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# LATEX PARTICLE NUCLEATION IN EMULSION POLYMERIZATION

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**Abstract**—Although it has been generally accepted for the past 45 years that the latex particles which are the principal locus of the emulsion polymerization reaction are nucleated from monomer solubilized in emulsifier micelles, conclusive evidence to support this supposition has been lacking. Twenty years ago it became apparent that in the case of monomers such as methyl methacrylate and vinyl acetate which have significant solubility in water, latex particles are nucleated by precipitation of oligomeric radicals formed in aqueous solution. Then it was found that even styrene, which has a very low solubility in water, could be polymerized in emulsion without an emulsifier or below the critical micelle concentration of the emulsifier when the latex particles must also be nucleated by oligomeric precipitation. However, such 'emulsifier-free emulsion polymerization' proves impossible with *p*-tert-butyl styrene which has only one tenth of the water solubility of styrene. Subsequently much evidence has been published to show that the ultimate latex particles are formed by coalescence of unstable precursor particles. It is argued that in the case of water-insoluble monomers, precursor particles may be formed by coalescence of monomer-swollen micelles destabilized by polymerization.

## INTRODUCTION

The ultimate latex particles formed by emulsion polymerization are much smaller than the droplets of the original emulsion; therefore, they are not formed simply by polymerization of the monomer droplets. Early work on emulsion polymerization was almost exclusively concerned with the preparation of styrene–butadiene and styrene–acrylonitrile copolymers for use in synthetic rubber. For experimental convenience styrene alone was used in many investigations. The solubility of styrene in water (Table 1) is very low and apparently negligible in comparison with the amounts which can be solubilized in solutions of surfactants. Consequently it has been generally accepted until very recently that polystyrene latex particles were nucleated by polymerization of monomer solubilized in micelles. The degree of polymerization of the polymer formed greatly exceeds the number of monomer molecules which can be solubilized in a single surfactant micelle so it is clear that monomer must be able to diffuse through the aqueous phase from other micelles and from emulsion droplets to latex particles containing growing radicals fast enough to maintain equilibrium swelling in the polymerizing particles (so that the reaction is not diffusion controlled). All estimates of the rate of diffusion support this conclusion [1, 2].

## EVIDENCE FOR MICELLAR NUCLEATION

However, the evidence that polystyrene latex particles are actually nucleated from monomer solubilized in emulsifier micelles is circumstantial.

(1) To total surface area of the micelles in a typical styrene emulsion greatly exceeds that of the emulsion droplets so that it is plausible that free radicals generated in the aqueous phase are more likely to enter micelles than emulsion droplets. Emulsion droplets can become the principal locus of polymerization if they are made small enough by special methods of emulsification—a technique now known as 'miniemulsion polymerization' [3, 4].

(2) It was found that some spacings in the X-ray diffraction pattern of very concentrated (20%) soap solutions increased when monomer was solubilized but reverted to their original values when the monomer was polymerized suggesting that the polymer had been expelled from the micelle [5]. However, there is a large excess of soap at the high concentration required to diffract X-rays so that most of the micelles remain when all the solubilized monomer has polymerized. What this experiment really shows is that solubilized monomer can polymerize. The latex particles formed do not contribute to the X-ray diffraction pattern and need not necessarily have been nucleated from micelles.

(3) The soap used in most early experiments in the U.S.A.—SF flakes—has a low critical micelle concentration so that there is little difference between the micellar emulsifier concentration and the total emulsifier concentration but this difference is significant for sodium dodecyl sulphate which has been used in many more recent experiments. Use of micellar rather than total emulsifier concentration improves agreement [6] between observed particle sizes and those calculated by Gardon's equations [7] derived from Smith–Ewart [8] theory. The increase in the number of latex particles formed with small increases in ionic strength when sodium dodecyl sulphate is the emulsifier can be accounted for by

Table 1. Solubility and solubilization [31]

| Solute | Solubility (% v/v) | Solubilization (% v/v) | Increase (%) |
|---|---|---|---|
| Ethyl benzene[a] | 0.015 | 0.035 | 233 |
| Vinyl acetate[a] | 2.94 | 0.03 | 1 |

[a] In $2.0 \times 10^{-3}$ mol dm$^{-3}$ sodium dodecyl sulphate solutions at *ca* 20°.

the increase in micellar emulsifier concentration consequent on the reduction in the critical micelle concentration although larger increases in ionic strength induce coalescence reducing particle numbers [9]. Equal micellar concentrations of emulsifiers in homologous series produce equal numbers of latex particles and consequently equal rates of polymerization [10] during Interval II (the period in which a constant polymerization rate is observed after the nucleation of latex particles—during Interval I—is supposed to have ceased) although the size (and consequently the number) of micelles and the amount of monomer which can be solubilized differs. With equal total concentrations of homologous emulsifiers the Interval II polymerization rate increases with the alkyl chain length of the emulsifier [11] although $a_S$, the area occupied by an emulsifier molecule in a saturated monolayer at the polymer/water interface decreases [12]. A decrease in the number of particles formed at the end of Interval I would have been expected according to the Smith–Ewart criterion for the cessation of particle formation [8] which is that the total surface area should have increased sufficiently to adsorb all the emulsifier present in a saturated monolayer (incidently implying the disappearance of micelles).

(4) The Interval I rate of polymerization of styrene–butadiene (and of styrene alone [10]) *is* proportional to the amount of monomer solubilized as was shown by Kolthoff, Meehan and Carr [13] whose rate results relate to the conversion after 3 hr: this is likely to be substantially the amount converted at the end of Interval I in the styrene–butadiene polymerization which is comparatively slow under the conditions normally used taking about 12 hr to react conversions over 80%.

## NUCLEATION BY OLIGOMERIC PRECIPITATION

The initial presence of micelles is not an essential feature of emulsion polymerization. The more water-soluble monomers e.g. methyl methacrylate and vinyl acetate and even styrene [14] can be polymerized in emulsion in absence of an emulsifier provided an initiator such as peroxydisulphate is used which will introduce charged end-groups into the polymer which can stabilize the latex electrostatically [15–17]. Uncharged hydroxyl end-groups from the decomposition of hydrogen peroxide catalysed by ferric ions do not stabilize latex particles sufficiently: precipitated polymer particles coalesce rapidly and become so large that they sediment under gravity in an unstirred system: most of the remaining monomer partitions into the polymer phase where radicals generated in the supernatant aqueous phase are unable to reach it so that the reaction slows down and stops at less than 50% conversion [16].

Model colloidal particles with clean surfaces (i.e. without adsorbed emulsifier) can conveniently be prepared by 'emulsifier-free emulsion polymerization' although the dispersion obtained is rather dilute and the particles rather large; however, the particle size distribution is monodisperse, which is a big advantage in this application. The average particle size can be reduced by addition of emulsifier at concentrations below its critical micelle concentration. In cases in which solubilization of monomer in emulsifier micelles is significant (e.g. styrene) a sharp increase in the number of latex particles formed is observed at the critical micelle concentration above which the particle size distribution becomes polydisperse. Until very recently this observation provided the most convincing evidence for the predominance of the micellar nucleation of latex particles above the critical micelle concentration of the emulsifier. The increase of particle number (and consequently of Interval II polymerization rate) even provides a possible method for the determination of the critical micelle concentration of the emulsifier [18].

Richards, Congalidis and Gilbert [19] claim that it is possible to reproduce Sütterlin's results [20] for the number of polystyrene latex particles formed as a function of sodium dodecyl sulphate concentration using their Emulsion Polymerization Model which involves only the coagulative nucleation of latex particles from unstable precursors formed by oligomeric precipitation without the need to consider micellar nucleation. However, although their model does reproduce the sharp increase in the number of latex particles formed at the critical micelle concentration, it predicts a zero order dependence of particle number on emulsifier concentration above the critical micelle concentration. This seems to be what is found [20] for methyl acrylate which is relatively soluble and for which the amount solubilized may be negligible in comparison with the amount in molecular solution. But for styrene, Sütterlin's results [20] reconfirm the previously established 0.6 order in emulsifier above the critical micelle concentration [21] consistent with the number of latex particles being limited by emulsifier exhaustion [8] although the order in emulsifier for styrene does vary somewhat with different emulsifiers [22] which is inconsistent with the Smith–Ewart hypothesis [12] for the cessation of particle formation. Observation of a 0.6 order in emulsifier, however, does not prove that latex particles are nucleated from micelles, only that the number of latex particles formed is limited by the amount of emulsifier available for adsorption as was first emphasised by Roe [23]. Thus there is no conclusive evidence that polystyrene latex particles are nucleated from micelles although, by contrast with more water-soluble monomers, micellar nucleation still seems probable for styrene on the basis of the argument [see (1)] that radicals generated in the aqueous phase are most likely to enter micelles during the initial stage of the reaction.

## COAGULATIVE NUCLEATION

Ample evidence has been accumulated recently which shows that the ultimate latex particles are not formed directly either by micellar nucleation or by oligomeric precipitation but from precursor particles which undergo limited coalescence during Interval I [24, 25]. The problem therefore becomes whether the precursors are formed from micelles or by oligomeric precipitation. There is no doubt that the latter mechanism is operative in the case of the more water-soluble monomers. Insoluble macromolecules with only one or two charged groups are not stable and coalesce until a surface charge density high enough to prevent further coalescence is attained. On the other hand, micelles and micelles swollen by solubilized monomer are thermodynamically stable: it has always been assumed that when solubilized monomer polymerized additional emulsifier would be adsorbed quickly enough to maintain a saturated monolayer at the polymer/water interface until the emulsifier was exhausted. This would be ample to prevent coalescence so that each of the minority of micelles in which polymerization was initiated (about 1 in 1000) would ultimately become a latex particle. However, there can be very little difference between the Gibbs energy of an emulsifier molecule in a monomer-swollen micelle and on a latex particle of similar size although this difference might be expected to increase with the size of the latex particles. Hence emulsifier adsorption might be slow initially. If the surface charge density of the latex particle decreases and its size (and van der Waals attractive energy) increases it might become unstable and coalesce until a surface charge density sufficient to prevent further coalescence with particles of similar size was attained. Thus evidence of the occurrence of coalescence need not preclude the formation of precursors from micelles in cases in which the amount of monomer solubilized exceeds the amount in solution.

### EMULSION POLYMERIZATION OF *p*-TERT-BUTYL STYRENE

*p*-Tert-butyl styrene has only one-tenth of the solubility in water of styrene [26]. Its solubilization in emulsifier solutions has not been measured but it is likely that it would be similar to, or somewhat greater than, that of styrene. By contrast with styrene, no latex is produced when emulsifier-free emulsion polymerization is attempted [27]. It is possible that some *soluble* oligomer might be produced which could be detected by a decrease of surface tension because of termination of dimer, trimer, etc. radicals formed in the aqueous phase before they could become large enough to precipitate, but this observation has yet to be attempted. However, a latex is formed immediately emulsifier is injected [27]. Evidently, in this case at least, the presence of micelles is essential for the formation of a high polymer. The glass transition temperature of poly-*p*-tert-butyl styrene (134°C) is considerably higher than that of polystyrene (81°C) [26]. The glass transition temperature of the polymers swollen to equilibrium with monomer will be much lower but, nevertheless, it is possible that poly-*p*-tert-butyl styrene latex particles are below their glass transition temperature at a polymerization temperature of 50°, so that they would not coalesce although they might coagulate. At any rate, the particles in electron micrographs of poly-*p*-tert-butyl styrene latex appeared to be very small. Figure 1 shows that the effect of varying the emulsifier concentration is entirely different for styrene and *p*-tert-butyl styrene

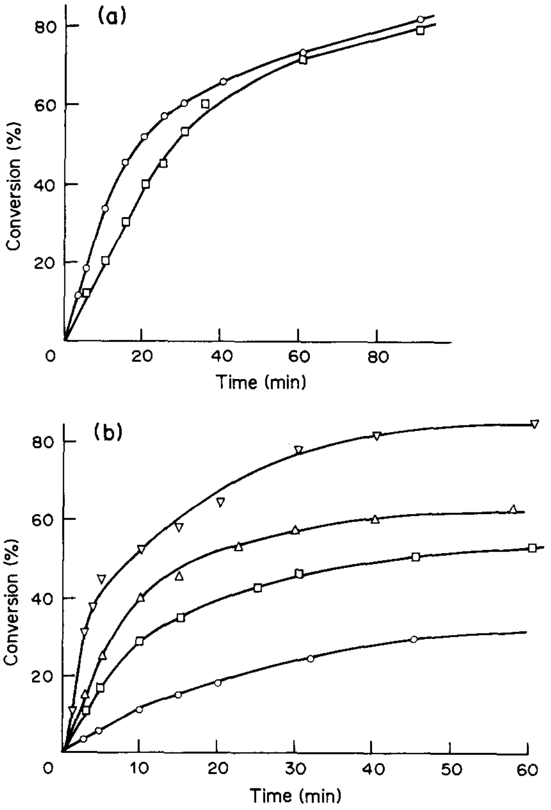

Fig. 1. (a) Polymerization of 2% styrene emulsion with 0.125% potassium persulphate at 50° (□) 0.5%; (○) 1% sodium dodecyl sulphate [27]. Polystyrene $T_g = 81°$. (b) Polymerization of a 2% *p*-tert-butyl styrene emulsion with 0.125% potassium persulphate at 50°. Poly-*p*-tert-butyl-styrene $T_g = 134°$. (○) 0.25%, (□) 0.50%, (△) 1.0%, (▽) 2.0% sodium dodecyl sulphate [27].

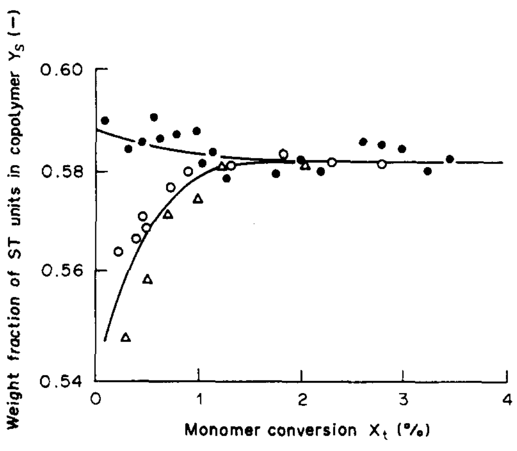

Fig. 2. Weight fraction of styrene residues in a styrene–methyl acrylate copolymer as a function of conversion with sodium dodecyl sulphate [28] below its c.m.c. (△) 0, (○) 0.2 g dm$^{-3}$, and above its c.m.c. (●) 12.5 g dm$^{-3}$. (Reprinted by permission from the *Journal of Polymer Science C Polymer Letters* © John Wiley & Sons Inc. 1988.)

under the same conditions. Whilst the styrene results are consistent with a 0.6 order in emulsifier, those on *p*-tert-butyl styrene suggest that the lower amounts of emulsifier used were insufficient to stabilize the latex which is consistent with the poly-*p*-tert-butyl styrene latex having a much larger total surface area. Similar results might be found with styrene if the reaction temperature were reduced far enough below the glass transition temperature with the use of redox initiation.

## DEPENDENCE OF COMPOSITION OF EMULSION COPOLYMERS ON EMULSIFIER CONCENTRATION

Recently Nomura and co-workers [28] have determined the composition of emulsion copolymers of a water-insoluble monomer (styrene) and a more water-soluble monomer (methyl acrylate or methyl methacrylate) at very low conversions (less than 1%) above and below the critical micelle concentration of the emulsifier. In absence of emulsifier or below its critical micelle concentration the composition of the initial copolymer is that expected from the concentrations of the monomers in the water phase whereas above the critical micelle concentration of the emulsifier the composition of the initial copolymer corresponds to the concentration of the monomers in the oil phase. The compositions converge rapidly with increasing conversion as the latex particles become the locus of the reaction. This experiment appears to provide conclusive evidence that the latex particles are nucleated from monomer-swollen micelles in this system. However, Gilbert [29] points out that the volume fraction of monomer in precursor particles is expected to vary with particle size in accordance with the Morton–Kaiserman–Altier equation [30] and that the function will be different for different monomers. This would explain the variation of composition with conversion as the average size of the latex particles increases but the aqueous phase should be saturated with each monomer in presence of monomer droplets whether micelles are present or not. The precursor particles should, therefore, have the same size and the same composition both above and below the critical micelle concentration of the emulsifier if precursor particles are not formed from micelles. Hence this experiment does indeed prove that precursor particles are formed from monomer solubilized in micelles when the amount of monomer solubilized exceeds the amount in molecular solution although these precursor particles subsequently undergo limited coalescence to form the ultimate latex particles most probably because the initial rate at which the surface area of very small particles increase by polymerization exceeds the initial rate of adsorption of monomer.

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