A NEW LOOK AT KINETICS AND STABILISATION PHENOMENA IN EMULSION POLYMERISATION

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SUMMARY **:** In order to obtain a well-defined particle size distribution in emulsion polymerisation, we have chosen a system composed of butyl acrylate (BuA), methyl methacrylate (MMA) and acrylic acid (AA) and will concentrate on the influence of BuA/MMA ratio, the influence of surfactant on particle number and size, and on the functionalisation of latices with carboxylic acids.

KEYWORDS : emulsion polymerisation, acrylic acid, stabilisation, kinetics, butyl acrylate, methyl methacrylate.

Introduction

Economic improvements to existing emulsion polymerisation processes can be achieved by several means, including: (i) improving control over rheological properties and viscosity (related to particle size and size distribution); (ii) increasing solids content of the latex (also related to particle size). High solids content without undesirably high viscosity can be obtained when the Particle Size Distribution (PSD) is polymodal [1,2]. However, although these studies provided recipes for obtaining a polymodal PSD and acceptable levels of viscosity, they did not attempt to examine the problem from a process engineering point of view: i.e. try to quantify the effect of particle size, and the concentration and type of surfactant on the evolution of the PSD and reaction kinetics. In order to obtain a well-defined PSD in emulsion polymerisation, it is necessary to have a complete understanding of several different, but interdependent phenomena, including particle nucleation, kinetics, latex stability, monomer type and concentration. We have chosen to study these parameters for a system composed of butyl acrylate (BuA), methyl methacrylate (MMA) and a carboxylic acid, and will concentrate on the influence of surfactant on particle number and size, and on the functionalisation of latices with carboxylic acids.

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Results and Discussion

Influence of ratio of BuA/MMA

The variation of the number of particles has been compared with the models of both micellar and coagulative nucleation. Figure 1 shows the influence of the initial composition of monomer on rate of batch polymerisation at a final solid content of 10%, $[APS]_0=0.75$ g/l, a stirring rate of 250 rpm, and T=70°C. It was observed that as one increased the amount of MMA in an BuA-MMA copolymerization, the contribution of homogeneous nucleation was greater since the amount of water soluble monomer increases. It was also observed that the nucleation process is more rapid when micellar nucleation is the dominant mechanism of particle formation. As shown in Figure 2, particle size regularly increases during the same reactions, and the data suggest that the ratio of BuA/MMA does not have a significant effect on the particle size.

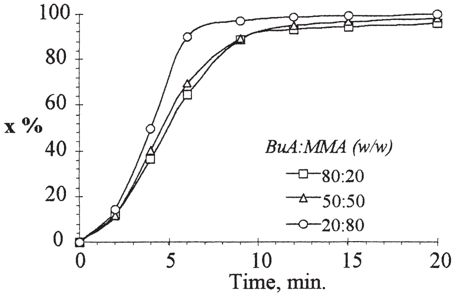

Figure 1: Conversion curves of emulsion copolymerization of BuA with MMA.

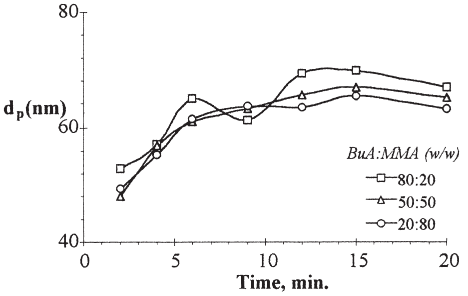

Figure 2: Effect of ratio of BuA/MMA on particle size.

Influence of anionic and non-ionic surfactants

Surfactants obviously play an important role in particle nucleation and growth. Here, we used both anionic (SDS) and non-ionic (Triton-X405) surfactants at different concentrations. The different mechanisms of stabilisation have very different influences on Np, and thus on kinetics and rheology. As shown in Figures 3 and 4 for the 50:50 (w/w) experiment, the rate of polymerisation and number of particles formed increase with the SDS concentration, essentially because the final number of particles does as well. (Note that the QELS technique used to estimate dp and thus Np is more sensitive to larger particle sizes, and Np might be underestimated). When SDS concentration was higher, the period of nucleation was shorter and Np reached its steady value faster.

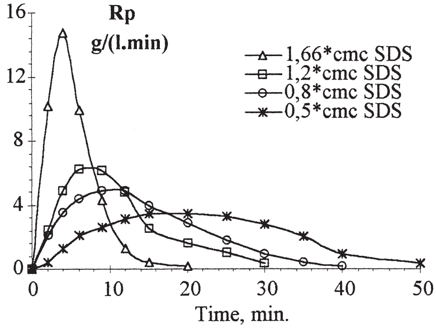

Figure 3: Rate curves of emulsion copolymerization of BuA with MMA.

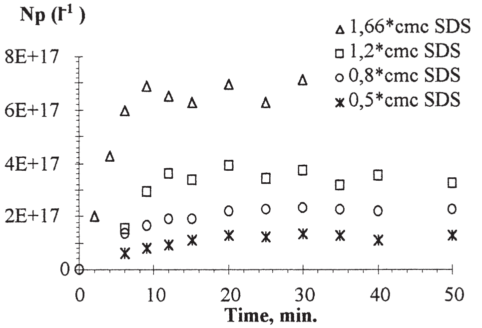

Figure 4: Effect of surfactant concentration on number of particles per litre.

For these experiments, where the surfactant concentration is greater than the CMC, values of $\bar{n}$, average number of radicals per particle, were calculated at the end of Stage II and varied in the range 0.46-0.63. This is close to those predicted for case II kinetics of Smith-Ewart, where it is assumed that termination takes place as soon as a new radical enters an active particle.

As shown in Figure 5 when the Triton surfactant was used in the same conditions as for Figures 3 and 4, the period of nucleation was long and the rate of polymerisation was lower than when SDS was used. And as can be seen in Figure 6 the final number of particles was also greatly reduced; and, consequently, the diameter of particles was higher. Thus, in these experiments we observed the formation of coagulums even when the surfactant concentration was higher than its CMC. These results suggest the greater instability of particles when these were stabilised with non-ionic surfactant. In this case, the calculation of the average number of radicals per particle at the end of Stage II gives values in the range 2.25-8.05 (Smith-Ewart case III kinetics). Secondary nucleation might occur during the polymerisation, producing small particles undetected by DDL. Radicals can also be captured by these particles. Our calculation of $\bar{n}$ did not take into account

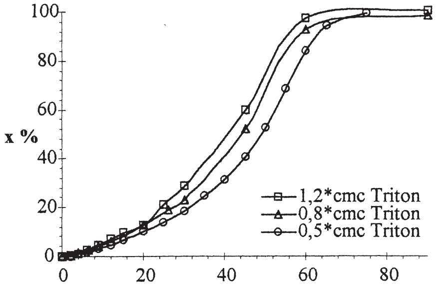

Figure 5: Conversion curves of emulsion copolymerization.

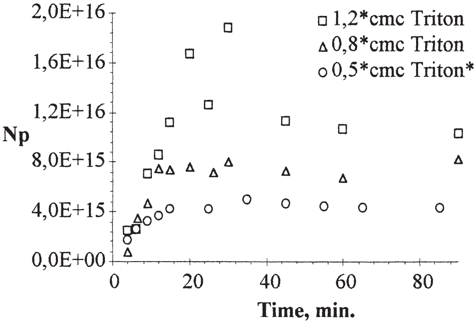

Figure 6: Effect of surfactant concentration on number of particles.

the secondary nucleation, and it is possible that these values over-estimate the true value of $\overline{n}$.

The profile of Np during the polymerisation process depends not only on the number of particles generated, but also on their stability. On one hand, according to the Smith-Ewart theory, which was based on the micellar nucleation mechanism, the number of latex particles is proportional to the surfactant concentration to the power 0.6. However, Novak [3] studied the semibatch emulsion copolymerization of methyl methacrylate and butyl acrylate, and used the coagulative nucleation model to describe particle nucleation and growth. This model predicts that the final particle size is proportional to the concentration of the surfactant to the power -1/3 and, consequently, of one directly proportional to Np.

Figure 7 shows the dependence of Np on the surfactant concentration. The parameter [TA] represents the concentration of surfactant in batch emulsion polymerisation systems. When the surfactant was SDS at concentrations below its CMC, the slope of the log(Np/l)-vs.-log[TA] is equal to 0.985. This result follow the Novak model quite well. On the other hand, when the SDS concentration is above its CMC, the parameter Np is more insensitive to [TA] and the slope is 0.42. This result is more according to the micellar mechanism. With Triton, the slope is equal to 1.31. This is slightly greater than the prediction with Novak model, and could be due to a significant flocculation phenomenon during the polymerisation process. Chern et al. [4] showed the slope of the log(Np/l)-vs.-log[TA] plot should lie between 0.5 and 1.2, this value was higher when the surfactant concentration was less. These results are consistent with those of Feeney et al. [5], who found a slope in the range 0.4-1.2.

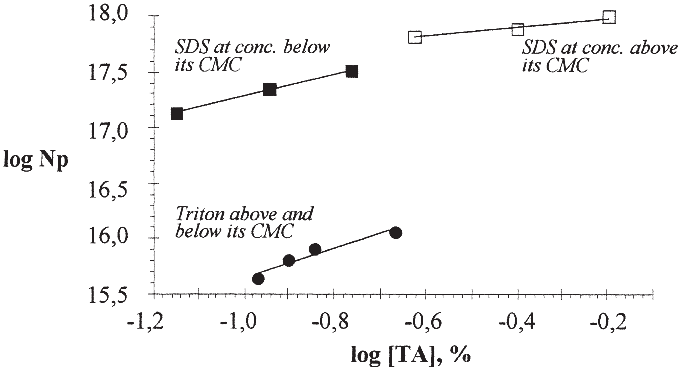

Figure 7: Number of final latex particles as a function of surfactant concentration.

Functionalisation with carboxylic acid

The functionalisation of a latex with carboxylic acids modifies physical properties of the final polymer and have also an influence on stability and colloidal behaviour. Carboxylic groups grafted on the particle surface are more useful than those in the particle, because they play a role in the stabilisation mechanism when the latex is neutralised and thus, the acid in its ionic form. We functionalised our latices with acrylic acid (AA), which is highly soluble in water, and used conductimetric titrations to estimate how it partitions between the aqueous phase, particle surface and particle interior.

As shown in Table 1, with both anionic and non-ionic surfactants, the fraction of acrylic acid grafted on the particle surface is very low (<15%mass.) compared to the fraction in aqueous phase (>50%mass.). In both experiments, the pH was low, varying between 2.5 and 2.9. In this pH range, acrylic acid exists in its molecular form -COOH and does not behave as a surfactant molecule, which would be generally be found on the particle surface. But even in its molecular form, AA is highly hydrophilic. Thus, the fraction of AA in aqueous phase is high. Santos et al.

[6] observed the same tendency. With a pH value of 2.2, there are this found 23% of AA on the particle surface and 46% in the aqueous phase. They also observed an increase in the fraction of carboxyl groups inside the particle in the case methacrylic acid because it is less hydrophobic. Bajaj et al. [7] proposed that the water solubility in of oligomeric radicals increases in the presence of carboxylated monomers. Thus, the degree of polymerisation before precipitation of these oligomeric radicals will increase as well as termination reaction in the aqueous phase. Otherwise, the fraction of carboxylated groups may increases to modify the strategy by wich the monomers are fed into the polymerisation system. Hoy [8] also investigated this last point.

Table 1 : Influence of surfactant type on AA partitioning

	average particle size	**surface charge density**	**AA partitioning**		
			surface	**aqueous phase**	**interior**
[SDS] =0,5 CMC	160 nm	26 μC/cm^2	7 (± 5) %	59 (± 5) %	34 (± 5) %
[Triton] = 0,5 CMC	400 nm	120 μC/cm^2	13 (± 5) %	67 (± 5) %	20 (± 5) %

Conditions: solid content 20%, [APS]=0,8g/l, BuA:MMA:AA (w/w) = 78.5 : 18.5 : 3, T=70°C)

We also calculated the surface charge density corresponding to AA in its ionic form, even it was not in this form during the polymerisation. The surface charge density was finally found to be higher with Triton than with SDS. This is explained by the relative size of particle : with non-ionic surfactant, particles are bigger than with anionic surfactant. The difference of AA partitioning between latices obtained with anionic and with non-ionic surfactants is not significant, considering the precision of the method.

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