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On-line Monitoring of Emulsion Polymerisation Using Conductivity Measurements

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Summary: This work investigates the feasibility of implementing conductivity measurements for the purpose of the on-line monitoring of particle generation by following the evolution of free surfactant concentration during SDS/styrene emulsion polymerisations. The conductivity and temperature were measured on-line during the reactant addition and reaction stages of a number of batch emulsion polymerisations. Samples were collected for off-line analysis of particle size and conversion. Observation of the evolution of the conductivity enabled us to measure the effect of surfactant and monomer addition. The maximum size of the monomer droplets was calculated from the decrease in conductivity that represented the adsorption of surfactant molecules onto the droplet surface. The division of SDS between the particle interface and the aqueous phase was also determined giving an indication of the particle stability.

Keywords: conductivity; droplet size; emulsion polymerisation; monitoring, on-line

Introduction

Carrying out in-line monitoring of free surfactant molecules in the media is of interest in the polymer reaction engineering because this provides information about nucleation phenomena and the degree of stabilization of polymeric latexes. Conductimetry is based on the fact that conductivity measurements offer a means of monitoring the evolution of concentrations of different species in the latex, and has been shown to be a promising tool [1,2,3]. Different studies have used a recirculation loop with an in-line probe for measurements of conductance during emulsion and miniemulsion polymerisations[4], for the design of surfactant addition profiles in encapsulation studies [5], to study nucleation in MMA miniemulsions with samples withdrawn from the reactor [6], and to look at surfactant partitioning [7]. With the exception of Janssen's study [5], most of these works used a sampling device, which is not always practical in industrial situations. Santos et al.[1,2,3] demonstrated that it is possible to infer the evolution of the number of stabilised particles in an emulsion polymerisation by following the response of the

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conductivity as a function of time.

The objective of the current work is to go beyond what was done in references [1,2,3], and to use conductimetry to understand emulsion polymerisation from a more fundamental, real-time point view, looking at the size of the monomer droplets and the partitioning of surfactant in the reactor. Before going further, it should be pointed out that emulsion polymerisation reactors are not the most suitable place to perform electrochemical studies. The occurrence of different phenomena in different phases, changes of viscosity and temperature represent complications that can make the interpretation of electrochemical measurements difficult, but not impossible.

Experimental procedures and techniques

Styrene, potassium persulphate (KPS), and sodium dodecyl sulphate (SDS) were obtained from Acros Organics and used as received. Emulsion homopolymerisations of styrene were run at 10% solids content (mass monomer with respect to total reaction mass), and the initiator concentration (KPS) was maintained at 1.00 g/L_{H2O} for the styrene runs, and 0.25 g/L_{H2O} for the MMA runs. The reaction volume (total) was 1830 ml (183 g monomer, 1650 g water, KPS, SDS). The only quantity that was varied was the mass of SDS, all other quantities remained constant. The reactor vessel and lid were jacketed, and water was circulated at a constant temperature of 60°C. Overall conversions were determined gravimetrically. Dynamic laser light scattering or quasi elastic light scattering (QELS) (Lo-C, Malvern Instruments Ltd.) was used to determine particle size and distribution. Measurements were recorded at a 90° angle and an average of ten measurements was recorded. Polymerisations were carried out in a 3-litre calorimetric reactor. There are four inlets in the vessel wall to allow for the insertion of sensors into the reaction mixture. A platinum sensor connected to a conductivity meter (TACUSSEL CD 810) was inserted into the reaction mass through one of these ports. Temperature and conductivity measurements were recorded by means of a data acquisition unit.

Results and Discussion

A series of 7 experiments at different surfactant concentrations was run to investigate the effect of changing surfactant concentration on styrene polymerisations. As can be seen in Figure 1, the conductivity increases when SDS is introduced and decreases when the monomer is added. This is then followed by a sharp increase due to the addition of the initiator since KPS generates negatively charged sulphate radicals in the aqueous phase. The signal subsequently evolves as the polymerisation proceeds and the amount of free surfactant (ions) changes.

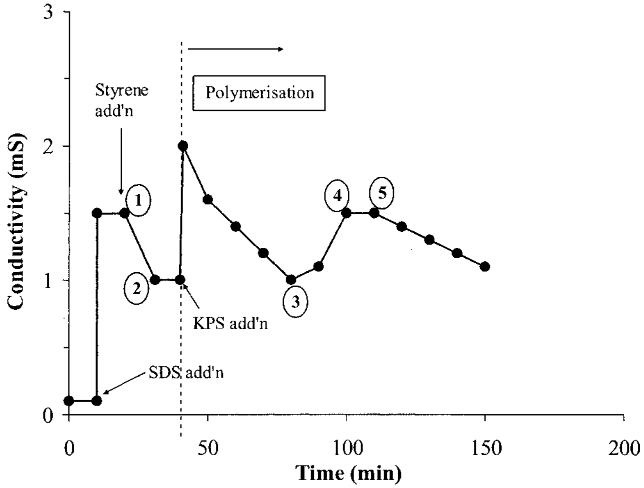

Figure 1. Evolution of the conductivity during the emulsion polymerisation of styrene.

The reduction of conductivity (at least in the absence of reaction) following the introduction of monomer is likely due to the decrease in the concentration of free surfactant in the aqueous phase as some of it is absorbed on the surface of the monomer droplets that are formed in the milieu. (Note that KPS decomposition does not noticeable influence the signal for the short times considered here). Thus, if we measure the change of conductivity from point 1 in Figure 1 (steady state conductivity in the presence of SDS, and after any micelles might have formed in the reactor) to that at point 2 (steady state in presence of monomer and SDS), and if we know the critical micelle concentration (CMC) and specific surface area of the surfactant molecules (a_S), we can calculate how much surfactant was absorbed at the surface of the organic phase. All experiments were run at 60°C, so the value of the CMC used here is 3.0 g/land $a_s = 50$

Å^2 [2]. A summary of the experiments, and the principle results are shown in Table 1.

Table 1. Summary of results of SDS partitioning before polymerisation for Styrene

× CMC	Mass SDS (Total, g)	SDS at interface	d_g (nm)	$\frac{SDS_{interface}}{SDS_{total}}$
0.7	3.3	0.055	21000	0.02
1	5	0.68	1693	0.14
2	9.2	4.7	244	0.51
3	13.9	6.0	192	0.43
4	18.5	9.3	124	0.50
5	23.2	7.1	162	0.31
6	27.9	6.1	190	0.22

d_g = droplet diameter

The total surface area, S_g, of the droplets is calculated by:

$$S_g = N_g(\pi d_g^2) \tag{1}$$

N_g, the number of droplets is related to the volume of monomer added to the reactor (V_m) and the droplet diameter as follows:

$$N_g = \frac{V_m}{\left(\frac{\pi d_g^3}{6}\right)} \tag{2}$$

Which means that the diameter of the droplets can be related to the total surface area by equation (3):

$$d_g = \frac{k\pi}{S_g} \text{ where } k = \frac{6V_m}{\pi} \tag{3}$$

Since we know how much surfactant was added, it is possible to use the correlation between the amount of free surfactant in the aqueous phase and the conductivity developed by Santos et al. [2] to calculate how much surfactant is in the water, and therefore how much surfactant is on the surface of the droplets. Once this is known, one can multiply the number of molecules of surfactant on the surface by a_s to find the total surface area, and therefore the droplet size.

It should be noted that these calculations of the droplet size, d_g, were made assuming that 100% of the droplet surface was covered before the reaction began. This might not be the case, as it is possible that surfactant is partitioned between the aqueous phase and the organic surface at levels below 100%. This means that the values presented in Table 1 are upper bounds and that if the surface coverage is lower than 100%, the droplets will be even smaller than the size calculated above. It is interesting to note here that the fraction of SDS situated at the interface increases very rapidly as the [SDS] concentration passes from just below to just above the CMC, and that it passes through a maximum at a point between 2-4 times the CMC. The reason for this is unclear, but it seems that there must be some sort of partitioning of surfactant going on in the system. We will return to this point below.

It can be seen from Figure 1 that the introduction of the initiator immediately provokes a rapid rise in the conductivity due to the addition of the sulphate ions from KPS, and that the signal then drops rapidly as the polymerisation begins. Although all of the results are not shown here for the sake of brevity, the form of all of the curves remains the same, but the first significant minimum (point 3 on Figure 1) occurs at different conversions. This minimum corresponds to a conversion of 14% for the case of 0.7×CMC, and increases to approximately 50% for 6×CMC, as shown in Figure 2. The conductivity then increases to a local maximum at Point 4, before decreasing once again after Point 5. The evolution of the conversion at these different points is shown in Figure 2 along with the evolution of the density of negative charges (SO_4^-) on the surface of the particles (KPS and SDS).

The increase from Point 3 to Point 4 must be due to a liberation of surfactant in the system. This "liberation" could have three origins: (1) disappearance of the droplets; (2) desorption of SDS from the particles as polymer content, and thus hydrophobicity of the particles increase; or (3) destruction of a certain number of particles due to auto-flocculation. Reasons (1) and (2) are unlikely. If we consider the experiments at 0.7 and 1 × CMC, the conversion is much lower than that corresponding to the well-known saturation level for PS. There are therefore droplets still present. In addition, Reason (2) is not correct since the concentration of polymer inside the particles remains constant between Points 3 and 4 for at least these 2 experiments.

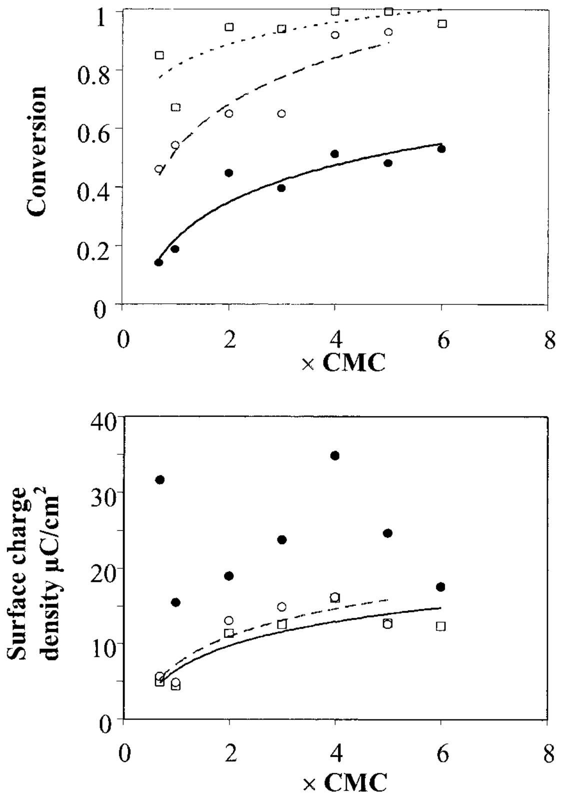

Figure 2. (Top) Evolution of conversion at Points 3, 4 and 5 on Figure 1 for the different PS experiments; and (bottom) evolution of the density of negative charges due to sulphate end groups on the particle surfaces for the same points. ●Point 3, ○Point 4, □ Point 5 (note curves are shown just to help distinguish the points and have no physical value).

We therefore postulate that the increase in the conductivity signal is due in large part to a reorganisation of the particle size distribution while the systems drives itself to more stable energy levels. In other words, between Points 1 and 2, the system is very rapidly generating a huge number of particles that grow quickly at first. It is quite possible that the kinetics of surface generation and the amount of surface to be covered are such that the system cannot respond, and a non-negligible fraction of these small 'metastable' particles flocculate onto each other, or onto well-stabilised particles. Note that the surface charge density proposed in Figure 2 is based on the surface area presented by the latex that is removed from the reactor, and not the latex in the state in which it is found during the reaction between Points 1 and 2. If we consider the graph in Figure 3, it can be seen that the particles are slightly smaller at Point 3 than the other two points. The difference here is not significant for large excesses of SDS, and above 3-4×CMC, it could be within the limit of experimental error of the apparatus. On the other hand, at low values of SDS concentrations there is a noticeable difference in d_p, and the particles continue to growth throughout the reaction, which supports the idea that the particles continue to flocculate until they reach a steady state.

Note that in the early stages of the polymerisation a large number of particles are nucleated very quickly, which gives us a very different dynamic from what we see at steady state at the end of the experiment. It will be much easier to stabilise any surface generated uniquely by particle growth than it would be to stabilise surfaces generated by nucleation. If one considers the graph at the bottom of Figure 3, it can be seen that changes in conductivity are significantly larger at lower concentrations of SDS than at higher ones. This is also consistent with the idea of a redistribution of surfactant to minimise the surface energy by pushing the system in the sense that small, unstable particles flocculate onto larger ones since the SDS would be fairly scarce at or below the CMC. In this case, the kinetics of particle stabilisation would be much slower and that the limited amount of SDS available would not be enough to fully stabilise all of the particles generated. On the other hand at higher SDS concentrations, the flux of surfactant to the surfaces generated during nucleation and growth would be higher, and we could stabilise relatively more particles.

Figure 4 shows that at low concentrations of SDS, a majority of the material is absorbed on the surface of the particles at the end of the reaction at values below 3 times the nominal CMC (note to convert g on the y-axis of this figure to CMC, divide by 1.65) However, above 3× CMC, we begin to accumulate SDS in the aqueous phase at levels above the CMC, which suggests that micelles and particles can coexist under certain conditions.

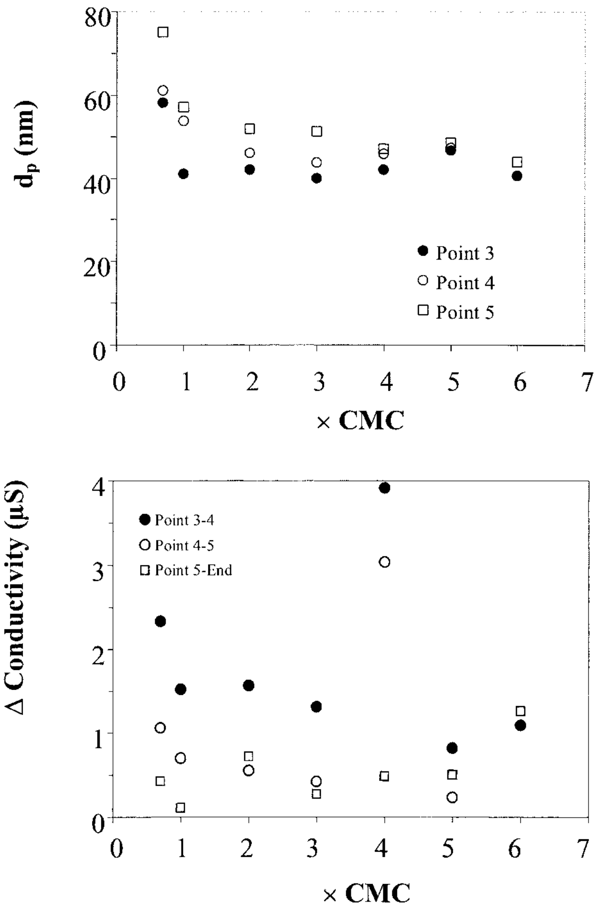

Figure 3. Evolution of measured particle diameter at Points 3, 4 and 5 on Figure 1 for the different PS experiments (top), and (bottom) measured value of the drop in conductivity between subsequent points in Figure 1. ●Point 3, ○Point 4, □ Point 5. (N.B. All d_p values monodisperse according to analytical software of the Malvern Lo-C QELS apparatus used for the measurements).

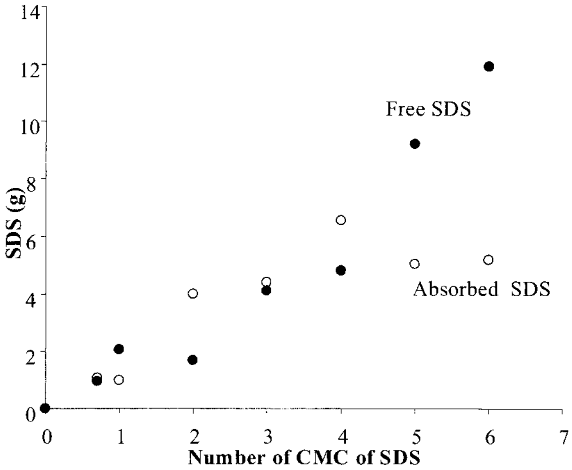

Figure 4. Amounts of SDS absorbed at the surface of the particles and of SDS free in the aqueous phase (as micelles or as dissociated molecules) as a function of the total amount of SDS added to the reactor. To convert g to number times CMC, divide by 1.65 (5 g = 1 CMC).

Conclusions

Conductivity can be a useful tool for the monitoring of styrene emulsion polymerisations, and the conductivity signal can be interpreted to allow us to understand the distribution of free surfactant in the reactor. This in turn allows us to follow the evolution of the PSD, and to have a better idea of how the surfactant is partitioned in the reactor.

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