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Kinetics of Miniemulsion Polymerization As Revealed by Calorimetry

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ABSTRACT: The kinetic behavior of styrene miniemulsions with a hydrophilic initiator was investigated by calorimetry, focusing on the studies of parameters such as (a) the amount of surfactant and (b) the quantity of the initiator. Their influence on the net reaction time of polymerization and on the nucleation mechanism in comparison to other heterophase polymerization types is discussed. The course of miniemulsion polymerization kinetics is characterized by three distinguishable intervals. The first two intervals can be defined by the average number of radicals per particle, $\bar{n}$: during the first interval, $\bar{n}$ increases until a plateau value of 0.5 is reached at the onset of the second interval. The beginning of the last interval is defined by a sharp increase of $\bar{n}$. Because of the nature of the first interval, all miniemulsion droplets are nucleated within this interval at a specific time, and therefore the individual conversion in each droplet has reached a different level. Every miniemulsion droplet can be perceived as a separate nanoreactor which does not interact with the others. Independent of the amount of initiator as well as the particle size, i.e., the number of active sites in the system, the limit value of $\bar{n}$ during the second interval remains 0.5. Therefore, the net polymerization time strongly decreases with decreasing particle size.

Introduction

Miniemulsions are classically defined as aqueous dispersions of relatively stable oil droplets within a size range of 50−500 nm[1] prepared by shearing a system containing oil, water, a surfactant, and a hydrophobe. Polymerization in carefully prepared miniemulsions results in latex particles which have about the same size as the initial droplets, as recently shown by a combination of small-angle neutron scattering (SANS), surface tension measurements, and conductometry.[2] Steady-state miniemulsification results in a system with “critical stability”; i.e., the final droplet size is caused by a rate equation of fission by ultrasound and fusion by collisions of the droplets. The droplet size in the steady state depends on the type and the amount of surfactant which is added prior to miniemulsification.[3] The use of different kinds of surfactants enables the synthesis of anionic and cationic charged and nonionic particles of various sizes.[4] The appropriate formulation of a miniemulsion suppresses coalescence of droplets and Ostwald ripening by using a hydrophobe, and a nearly 1:1 copy of the droplets to the particles can be achieved. This paper deals with the kinetics in such miniemulsions started with a hydrophilic initiator. It focuses on calorimetric studies of miniemulsions with the objective to study parameters influencing the reaction time of the polymerization such as (a) the amount of surfactant and (b) the quantity of the initiator and to further enlighten the nucleation mechanism in contrast to other heterophase polymerization types.

In principle, for heterophase polymerizations three particle nucleation mechanisms are currently discussed in the literature: micellar nucleation, homogeneous nucleation, and droplet nucleation. These mechanisms are summarized in Figure 1.

To get an insight into the polymerization mechanism of miniemulsion polymerization, several studies have focused on the particle size development during the polymerization and its dependence on the initiator amount.[5] Generally, it can be stated that droplet nucleation is the predominant nucleation mechanism when the nucleation efficiency is independent of the initiator concentration.[6] In this case the overall reaction rate in miniemulsions should only be influenced by the number of droplets, e.g., their size.

The droplet nucleation mechanism (C in Figure 1) suggests that the droplets formed during the emulsification step are polymerized directly via a radical which enters these monomer droplets and reacts with the monomer present there. Monomer diffusion to the reaction sites can be neglected in the case of a batch styrene miniemulsion polymerization since there is already sufficient monomer present at the reaction site. For an ideal miniemulsion system, droplet nucleation is the preferred mechanism, and thus every single droplet is nucleated; the particle number does not change during the polymerization. This mechanism also explains the successful usage of oil-soluble initiators in miniemulsion polymerization.[4]

The homogeneous nucleation is a second possible mechanism for miniemulsion polymerization (B in Figure 1); its importance for the so-called surfactant-free emulsion polymerization was recently delineated.[7] In this case, the latex seeds are created from oligomers in the water phase, and the monomer is brought to the nucleation site by diffusion. Usually, this mechanism is sensitive to the overall initiator concentration and depends on the solubility of the employed monomer. It is discussed to be of minor significance in styrene miniemulsions, too. It is an agreed upon fact that the nucleation of the particles mainly starts in the monomer droplets themselves, but the relative importance of homogeneous nucleation is less clear: Choi et al.[8] described that only 20% of the droplets are nucleated, whereas Reimers and Schork[9] reported a droplet nucleation of 95%. The seemingly marginal difference toward

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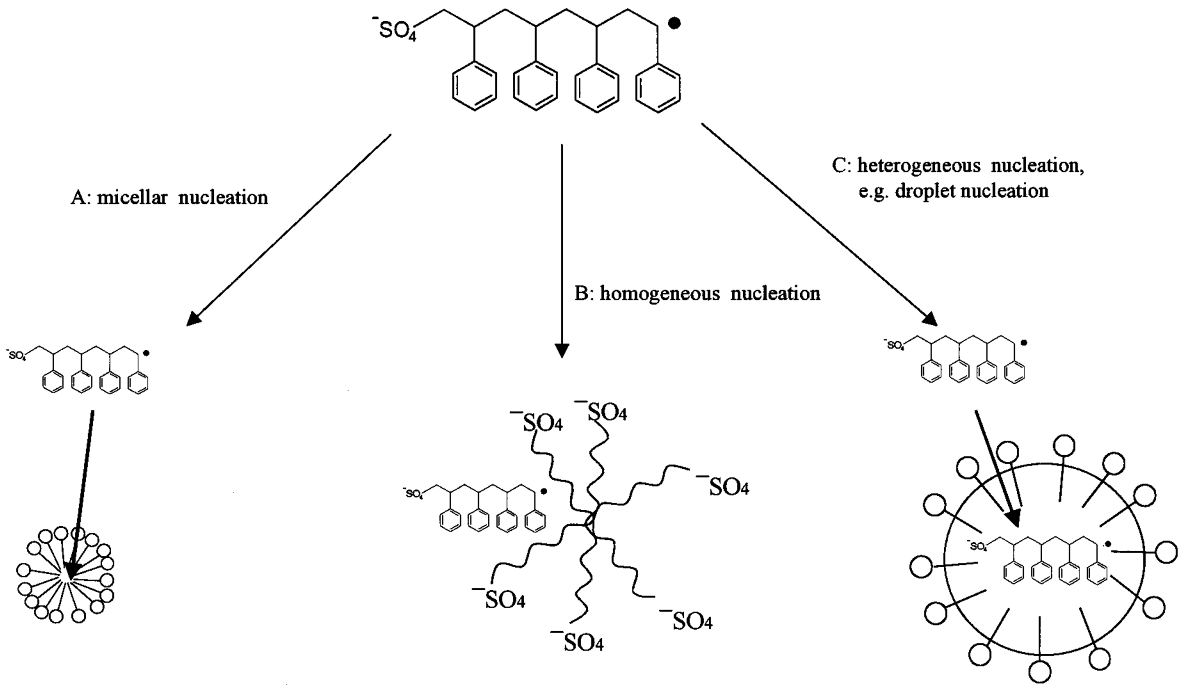

Figure 1. Schematic diagram of nucleation mechanisms.

complete droplet nucleation would be disturbing the interesting properties miniemulsion latexes are renown for due to the different sizes and compositions of these secondary homogeneously nucleated particles.

The micellar nucleation mechanism is very unlikely for miniemulsion polymerizations. In the micellar nucleation mechanism (A in Figure 1) the radical enters a micelle, which is swollen with monomer, and reacts with the monomer to form a polymer chain. Further monomer diffuses from other monomer-swollen micelles which serve as monomer reservoirs. This mechanism seems to be typical for microemulsion polymerizations started from the continuous phase. Because of its nature, it can only occur above the critical micelle concentration of the applied surfactant and results in a broad particle size distribution. However, surface tensions of miniemulsions are mostly well above saturated surfactant solutions;[3] i.e., there are no micelles present.

Experimental Section

Synthesis of the Latexes. An 18 g sample of styrene and the hydrophobe (750 mg or 3.3 mmol of hexadecane unless stated otherwise) were mixed and added to a solution of different amounts of sodium dodecyl sulfate (SDS) in water (72 g). After stirring for 1 h, emulsification was achieved by ultrasonicating the mixture for a distinct time until the steady state was reached, typically 600 s, at 90% amplitude with a Branson sonifier W450 Digital. To avoid polymerization due to heating, the mixture was ice-cooled during homogenization. To start the polymerization, the temperature was increased to 72 °C, and 120 mg of potassium persulfate (KPS) was added unless stated otherwise. For the samples with preadded polymer, 360 mg (2 wt %) of anionically synthesized polystyrene ($M_w = 244\ 500$ g mol^{-1}) were dissolved in the monomer phase.

Analytical Methods. The calorimetric measurements were carried out in a reaction calorimeter RM2-S from ChemiSens (Lund, Sweden) with a volume of 100 mL equipped with a stainless steel stirrer and a heating device through the reaction bottom. For the determination of the net reaction time the end of the reaction was defined to be when 95% of the conversion was reached, and the heat flow was back to a value of roughly zero.

The calorimeter measures directly the heat of reaction which can be transformed into the rate of polymerization via the following formula:

$$R_P = \frac{Q_r}{V_{aq}\Delta H_P} \tag{1}$$

The heat of polymerization R_P is the quotient of the heat of reaction Q_r and the volume of the aqueous phase V_{aq} with the molecular heat of polymerization ΔH_P, which for styrene is 73 kJ mol^{-1}.[10] The fractional conversion can be obtained by integrating the reaction heat curve.

Another important parameter when discussing calorimetric data is $\bar{n}$, which denotes the average number of radicals per particle. For the evaluation of $\bar{n}$ the number of particles per liter of aqueous phase (N_P) needs to be known. Taking a nearly 1:1 copying process of the miniemulsion droplets to the final latex as a prerequisite, N_P can be calculated from the final latex size obtained by dynamic light scattering and is assumed to be constant throughout the polymerization. The monomer concentration in the particles $[M]_P$ can be calculated as follows:

$$[M]_P = \frac{\dfrac{1-x}{M_0}}{\dfrac{(1-x)}{\rho_M} + \dfrac{x}{\rho_P}} \tag{2}$$

x is the fractional conversion obtained by integrating the heat flow curve which is directly measured with the calorimeter, M_0 is the molar mass of the monomer, ρ_M is the density of the monomer, and ρ_P is the density of the corresponding polymer.

After having determined all these parameters, $\bar{n}$ can then be determined by

$$\bar{n} = \frac{N_A R_P}{k_p[M]_P N_P} \tag{3}$$

with N_A being Avogadro's number.

The samples drawn during the polymerization process were prepared by diluting 1 mL of the forming latex in 30 mL of a 0.1 wt % solution of SDS and subsequent removal of the remaining monomer by distillation.[11]

The particle size analysis was conducted using a Nicomp particle sizer (model 370, PSS Santa Barbara, USA) at a fixed scattering angle of 90°.

The polymer molecular weights were determined by GPC analysis performed on a P1000 pump with UV1000 detector ($\lambda = 260$ nm) (both from Thermo Separation Products) with 5 μm 8 × 300 mm SDV columns with 10^6, 10^5, and 10^3 Å from Polymer Standard Service in THF with a flow rate of 1 mL min^{-1} at 30 °C. The molecular weights were calculated with a calibration relative to PS standards.

For the TEM micrographs the samples were diluted and mounted on copper grids, which were coated with carbon. These grids where then examined in an EM 902 (Zeiss, Germany).

Results

A Characteristic Calorimetric Curve of a Miniemulsion. To be able to discuss a typical calorimetric curve for a miniemulsion polymerization and to compare this within the framework of other techniques of heterophase polymerizations, a short overview of the reaction mechanism of the classical emulsion polymerization is given. Harkins[12] depicted three major intervals which play an integral part in the reaction course of a classical emulsion polymerization.

The initiator is dissolved in water, and therefore the formation of free primary radicals takes place in the water phase. Because of the ratio of micelles to monomer droplets of about 10^8 to 1 present in the system, the probability that these radicals enter micelles is far greater than radical entry into the monomer droplets. This first interval is named the particle nucleation interval (interval I). As soon as the entire surfactant is adsorbed on the growing latex particles, the second interval begins (interval II) in which the existing particles grow through reacting with monomer which diffuses into them from the monomer droplets. These monomer droplets act as reservoirs, and the overall reaction speed is constant because it is governed by the diffusivity of the monomer. When the monomer is consumed, the reaction speed decreases exponentially (interval III); sometimes a gel effect ("Trommsdorff–Norrish effect") can be observed due to the higher viscosity of the polymer latices swollen with monomer (interval IV, optional).

The characteristics of a calorimetric curve for a (macro)emulsion polymerization are a maximum of the reaction rate ($v_{\max}$), which is observed between 30 and 50% of conversion, and a gel peak.

A very similar mechanism is assumed for the microemulsion polymerization. Here, the second interval is missing due to the fact that the surfactant concentration in these systems is so high that there are no monomer droplets but only monomer-swollen micelles or microdroplets. Only some of these are nucleated during interval I, while the others are depleted of the monomer contained inside them during interval I. Then interval III directly follows where the reaction speed abates continually since there is no further monomer which can diffuse to the reaction loci. Usually, no Trommsdorff–Norrish effect is observed in microemulsions since the droplets are too small.

Typical for the reaction profiles of polymerizable microemulsions is that interval II is missing, there is no gel peak, and $v_{\max}$ lies at about 39% conversion.[13]

In Figure 2, the calorimetric curve of a typical miniemulsion polymerization with styrene is shown. The reaction course can be divided into three different intervals, which were assigned corresponding to those for the macroemulsion system[12] to indicate similarities and differences. Similarly to microemulsions, there is no interval II of constant reaction rate. This points already to one of the big differences to emulsion polymerization as the diffusion of monomer does not contribute to the rate-determining step.

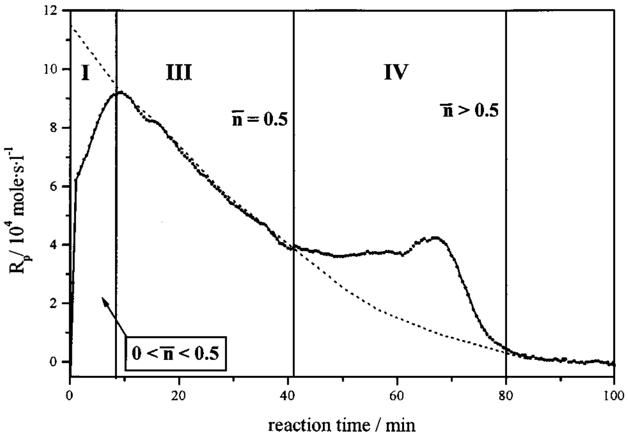

Figure 2. Calorimetric curve of a typical miniemulsion.

The first interval is the particle nucleation interval (interval I), but as compared to emulsion and microemulsion polymerization, this interval is shorter in miniemulsion polymerization and ends at the reaction rate maximum $v_{\max}$ of about 20% conversion. In the present case particle nucleation denotes the time interval needed to reach an equilibrium radical concentration within every droplet formed during emulsification.

The starting interval lasts for about 8 min and could not be observed if the persulfate radicals would be able to enter directly into the oil droplets. One possible reason for the very slow radical entry is the electrostatic repulsion between the negatively charged surfactant, SDS, and the likewise negatively charged radical. Another explanation is that the highly hydrophilic radical with its shell of water molecules cannot penetrate into the hydrophobic oil droplet. Comparable experiments with cationic and nonionic initiators show that the second reason is of more importance. Obviously, a radical can only penetrate into the droplet after the sulfate radical has reacted with a few monomer molecules solubilized in the water phase. Because of the very low concentration of monomer in water, this process inevitably takes some minutes.[7] It will be shown below that the duration of interval I does not denote the average time of radical entry, but a related time during which the average radical number per particle of $\bar{n} \approx 0.5$ is established.

During interval III the kinetics follow those of a bulk or a suspension polymerization (dotted line in Figure 2). As is constituted by the droplet nucleation mechanism, only the monomer in the droplet is available for polymerization, and this is exponentially depleted from the reaction site. It will be shown below that the average number of radicals per particle, $\bar{n}$, during interval III is quite accurately kept at 0.5, implying that the on/off mechanism upon entry of additional radicals into such small latex particles is strictly valid.

Interval IV then boosts the typical gel peak which is due to the viscosity increase inside the particles. The steep rise of $\bar{n}$ during this interval is due to the kinetic hindrance of recombination.

Evolution of the Sample during Polymerization. A close examination of the characteristics of a typical

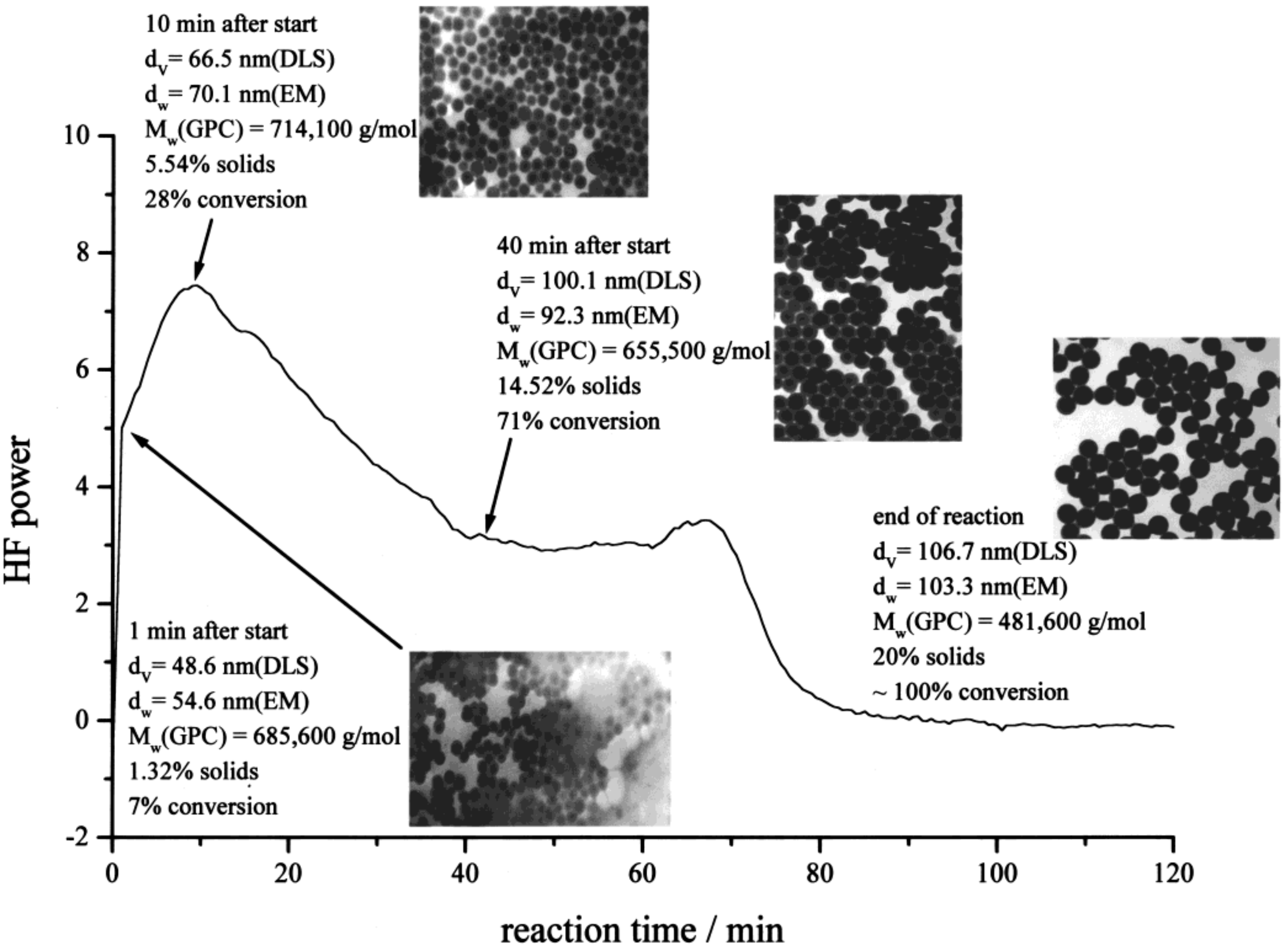

Figure 3. Polymerization curve and conversion in dependence of the reaction time.

miniemulsion polymerization is presented in the following section. During the course of the miniemulsion reaction started from the water phase, whose calorimetric curve is shown in Figure 3, samples were drawn and analyzed with regard to particle size (studied by DLS and transmission electron microscopy) and molecular weight. The monomer was converted within an experimental error to 100% to form a latex with a solid content of 20 wt %.

It is noted that the unreacted monomer is removed from the latex by the method of El-Aasser;[11] i.e., the shown particles do not represent the monomer swollen state found in the original miniemulsion, but the polymer-only part. Comparison of this particle diameter determined via electron microscopy (insets in Figure 3) with the corresponding conversion (obtained by gravimetry) at different times throughout the reaction course reveals a good agreement with the calculated particle size from the calorimetric conversion: e.g., a particle diameter of 92.2 nm at 71% conversion is calculated, and 92.3 nm was experimentally determined. At 28% conversion, the experimental value of 70.1 nm compares with a calculated value of 67.6 nm. The agreement at 7% conversion is less accurate, because the experimental value lies at 54.6 nm whereas the simple conversion leads to an expected value of 42.6 nm. In addition to that, the particle size distribution is also broader with a decreasing degree of conversion as can be depicted from the electron micrographs in Figure 3. At 1 min, the standard deviation is 0.144 and decreases from 0.136 at 10 min to 0.07 at the end of the polymerization. The standard deviation of the final latex is as low as 0.056. The good agreement of experimental and calculated particle sizes at higher conversions again underlines the fact that each droplet acts as a separate nanoreactor and that the particle number throughout the reaction course is constant. The increasing standard deviation at smaller conversions and the increasing deviations in particle size is related to the relatively slow onset of nucleation already seen in the heat flow curve: at 7% conversion, the amount of formed polymer in each droplet is different, and there are presumably even a few droplets that have not been nucleated at all. Therefore, the structural data shown as insets in Figure 3 conform with the calorimetric curve and the assorted kinetic scenario.

The molecular weights as determined by GPC are found to be rather high and almost constant throughout the intervals I and III, while later on the molecular weight increases. At the end of the polymerization, the molecular weight is decreased. This is due to the fact that the molecular weights obtained are only the cumulative ones rather than the instantaneous ones so that no deduction can be made as to whether during the gel peak interval (interval IV) there are chains with a higher molecular weight.

While discussing Figure 3, the average radical number per particle $\bar{n}$, which is calculated from the heat flow and eq 3, was introduced, which is usually plotted against conversion. For the reaction shown in Figure

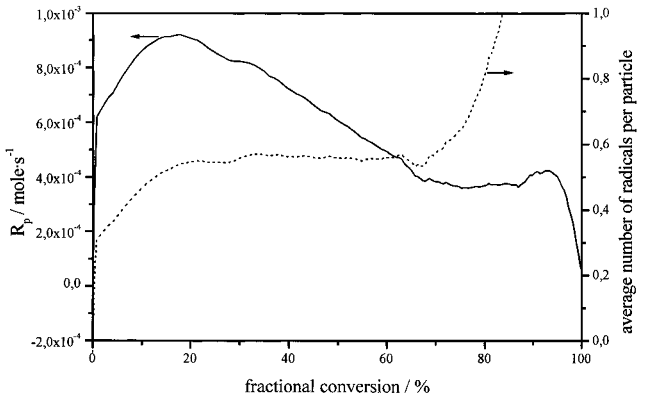

Figure 4. Development of the average number of radicals per particles through the course of reaction.

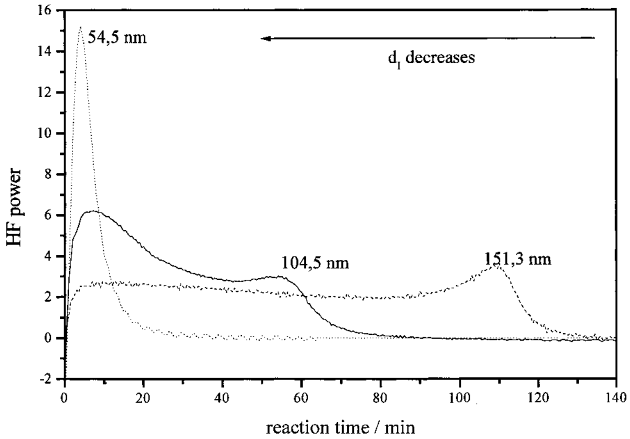

Figure 5. Calorimeter curves of miniemulsions with different surfactant amounts, e.g., particle sizes but all started with same amount of KPS (0.4 mmol).

3, this is done in Figure 4. During interval I which ranges up to 15% conversion, $\bar{n}$ rises quite rapidly from 0 to 0.5, while throughout interval III it stays constant at about 0.5 until 70% conversion. The sharp rise in reaction rate at the gel peak beyond 70% conversion is manifested in a strong increase of radical numbers since during this interval a quick termination of the radicals in the particles is no longer possible due to the high viscosity (interval IV).

Since the value for $\bar{n}$ lies slightly above 0.5, Smith–Ewart case 3 kinetics is observed.[14] Smith and Ewart stated that such kinetics can be compared to an oil phase type of polymerization in suspended particles, e.g., a bulk polymerization, which are supplied with free radicals from the water phase. This statement clearly describes our miniemulsion started with a water-soluble initiator.

Influence of the Particle Size on the Polymerization Rate. After the kinetic analysis of one particular latex, a number of other experimental features, such as the influence of the particle size on the polymerization rate, are discussed. In miniemulsions, the droplet size is easily varied by variation of the amount of surfactant, in this case from 0.075 to 15.7 mmol of SDS. The amount of initiator to start the polymerization was kept constant (0.4 mmol of KPS). Depending on the droplet size of the miniemulsions, calorimetric curves with various kinetic features are obtained (Figure 5).

The reactions can directly be compared, since the same amount of monomer was used, which ensures that the total reaction heat is always the same. It is clearly seen that the calorimetric curves are quite different. In all three cases, interval I has a similar duration and takes about 5 min. This clearly underlines that the kinetics of interval I are determined by processes in the continuous aqueous phase which do not depend on the droplet size.

Table 1. $\bar{n}$ and $N_{\text{chains/particle}}$ for Different Diameters

sample no.	initiator	d_l/nm	$\bar{n}_{av}$[a]	$\bar{n}_{max}$	$N_{\text{chains/particle}}$
NBKL8	KPS	55	0.35	0.44	30
NBKL16.5	KPS	105	0.43	1.1	460
NBKL16	KPS	151	0.5	4.9	2156

[a] $\bar{n}_{av}$ at 20%.

The maximum reaction speed however shows a strong particle size dependence and is proportional to the particle number; i.e., the smaller the particles, the faster is the reaction. It is underlined that polystyrene latexes can be polymerized as fast as within 20 min, as long as the particle size is small enough. This is much faster than any comparable emulsion polymerization reaction and related to the simplicity of miniemulsion kinetics.

The gel peak is not observed for the smallest particles (54 nm) and becomes more pronounced for the larger particles. In addition, its onset also depends on particle size (at 45% conversion for a 150 nm latex and at 60% for a 105 nm latex). Both intensity and onset show that the gel effect is a bulk effect and not found close to the particle interface where the radical flux is still in equilibrium.

The molecular weights of the polymer chains constituting these latexes synthesized with the same amount of initiator all lie in a very narrow range around 500 000 g mol^{-1}. This conforms with the expected behavior. These data are summarized in Table 1.

A calculation of the average number of radicals in each droplet in interval III results in values between 0.35 and 0.55. Even though the particle number of the latexes increased drastically, the number of radicals per particle is about constant, which underlines the on/off mechanism being valid throughout the radical flow. The minor deviations from the $\bar{n} = 0.5$ behavior for the smaller particles are presumably due to statistics: the calculated average number of chains per particle decreases significantly from 2156 to 30 for the large (150 nm) and the small droplet size (54 nm), respectively (Table 1); i.e., after the equilibrium is reached the small particles experience just a few on/off cycles, making secondary effects (such as termination by impurities) more important. It is worth noting that, within 20 min of overall reaction time (54 nm latexes), just about 60 radicals have crossed the particle interface. The effective radical flow is comparably low; just a fraction of the radicals created by initiator decomposition ends up in the hydrophobic particles which is analyzed below.

Generally it can be stated that the miniemulsions with small particles show a reaction profile associated mainly with microemulsions whereas the miniemulsions with large droplets display a gel peak more common for macroemulsions. For intermediate particle sizes the two reaction types merge. Again, the particle size dependence indicates that droplet nucleation is the predominant mechanism. An additional argument for that was given by Schork et al.,[15] who stated that for continuous polymerizations the absence of oscillations in the conversion curve is an indication for the dominance of droplet nucleation.

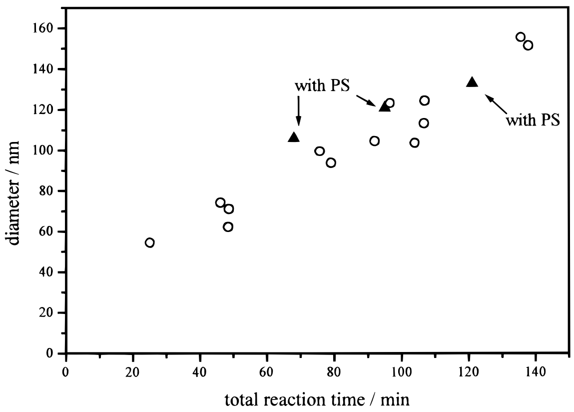

Figure 6. Dependence of the total reaction time on the diameter of the resulting latexes, all started from the water phase with 0.4 mmol of KPS.

For practical reasons, a net reaction time (reaction exceeds 95% conversion) is defined and plotted against particle size. This is done for a whole set of calorimetric data of various miniemulsions described in this paper with varying amounts of SDS as surfactant and varying hydrophobes (Figure 6).

Disregarding the complexity of the kinetics and the existence of the three intervals, the reaction time averages out to depend about linearly on the particle size and thus varies between 20 and 120 min. Contrary to previous reports on miniemulsion kinetics,[16] we found that the addition of 2 wt % of polystyrene to the reaction mixture does not have a pronounced (accelerating) effect. The corresponding data fit into a linear relationship, suggesting that the addition of polystyrene has only a minor influence, which was however expected for the scenario of droplet nucleation.

Influence of the Initiator Amount on the Reaction Time. In the next set of experiments, the particle size was kept constant while changing the amount of initiator. This is easily accomplished since in the miniemulsion process the particle size does not depend on the initiator amount (as is the case for macroemulsions).

In Figure 7, a set of calorimetric curves is displayed, all of which have a similar particle size of about 120 nm, whereas the amount of initiator was varied over a factor of 6 (numeric data are also summarized in Table 2).

The comparison of reaction courses for miniemulsions with varying initiator concentrations (Figure 7a,b) reveals that the reactions are surprisingly similar.

The particle nucleation interval, interval I, depends just slightly on initiator concentration and requires a longer time interval when less initiator is present. In the case of the lowest concentration, it takes about 20 min to reach the radical equilibrium, whereas for all other reactions, there seems to be a threshold below which interval I cannot be further shortened. This is speculatively attributed to the fact that the radicals need to oligomerize before they can pass through the droplet interface. Therefore, it is not the overall radical production but the equilibrium concentration of monomer dissolved in the aqueous phase which determines the length of interval I confirming all quantitative observations made above.

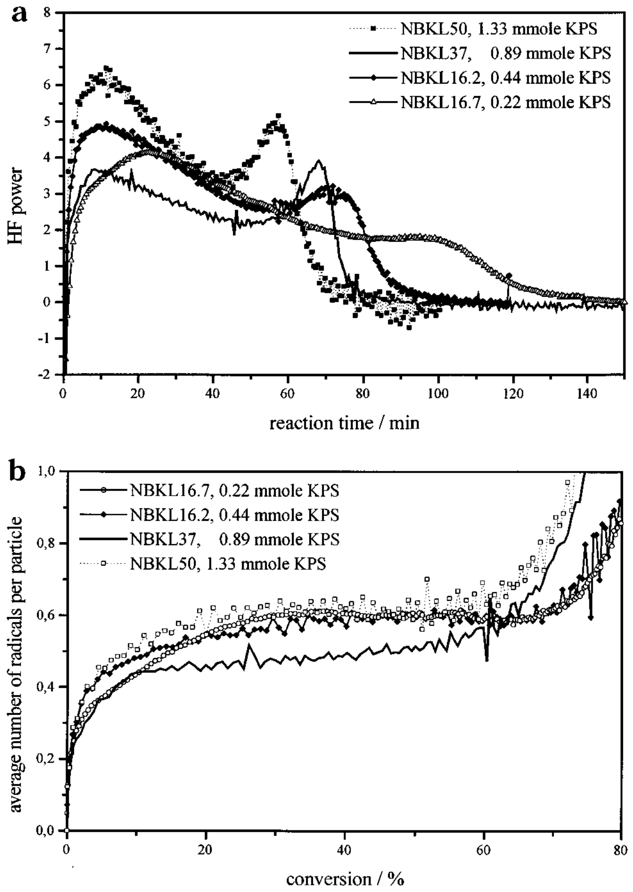

Figure 7. (a) Reaction curves depending on the initiator concentration. (b) Comparison of the average number of radicals per particle in dependence of the initiator amount.

Table 2. Kinetic Parameters for Different Amounts of Initiator

sample no.	initiator	initiator amount/mmol	d_1/ nm	PSD/σ	R_t/ min	M_w/ g mol^{-1}
NBKL50	KPS	1.33	123	0.099	90	295 400
NBKL37	KPS	0.89	126	0.403	95	338 900
NBKL16.2	KPS	0.44	124	0.082	107	572 000
NBKL16.7	KPS	0.22	125	0.115	145	795 100

Once all the droplets are nucleated, the monomer inside these droplets is steadily consumed (interval III). This mechanism is obviously unaffected by the amount of initiator added, meaning that the heat flow in interval III is equal in all four cases of Figure 7. The average numbers of radicals per particle all have values of about 0.5 (see also Table 2), so that it is not the overall reaction rate which is affected but rather the frequency of the on/off process.

The main difference in the four reaction curves however is the onset of the gel peak which shifts to shorter overall reaction times or lower conversions with increasing initiator concentrations; this also results in a reduction of the overall net reaction time needed for complete conversion. Except for the lowest initiator concentration, this change of the net rate however is low and just results in a difference between 70 and 90 min. An earlier onset of the gel effect with an increasing radical flux is consistent with the concept of a sterically hindered termination of radicals. That is, the more radicals can enter, the faster the chains have to find each other and the earlier the viscous hindrance becomes important.

Increasing the initiator concentration causes only a slight increase in the reaction rate but has to result in a reduction of the degree of polymerization, which should directly depend on the frequency of the on/off

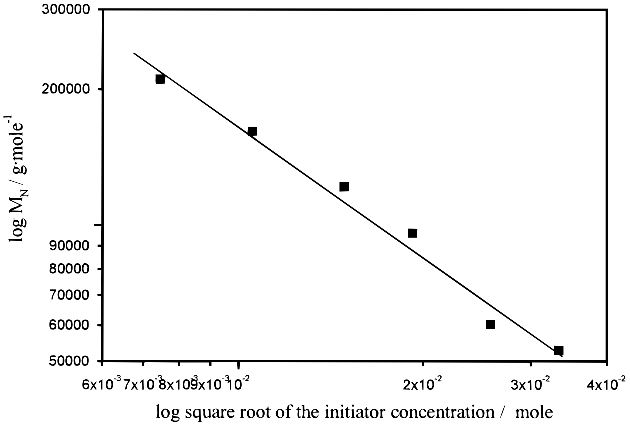

Figure 8. Dependence of the molecular weight on the amount of initiator.

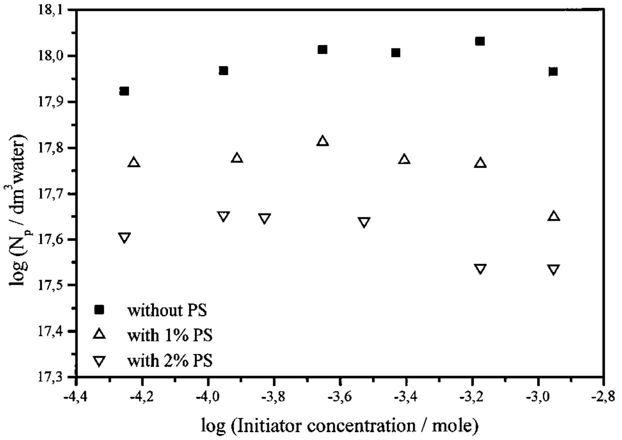

Figure 9. Effect of the KPS concentration on the particle number.

cycles. For those reasons, all four latexes were characterized with respect to the molecular weight of their constituting polymer chains in dependence of the initiator amount added to start the reaction.

Figure 8 shows the resulting data in dependence on the initiator concentration: it is found that the chain length of the resulting polymer is inversely proportional to the square root of the initiator amount. The points form a straight line and fulfill the theoretical expectations very accurately (Figure 8). This also means that the reaction in a miniemulsion is rather direct and an ideal radical polymerization.

Because of this ideality, the percentage of initiator radicals that actually started a polymer chain can be calculated from the overall initiator concentration, the net reaction time, the molecular weight, and the number of polystyrene chains. Assuming that the half-life time of KPS under reaction conditions is 230 min (determined by potentiometry in pure water), it is found that, independent of the total initiator concentration available to the system, about 15% of initiator radicals lead to the formation of a polymer chain.

Another important piece of information about the reaction scenario is obtained by plotting the resulting latex size against initiator concentration. It is seen in Figure 9 that the amount of initiator used for polymerizing the latex does not have an effect on the number of nucleated droplets. The slight deviations in the particle number for the system are only due to minor particle size variations for the different latexes. This fact in addition with the very low polydispersity of all latexes (which is below 10% Gaussian width) shows that droplet nucleation is by far the dominant mechanism over the whole range of initiator concentrations. This is not necessarily the case, since an increased initiator concentration also results in an increased probability for homogeneous nucleation, but the kinetics of miniemulsions are obviously even stable against high initiator concentrations. Still higher initiator concentrations are not accessible with the KPS system, since as a salt it also contributes to the ionic background and influences the colloidal stability in a negative fashion, which is not related to kinetic effects.

The addition of polystyrene to our system has only a slightly negative effect on the particle number, but the number of particles also does not change in dependence of the amount of initiator (Figure 9). This is in good agreement with the kinetic scenario which is not affected by the nature of the hydrophobe, but it is in contradiction to observations found in the literature.[5] This further sustains the concept of a miniemulsion polymerization ideally being a 1:1 copy process from the droplet to the final latex particle.

Influence of the Hydrophobe on the Kinetic Behavior. The nature of the hydrophobe was not expected to have an influence on the kinetic behavior of miniemulsions since its sole purpose lies in the suppression of the Ostwald ripening of the miniemulsion droplets. The most efficient hydrophobes are very water-insoluble, surface-inactive reagents.[3] In this context other characteristics such as the exact chemical nature or the molecular weight of the hydrophobe have no influence whatsoever. Polymeric additives such as polystyrene[9] can be used as well as a wide variety of other substances.

Looking more closely at the calorimetric results obtained for the same recipe synthesized with and without the addition of polystyrene (PS) prior to emulsification, however, it becomes obvious that the two reactions differ from each other, although their obvious characteristics such as particle size, particle size distribution, and net reaction time are very similar (Figure 10a,b).

The latex without PS starts off very quickly and has a gel peak toward the end of the reaction whereas the one with 2 wt % PS begins rather slowly, reaches its maximum heat flow near the middle of the reaction, and shows no pronounced gel peak. Transferred to the concept of average radical numbers, the sample without polystyrene reaches its equilibrium $\bar{n}$ of 0.5 already after 20% conversion. As discussed above, whereas in the presence of 2 wt % PS, $\bar{n}$ is constantly increasing, and 0.5 is reached after 60% conversion and continues to increase to end up in the gel effect (Figure 10b). Increasing the amount of PS has only a weak effect on the development of $\bar{n}$, as shown in Figure 10b by addition of 10% of polystyrene.

We can only speculate about the reason for this very systematic expansion of interval I. A related explanation is that the radical flux through the droplet interface is decreased because of the presence of a hydrophobe inside the droplets which elevates the osmotic pressure inside the droplets so that less monomer is available in the continuous phase. A lowered amount of monomer however would slow the reaction between KPS radicals and monomer to form the necessary oligomeric radicals which are able to penetrate into the droplets. This

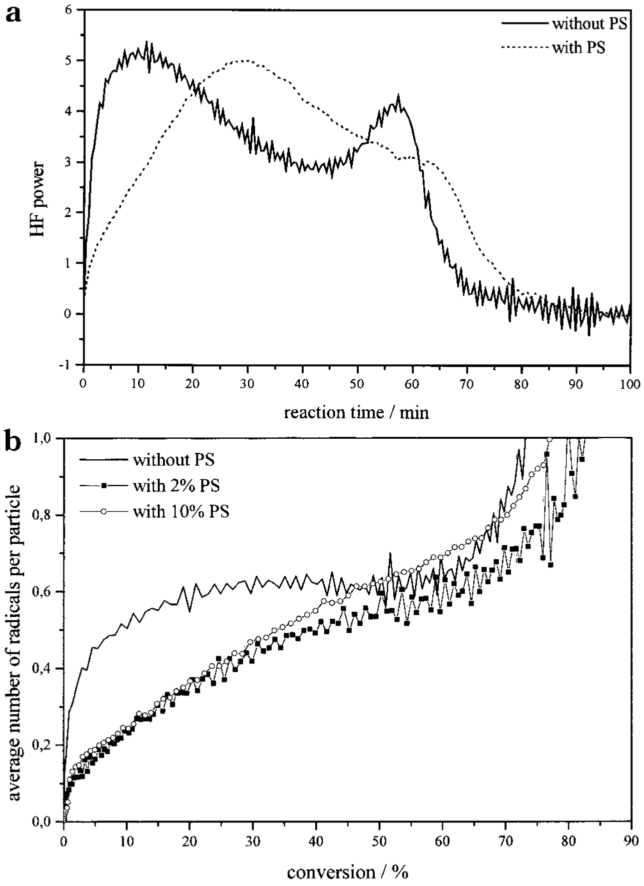

Figure 10. (a) Calorimetric curves of the same reaction with and without the addition of 2 wt % polystyrene to the monomer phase prior to emulsification. (b) Development of $\bar{n}$ through the course of polymerization for latexes with 0, 2, and 10 wt % of polystyrene.

interpretation is further sustained by the fact that the differences in reaction courses with and without pre-added polystyrene are not to be observed for the still water-soluble, but however more hydrophobic (and thereby having easier access to the droplet interior), initiator V50.[4] On the other hand, these effects cannot be explained by impurities in the hydrophobe, because all effects can be accurately reproduced. A more decisive answer has to await further experiments with other monomers with a different water solubility which are currently being performed.

Conclusion

In this paper, the kinetic behavior of miniemulsion polymerization using water-soluble initiators was examined by calorimetry with the objective to further enlighten the miniemulsion polymerization process by selectively changing parameters such as the initiator and surfactant amount. Three distinguished intervals can be categorized for miniemulsion polymerization kinetic courses. As derived from Harkins definition for macroemulsion polymerization, only intervals I and III are found in the miniemulsion process. Additionally, interval IV describes the gel peak. Intervals I and III can be defined by the average number of radicals per particle, $\bar{n}$: during interval I, $\bar{n}$ increases until a plateau value of 0.5 is reached at the onset of interval III. A sharp increase of $\bar{n}$ indicates the beginning of interval IV. Interval III reveals the similarity toward a suspension polymerization. The droplet nucleation interval (interval I) is unexpectedly short as after only 10 min (15% conversion) every droplet is nucleated and $\bar{n} = 0.5$ is reached.

The slow increase of $\bar{n}$ is due to a slow radical flux through the droplet interface. Therefore, the start of the polymerization in each miniemulsion droplet is not simultaneous, so that the evolution of conversion in each droplet is different, as was shown by TEM. Every miniemulsion droplet can be perceived as a separate nanoreactor which does not interact with others. It could be shown that the value of $\bar{n} = 0.5$ during interval III is independent of the amount of initiator, and therefore the increase of the initiator concentration does not result in an acceleration of the polymerization process in this interval. Independent of the particle size the limit value of $\bar{n}$ during stage III remains 0.5. Therefore, only the number of active sites defines the net polymerization time: the smaller the particles, the shorter the net polymerization time.

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