Effect of composition drift on emulsion copolymerization rate

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With potassium persulphate as initiator and sodium dodecyl sulphate as emulsifier, the batch emulsion copolymerization rate behaviour of styrene (S) and methyl acrylate (MA) was investigated at 50°C, varying the monomer ratio and the monomer to water ratio. The composition drift occurring during the copolymerization is determined by the reactivity ratios and by the monomer partitioning between the various phases present in the emulsion system. Monomer partitioning studies show that the monomer ratio in the latex particles is equal to the monomer ratio in the droplets, although the total monomer swellability of the (co)polymer latex particles depends upon copolymer composition and monomer droplet composition. In the absence of monomer droplets the equilibrium monomer concentration in the aqueous phase is closer to its saturation value (i.e. water solubility) than the monomer concentration in the latex particles. As a consequence of the composition drift, the kinetic behaviour differs widely from the homopolymerizations depending upon the initial monomer ratio. The copolymerization rate strongly varies during copolymerization resulting in a conversion-time plot differing in shape from the sigmoidal shape usually observed in emulsion homopolymerization. The penultimate effect in S-MA copolymerization has been proved to be responsible for this, as can be seen clearly from the conversion dependence of the copolymerization rate during batch emulsion copolymerizations starting from an MA-rich monomer feed, leading to a strong composition drift.

(Keywords: emulsion copolymerization; composition drift; penultimate model; styrene; methyl acrylate)

INTRODUCTION

Batch (emulsion) copolymerization processes often produce highly heterogeneous copolymers with respect to chemical composition. This heterogeneity may affect the product properties either beneficially or adversely. If required, this can be avoided by using more sophisticated processes such as semi-continuous (sometimes called semi-batch) processes or controlled composition processes. Before studying semi-continuous processes it is necessary to obtain a good knowledge of the conventional batch process.

Copolymerization rate is one of the important aspects of emulsion copolymerization, since it involves many complicated chemical and physical rate processes. Generally, the rate of emulsion polymerization strongly depends on temperature and the kind and amount of monomers, initiator and surfactants. A very important factor is the number of latex particles. The overall polymerization rate is proportional to the particle number, average number of radicals per particle and the monomer concentration inside the particles, the last being the main loci of polymerization. Normally, a conversion-time plot of an emulsion polymerization exhibits the well-known characteristic sigmoidal shape. Sometimes a sudden increase in polymerization rate at high conversion can be observed due to the gel effect.

For instance, this effect was reported by Nomura et al. for styrene (S)-methyl methacrylate (MMA) emulsion copolymerization.

As compared with homopolymerizations, in copolymerizations the monomer feed ratio is an additional parameter significantly affecting copolymerization rate. This may result in an even more complex rate behaviour. Due to the occurrence of composition drift during emulsion copolymerization the conversion-time plot may exhibit different shapes. For the emulsion copolymerizations of vinyl acetate (VAc) with MMA, VAc with n-butyl acrylate (BA) and VAc with methyl acrylate (MA) it has been demonstrated that the conversion-time plots can exhibit a double bend. This was attributed to the fact that in these cases there is a large difference between the values of the reactivity ratios (r_{VAc} < 0.1 and \( r_{(meth)acrylate} > 5 \)) in combination with a large difference between the propagation rate constants of the pertaining homopolymerizations. The large difference in reactivity ratios results in a strong composition drift. Vinyl acetate is polymerized in two stages. The first stage comprises a real copolymerization with the (meth)acrylate and during the second stage, after the (meth)acrylate has been depleted, a sudden increase in polymerization rate is observed and VAc practically homopolymerizes. According to the well-known ultimate model (Alfrey-Mayo kinetics) the average rate constant (k_p) depends on the propagation rate constants of the homopolymers and is also a function of the reactivity ratios...
and the (local) monomer feed ratio. In these systems the (average) $k_p$ strongly depends upon the monomer ratio, because the $k_p$s of the homopolymerizations are very different.

The aim of the current investigation is to furnish further fundamental information about the kinetic mechanism of S–MA emulsion copolymerization. It might be expected that the emulsion copolymerization of S and MA exhibits a similar kind of kinetic behaviour as VAc–BA, because the reactivity ($k_p$) of MA is high as compared with that of S and the values of the reactivity ratios in combination with the higher water solubility of MA result in a significant composition drift. Moreover, Davis et al. recently found a penultimate effect for the copolymerizations of S–MA and S–BA, where $k_p$ is strongly dependent on monomer ratio. Ramirez-Marquez et al. investigated the effect of initiator concentration, emulsifier concentration and monomer to water ratio on the (co)polymerization rate of S–MA emulsion copolymerization. Although they observed the occurrence of a strong composition drift in MA-rich recipes, from their limited conversion–time data they did not notice a sudden increase in polymerization rate at the moment S is almost totally depleted. As a result they were able to describe the S–MA emulsion copolymerization rate by means of the ultimate model. This obligated us to perform very accurate kinetic measurements in order to investigate whether the occurrence of composition drift would affect the average propagation rate constant and whether this phenomenon is reflected in the conversion–time curves.

In order to accurately describe emulsion copolymerization by means of a model, it is of paramount importance to implement a reliable description of the monomer concentrations within the latex particles. The monomers are distributed between the particles, the aqueous phase and, if present, the monomer droplets. In emulsion (co)polymerization it is generally recognized that the monomer partitioning is determined by thermodynamic equilibrium. Equilibrium requires the chemical potential of the monomers to be equal in all phases present. Morton et al. developed a model that describes the monomer partitioning in the case of one monomer. This model is based on the classical Flory–Huggins lattice theory for monomer–(homo)polymer mixtures and includes an interfacial energy term. Morton stated that even in those cases where the monomer is a good solvent for the polymer only a limited amount of monomer is absorbed by the latex particles, because the increase of surface energy on swelling compensates for the free energy gain of mixing.

Guillot extended the thermodynamic monomer partitioning treatment of Morton, in an effort to describe the monomer partitioning during emulsion copolymerization by introducing interaction terms for the monomers. Guillot gave equations to calculate the monomer and polymer volume fractions and (partial molar) free energies of both monomers in the three phases.

In the last few years the thermodynamic treatment has been applied by several investigators. However, at present no reliable method of predicting the free energy of a monomer swollen latex particle is available. The use of models to describe the very complicated phenomena of monomer partitioning and also the lack of sufficient and accurate experimental monomer partitioning data frequently results in unreliable or unrealistic estimations of interaction parameters.

Among all emulsion copolymerization systems the monomer partitioning behaviour of S–MMA has been most extensively described. Nomura performed numerous monomer equilibrium experiments on S–MMA, determining the effect of monomer ratio, particle size, copolymer composition, interfacial tension and ionic strength on the latex particle swellability. For other copolymer systems such detailed data are not available.

The above considerations provided sufficient motives to perform a set of equilibrium experiments to study the effect of several parameters (monomer ratio, copolymer composition and molecular mass, crosslink density and particle size) on the monomer partitioning in S–MA emulsion copolymerization systems. Experiments were carried out with or without the presence of a separate monomer layer. The experiments with a monomer layer are representative for intervals I and II of the emulsion copolymerization, whereas the experiments without a separate monomer layer are representative for interval III of the emulsion copolymerization.

**EXPERIMENTAL**

**Equilibrium monomer partitioning experiments**

A latex of known solid content (determined by means of standard dry solid content analysis) and copolymer composition was mixed with known amounts of the two monomers in the absence of initiator. Prior to use the latex had been heated (90°C) for 24 h in order to remove the last traces of the initiator. The system was allowed to reach equilibrium by shaking (for at least 24 h) while thermostatically controlled at the chosen temperature. The phases (swollen polymer particles, aqueous phase and monomer layer) were separated using an ultracentrifuge (380 000g, Centrikon, T-2600, 1–3 h) thermostatically controlled at a maximum temperature of 45°C. The swollen particles could not be analysed without including a small part of the adhering aqueous phase. Monomer concentrations in the particle phase were determined by means of gas–liquid chromatography (g.l.c.) after dissolving the monomer swollen (co)polymer phase (with minor aqueous phase content) in acetone with toluene as an internal standard or, alternatively in the case of polystyrene (PS) lattices, after dissolving in toluene with 2-propanol (IPA) as internal standard. Determination of dry solid content of the sample gave the copolymer content. The concentration of MA in the aqueous phase was determined after adding a standard IPA solution in water to the aqueous layer. The presence of styrene ($<3\text{mmol}\text{l}^{-1}$) in the water phase was neglected. For the determination of the monomer concentrations in the particles, appropriate corrections were performed for the MA content in the sample, dissolved in the aqueous phase. If present, the monomer layer was analysed by means of g.l.c. in terms of molar monomer ratio. This monomer ratio was always in very good agreement with the value calculated from the mass balance equations. To calculate the monomer concentrations inside the particles, the volumes of all components (monomers and (co)polymer) present in the monomer swollen latex particles were assumed to be additive. Copolymer density was calculated by the appropriate averaging of the densities of the homopolymers (Table 1).

The reliability of the method mentioned above was confirmed by means of additional monomer equilibrium
equilibrium was always achieved within 30 min.

aqueous phase serum from the latex particles. Phase experiments (without a separate monomer phase present) using common dialysis tubing for the separation of the monomer to water ratio, and the NDM concentration concentration of 1.233 mmol 1⁻¹. The monomer ratio, the monomer to water ratio, and the NDM concentration (usually 1 wt% on monomer basis) were varied. NaHCO₃ (usually >3 mmol l⁻¹ and can be neglected in the emulsion copolymerization model calculations. The concentration of MA in the aqueous phase linearly increases when the mole fraction of MA in the monomer phase increases (Figure 1). The partitioning coefficient 

\[
K_{MA} = \frac{[MA]_{w}}{[MA]_{m}} \approx 0.05.
\]

As already pointed out by Emelie et al.28 for BA and MMA the type and concentration of surfactants can affect the water solubility of a monomer. Above the critical micelle concentration (\(\sim 2.2 \text{ g l}^{-1} \text{ l}^{-1}\) for SDS) this effect is reinforced by the monomer solubilization within micelles. In Figure 2 it is demonstrated, however, that the effect of SDS concentration \((<4 \text{ g l}^{-1})\) on the water solubility of MA is negligible.

**RESULTS**

**Monomer partitioning**

Methyl acrylate concentration in the aqueous phase as a function of composition of monomer phase, and SDS concentration. In the presence of a separate monomer phase the aqueous phase concentration of S is always <3 mmol l⁻¹ and can be neglected in the emulsion copolymerization model calculations. The concentration of MA in the aqueous phase linearly increases when the mole fraction of MA in the monomer phase increases (Figure 1). The partitioning coefficient 

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**Table 1** Densities of monomers and polymers used

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Density (g cm⁻³)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>0.9060</td>
<td>20</td>
</tr>
<tr>
<td>Methyl acrylate</td>
<td>0.9535</td>
<td>20</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>1.05</td>
<td>20</td>
</tr>
<tr>
<td>Poly(methyl acrylate)</td>
<td>1.2</td>
<td>20</td>
</tr>
</tbody>
</table>
Composition drift and copolymerization rate. G. H. J. van Doremaele et al.

**Figure 1** MA concentration in the aqueous phase as a function of monomer phase composition at 50°C

**Figure 2** Water solubility of MA depending upon SDS concentration and temperature: (O) 45°C; (+) 50°C

Methyl acrylate partitioning between aqueous phase and polymer particles in the absence of a separate monomer phase. During S–MA batch emulsion copolymerization, especially in the case of the very interesting MA-rich recipes, at moderate total conversion the major part of the S has already been depleted while a major part of the MA is still present. Therefore, the MA concentration inside the particles ([MA]_p) versus the MA concentration in the aqueous phase ([MA]_w) was determined in the absence of S. All these experiments were carried out at 45°C. In Figure 3a it is demonstrated that in the absence of a separate monomer phase, [MA]_w is closer to the saturation value (i.e. water solubility) than [MA]_p in poly(methyl acrylate) (PMA) latex particles (i.e. [MA]_w/[MA]_w > [MA]_w/[MA]_w). This swelling behaviour of MA is similar to that of S in PS particles and MMA in poly(methyl methacrylate) particles. Furthermore, it is shown that the presence of crosslinks in the PMA particle on the swellability is negligible. Apparently, the extent of crosslinking is too low to restrict the monomer swelling of the latex particles. The crosslinked PMA latex was prepared in the presence of 5 mol% ethylene diacrylate.

In Figures 3b, c and d the effect of copolymer composition (of S–MA (co)polymer), particle size and molar mass on MA partitioning is shown. At MA concentrations close to saturation a very small influence...
is noticed. This effect, however, is negligible in practical simulations. Lower molar mass, larger MA content in the (co)polymer and larger particle size increase the simulations. Lower molar mass, larger MA content in is noticed. This effect, however, is negligible in practical composition of the monomer phase (20°C). The lines concentrations of the pure monomers are: S 8.7 mol 1\(^{-1}\) and MA 11.1 mol 1\(^{-1}\). In Figure 5 the monomer composition in the particles is compared with the monomer composition of the monomer phase.

From Figure 4 it is concluded that the monomer swellability of polymer particles increases with increasing MA content. The monomer ratio in the droplets is equal to the monomer ratio in the swollen particles for all monomer ratios and all copolymer chemical compositions studied (Figure 5). Copolymer composition only affects the total monomer concentration inside the latex particles. The curves of the monomer concentrations in the particles versus the mole fraction of the same monomer in the monomer phase are curved in such a manner that, independent of the monomer ratio in the monomer phase (droplets), the monomer ratio in the particles is equal to the monomer ratio in the monomer phase, although the total monomer concentration may still depend on the monomer ratio in the monomer phase. Nomura and Fujita found a similar behaviour for S-MMA. 

It is known that solution copolymerizations of monomers strongly differing in polarity (e.g. S and acrylic acid) only can be described by 'apparent' reactivity ratios that depend on the solvent used. This can be explained by the 'bootstrap' model, presented by Harwood, that accounts for local monomer concentrations in the environment of the growing radical chains differing from the overall monomer concentrations. The result of Figure 5 (monomer ratio independent of the composition of the (co) polymer present) suggests the absence of a 'bootstrap' effect. This is in agreement with the findings that reactivity ratios of these systems are only weakly dependent on solvent. Similar monomer partitioning behaviour has also been found for the MA-BA and S-BA systems.

**Copolymerization rate behaviour**

A typical conversion–time curve of a batch emulsion copolymerization of S with MA is given in Figure 6a. The initial monomer ratio (S/MA)\(_0\) was 0.33 mol\(^{-1}\) with a monomer to water ratio (M/W)\(_0\) of 0.2 g g\(^{-1}\). From this plot it is obvious that the S-MA copolymerization passes through several stages. Polymerization starts with the particle nucleation stage. After 10% conversion an almost constant copolymerization rate is observed until 40% conversion. Copolymerization rate then decreases between 40% and 55% conversion. This decrease in copolymerization rate is attributed to a decrease in monomer concentrations in the latex particles. At the point at which S is (almost) totally depleted, the polymerization rate is at a minimum. From this point on the reaction rate suddenly increases MA homopolymerizes. Depletion of MA, the preferential presence of MA in the aqueous phase, and diffusion controlled propagation, result in a final decrease of polymerization rate at high conversions. This indicates that composition drift strongly affects the S-MA copolymerization rate.

In order to obtain further insight in the underlying mechanisms that control the sudden acceleration of the polymerization rate, the (S/MA)\(_0\) (Figure 7) and (M/W)\(_0\) (Figure 8) have been changed. All experiments with a S content of < 50% were found to exhibit a sudden increase in polymerization rate at the moment where S has almost totally been consumed. No sudden increase in polymerization rate was noticed in the case of higher S contents. As has already been noted by Ramirez-Marquez and Guillot, higher MA fractions in the initial monomer feed result in a higher polymerization rate. As depicted in Figure 7 at lower (S/MA)\(_0\) ratios acceleration and pure PMA formation occurs at a lower conversion. As depicted in Figure 8 a decrease of

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**Figure 4** Monomer (S and MA) concentrations inside the latex particles as a function of the composition of the monomer phase: (\(\triangle\)) [MA]\(_p\), PS; (\(\bullet\)) [MA]\(_p\), PS–MA (with \(F_s = 0.5\)); (\(\square\)) [MA]\(_p\), PMA; (\(\triangle\)) [S]\(_p\), PS; (\(\circ\)) [S]\(_p\), PS–MA (with \(F_s = 0.5\)); (\(\square\)) [S]\(_p\), PMA

**Figure 5** Monomer fraction in the latex particles as a function of the composition of the monomer phase: (\(\square\)) PMA; (\(\circ\)) PS–MA (with \(F_s = 0.5\)); (\(\triangle\)) PS

The initial monomer ratio (S/MA)\(_0\) was 0.33 mol\(^{-1}\) with a monomer to water ratio (M/W)\(_0\) of 0.2 g g\(^{-1}\). From this plot it is obvious that the S-MA copolymerization passes through several stages. Polymerization starts with the particle nucleation stage. After 10% conversion an almost constant copolymerization rate is observed until 40% conversion. Copolymerization rate then decreases between 40% and 55% conversion. This decrease in copolymerization rate is attributed to a decrease in monomer concentrations in the latex particles. At the point at which S is (almost) totally depleted, the polymerization rate is at a minimum. From this point on the reaction rate suddenly increases MA homopolymerizes. Depletion of MA, the preferential presence of MA in the aqueous phase, and diffusion controlled propagation, result in a final decrease of polymerization rate at high conversions. This indicates that composition drift strongly affects the S-MA copolymerization rate.

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Composition drift and copolymerization rate: G. H. J. van Doremale et al.

monomer to water ratio results in a higher fractional (co)polymerization rate. Because of the stronger composition drift due to the buffer capacity of water for MA, this also results in a lower critical conversion at which the acceleration of polymerization rate occurs (Figure 9).

From these experiments it can be concluded that composition drift is an important factor determining copolymerization rate behaviour. In principle this behaviour could be attributed to several possible mechanisms, since the polymerization rate is proportional to: (a) the number of latex particles; (b) the monomer concentration inside the particles; (c) the number of radicals per particle (influenced by a gel effect); and (d) the average propagation rate constant.

Mechanism (a). The acceleration observed could be attributed to a sudden increase in particle number (secondary nucleation) at the moment at which the homopolymerization of the more water soluble monomer (in this case MA) starts. More water soluble (hydrophilic) monomers have the tendency to form more latex particles in emulsion polymerization as compared with less water soluble monomers. However, d.l.s. measurements and transmission electron micrographs (after u.v. hardening of the latex) did not indicate a significant amount of small PMA particles at high conversion (Figure 10). Only a very small, gradual increase in particle number was...
Composition drift and copolymerization rate: G. H. J. van Doremaele et al.

Figure 10 Particle number calculated from d.l.s. data versus conversion of a S–MA batch emulsion copolymerization at 50°C: (S/MA)$_0$ = 0.33 mol mol$^{-1}$, (M/W)$_0$ = 0.2 g g$^{-1}$, SDS concentration = 0.0116 mol l$^{-1}$, NaHCO$_3$ concentration = 1.233 mmol l$^{-1}$, 1 wt% NDM and K$_2$S$_2$O$_8$ concentration = 1.233 mmol l$^{-1}$

Figure 11 Average propagation rate constant for S–MA copolymerizations at 50°C as a function of the fraction of MA at the locus of reaction calculated according to the ultimate model (——) and the penultimate model (---)$^{13}$

Table 2 Initial overall monomer ratio (S/MA)$_0$ and composition ($f_{m,0}$) of various batch emulsion copolymerizations, together with the critical mole fraction of the monomer inside the swollen latex particles ($f_{c,1}$), the critical volume fraction of polymer ($v_v$) in the swollen latex particles and the critical copolymer composition ($F_{c}$) at which acceleration occurs.

<table>
<thead>
<tr>
<th>(S/MA)$_0$</th>
<th>$f_{m,0}$</th>
<th>$f_{c,1}$</th>
<th>$v_v$</th>
<th>$F_{c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/3</td>
<td>0.75</td>
<td>0.93</td>
<td>0.74</td>
<td>0.62</td>
</tr>
<tr>
<td>1/7</td>
<td>0.88</td>
<td>0.99</td>
<td>0.53</td>
<td>0.72</td>
</tr>
<tr>
<td>1/11</td>
<td>0.92</td>
<td>0.98</td>
<td>0.38</td>
<td>0.75</td>
</tr>
<tr>
<td>1/19</td>
<td>0.95</td>
<td>0.97</td>
<td>0.26</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Sometimes observed$^{15}$. The final latex particles appeared to exhibit a core–shell type of morphology, as can be explained by the composition drift and the incompatibility of the (co)polymers formed. Furthermore, a significant increase in latex particle number is unlikely to occur, since the monomer droplets already disappeared below 50% conversion and, as a consequence, at 50% conversion the major part of the unreacted monomer MA is already inside the latex particles. Only a small part of the MA (< 0.6 mol l$^{-1}$) is dissolved in the aqueous phase.

Mechanism (b). During interval III of the emulsion polymerization an increase in (average) [MA]$_p$ is of course impossible. However, an increase in local MA concentration in the shells of the polymer particles cannot be completely ruled out. The equilibrium concentration of MA is higher in PMA latex particles than in PS latex particles, 8.5 and 6 mol l$^{-1}$, respectively. Given these data, however, this phenomenon cannot be a major factor causing the sudden strong increase in rate. Therefore, a possible monomer concentration gradient inside the particles, due to differences between the thermodynamic interactions of MA with PMA and MA with copolymer (PS–MA), could only be slightly responsible for the observed increase in polymerization rate.

Mechanism (c). At first sight the gel effect, causing an increase of the average number of radicals per particle ($\bar{n}$), might cause the observed acceleration. MA is well-known for its gel effect. However, for several reasons the gel effect must be ruled out as a main cause in suddenly increasing the polymerization rate, although it will probably affect the rate to some extent. This is because, when varying initial monomer ratios, the increase in polymerization rate was found to occur at different conversions, and thus at different monomer concentrations, different volume fractions and different chemical compositions of the copolymer in the monomer swollen latex particles (Table 2). Invariably, in all cases the increase in rate was found to occur just at the moment S was exhausted.

Moreover, it was found that the presence and the amount (ranging from 0 to 10 wt% on monomer basis) of NDM, having a paramount effect on molar mass of the copolymer formed, did not affect polymerization rate. As a consequence, the occurrence of an important gel effect can be ruled out, because, as reported by Matheson et al.$^{33}$, the gel effect occurring during bulk polymerization of MA is eliminated by the presence of a small amount of chain transfer agent.

The average number of radicals inside latex particles was calculated at any moment from polymerization rate data, the $k_p$ (Figure 11), the monomer concentrations inside the latex particles and the number of latex particles. For the experiment given in Figure 6 the calculated values of $\bar{n}$ were ~ 0.3. However, due to errors and uncertainties in all parameters the values of $\bar{n}$ must be regarded as an approximation and not as absolute values, and therefore should be prudently used.

Mechanism (d). The cause of the sudden increase in rate may also be found in $k_p$. The composition and sequence distribution of the copolymer formed and the composition drift during a copolymerization of S and MA can be adequately described by the ultimate model$^{34}$. However, recent measurements of $k_p$ as a function of monomer ratio by Davis et al.$^{14}$ using the laser-flash technique (comparable to the well-known rotating sector method) in low-conversion bulk and solution systems revealed that the kinetic behaviour of the S–MA system cannot be adequately described by the ultimate model. Instead the penultimate model proved to be...
appropriate in this case. Given the fact that composition drift is well described by the ultimate model, it can easily be demonstrated that from the six reactivity ratios in the penultimate model, two pairs of reactivity ratios are equal. Given the homopropagation rate constants of the ultimate model, two pairs of reactivity ratios are demonstrated that from the six reactivity ratios in the appropriate in this case. Given the fact that composition drift is determined by the reactivity ratios (Figure 9).

CONCLUSIONS

In the acrylate-rich batch emulsion copolymerizations of S with MA a strong composition drift is observed. The composition drift is determined by the reactivity ratios and the monomer partitioning.

From the equilibrium monomer partitioning experiments in the absence of a separate monomer layer it can be concluded that the MA concentration in the aqueous phase is closer to the saturation value than the MA concentration in the latex particles. The monomer partitioning in the systems investigated is only marginally affected by particle size, copolymer composition and copolymer composition and upon monomer ratio in the droplets.

The occurrence of a penultimate effect in the propagation rate of the sudden acceleration occurs (Figure 9).

Figure 12  Experimental data of partial conversions of S (Δ) and MA (Δ) versus overall mole conversion compared to model calculations of an emulsion copolymerization with (S/MA)₀ = 0.33 mol m⁻¹ and (M/W)₀ = 0.2 g g⁻¹.

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