

Emulsion Polymerization of Styrene Using Mixtures of Hydrophobically Modified Inulin (Polyfructose) Polymeric Surfactant and Nonionic Surfactants

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ABSTRACT: Polystyrene latex dispersions were prepared by emulsion polymerization, using a mixture of hydrophobically modified inulin (INUTE[®] SP1) and various nonionic surfactants (cosurfactants). Two series of nonionic surfactants were used, namely Synperonic A (C_{13–15} alkyl chain with 7, 11, and 20 moles of ethylene oxide, EO) and Synperonic NP (nonylphenol with 10 and 15 moles of EO). For 5 wt % latex, the INUTE[®] SP1 concentration was kept constant at 0.0165 wt % and the initiator concentration was also kept constant at 0.0125 wt %, whereas the cosurfactant concentration was varied between 0.1 and 0.5 wt %. With the exception of Synperonic A20, all other cosurfactants showed an initial increase in particle diameter followed by a decreased reaching a value comparable with that obtained using INUTE[®] SP1 alone. However, A20 produced a continuous reduction in particle diameter with

increase of surfactant concentration, reaching a value of 100 nm at 0.5 wt % which is lower than the value obtained using INUTE[®] SP1 alone (188 nm). In all cases, addition of a cosurfactant enhanced the stability of latexes by co-adsorption at the solid–liquid interface. The enhanced stability produced by the addition of cosurfactants to INUTE[®] SP1 could be illustrated by using the mixture of INUTE[®] SP1 and Synperonic A7 at 40 wt % of styrene latex concentration. In this case, the mixture produced lower particle size, much lower polydispersity index and much higher stability. These results are of significant value for industrial applications.   2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 811–815, 2008

Key words: emulsion polymerization; polystyrene; self-assembly; stabilization; surfactants

INTRODUCTION

Recently, we have prepared polystyrene (PS) latexes by emulsion polymerization using a hydrophobically modified inulin (INUTE[®] SP1).^{1,2} One of the most interesting findings of this previous work was the low [INUTE[®] SP1]/[Monomer] ratio that was sufficient to produce stable aqueous latexes up to 50 wt % PS.² This ratio was 0.0033. The stability is attributed to the multipoint anchor attachment of the polymeric surfactant by several alkyl chains and the strong hydration of the polyfructose loops and tails. This is the principle of enhanced steric stabilization.³ Latexes produced with INUTE[®] SP1 at such low [INUTE[®]]/[monomer] ratio have a low Critical Coagulation Concentration (CCC) with CaCl₂ of 0.05 mol dm^{–3} which is still higher than that of the surfactant-free latex. In addition, the polydispersity of

the latexes increases with the increase of solid content. However, the stability in electrolyte solution could be significantly increased by post-addition of the polymeric surfactant. For example, by adding 0.05 wt % INUTE[®] SP1 the CCC_{CaCl₂} increased from 0.05 to 0.4 mol dm^{–3}. This enhanced stability was attributed to the adsorption of INUTE[®] SP1 on the bare patches present on the latex particles. The enhanced steric stabilization in the presence of high electrolyte concentration could also be obtained for oil/water emulsions.^{4,5}

To explain the high stability of dispersions, we have carried out Atomic Force Microscopy (AFM).⁶ In these measurements, the force-distance curves between the hydrophobically modified glass sphere and glass plate, both containing adsorbed INUTE[®] SP1 molecules were obtained at 25 C. These results showed strong repulsion, both in water and in the presence of sodium sulphate up to 1.5 mol dm^{–3}. This clearly showed that the polyfructose loops remained hydrated up to this high electrolyte concentration. The adsorbed layer thickness measured by AFM was about 9 nm in water and it is decreased to about 3 nm in 1.5 mol dm^{–3} Na₂SO₄.⁶ The preparation of latex dispersions using polymeric surfactants,

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at high solid content, results in large particles, which are also polydisperse. This could be due to the slow diffusion of the high-molecular weight surfactants to the solid/liquid interface. To enhance diffusion, one needs to have molecules with lower weight, and that is usually the case for most industrial applications. However, in the latter case, very high surfactant concentrations, well above the CMC (Critical Micellar Concentration), are usually used.

Consequently, there is a high interest in achieving the preparation of stable latex particles with high-solid content, low polydispersity and using low surfactant concentrations, for the production of synthetic rubbers, paints, adhesives, drug delivery systems, etc. In this context, the aim of this work is to obtain such latex particles by using mixtures of a novel graft copolymer surfactant with several nonionic surfactants. Previous studies have demonstrated that the CCC of latex particles can be greatly increased by the addition, after the polymerization, of the copolymer surfactant.^{1,2} In this article, we investigate the synergy of the copolymer surfactant with conventional nonionic surfactants.

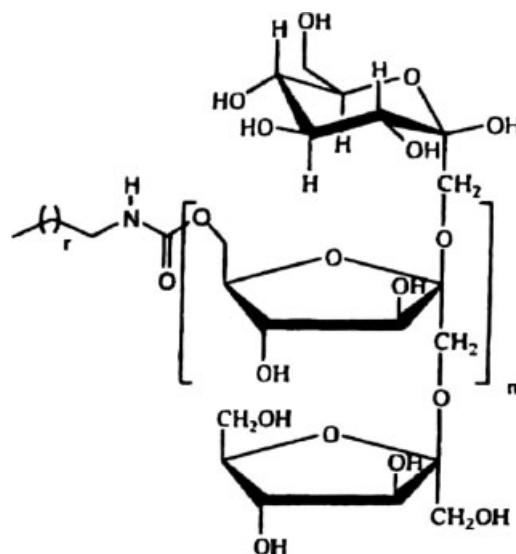
EXPERIMENTAL

Materials

Styrene monomer was purified by passing it through basic chromatographic aluminum oxide in order to remove the hydroquinone inhibitor. As initiator, $K_2S_2O_8$ from Fluka with purity higher than 99% was used. Deionized water was further purified by filtration through a milli-Q system. The electrolyte used was $CaCl_2 \cdot 2H_2O$ (purity > 99%) supplied by SIGMA. It was dried at 200°C during 5 h in order to obtain a dehydrated electrolyte.

The polymeric surfactant used in this study was hydrophobically modified inulin, INUTEK SP1, supplied by ORAFI Bio Based Chemicals (Tienen, Belgium), and it was synthesized as described earlier.^{7,8} It is a randomly graft copolymer made of a polyfructose backbone on which some alkyl groups are grafted. Its average molecular weight is approximately 5000 g mol^{-1} and it is quite polydisperse since inulin has a wide molecular weight distribution. The purity of such surfactant was higher than 97% and it makes a clear solution in water at concentrations lower than 0.1 wt %, above which a turbid solution appears that could be due to some association of the polymeric chains. The general structure of INUTEK SP1 is shown in Scheme 1.

INUTEK SP1 was used in combination with several nonionic surfactants (to be referred to as cosurfactants) all supplied by UNIQEMA: (a) $C_{13-15}(EO)_7$ (Synperonic A7), $C_{13-15}(EO)_{11}$ (Synperonic A11), $C_{13-15}(EO)_{20}$ (Synperonic A20), and (b) nonylphenol



Scheme 1 General structure of the graft copolymer surfactant (Reproduced from Ref 8, with permission from American Chemical Society).

ethoxylates Synperonic NP10 which is nonylphenol with 10 moles of ethylene oxide, and Synperonic NP 15 which is nonylphenol with 15 moles of ethylene oxide.

Methods

Emulsion polymerization

All latexes were prepared by emulsion polymerization in a round-bottle batch reactor (volume 500 mL) and dispersions were agitated with a U-shaped Teflon stirrer (300 rpm) located at 1 cm over the bottom of the vessel. The reactions were carried out for 24 h, at a constant temperature of 80°C under controlled nitrogen atmosphere. The polymerization method including the reaction time was the same as described earlier.² These conditions ensured that the conversion rate was always higher than 95%. The conversions were determined at the end of the reaction for each latex synthesized, by gravimetric method after evaporation of all volatile components of the dispersion, at 50°C during 12 h.

Particle size determination

The mean particle size of the latex dispersions was determined by Photon Correlation Spectroscopy (PCS). A Malvern 4700 instrument (Malvern Instruments, Malvern, United Kingdom) was used for this purpose. This instrument was equipped with an argon laser ($\lambda = 488 \text{ nm}$) with variable intensity to cover the wide size range involved. Measurements were carried out at different scattering angles and at a constant temperature of 25°C. The PCS data were analyzed by the CONTIN method and a constrained regularization

TABLE I
Variation of the Diameter, Polydispersity Index, CCC_{CaCl_2} , and Diffuse Layer Potential, ψ_d , as a Function of the wt % of the Various Cosurfactant Concentration in the Surfactant Mixture, for Latex Synthesized with 5 wt % Styrene

Cosurfactant	Cosurfactant (wt %)	Diameter (nm)	Polydispersity index	CCC_{CaCl_2} (mol dm ⁻³)	ψ_d (mV)
None	0	186.0	0.02	0.05	-8.6
Synperonic A7	0.1	246.0	0.02	0.19	-6.4
	0.3	218.0	0.04	0.23	-8.1
	0.5	169.4	0.02	>1.33	-
	0.1	210.8	0.002	0.46	-8.6
Synperonic A11	0.3	232.0	0.02	>1.33	-
	0.5	161.0	0.08	>1.33	-
	0.1	155.0	0.02	0.54	-9.1
Synperonic A20	0.3	109.0	0.03	>1.33	-
	0.5	98.0	0.04	>1.33	-
	0.1	279.8	0.05	0.08	-8.1
Synperonic NP10	0.3	219.0	0.05	0.35	-8.8
	0.5	196.1	0.01	0.76	-8.6
	0.1	240.0	0.06	0.29	-6.6
Synperonic NP15	0.3	196.7	0.07	0.78	-6.3
	0.5	173.7	0.09	>1.33	-

The INUTEC[®] SP1 concentration was kept constant at 0.0165 wt %.

calculation algorithm known as REPES incorporated in the analysis package GENDIST (interactive program for the analysis of homodyne PCS data).

Transmission Electron micrographs (Hitachi H-800) were also obtained to check particle size, polydispersity, and particle shape. The latex suspensions were diluted, placed on a copper-carbon grid and then dried. Observations were carried out in an electric field of 200 kV.

Critical coagulation concentrations and diffuse double layer potential (ψ_d) determinations

The stability of the dispersion in the presence of electrolytes was assessed by determining the CCC using calcium chlorides. It was obtained by measuring the turbidity at a wavelength of 633 nm as a function of time for different electrolyte concentrations using a Spectrophotometer (Varian, Cary 300 Bio UV-visible). The wavelength of 633 nm, in the visible range, was chosen because of the low absorption of PS particles at this wavelength. The initial slopes of these curves are directly proportional to the initial coagulation rate. The slopes increased with increasing electrolyte concentration until a maximum was reached at the CCC. Above the CCC there was no further increase in the slope. Therefore, the stability can be expressed in terms of the stability factor W ,^{9,10} obtained as the ratio of the rate constants for rapid, k_r , and slow coagulation, k_s :

$$W = \frac{k_r}{k_s} \quad (1)$$

In rapid coagulation $W = 1$, while higher values of W_{exp} are obtained for aggregations under conditions of slow coagulation. The CCC can be obtained from a plot of the log of the stability factor, $\log W$, vs. the log of the

electrolyte concentration, the CCC corresponds to the intersection to the break point at which $\log W = 1$.

From the same plot, ψ_d , which is related to the electrical double layer repulsion, can be calculated using Reerink and Overbeek¹¹ approximations. The slope of the stability curve, $-d \log W / d \log C_e$, is related to the particle radius, a , to the diffuse potential associated with the charge polymer surface, ψ_d , and to the electrolyte valence, z , by the expression

$$-d \log W / d \log C_e = 2.15 \times 10^9 a \gamma^2 / z^2 \quad (2)$$

where

$$\gamma = \tanh(z e \psi_d / 4 k T) \quad (3)$$

Where, e is the elementary charge, k the Boltzman constant, and T the temperature.

All CCC measurements were carried out at 25°C using $CaCl_2$ as electrolyte, because the latex dispersions were stable against 1 : 1 electrolytes, such as NaCl. For a 2 : 1 electrolyte the valency, z , is $3^{1/2}$ as described by Israelachvili.¹²

RESULTS AND DISCUSSION

PS particles were selected as model systems because its glass transition temperature (T_g) is high, and it facilitates the preparation of stable and rigid particles. Emulsion polymerization of styrene was carried out stabilizing by INUTEC SP1/nonionic surfactants mixtures. Different fatty alcohol ethoxylates (Synperonic A7, A11, A20) and different nonylphenol ethoxylates (Synperonic NP10 and NP15) were used in the emulsion polymerization of styrene to produce particles with 5 wt % styrene. Table I shows a summary of the results obtained at 5 wt % of

TABLE II
Diameter, Polydispersity Index, CCC_{CaCl_2} , and ψ_d Obtained for PS Particles Prepared at 40 wt % Styrene for Different Surfactant, INUTEC, and Cosurfactant, $C_{13-15}(EO)_7$, Mixtures

[INUTEC [®] SP1] wt %	[$C_{13-15}(EO)_7$] wt %	Diameter (nm)	Polydispersity index	CCC (mol dm ⁻³)	ψ_d (mV)
0	4	Aggregated			
0.133	0	306	0.31	0.03	-6.2
0.133	4	262	0.05	>1.33	-

The initiator concentration was 0.0125 wt %.

styrene, using SP1 concentration of 0.0165 wt % and initiator concentration of 0.0125 wt % $K_2S_2O_8$, and various cosurfactant concentrations in the mixture.

The results for A7, A11, A20, NP10, and NP15 show roughly the same trend for the change of particle diameter with surfactant concentration: an initial increase after addition of 0.1 wt % of cosurfactant, followed by a decrease with further increase in concentration. However, with A20, independently on surfactant concentration, there is a decrease in diameter with the addition of cosurfactant, reaching a value of 98 nm at 0.5 wt %. These results show that, at 5 wt % styrene, only A20 added to SP1 is efficient in reducing significantly the diameter below that obtained using SP1 alone.

In all cases, as shown in Table I, the polydispersity index (PI) is quite low that is less than 0.1. It should be mentioned that in the absence of SP1, all latexes prepared with cosurfactant alone were strongly coagulated.

The stability of the dispersions was determined by calculating the CCC_{CaCl_2} and the diffuse double layer potentials (ψ_d), as described in the experimental section. $CaCl_2$ was used as a model electrolyte because the dispersions were very stable against 1 : 1 electrolytes, such as NaCl. The results of CCC_{CaCl_2} and ψ_d are also shown in Table I. The main advantage of addition of cosurfactant is the enhancement of latex stability, as shown by a dramatic increase of CCC with the increase in cosurfactant concentration.

This enhanced stability can be accounted for by the presence of PEO chains at the solid/liquid interface.¹³ The longer the PEO chains, the higher the CCC_{CaCl_2} . This indicates that the cosurfactant provides an effective steric barrier by the formation of a thick dense polyethylene oxide layer at the surface of the particles. It might be due to the coadsorption of the surfactant with INUTEC SP1 at the particle surface, because there is no significant change in the electrostatic repulsion, since ψ_d values remain approximately constant, indicating a small contribution of electrostatic repulsion.

The above enhancement of stability on addition of cosurfactant to SP1, could also be demonstrated by preparing PS latexes at higher styrene concentration (40 wt %). The initiator concentration was fixed at 0.0125 wt % and the cosurfactant concentration was increased to 4 wt % proportionally to the styrene

concentration, keeping the ratios [cosurfactant]/[styrene] and [INUTEC]/[styrene] constants to 0.1 and 0.0033, respectively.

It is interesting to point out that for the concentrated latex prepared using Synperonic A7 alone at 4 wt %, the dispersion was not stable and aggregation occurred during the polymerization (Table II). On the other hand, when using INUTEC SP1 alone at 0.133 wt %, a stable dispersion could be obtained at such high styrene concentration, but the PI (0.31) was rather high. However, a stable dispersion, with low polydispersity, could be obtained using a mixture of INUTEC SP1 and $C_{13-15}(EO)_7$.

The stability of the concentrated dispersions (40 wt %) was also evaluated by determining the CCC of $CaCl_2$. As illustrated, the stability factor corresponding to the particle dispersion prepared using 0.133 wt % INUTEC SP1 is shown in Figure 1. The CCC_{CaCl_2} of this sample is 0.03 mol dm⁻³, as indicated by the arrow inserted in Figure 1, and the diffuse double layer potential (ψ_d) is -6.2 mV, as also shown in Figure 1.

The addition of the cosurfactant $C_{13-15}(EO)_7$ produced a great increase in stability, and the CCC_{CaCl_2}

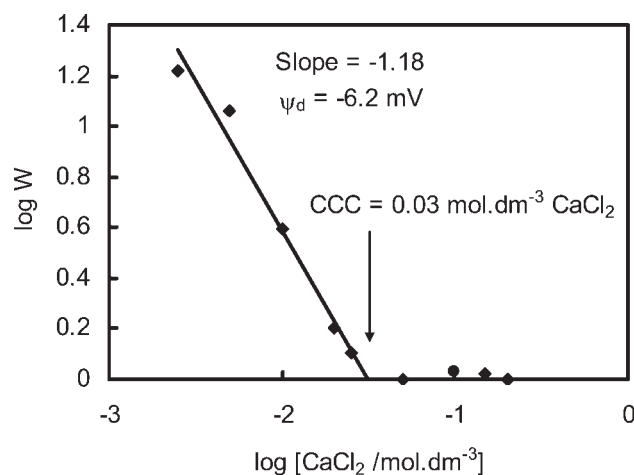


Figure 1 Determination of the critical coagulation concentration (CCC_{CaCl_2}) and the diffuse double layer potential (ψ_d) from the plot of the log of stability factor ($\log W$) versus the log of electrolyte concentration, for the latex dispersion obtained using INUTEC SP1 at 0.133 wt %, at 40 wt % styrene.

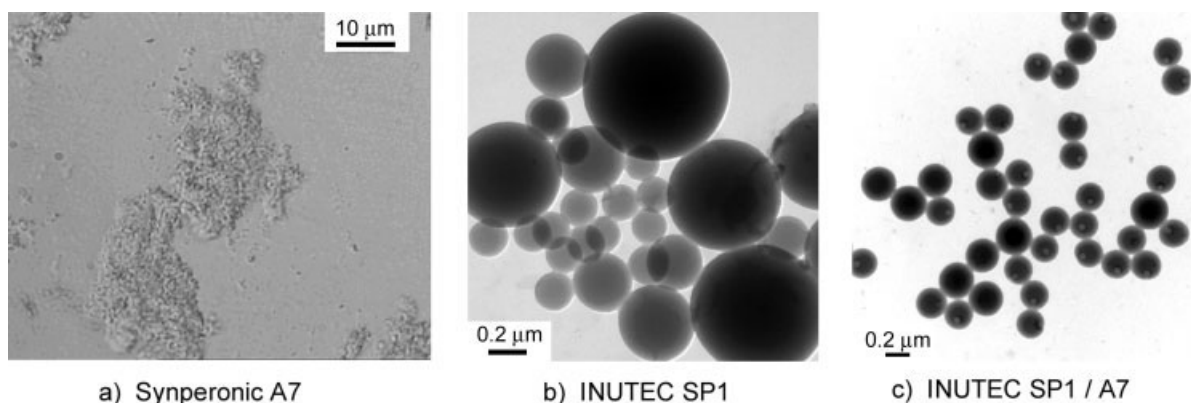


Figure 2 Comparison of latex dispersions prepared using (a) Synperonic A7 at 4 wt % (optical micrograph), (b) INUTEC SP1 at 0.133 wt % (TEM micrograph), and (c) mixture of INUTEC SP1 at 0.133 wt % and Synperonic A7 at 4 wt % (TEM micrograph). The solid content is 40 wt % in all cases, as described in Table II.

could not be calculated because it was higher than the maximum CaCl_2 concentration of 1.33 mol dm^{-3} . Consequently, the particle dispersion prepared by using the mixture of INUTEC SP1 and A7 ($\text{C}_{13-15}(\text{EO})_7$) had a very high stability, compared to the samples prepared using single surfactants. These results are summarized in Table II.

Figure 2 shows images of the latexes described in Table II, obtained by optical microscopy [Fig. 2(a)] and transmission electron microscopy [Fig. 2(b,c)]. The concentrated latex prepared solely with Synperonic A7 was aggregated [Fig. 2(a)], as discussed earlier. The TEM micrographs of the latexes containing INUTEC SP1 confirmed the particle sizes determined by PCS. The mixed surfactant system (INUTEC SP1/A7) shown in Figure 2(c) gave smaller particles of 262 nm with a much lower PI (0.05) when compared with the results using INUTEC SP1 alone [Fig. 2(b)]. This shows that A7 is very effective, as cosurfactant, for stabilizing the growing latex particles during polymerization.

As discussed earlier, the particles obtained with a mixture of surfactants showed a much higher CCC when compared with the latex prepared using INUTEC SP1 alone. This enhanced stability when using INUTEC SP1 and Synperonic A7 may be due to interaction between the two molecules at the solid-liquid interface and possibility of enhanced stabilization of the latex during preparation of dispersions. The lower molecular weight Synperonic A7 is expected to diffuse faster to the interface, thus capturing the particles and preventing their aggregation during the particle growth. Such effect, not only reduces the polydispersity of the resulting latexes, but also enhances stabilization against flocculation by electrolyte.

CONCLUSIONS

Stable concentrated latex dispersions (40 wt %), with narrow size distribution, have been obtained in a simple batch process using a mixture of a polymeric sur-

factant and a conventional nonionic surfactant. The stability of PS latexes prepared in these mixed surfactant systems can be enhanced by the coadsorption and formation of a dense polyethylene oxide chain steric barrier at the solid/liquid interface. Some nonionic cosurfactants, such as synperonic A7 ($\text{C}_{13-15}(\text{EO})_7$), added to INUTEC SP1 can cause a significant reduction in latex diameter and latex PI below the value obtained using INUTEC SP1 alone. Furthermore, this work demonstrated that the use of mixed surfactant systems has the advantage of obtaining stable particle dispersions at high solid content (40 wt % styrene), with small particle size (262 nm) and low polydispersity (PI = 0.05). This synergy is of great interest in industrial applications for preparation of latexes.

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