier the average particle

diameter also decreases as the emulsifier content increases.

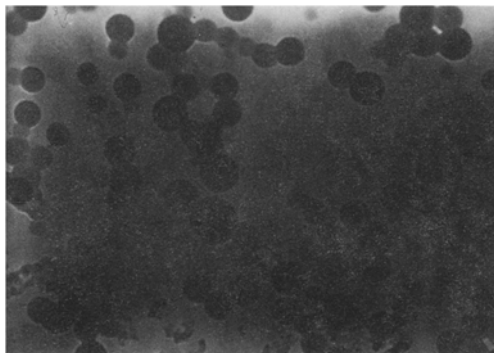


Figure 5: Electron micrograph of latex particles (sample 1) (8)
DB2 = 1.0g/100g water
APD = 145 nm
Magnification = 40.000 X

The particle distribution seen by TEM was confirmed by LLS. For this emulsifier a bimodal distribution was obtained. In an emulsion that shows bimodal distribution the error of LLS analysis is higher. This can be seen in Table 2, which shows that for the same sample different average particle diameters were obtained. This problem did not occur with the anionic emulsifier because monodisperse latex was formed.

Effect of Mixture of Emulsifiers on the Copolymerization

In order to have an homogeneous copolymerization, a final emulsifier concentration well above the CMC of each emulsifier (0.7g/100g water) was chosen.

Table 2: Average particle diameter vs emulsifier concentration. Effect of the nonionic emulsifier on the latex morphology(8).

EMULSIFIER (g/100g water)	AVERAGE PARTICLE DIAMETER (nm)	
	LLS	TEM
1.0	126	145
1.2	114	154
1.4	104	131
1.5	97	155
1.6	102	146
1.7	89	141
1.8	99	106
1.9	107	116
2.0	87	107

BuA = 3.1×10^{-2} mol, STY = 2.2×10^{-1} mol, AP = 1.0×10^{-4} mol,
SHF = 1.7×10^{-4} mol, Water = 200g, T = 70°C, Time = 150 min.

Figure 6 shows the effect of mixture of emulsifier on the overall conversion of copolymerization.

As can be observed an increasing proportion of LSS led to a value of maximum conversion much higher than that obtained using the nonionic emulsifier alone, even at concentrations above 0.7g/100g water.

The limiting conversion for the mixture of emulsifiers was analogous to that attained with the anionic emulsifier at the same concentration.

As can be seen in Table 3 the average particle diameter decreased as the proportion of the nonionic emulsifier increased.

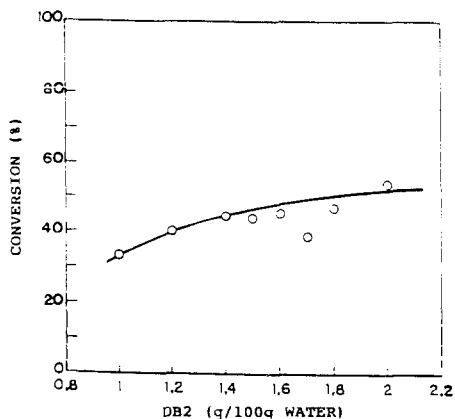


Figure 4: Overall conversion vs emulsifier concentration. Effect of the nonionic emulsifier on the copolymerization (8).
 BuA = 3.1×10^{-2} mol,
 STY = 2.2×10^{-1} mol,
 AP = 1.0×10^{-4} mol,
 SHF = 1.7×10^{-4} mol,
 Water = 200g, T = 70°C,
 Time = 150 min.

Above 40% of nonionic emulsifier, the average particle diameter increased. This composition could be a point of synergism for the mixture of emulsifiers(1,12). Therefore a more accurate analysis should be done to confirm the synergism found.

In this study the particle size distribution was slightly narrower than that obtained with the nonionic emulsifier alone. The latex morphology was strongly affected by the anionic emulsifier and in some cases monomodal distribution was obtained. Using LLS it was possible to verify a more uniform particle size distribution even at relative low concentration of the anionic emulsifier. On the other hand, as expected, at very low anionic emulsifier concentration bimodal distribution was obtained.

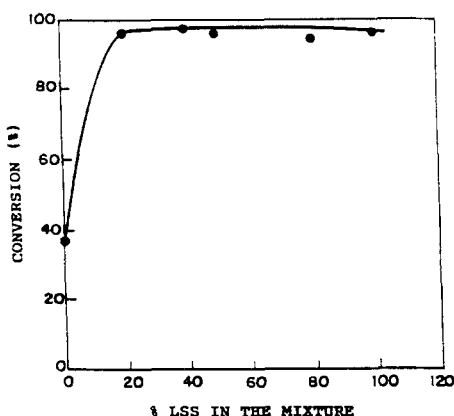


Figure 6: Overall conversion vs % LSS in the mixture. Effect of the mixture of emulsifiers on the copolymerization (8). BuA = 3.1×10^{-2} mol,
 STY = 2.2×10^{-1} mol,
 AP = 1.0×10^{-4} mol,
 SHF = 1.7×10^{-4} mol,
 Water = 200g, T = 70°C,
 Time = 150 min.

Table 3: Average particle diameter vs the amount of DB2 in the mixture. Effect of the mixture of emulsifiers on the latex morphology(8).

% DB2 IN THE MIXTURE	AVERAGE PARTICLE DIAMETER (nm)	
	LLS	TEM
0	94	104
20	90	100
40	83	67
50	93	99
60	108	88
80	87	94
100	164	178

BuA = 3.1×10^{-2} mol, STY = 2.2×10^{-1} mol, AP = 1.0×10^{-4} mol,
SHF = 1.7×10^{-4} mol, Water = 200g, T = 70°C, Time = 150 min.

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