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Nucleation in Emulsion Polymerization: Another Step towards Non-Micellar Nucleation Theory

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Summary: Comprehensive experimental results of the nucleation stage of styrene emulsion polymerization in the absence as well as in the presence of emulsifier at different concentrations are presented. In addition, the influence of initiator type and presence of seed particles are studied. The nucleation mechanism is verified by means of on-line monitoring of the optical transmission and the conductivity of the aqueous phase. Results prove that micelles do not alter the nucleation mechanism which comprises the initiation of water soluble oligomers in the aqueous phase followed by their aggregation into colloidally stable latex particles. Surfactants assist with nucleation as they lower the activation free energy of particle formation. Contrary, in the presence of seed particles above a critical volume fraction the formation of new particles can be suppressed.

Keywords: 2,2′-azobisisobutyronitrile; emulsion polymerization; particle nucleation; seeded emulsion polymerization

Introduction

Since several decades understanding of the mechanism of emulsion polymerization has been one of the most challenging issues in heterophase polymerization research. Although emulsion polymerization is widely used commercially and an enormous number of studies has been carried out on various aspects of the polymerization mechanism, there is still a huge uncertainty with respect to an unambiguous experimental proof of the mechanism of important reaction steps.[1] For instance, the mechanism of the formation of latex particles in both the presence and the absence of added surfactants remains a matter of experimental investigations and scientific debate.[2] Several theories have been proposed to account for particle nucleation in emulsion polymerization. First, micellar Nucleation assumes the simple conversion of monomer swollen micelles into particles by the entry and subsequent growth of free radicals in micelles.[3,4] Second, homogeneous nucleation considers the precipitation of a single growing oligomer chain above a critical chain length.[5–7] Third, the coagulative nucleation mechanism assumes the coagulation of small primary particles to stable particles.[8,9] So far it was not possible to get direct experimental proof to support or to refute a particular nucleation mechanism. One of the difficulties on this way is the high rate of nucleation which requires a fast and sensitive method for online investigation. The other complexity is the existence of at least two reaction loci: the continuous phase and the dispersed phase.[10,11] Within this work a comprehensive experimental study of particle nucleation in emulsion polymerization of styrene at 70 °C with ionic and nonionic initiators (hydrophilic and hydrophobic types) has been performed. The initial period of batch ab-initio polymerizations in the absence as well as in

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the presence of surfactants (concentrations above and below the critical micelle concentration) and also in the presence of seed particles has been investigated by means of online conductivity and turbidity measurements. The initial period means polymer content in the range from zero to approximately 1%. Indeed, the experimental results reported here show that the experimental setup allows the monitoring of the onset of particle formation clearly and the differentiation between various nucleation models.

Experimental Part

Styrene (Sigma Aldrich) was purified by standard procedures to remove stabilizers, distilled under vacuum, and stored in the refrigerator until use. Potassium peroxydisulfate (KPS) from Fluka, sodium dodecylsulfate (SDS) ultrapure from Roth and 2,2-azobisisobutyronitrile (AIBN) from Wako were used as received. De-ionized water was taken from a Seral purification system (PURELAB Plus) with a conductivity of 0.06 μS/cm and degassed prior to use for polymerization. Polystyrene seed particles were prepared by batch emulsion polymerization in a 2000 mL all glass reactor, equipped with stirrer, reflux condenser, nitrogen inlet and outlet, heating jacket to control the temperature. The seed latex was produced by polymerizing 24 g of styrene in 2000 g of water containing 8.5 g of a reactive surfactant (APG2019 from Clarient with an allyl reactive group) and 3.2 g of KPS initiator at 70 °C at slow stirrer speed (50 rpm) for 24 hours under N_2 atmosphere. The seed latex was cleaned by ultrafiltration through DIAFLO membranes with a molecular weight cut-off of 10^4 g/mol (type YM 10 from Amicon, Inc., USA) as long as the amount of original water was replaced at least five times. The final seed particles are quite mono disperse with an average diameter of 30.5 nm (measured by analytical ultracentrifuge).

All polymerizations to investigate particle nucleation were carried out at 70 °C in a specially constructed 500 mL all-Teflon reactor equipped with a stirrer working at 70 rpm, probes for on-line measurement of the temperature and conductivity, and two optical windows for an on-line monitoring of optical transmission in the aqueous phase, as described previously.[1,12] The general polymerization procedure is as follows. First, the reactor was filled with 400 g of water containing if necessary the surfactant or the seed particles. Then, monomer was placed on top of the water confined in a glass funnel maintaining a constant monomer-water interface of 31 cm^2 throughout the experiment (the remaining water – air interface is 80 cm^2). The stirrer speed is so slow that the monomer phase is not comminuted but only the water phase mixed thoroughly. At defined times after placing the styrene the polymerizations were started by injection the initiator solution. The amounts of monomer and initiator in the reaction mixture for KPS initiated polymerizations were 3.3 g and 0.0672 g, respectively. For the polymerizations with AIBN 2.8 g of styrene was added to the reactor as the monomer reservoir and 0.9 g was kept to prepare the initiator solution by dissolving 0.076 g of AIBN in that. This solution was then added directly into the aqueous phase. At the end of the polymerizations the monomer phase was separated from the aqueous phase and the polymers formed in the latex phase were characterized regarding their particle size and size distribution. The particle size (D_i, intensity weighted average particle size) was measured using a NICOMP particle sizer (model 370). Additionally, some samples were investigated regarding their morphology by transmission electron microscopy (TEM) with a Zeiss EM 912 Omega microscope operating at 100 kV with sample preparation according to the suspension preparation technique. Nuclear Magnetic Resonance (NMR) studies were carried out on the AIBN-initiated products by dissolving ppm amount of the solid extracted from the latex in $CDCl_3$. The spectra were recorded on a Bruker DPX-400 Spectrometer at 400 MHz.

^1H chemical shifts were referenced to TMS via the residual non-deuterated solvent signal.

Results and Discussions

Nucleation in the Surfactant-Free Emulsion Polymerization

Surfactant-free emulsion polymerization is the simplest system to investigate particle nucleation as it contains only three starting components: water, monomer, and initiator. Moreover, in such systems the possibility of particle nucleation via the micellar nucleation mechanism is virtually precluded.

Surfactant-free emulsion polymerization has inspired continuous scientific interest in heterophase polymerization research for over 30 years. Special interest has been devoted to peculiarities of particle nucleation, in situ stabilizer formation, and polymerization kinetics.[1,2,13–19] The primary free radicals derived from the initiator which are present in the polymer as end groups have to ensure latex stability either electrostatically or sterically. Thus, the application of various types of hydrophilic initiators is straightforward. Surprisingly, it was found that surfactant-free emulsion polymerizations with non-ionic, oil soluble initiators such as AIBN can be carried out. However, the attainable solids content is much lower compared with hydrophilic initiators. Figure 1 shows typical results as obtained for the surfactant-free emulsion polymerization of styrene initiated with AIBN and KPS. Clearly, the general behavior for both types of initiators is identical.

The conductivity rises after injection of the initiators (points *A* of Figure 1). After a particular time, at point *B*, the slope of the conductivity curves changes. This bend in the conductivity curve, indicates appearance of the first particles, i.e., the onset of the nucleation.[1,2,12–14] Thus, the duration *A-B* corresponds to the pre-nucleation period meaning that the reaction takes place under homogeneous conditions in the aqueous phase. The initiator decomposes and generates primary free radicals which subsequently react with water or monomer molecules as discussed for KPS in.[13] As the initiator molecules are surrounded by orders of magnitude more water than styrene molecules the free radicals attack water molecules. These side reactions lead obviously also for AIBN to conducting species and cause the increase in conductivity; reasonably, with a slower rate than that observed for KPS. At point *B*, where particle nucleation sets on, conducting

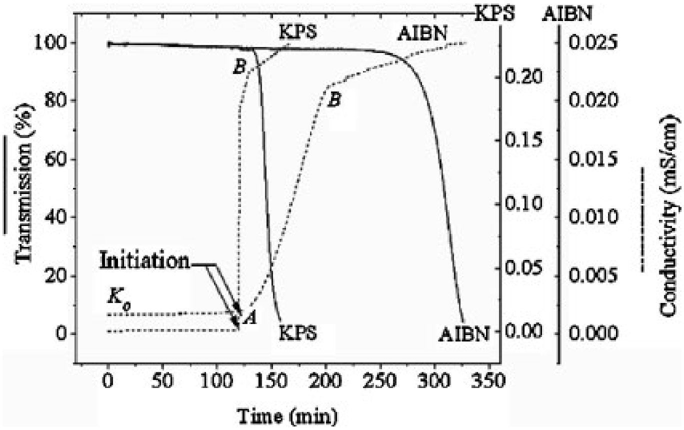

Figure 1.

On-line monitoring of transmission (solid lines) and conductivity (dashed lines) during an ab-initio surfactant-free styrene emulsion polymerization; the polymerizations initiated with KPS and AIBN are indicated on each curve; K_0 is the initial conductivity of water plus styrene.

species are bound due to their charges to the electrical double layer and loose mobility, which causes a decrease in conductivity. This picture of particle formation can be nicely described within the frame of aggregative particle nucleation theory.[1] The fact that the rise in conductivity curve takes place with a much slower slope in the case of AIBN compared with that of KPS can be explained with much lower water solubility of AIBN. Consequently, both a lower concentration of initiating species and a lower concentration of oligomers are present in water at given time. Therefore, the onset of nucleation which is controlled by the concentration of cluster forming species, as well as the decrease in transmission which is determined by the formation of a corresponding number of larger particles are delayed. This different behavior between water and oil soluble initiators is also reflected by the development of the average particle size and particle number with time as shown in Figure 2.

After the bend in the conductivity curves indicating the formation of the heterogeneous reaction system it is possible to follow the growth of the particles. Samples were taken at given turbidity (or transmission) and analyzed with dynamic light scattering regarding the average particle size. Knowing the particle size and the turbidity data it is possible with the table of scattering functions to calculate the number of polymer particles.[1] The results confirm the generation of less but bigger particles after longer reaction times for AIBN compared with KPS as initiator.

It must be mentioned that the use of hydrophobic instead of hydrophilic initiators influences the availability of the monomer in water phase. In fact, the major part of the oil soluble initiator remains in the monomer phase on top of the reaction mixture leading to a rather high amount of bulk polymer. As a consequence, the monomer supply to the water phase is restricted in the course of polymerization as the presence of polymer in the monomer hinders its distribution to the water and the latex particles. This phenomenon is described in more details elsewhere.[12] Detailed analytical studies on the AIBN-initiated polymer show that the final latex particles are electrostatically stabilized. TEM images of the final latex particles are shown in Figure 3. The zeta-potential of these particles is pH-dependent and has a value typically of about -50 ± 10 mV at pH of 7.

The experimental fact that the nonionic AIBN can generate stable latex particles by surfactant-free emulsion polymerization and the high zeta potential of the particles arise the question regarding the origin of the charges. In the NMR spectra of the polymer extracted from the latex besides the polystyrene and the cyanoisopropyl signals additional signals indicating carboxylic or benzoic acid groups can be seen

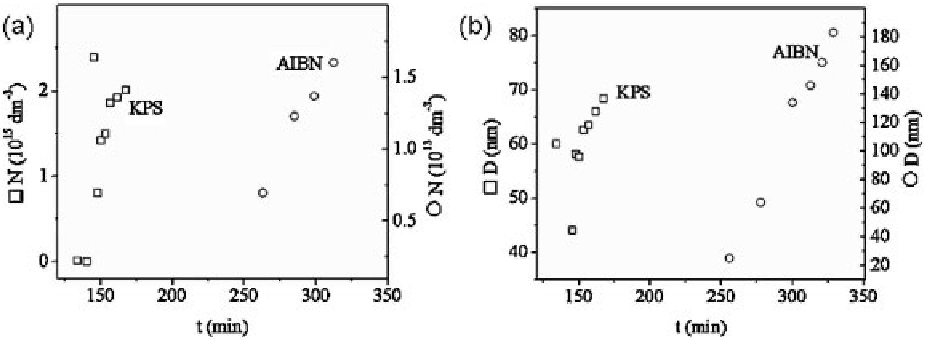

Figure 2.

Comparison of the development of the particle number, N, (a) and the average particle size, D, (b) during the surfactant-free emulsion polymerization of styrene initiated with KPS (squares) and AIBN (circles).

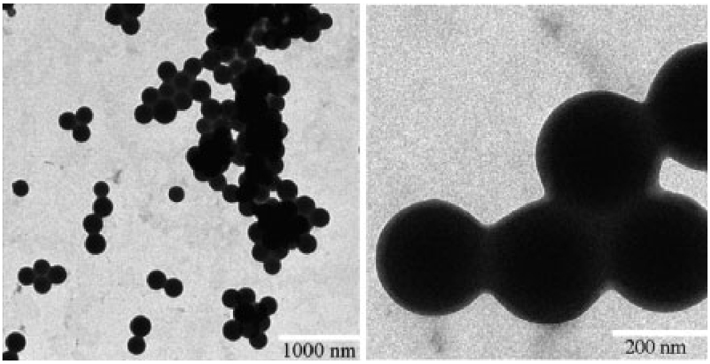

Figure 3.
TEM images of final latex particles obtained by surfactant-free emulsion polymerization of styrene initiated with AIBN.

(Figure 4 and Table 1). Similar observation is reported for the emulsion polymerization of styrene initiated with poly(ethylene glycol)-azo-initiators,[21] where side oxidation reactions of carbon radicals and water molecules is discussed as the origin of these signals.

The formation of conducting species during the AIBN – initiated emulsion polymerization is an experimental fact and a possible reaction path of the cyano-isopropyl radicals with water leading to hydroxyl radicals and subsequently to hydrogen peroxide is shown in Figure 5. Hydroxyl radicals can either initiate the polymerization or recombine to hydrogen peroxide. The ability of the latter to oxidize hydroxyl chain ends of oligomer or polymer molecules to carboxylic groups is well known.[22]

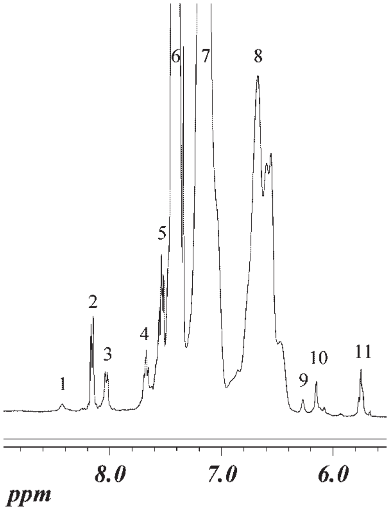

Figure 4.
Part of the 400 MHz ^{1}H-NMR spectrum of the final latex obtained by surfactant-free emulsion polymerization of styrene initiated with AIBN.

The initiation of surfactant-free emulsion polymerization with oil-soluble initiators offers the unique possibility to control the duration of the pre-nucleation period by the interfacial area between the monomer and the water.[12] If the AIBN solution is injected to the monomer phase which is confined in a glass funnel on top of the aqueous phase with an area of 31 cm^2 the interface through which the AIBN can diffuse into the water is reduced by more than a factor of two. Consequently, the duration of the pre-nucleation period is prolonged, the slope of the conductivity decreased, and the transmission starts later to decrease.

Another possibility to influence the duration of the pre-nucleation period is to control the equilibration time of the monomer with water before the initiator addition (cf. Figure 6).

The data of Figure 6 clearly prove the strong influence of the monomer equilibration time on the course of the reaction. Obviously, a longer equilibration time leads to a better availability of the monomer

Table 1.
Chemical shifts in 400 MHz ^{1}H-NMR spectrum of the final latex obtained by surfactant-free emulsion polymerization of styrene initiated with AIBN, numbers correspond to the signals in Figure 4

Peak number	1–4	5	6	7	8	9–11
Polystyrene peaks		$1H_4$ at 7.53	$2H_3$ at 7.44	Solvent peak	$2H_2$ at 7.18	
Functional groups	$C_6H_5COO^-$ COO^- C_6H_5OH					$CONH_2$

during the reaction. The effect is more pronounced during the particle growth period (Figure 6a) that is after particle nucleation. This is reasonable as the behavior during the pre-nucleation period is essentially co-determined by the initiator concentration which is however not changed during these experiments. Nevertheless, the duration of pre-nucleation period reduces from about 85 to about 65 min at 40 and 140 min of monomer equilibration time, respectively. The influence of the reaction kinetics on the duration of the pre-nucleation period can be understood within the frame of the classical nucleation theory which is the base of the aggregative nucleation mechanism.[23,24] Within this framework the rate of nucleation (r_N) is given by Equation (1).

$$r_N = PEF \exp\left(-\frac{\sigma^3 \cdot v^2}{(k_B T)^3 \ln^2 S}\right) \tag{1}$$

In Equation (1) PEF is a pre-exponential factor, σ is the interfacial tension between nucleus and water, v is the molar volume of the nucleating species, $k_B T$ is the thermal energy, and S is the supersaturation defined as the ratio of concentration to solubility of the nucleating species. Nucleation occurs as soon as a critical supersaturation is reached. The higher is the availability of monomer in water the faster the critical supersaturation is reached and hence, the shorter the pre-nucleation period.

Nucleation in the Presence of Surfactants

The experimental data for the surfactant-free emulsion polymerization of styrene, despite whether hydrophilic or hydrophobic initiators were used, can all be explained with the aggregative nucleation mechanism.

Principally, two possibilities exist to start the reaction: either by the addition of the

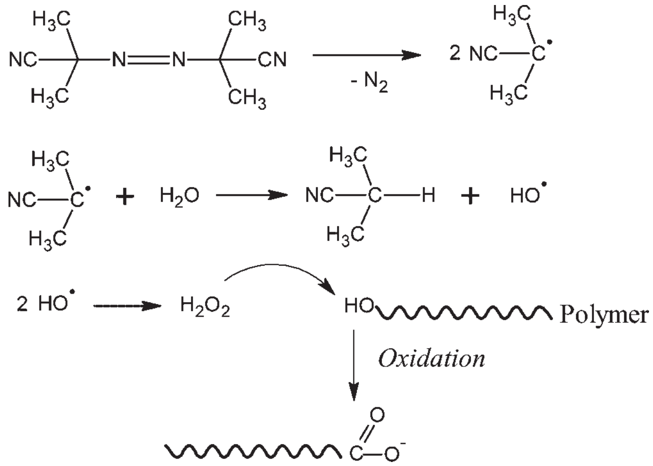

Figure 5.
Possible sequence side oxidation reactions initiated by the reaction of cyanoisopropyl radicals during aqueous emulsion polymerization.

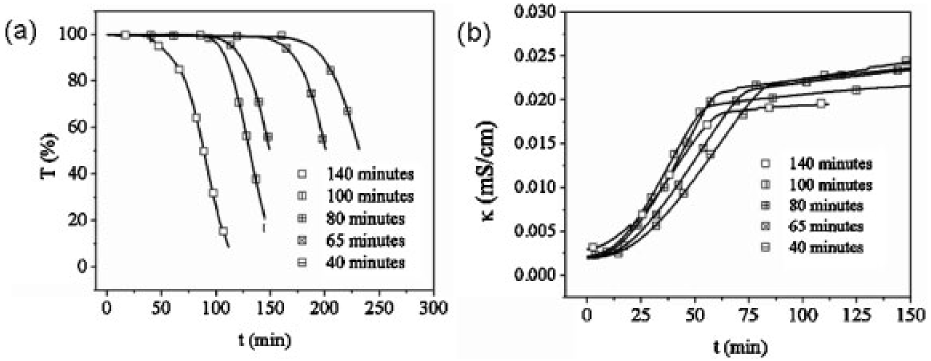

Figure 6.
On-line monitoring of (a) transmission (T) and (b) conductivity (κ) during an ab initio surfactant-free styrene emulsion polymerization initiated with AIBN, different curves correspond to different monomer-water equilibration times; the symbols are just for guiding the eyes.

initiator to a monomer in water emulsion or by the addition of the monomer to an initiator solution. In the presence of surfactant micelles both situations might lead to different results as the former scenario corresponds to the assumption of swollen micelles in which initiator free radicals could enter (cf. data of Figure 7). In the latter situation initiator free radicals and micelles compete for the monomer molecules. The experimental results show for both situations after the pre-nucleation period a bend in the conductivity – time curves thus, these data rule out micellar nucleation. Despite the occurrence of the bend under both conditions the conductivity curves are, compared with the surfactant-free experiments, significantly influenced by the presence of SDS in the reaction system (cf. Figure 8).

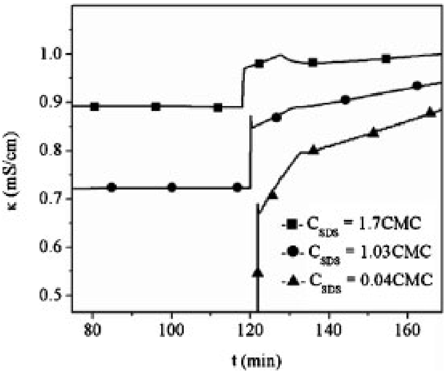

Figure 7.
Change of the conductivity during ab initio styrene emulsion polymerizations of styrene initiated with KPS two hours after monomer addition in the presence of different concentrations of SDS surfactant below and above the critical micelle concentration; the conductivity values are normalized for each plot to the highest value measured; the symbols are just for guiding the eyes.

In general, the decomposition of KPS is strongly influenced by the presence of foreign matter as it is a strong oxidizing agent.[25] Also surfactants such as SDS and polymer particles such as polystyrene influence the decomposition rate; although contradictory results have been published.[26,27] The consequences for the conductivity measurements are enormous as even in the absence of styrene monomer chaotic changes of the conductivity were observed starting after a few minutes and lasting only a few minutes. This period exhibits a tendency to oscillations before again a constant slope is observed. A similar behavior is also found in the presence of monomer as indicated already by the data depicted in Figure 7. For SDS concentrations higher than two times the CMC the conductivity drops after the pre-nucleation period quite sharply before it returns to a linear increase with lower slope. Despite these peculiarities an evaluation of two slopes is possible (again before and after

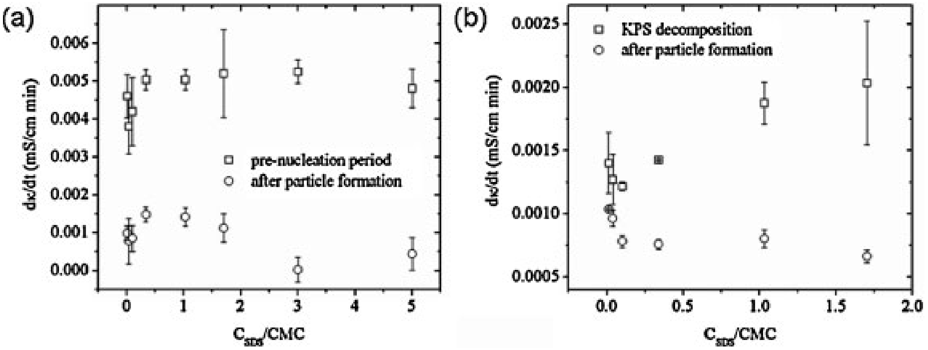

Figure 8.

Dependence of the slopes of the conductivity curves during styrene emulsion polymerizations in the presence of SDS initiated with KPS; (a) polymerizations started by initiator addition 2 hours after monomer addition to the aqueous SDS solution, (b) polymerizations started by the addition of monomer to the aqueous solution containing KPS and SDS; the squares of graph (b) describing the KPS decomposition in the presence of SDS without polymerization.

nucleation) which for the scenario without monomer equilibration means that the first slope corresponds to the KPS decomposition in the absence of monomer.

For the scenario that the reaction is started after 2 hours of monomer equilibration, the slopes before and after the bend are almost independent of the SDS concentration (Figure 8a). Moreover, the slopes before particle nucleation are about a factor of five higher than those after particle nucleation. This is an interesting result as it proves that reactions inside micelles are only of minor importance during the initial period of emulsion polymerizations. If the polymerization is started with the addition of monomer the slopes of the conductivity curves behave differently. The data before the polymerization show that the KPS decomposition is enhanced by the presence of SDS micelles. After particle nucleation the slope is smaller and the difference is the larger the higher the SDS concentration. This is an expected behavior as more conducting species can be bound in the larger interface.

The data obtained in the presence of SDS allow an experimental verification of the influence of surfactants on the nucleation rate or the duration of the pre-nucleation period (t_N) as predicted by different nucleation theories. If surfactants lower the interfacial tension between the nucleating particles and the continuous phase the nucleation rate should be increased according to the classical nucleation theory.[23] Assuming that surfactants lower the interfacial tension r_N should increase that is t_N should decrease. However, for the conditions during emulsion polymerization with KPS as initiator one might expect only a minor influence of SDS as both the nucleating polystyrene oligomers and the surfactant molecules contain hydrophilic sulfate groups. Indeed, the experimental data put together in Figure 9 reveal only a week influence of the SDS concentration on t_N. The difference between surfactant-free polymerization ($t_N = 10.5 \pm 1$ min) and the highest SDS concentration at 5 times the CMC is only 20% ($t_N = 8.2 \pm 1$ min) and

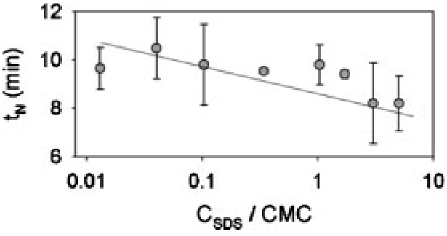

Figure 9.

Dependence of the duration of pre-nucleation period (t_N) on the SDS concentration during styrene emulsion polymerizations initiated with KPS.

not really significant due to the inherent scatter of any nucleation experiment.[23]

The experimental nucleation data for styrene emulsions polymerization in the presence of SDS covering a huge concentration range below and above the CMC give no hints that micelles are somehow involved in the particle nucleation process.

Nucleation in the Presence of Seed Particles

Seeded emulsion polymerizations are an important procedure to carry out emulsion polymerizations in industry.[28] One important reason for the application of seeded instead of ab-initio emulsion polymerizations in industrial scale is the possibility to avoid the uncertainties connected with the particle nucleation. Therefore, it is mandatory to check the conductivity method to study particle nucleation for seeded polymerizations where above a critical volume fraction of seed particles the nucleation of new particles is suppressed. Under such conditions no bend in the conductivity time curve should be observed. Also with seed particle the two possibilities to start the polymerization must be studied as both conditions are of practical importance. Starting the polymerization by initiator addition after monomer equilibration means that the seed particles are swollen with the monomer and the aqueous phase is saturated. This situation is useful for the production of composite latex particles. Contrary, the other scenario where the polymerization starts with the addition of monomer and the seed particle remain unswollen allows the formation of core - shell particles.

Happily, the data put together in Figure 10 prove the applicability of conductivity measurements as depending on the volume fraction of seed particles either a bend in the conductivity curve is observed or not.

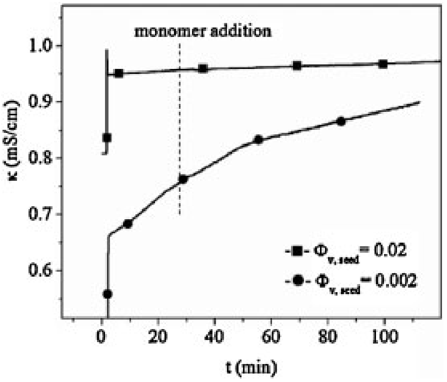

Figure 10.
Conductivity – time curves recorded during the initial period of seeded emulsion polymerizations of styrene with KPS at two different volume fractions of polystyrene seed particles ($\Phi_{v,seed}$) as indicated in the graph; the polymerization was started with monomer addition; the conductivity values are normalized for each plot to the highest value measured; the filled squares and circles are just for guiding the eyes.

Expectedly, at higher seed volume fractions (upper curve of Figure 10) no bend in the conductivity time is observed. Also for the other scenario where the polymerization is started by KPS addition after equilibration of the seed latex with the monomer no bend towards a lower slope in the conductivity – time curve is found for seed volume fractions above 2% (data not shown).

Conclusions

On-line conductivity measurements are a valuable tool to investigate particle nucleation during the initial state of ab-initio emulsion polymerizations. This technique allows clearly to detect the onset of particle nucleation and to find experimental conditions where it is suppressed. The experimental data presented here rule out the micellar nucleation mechanism as no hints have been found that even at SDS concentration 5 times higher than the CMC the micelles are the locus of particle nucleation.

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