

The Preparation of Uniform Polystyrene Latices by True Emulsion Polymerization

JOHN R. McCracken and ARVED DATYNER, *University of New South Wales, School of Textile Technology, Kensington, N.S.W. Australia*

Synopsis

Conventional emulsion polymerization of styrene produces some polydispersion in particle sizes in the latex. By carrying out a one-stage polymerization of finely emulsified monomer droplets of styrene formed in a mixture of methanol and water, it is possible to prepare stable latices of polystyrene in which the particles are perfectly uniform in size. The polymer has a relatively low molecular weight, but it is more stable to fragmentation by surfactant solutions than polystyrene prepared by conventional emulsion polymerization, the molecular weight of which is greater. The surface charge density of the particles is higher than that of particles produced by emulsion polymerization, and this probably accounts for the stability of the dispersion during polymerization and of the latex.

INTRODUCTION

Interest has recently been shown in the use of polymer latices for studies of adsorption.^{1,2} For this purpose, dispersions should be stable, monodisperse, and contain smooth spherical particles. Polystyrene latices can be prepared from seed dispersions by emulsion polymerization followed by a number of surface-initiated growth stages, and detailed accounts of this technique have been described elsewhere.^{3,4}

During an investigation by the authors of the adsorption of nonionic surfactants by polystyrene latex particles prepared in the above way, it was found that the particles partially disintegrated at surfactant concentrations in excess of the critical micelle concentration (c.m.c.). Evidence of disintegration was obtained from the ultraviolet spectra of the dispersing medium obtained from centrifugal separation at $50,000 \times g$ of the latex particles. A spectrum typical of polystyrene was obviously superimposed on the spectra of the nonionic surfactant, suggesting that solubilization of polymer fragments, particularly the low molecular weight oligomers, in the surfactant micelles had taken place. Anionic surfactants at concentrations in excess of their c.m.c. produced similar results. Hearn et al.⁵ obtained evidence of a decrease in molecular weight with increase in latex particle size, and Williams and Bobalek⁶ and Grancio and Williams⁷ found that during each growth stage the molecular weight first increased and then decreased, indicating that relatively short polymer chains persist at the

periphery of the latex particles. It is thus feasible that these shorter polymer chains near the surfaces of the particles were leached out by the surfactants. It was thought that fragmentation of the polymer could be avoided by producing latex particles of higher molecular weight and/or a greater degree of entanglement of the polymer chains.

The present work describes a method of true emulsion polymerization of styrene in the presence of methanol but in the absence of surfactant, a method which differs from the technique recently proposed by Ugelstad et al.⁸ in which both a long-chain fatty alcohol and an anionic emulsifier are used to create small, stable, emulsified droplets of monomer which act as the principal loci of polymerization in preference to monomer solubilized in surfactant micelles. The present method is based on the following considerations: The solubility of styrene in water is very small (0.0271% w/v at 20°C and 0.0382% w/v at 50°C),⁹ but it can be increased by the addition of water-miscible solvents for styrene. For example, the solubility of styrene at 20°C in a mixture of methanol-water in proportions 55:45 by volume is 1% w/v. Polystyrene is virtually insoluble in this mixture. When the mixture contains a lower proportion of methanol, styrene forms a fine, stable dispersion of a large number of small, separate particles which act as loci for polymerization, and the rate of polymerization and molecular weight achieved are both high.

EXPERIMENTAL

Materials

Inhibitor was removed from styrene monomer supplied by B. D. H. Ltd. by washing with five portions of 0.1*M* NaOH. Ammonium persulfate, sodium hydroxide, methanol, benzene, and methyl ethyl ketone (MEK) were all A.R. grade. The solvents were distilled before use. Sodium dodecyl sulfate (NaDoS) was also of A.R. grade, and its c.m.c. at 20°C was measured with a Du Nòuy surface tension balance and found to be $7.28 \times 10^{-3}M$. The nonionic surfactants were of the Teric N series supplied by I.C.I. Ltd.

Preparation of Latex E by Conventional Emulsion Polymerization

A seed dispersion was made by adding 100 g styrene to 250 ml water containing 6 g NaDoS. The pH was adjusted to 10 and maintained at 9-10 by periodic addition of 0.1*M* NaOH. The mixture was stirred vigorously and heated to 60°C. Ammonium persulfate, 1g, dissolved in 50 ml water was then added. After 2 hr, the stirring speed was progressively reduced, and stirring was stopped after 6 hr. The atmosphere in the reaction vessel throughout the polymerization was purged with nitrogen.

For the first growth stage, 100 g styrene and 100 ml seed dispersion were added to 1 liter water. The pH was adjusted to 10, and the same procedure was followed as for the seed dispersion. Subsequent growth

stages (to a fourth-stage latex E) differed only in that it was found necessary to decrease progressively the concentration of latex particles to about one third of that in the previous stage.

Preparation of Latex S by True Emulsion Polymerization

Styrene was dissolved in methanol and the solution added to water to give the required volumetric ratio of methanol to water and 1% v/v of styrene in the final mixture. The pH was adjusted to 10 and the temperature raised to 60°C in a thermostated shaker bath. A 0.5% w/v solution of ammonium persulfate in water was prepared and added to the above mixture. The latex S described here was prepared by using 40 ml styrene, 800 ml methanol, 3200 ml water, and $2 \times 10^{-3}M$ ammonium persulfate in the total volume. The pH was maintained at 9–10 during polymerization, which was allowed to proceed for 10 hr. The atmosphere in the reaction vessel was purged with nitrogen throughout that time.

Dialysis of Latices

Both latices E and S were dialyzed in boiled-out Visking (Visking Co., Illinois) dialysis tubing with water, and the dialyzate was changed daily. The surface tension of the dialyzates of latex E was measured, and one month was required for the surface tension to reach exactly that of water, but latex S required only one week to achieve the same result. However, both latices E and S were dialyzed for periods in excess of two months before characterization studies were commenced.

Particle Size Determination

Particle sizes were determined in an ultracentrifuge (Beckman Spinco, Model E) by the sedimentation velocity method. Ultracentrifugation was preferred to electron microscopy because of the possible shrinkage of the particles upon exposure to the electron beam.¹⁰ The average diameter d (in Å) of the latex particles was calculated using the following formula, derived from Stokes' law:

$$d = \frac{10^8}{\omega} \sqrt{\frac{18\eta}{(\rho_p - \rho_w)} \cdot \frac{d \ln(X_t/X_0)}{dt}} \quad (1)$$

where ω = angular velocity of rotation (radian · s⁻¹); t = time (s) of centrifuging at constant angular velocity, X_t = radius of curvature of the Schlieren peak at time t ; η = viscosity of water at 20°C (1.04×10^{-2} poise); ρ_p = density of the polymer at 20°C ($1.045 \text{ g} \cdot \text{cm}^{-3}$); and ρ_w = density of water at 20°C ($0.998 \text{ g} \cdot \text{cm}^{-3}$).

The main error in particle size determination of the latices by ultracentrifugation lies in the measurement of the small difference in density between the polymer and aqueous phase. Pycnometry was used to determine the density of the polymer, giving a value of $1.045 \pm 0.001 \text{ g} \cdot \text{cm}^{-3}$ at 20°C for both latices E and S. This result was confirmed by centrifuging

latex particles in solutions of sodium sulfate of known densities; the particles did not separate from the solution when both had the same density. This also indicated that the latex particles were not swollen by absorption of water. The error associated with the density value does not contribute more than $\pm 1\%$ in the estimate of the average diameter of the latex particles.

Particle size distributions were determined by measuring the diameters of about 500 particles on electron micrographs (Philips Electron Microscope, Model 300). Monolayers of particles were also examined by electron scanning microscopy (JEOL JSM-2) to deduce monodispersivity from close packing. The monolayers were prepared by smearing glass slides with a nonionic surfactant, placing a drop of dilute latex on the slide and evaporating to dryness under ambient conditions.

Molecular Weight Determinations

The latices were dried under vacuum at 50°C for 7 hr and the viscosity-average molecular weight was determined in triplicate in a B.S. U-tube Type M2 Microviscometer using the data of Krigbaum and Flory¹¹ or Outer et al.¹² for polystyrene dissolved in benzene or MEK, respectively.

Surface Charge Measurements

Surface charge densities were determined by potentiometric titrations with $0.005M$ NaOH. The average area A occupied by a monovalent group and the corresponding average number B of monovalent groups per latex particle for both latices were then calculated:

$$A = \frac{6 \times 10^{30}}{mNd\rho_p} \text{ \AA}^2/\text{monovalent group} \quad (2)$$

$$B = \frac{\pi \times 2070^2}{A} \text{ monovalent groups/latex particle of } 2070\text{-\AA diameter} \quad (3)$$

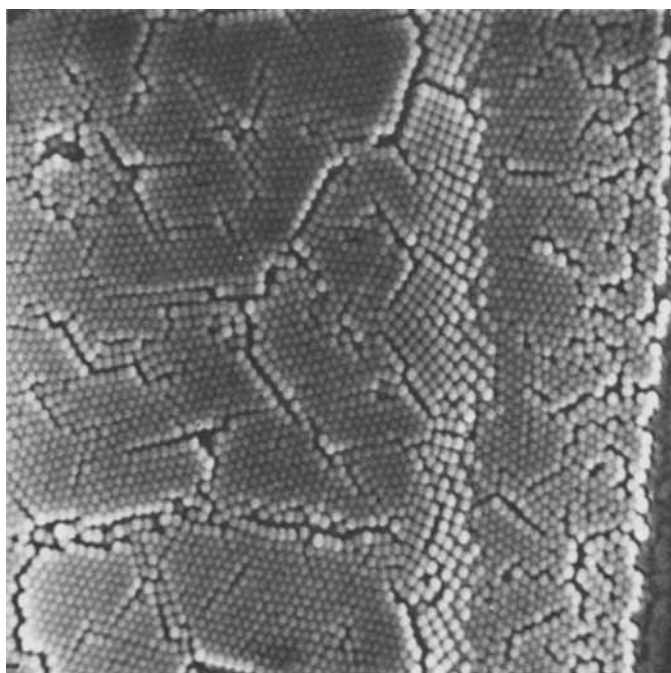
where N is Avogadro's number and m is the number of micromoles of NaOH per g of latex. The groups referred to are mainly carboxylate and, to a smaller extent, sulfate and because of their high polarity are largely located at the particle surface.^{5,13}

Infrared Spectra

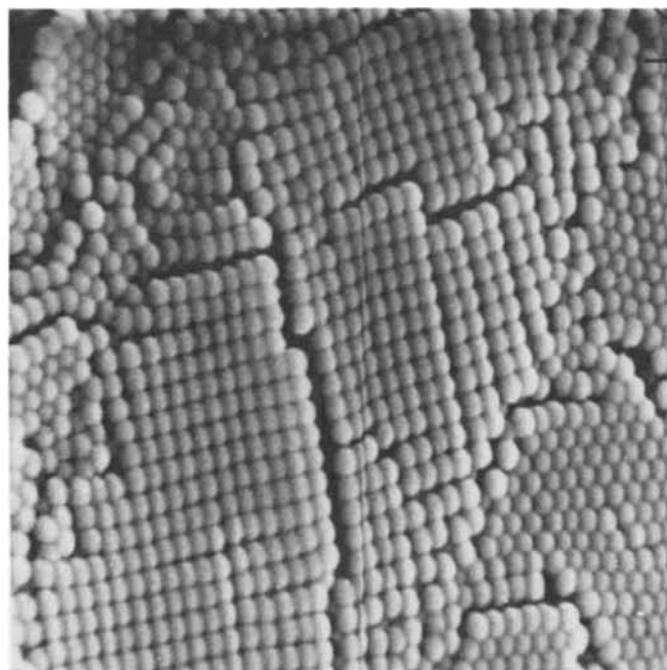
The infrared spectra of both latices were recorded (Perkin-Elmer spectrophotometer, Model 337) over the region $400\text{--}4000 \text{ cm}^{-1}$ by first vacuum drying the polymer and then dissolving in benzene to give a concentration of 0.3% w/v and placing the solution in potassium bromide cells provided with 1-mm spacers.

RESULTS AND DISCUSSION

The true emulsion polymerization of styrene provides a simple means of producing a stable latex of spherical particles which are almost perfectly



(a)



(b)

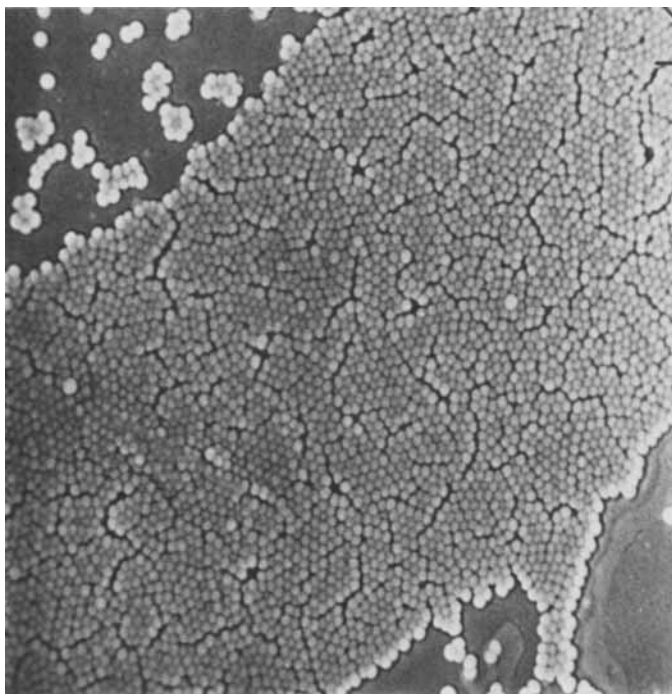
Fig. 1. Scanning electron micrograph of monolayers of latex S; (a) not tilted, $\times 10,000$; (b) tilted 30° to the normal, $\times 20,000$.

monodisperse, as shown in Figures 1a and 1b. The latex produced by conventional emulsion polymerization is not quite monodisperse (Figs. 2a and 2b). These observations were confirmed by measurements of latex particle diameters on electron micrographs (Table I). Ultracentrifugation of latices E and S confirmed the above results of particle sizes and distributions; latex S gave a very sharp Schlieren peak and latex E, a somewhat broader peak over a more diffuse separation boundary.

Latex E particles, when shaken in surfactant solutions above their c.m.c.'s, partially disintegrated but latex S particles did not, although the polymer in latex S has a molecular weight of about $1/11$ of the polymer in latex E (Table II) which, contrary to the results of Hearn et al.⁵ appeared

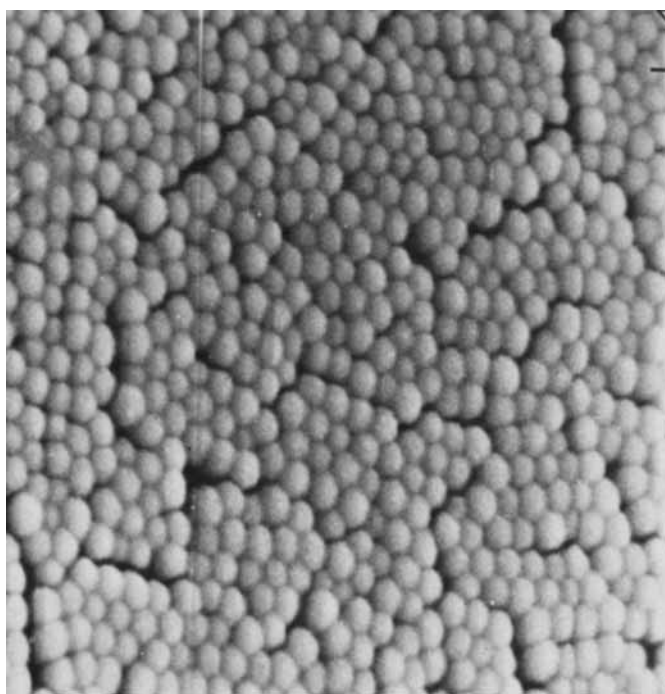
TABLE I
Latex Particle Sizes

Latex	Average particle diameter (from ultracentrifugation), Å (from eq. (1))	Coefficient of variation of the average diameter of 500 latex particles (from electron micrographs)
S	2070 ± 25	0
E	1400 ± 30	0.041



(a)

Fig. 2 (continued)



(b)

Fig. 2. Scanning electron micrograph of a monolayer of latex E; (a) not tilted, $\times 10,000$; (b) tilted 30° to the normal, $\times 30,000$.

TABLE II
Average Molecular Weights

Latex	Intrinsic viscosity, dl/g		Viscosity-average molecular weight $\times 10^{-6}$	
	Benzene	MEK ^a	Benzene ¹¹	MEK ¹²
S	0.500	0.320	0.096	0.106
E				
Growth 1	3.02	1.31	1.09	1.20
Growth 2	3.20	1.37	1.18	1.30
Growth 3	3.11	1.34	1.13	1.25
Growth 4	3.00	1.30	1.08	1.19

^a MEK = Methyl ethyl ketone.

to have approximately the same average molecular weight throughout all growth stages.

The resistance to fragmentation of latex S by surfactant is possibly due to the greater uniformity in the length of polymer chains which are formed in one polymerization stage and extend through the bulk of the particle, whereas each growth stage in latex E produces progressively thinner overlapping shells of polymer, permitting the polymer chains close to the sur-

TABLE III
 Monovalent Surface Groups

Latex	m , μ moles of NaOH/g latex	A , \AA^2 /monovalent group	B , monovalent groups/ latex particle of 2070- \AA diameter
S	4.81	960	14,000
E	1.14	5,970	2,260

face of the spherical particles to be arranged so that surfactant molecules are able to leach out at least the shorter oligomers in the outer shell.

The infrared spectra of polymers E and S were identical and typical of polystyrene.¹³

Table III gives the respective surface charge densities of latices E and S. The smaller areas per monovalent negatively charged group in latex S possibly explain why these particles were completely stable in dispersion at 60°C during polymerization.

SUMMARY

A simple method has been proposed for the polymerization of styrene in a solution of methanol and water to give a stable latex of uniform, spherical particles. The stability of the latex in dispersion seems to be due to a higher surface charge density of the particles compared with latex particles prepared by conventional emulsion polymerization. The new method involves only one polymerization stage in which no emulsification of monomer with surfactants is necessary and so dialysis against water proceeds very rapidly. The latex particles are stable in surfactant solutions above their c.m.c.'s, unlike latex particles prepared by conventional emulsion polymerization.

References

1. D. J. M. Robb and A. E. Alexander, *Soc. Chem. Ind., Symposium on Wetting* **25**, 292 (1967).
2. P. Connor and R. H. Ottewill, *J. Colloid Interfac. Sci.*, **37**, 642 (1971).
3. B. M. E. van der Hoff, in *Solvent Properties of Surfactant Solutions*, Vol. II, K. Shinoda, Ed., Marcel Dekker, New York, 1967, p. 285.
4. R. H. Ottewill and J. N. Shaw, *Kolloid-Z. Z. Polym.*, **215**, 161 (1967).
5. J. Hearn, R. H. Ottewill, and J. N. Shaw, *Brit. Polym. J.*, **2**, 116 (1970).
6. D. J. Williams and E. G. Bobalek, *J. Polym. Sci.*, **4**, 3065 (1966).
7. M. R. Grancio and D. J. Williams, *J. Polym. Sci. A-1*, **8**, 2733 (1970).
8. J. Ugelstad, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci., Polym. Lett.*, **11**, 503 (1973).
9. F. A. Bovey and I. M. Kolthoff, *J. Polym. Sci.*, **5**, 487 (1950).
10. E. B. Bradford and J. W. Vanderhoff, *J. Polym. Sci., Polym. Symposia*, **3**, 41 (1963).
11. W. R. Krigbaum and P. J. Flory, *J. Polym. Sci.*, **11**, 37 (1953).
12. P. Outer, C. I. Carr, and B. H. Zimm, *J. Chem. Phys.*, **18**, 830 (1950).
13. J. N. Shaw and M. C. Marshall, *J. Polym. Sci. A-1*, **6**, 449 (1968).

Received November 27, 1973

Revised February 13, 1974