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Analysis of Mass Transport Limitation during Emulsion Polymerization Using Reaction Calorimetry and Conductivity Measurement

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Summary: The seeded emulsion polymerization of styrene was investigated by reaction calorimetry in combination with conductivity measurements using the RC1e calorimeter (Mettler Toledo). Varying the stirrer speed showed the existence of mass transport limitation in the lower speed range. For the case of using the autoclave HP60 with an anchor stirrer a minimum stirrer speed of 400 rpm is required to be sure of adequate mixing in the reactor.

Keywords: calorimetry; conductivity, emulsion; mass transport; styrene

Introduction

Emulsion polymerization is a multiphase system composing of polymer particles, aqueous phase and monomer droplets. The water-soluble initiator decomposes into radicals and may initiate a propagating chain in the water phase, which enters a micelle and a new latex particle is formed. During the propagation reaction monomer is consumed within the latex particle and is replaced with monomer from the monomer droplets transported through the aqueous phase.

The growing latex particles consume emulsifier to cover their gradually increasing surface. Subsequently, the concentration of free emulsifier in the water phase decreases. Particle formation via micellar mechanism predominantly stops once the emulsifier concentration falls below the critical micelle concentration (cmc). In terms of the Harkins theory, the particle nucleation period (Interval I) ends and the particle growth period (Interval II) starts [1].

Interval II is characterized by transport of monomer from the monomer droplets into the growing latex particles and by monomer conversion within the particles.

At the end of Interval II the monomer droplets disappear and the monomer concentration in the latex particles decrease in Interval III that follows.

Particularly the Interval II is interesting for kinetic studies. The number of latex particles is

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supposed to be constant and the reaction rate is only affected by the number of radicals and the monomer concentration within the latex particles [2]. Therefore, it is useful to start an emulsion polymerization in Interval II. Using the seeded emulsion polymerization technique the number of particles is defined by the particle size and the amount of added seed latex.

In most academic studies the monomer transport from the monomer droplets into the latex particles is assumed to be quite fast and not the limiting step, so that the emulsion polymerization is kinetically controlled. However, there are some indications that, under certain conditions, monomer transport may be slower than monomer consumption by propagation reaction [3,4]. E.g. mass transport limitation during batch and semicontinuous emulsion polymerization of different monomers was investigated and modeled by Asua et al [5].

In the present work monomer transport limitation during emulsion polymerization of styrene was investigated by reaction calorimetry using the RC1e calorimeter (Mettler Toledo) equipped with a conductivity cell as an additional sensor.

Experimental

Polymerization was carried out in the reaction calorimeter RC1e (Mettler Toledo) using the stainless steal autoclave HP60 reactor (1.8L) fitted with the standard anchor type stirrer ($D_{stirrer}$ = 90 mm), calibration heater, temperature sensor and a conductivity sensor. The visualization experiments were carried out in the glass reactor MP10. The seed latex was produced in a 1-L glass reactor fitted with a reflux condenser and a pitched blade propeller.

Styrene (Fluka) was distilled to remove inhibitor, Aerosol MA80 (Cytec), sodium bicarbonate ($NaHCO_3$) and potassium persulfate (PPS, Merck) were used as received. Deionized water was used throughout the work.

The recipe for the seed latex contains 160 g styrene, 820 g water, 16 g Aerosol MA80, 1 g $NaHCO_3$ and 2.4 g PPS.

The RC1e reactor was typically filled with 950 g water, 250 g seed latex (16 % solid content by weight), 5 g Aerosol MA80 and 0.4 g $NaHCO_3$. The amount of initiator KPS was dissolved in a small amount of water before added.

For all reactions the final conversion was detected by gas chromatography. The propagation rate coefficient k_p is used as reported in [6] for all calculations.

Thermal Kinetics

Using reaction calorimetry the heat flow rate of the chemical reaction is calculated from the heat balance of the reactor by

$$\dot{Q}_{reaction} = \dot{T}_R c_{pR} + U \cdot A \cdot (T_R - T_J) - \dot{Q}_{stirrer} + \dot{Q}_L$$

where $\dot{Q}_{reaction}$ is the reaction heat flow rate, c_{pR} is the heat capacity of the reactor, U is the overall heat transfer coefficient with A as the heat exchange area, $\dot{Q}_{Stirrer}$ is the power input rate by agitation and $\dot{Q}_L$ indicates heat loss to the surroundings. T_R and T_J are the temperatures in the reactor and the jacket, respectively.

The conversion rate of emulsion polymerization is proportional to the heat flow rate of reaction:

$$\frac{\dot{Q}_R}{(-\Delta H_R) V_R [M]_0} = \frac{dX}{dt} = -k_P \frac{[M]}{[M]_0} \frac{N_P \bar{n}}{N_A V_P}$$

where [M] is concentration of monomer within the particles, N_P is the total number of particles, $\bar{n}$ is the average number of radicals per particle, V_R is the volume of reaction mass, V_P is the volume of one particle, ($-\Delta H_R$) is the reaction enthalpy, k_p is the propagation rate coefficient and X is the monomer conversion.

Due to the changing volume during polymerization, it is necessary to evaluate the particle volume during the course of polymerization by

$$V_p(t) = \frac{m_{Polymer}}{N_P \cdot \rho_P} + \frac{n_{Monomer,P}(t) \cdot M_M}{\rho_M} + \frac{X(t) \cdot m_M^0}{N_P \cdot \rho_P}$$

where $m_{Polymer}$ is the mass of polymer, ρ_P and ρ_M are the density of polymer and monomer, respectively.

Thus an equation is obtained where calorimetric heat flow rate and monomer concentration are combined:

$$\frac{\dot{Q}_R(t)}{V_R \Delta H_R} = k_P(t) \cdot \frac{n_{Monomer,P}(t)}{V_P(t)} \cdot \frac{N_P \cdot \bar{n}}{N_A \cdot V_P(t)}$$

This equation can be applied to evaluate only the product of monomer concentration and average radical number per particle through reaction calorimetry but not the separated quantities. To calculate the individual values other methods have to be used to determine one of this values or one value has to be estimated.

In literature, it is frequently postulated that the monomer concentration within the particles is equal to its swelling equilibrium concentration. Another possibility is to estimate the average number of radicals per particle, e.g. zero-one kinetics.

In the present work the end of Interval II is determined by different methods of measurement. On the one hand the monomer concentration is postulated to be equal to the swelling equilibrium concentration and subsequently the end of Interval II is calculated from the mass balance equation. On the other hand the average number of radical is postulated to be equal to 0.5 and the monomer concentration is calculated from the calorimetrical data.

These calculations were compared with the experimental data from conductivity measurements.

Conductivity measurements

During emulsion polymerization significant changes in interfacial area take place due to latex particle formation and particle growth. If ionic emulsifiers are used as in the present work, the amount of free emulsifier and thus changes in surface area can be detected by conductivity measurements. The contribution of emulsifier molecules located at the interface to conductivity can be neglected. Therefore, this method of measurement can be also applied to determine precisely the cmc, as shown in Fig.1.

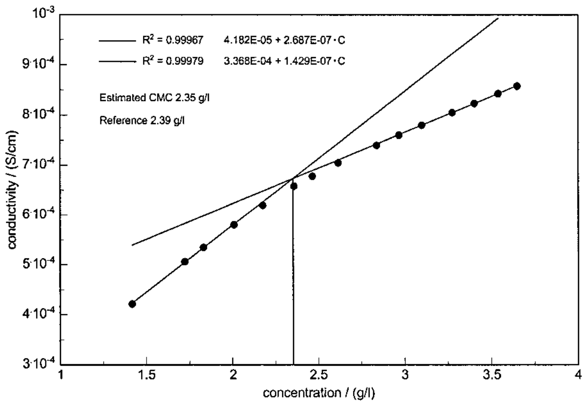

Figure 1: Determination of the critical micelle concentration of SDS.

The use of conductivity measurements facilitates the investigation of stability of emulsions and dispersions. Furthermore, the conductivity cell can be used as an online sensor for the detection of the transition from Interval II to Interval III of emulsion polymerization [7,8]. In this transition stage numerous emulsifier molecules are released from the disappearing monomer droplets, resulting in a significant increase of conductivity.

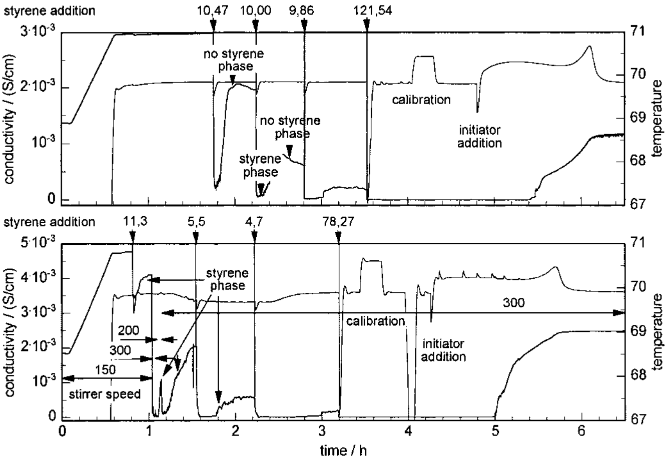

Figure 2: Conductivity and temperature profiles of two seeded emulsion polymerization runs. Latex particle swelling, monomer droplets formation and diminishing are monitored by conductivity measurements. a) four portions of styrene (in g) were added. b) four portions of styrene were added and the agitator speed was varied additionally. The temperature profiles after the initiator addition correspond with the heat release rate versus time curves in Fig. 4.

In order to proof the feasibility of conductivity measurements for monitoring emulsion polymerization, two experiments were carried out by adding monomer in small portions to the reaction mass before initiating the reaction as shown in Fig. 2. After adding a small portion of styrene the conductivity decreases very rapidly and then increases again slowly after some minutes. This is due to the swelling of the particles. Right after the monomer addition the free emulsifier is captured by the droplets to stabilize them. By latex particle swelling the monomer droplets disappear and the emulsifier is released to the water phase again whereby the conductivity increases. Because of the greater surface area of the swollen particles the amount of free emulsifier molecules is smaller and thus the conductivity is lower than before. Varying the stirrer speed after the first addition of monomer shows that there is a certain amount of monomer inadequately mixed in the system. Increasing the stirrer speed causes a decreasing conductivity. This is explained by an increase in specific power input and consequently, results in better mixing, smaller monomer droplet and hence it follows an increase in specific interfacial area that adsorbs emulsifier molecules.

Seeded Emulsion Polymerization

For the kinetic calculations, it is very important to know the number of particles in the reaction system. Therefore, a small seed latex with a narrow particle size distribution (PSD) was produced and characterized by TEM and disk centrifuge.

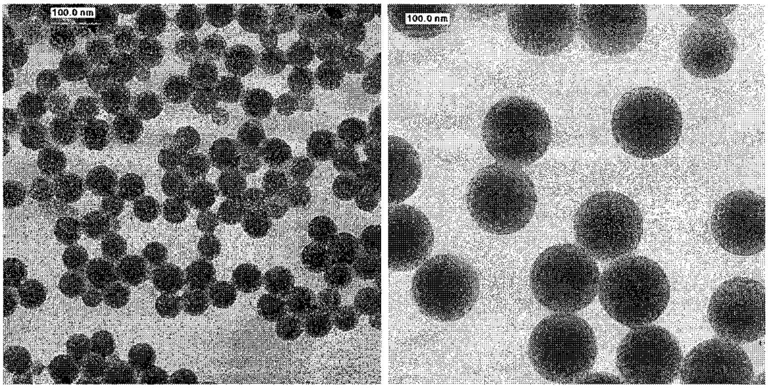

Figure 3: TEM photography of the seed latex with an average particle diameter of 63 nm (left) and the product latex with an average particle diameter of 118 nm (right).

Fig. 3 shows the TEM pictures of the seed latex and the final polystyrene latex. Both have a narrow PSD so that it is justified to assume the absence of particle formation during the course of the seeded emulsion polymerization. The number of particles is calculated from particle diameter and the amount of seed latex in the reaction mass.

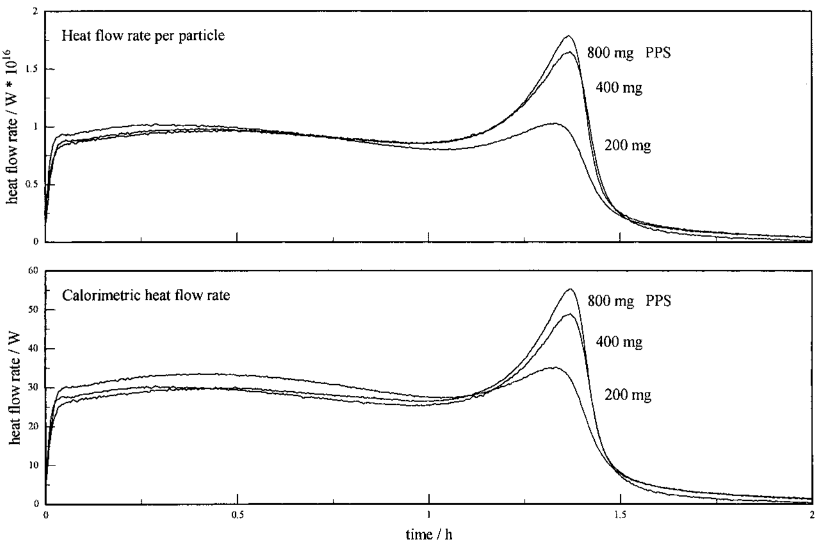

Figure 4: Comparison of the heat flow rate determined by calorimetric measurement and heat balance evaluation using different initiator concentrations. The specific heat flow rate per particle was calculated by considering the number of particles N_P. The reaction temperature was 70 °C.

To calculate the monomer concentration within the particle from the calorimetric data as described before, the average number of radicals is postulated to be equal to 0.5. This is equivalent with the assumption of zero one kinetics. From Fig. 4 it can be seen that doubling and halving of initiator concentration has almost no influence on reaction rate during Interval II, which supplies evidence of zero-one kinetics.

Consequently, the actual monomer concentration in the polymer phase can be calculated on the basis of zero-one conditions. However, Trommsdorff effect predominates in Interval III and therefore, initiator concentration influences reaction rate at that late stage of polymerization as expected.

Visualization

A typical indication for a mass transfer limitation during the reaction is the late transition from Interval II to III. The easiest way to detect this transition is the visualization of the monomer droplet phase in the reaction vessel. Therefore, the stirrer was stopped for a few seconds several times while carrying out the emulsion polymerization of styrene in a glass reactor to allow creaming of the monomer droplets. All these experiments showed that three phases coexist in the conversion range from 30 up to 70 % (Fig.5), which can be explained easily by considering mass transfer limitations. This experimental finding is in contrast with a kinetically controlled reaction, which assumes an equilibrium concentration of monomer in the polymer particles of about 5.5 mol/l or a corresponding conversion of about 35 %.

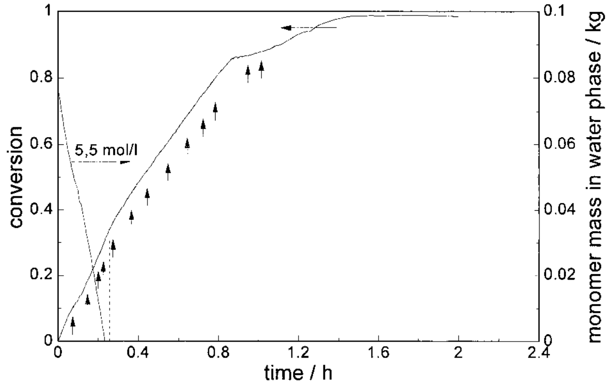

Figure 5: Typical monomer conversion calculated from measured heat flow rate for a seeded emulsion polymerization. Marked points are points with a stopped stirrer. The number and volume of phases was observed. The calculated amount of monomer in the water phase (means dissolved monomer and monomer in the droplets) assuming swelling equilibrium shows an expected transition in Interval III at a conversion of ca. 35 %.

Temperature Effects

If the conversion rate is not only affected by the kinetics the influence of temperature should be investigated. As Figure 6 shows, the increase of temperature does not lead to increased conversion rate as it is expected for a kinetically controlled reaction. Assuming zero-one kinetics, the calculated end of stage II was found at higher conversion as expected for no diffusional limitation. This is in a good agreement with results from conductivity measurement.

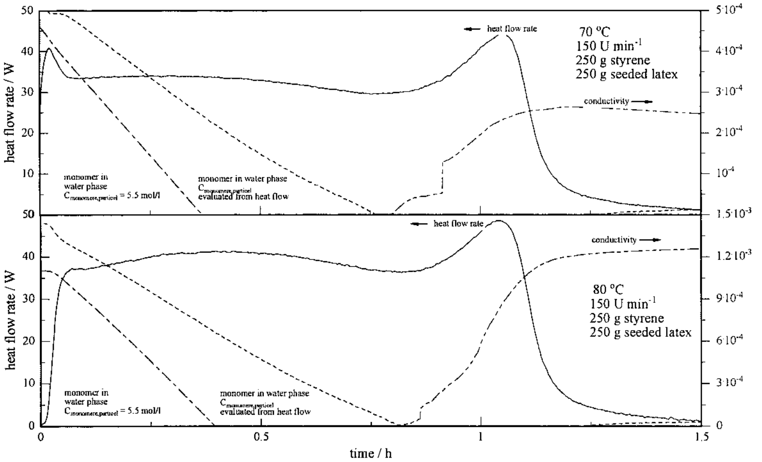

Figure 6: Temperature dependence of the reaction rate. Increasing temperature shows no effect on the reaction rate as should be expected for a kinetically controlled reaction. In both experiments the transition from Interval II to Interval III takes place at a later point of time than expected in case of equilibrium concentration within the latex particles.

Influence of Stirrer Speed

The experimental results show that the swelling equilibrium is not reached throughout the reaction. Therefore, it should be possible to show an influence of stirrer speed and stirrer type which are typical for a mass transport limited reaction. Figure 7 shows the increase of reaction rate as a result of increasing stirrer speed. Additionally, a modified 4-paddle-anchor-stirrer was used instead of the 2-paddel-anchor (horse shoe typ). The modification of the anchor results in a better emulsification of monomer droplets and in an increase in reaction rate.

All measurements show a good agreement between the calculated end of Interval II assuming zero-one kinetic and observed end of Interval II by conductivity measurements.

Looking at the curves for a stirrer speed of 300 rpm there are still differences between the transitions from stage II to III. This means that calculations need to bear the non equilibrium in mind.

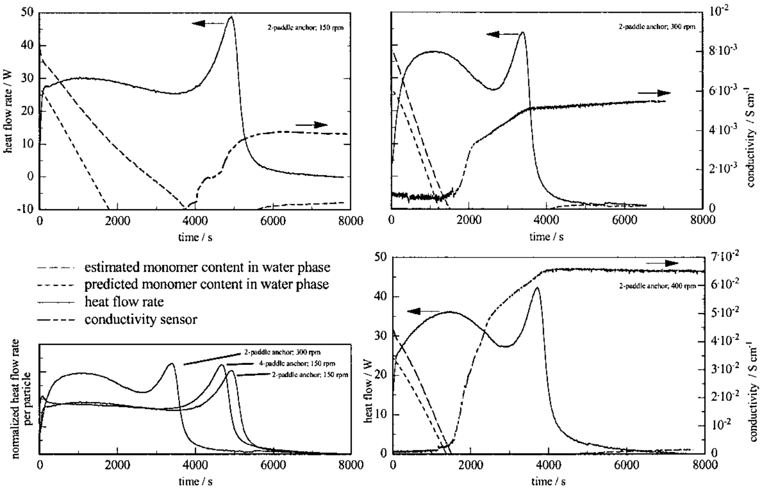

Figure 7: Effect of stirrer speed on the reaction rate.

Conclusion

Influences of temperature, initiator concentration and stirrer speed on seeded emulsion polymerisation were investigated using calorimetry, conductometry and visualization experiments. The existence of mass transport limitation at lower stirrer speed was shown. Furthermore, the determination of the monomer concentration in latex particles using calorimetrical data and conductivity measurements were shown. All these methods of measurement indicate an existence of three phases at higher conversions than 30 to 40 percent even at higher stirrer speed.

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