Rate-Determining Kinetic Mechanisms in the Seeded Emulsion Copolymerization of Styrene and Methyl Acrylate

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ABSTRACT: A kinetic study of the seeded emulsion copolymerization of styrene (S) and the relatively water-soluble methyl acrylate (MA) was carried out so as to investigate the mechanisms of radical entry into latex particles, radical exit from the latex particles, and the fate of radical species in the aqueous phase. Three seed latices of differing size were used, two of poly(S-*co*-MA) latices and one poly(S) latex. This way of determining kinetic parameters of emulsion copolymerization on a homopolymer seed ("heteroseeded polymerization") is possible because the techniques used involve only a relative small change in conversion. This means that phase separation will not be a problem at the high monomer concentrations used and that composition drift is negligible. Conditions were such that the system followed zero–one kinetics (Smith–Ewart cases 1 and 2), which means that no latex particles contain more than one growing chain. Data were obtained for the steady-state rate of polymerization with persulfate as initiator and for the non-steady-state relaxation kinetics in γ-radiolysis initiation experiments. The latter kinetics are dominated by radical loss mechanisms such as radical exit and termination. It was possible to obtain a value for the chain transfer constant of styrene-terminated radicals to methyl acrylate from the molecular weight distributions. It was found that this copolymer system is retarded at very low conversions, possibly by oxygen. The data can be explained with the following mechanisms. Radical exit occurs via the same transfer–diffusion mechanism as found in a number of other systems, *i.e.*, transfer of the radical activity to monomer(s) and subsequent desorption into the aqueous phase. These desorbed monomeric radicals re-enter the particles and either terminate or propagate therein. The entry efficiency of persulfate is low, with 50–95% of the persulfate-derived radicals undergoing termination in the aqueous phase. This is in accord with the mechanism for entry that states that the rate-determining events are aqueous-phase propagation and termination; radicals of a critical degree of polymerization enter a particle irreversibly and instantaneously. At high fractions of S in the S–MA system, although MA polymerizes quickly (high propagation rate constant), the occasional addition of S in the aqueous phase slows the propagation rate down considerably. Thereby it also decreases the probability of the attainment of a sufficiently high degree of polymerization for surface activity, perhaps 10–20 monomer units with the relatively water-soluble MA.

Introduction

In emulsion copolymerization monomer partitioning and composition drift are now well understood, and this allows copolymer composition control to some extent.[1] To have more flexible composition control or good control of other product properties, such as the molecular weight distribution, a good understanding of the kinetics of emulsion copolymerization is also very important. Recently, extensive models for the rate-determining kinetic mechanisms in emulsion polymerizations have been developed for and applied to the homopolymerizations of styrene[2–4] and methyl methacrylate.[3] These models mainly involve descriptions of radical entry[2,5] and exit,[3,4] the kinetic processes that are typical for compartmentalized systems such as emulsion polymerizations, and (chain length dependent) termination.[6]

Some researchers have also paid attention to copolymerizations such as styrene–methyl methacrylate copolymerization.[7,8] However, most industrial recipes involve more water-soluble monomers. As it is now well established that the aqueous phase plays a dominant role in the kinetics,[2] the question rises whether the same kinetic mechanisms are dominant if monomers with a higher water solubility are used. The objective of the present study therefore will be to investigate an emulsion copolymerization that displays zero–one kinetics, *i.e.*, where intraparticle termination reactions are not rate-determining and where one monomer is water insoluble (styrene (S)) and the other monomer moderately water soluble (methyl acrylate (MA)). It will be investigated whether the kinetic scheme shown to be valid for water-insoluble monomers can be applied in this case. By looking at seeded emulsion polymerizations, particle nucleation is avoided and particle growth can be studied. In a zero–one system this is controlled by entry and exit of radicals and by the fate of desorbed radicals in the aqueous phase.

In the description of the rate-determining steps in an emulsion copolymerization, the extensive treatment by Casey *et al.*[3] of zero–one emulsion polymerization systems will be followed. Accordingly, a brief summary of their treatment will be given with the resulting rate equations. Then the corresponding rate equations for a copolymerization system will be derived, followed by a discussion of the assumptions that are made in the derivation of the rate equations with respect to applicability to the comonomer system studied experimentally. Predictions will be given for radical entry and exit based on the rate equations and parameter estimations. Subsequently, the experimental setup used to check the predictions will be described, and the experimental results will be discussed.

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Zero–One Seeded Emulsion Polymerization

A. Rate-Determining Mechanisms in Zero–One Seeded Emulsion Polymerizations. (1) Radical Entry. Radical entry is determined by the rate of generation in the aqueous phase of oligomeric radicals capable of entering irreversibly and instantaneously. This rate is determined by both propagation and termination in the aqueous phase. When persulfate is used as the initiator, the following processes are involved: after decomposition a sulfate radical reacts with monomer that is dissolved in the aqueous phase and an oligomeric species is formed that is water soluble. This can undergo propagation as well as termination. If the oligomeric species keeps propagating, it will eventually reach a certain length z at which it has surface-active properties or is water insoluble (*N.B.*: $z < j_{\mathrm{crit}}$; j_{crit} is the critical degree of polymerization at which an oligomer can form a precursor particle (nucleation)). If the number of particles is sufficiently high, oligomeric radicals will enter the particles and not form any new particles. If the actual entry event is so fast as not to be rate-determining, the propagation of the oligomer in the aqueous phase becomes rate-determining, and a mathematical expression according to the entry theory of Maxwell *et al.*[5,9] is applicable. Other researchers (*e.g.*, ref 10) take into account that there is a range of oligomers that can enter a particle, each with its own partitioning coefficient for the aqueous phase and particle phase. However, such an approach will most likely lead to an average value for z, so here the approach of Maxwell *et al.*[5] is used. This treatment has been shown to be applicable to styrene and also to methyl methacrylate. The entry efficiency, defined as the fraction of initiator radicals that actually end up entering a particle, defined as the fraction of initiator radicals that actually end up entering a particle, depends mainly upon intrinsic parameters: the propagation rate constant, k_{p}, the monomer concentration in the aqueous phase C_{aq}, the termination rate constant $k_{\mathrm{t,aq}}$, and the critical degree of polymerization for irreversible entry z. It should be noted that the termination reaction between two radicals in the aqueous phase is assumed to be in the diffusion limit and therefore not very dependent upon monomer type. In general, the smaller the time scale for propagation ($1/k_{\mathrm{p}}C_{\mathrm{aq}}$) or the lower the critical degree of polymerization, the higher is the fraction of initiator radicals that actually enter. This explains why the efficiency for styrene is generally lower than 100%: this monomer has both a low C_{aq} and a relatively low propagation rate constant (z is low, too). Entry efficiency of persulfate in emulsion polymerizations of methyl methacrylate is close to 100%[6] (higher k_{p}, high C_{aq}, and relatively low z).

(2) Exit of Radicals. The extensive discussion of exit by Casey *et al.*[3] (encompassing descriptions given by Ugelstad and Hansen and by Nomura and coworkers) has been tested for styrene and methyl methacrylate. Morrison *et al.*[4] provided an extended means for verification of exit models. It has been generally accepted that the first step in exit is transfer to a small species that is capable of rapidly diffusing away from the particle. This species is normally a monomer but can also be a transfer agent. Only transfer to monomer will be considered. Once transfer to monomer has occurred, the monomeric radical has in principle three fates: (1) escape from the particle, (2) termination with another radical, and (3) propagation, after which escape is assumed to be impossible. If the last process occurs, there is no direct influence on the radical concentration in a zero–one system, and it is therefore kinetically unimportant. It is normally assumed that transport in the aqueous phase is rate-determining for desorption.[11]

(3) Fates of Desorbed Free Radicals. The effect of exit on the overall kinetics is greatly dependent on the fates of the escaped monomeric radical in the aqueous phase: (1) termination in the aqueous phase, (2) re-entry into a particle which is not necessarily the particle it escaped from, and (3) propagation in the aqueous phase, which is normally very unlikely, except maybe for very water-soluble monomers with a high k_{p}. The absence of a hydrophilic part as in persulfate-derived radicals considerably shortens the residence time of monomeric radicals in the aqueous phase, which decreases the probability of propagation. Casey *et al.*[3] took these fates into account, and this resulted in a number of limits for the resulting rate equation. Below are given the most important assumptions Casey *et al.* made in the derivation and the resulting rate equations for homopolymerizations.

B. Rate Equations for Zero–One Seeded Emulsion Homopolymerizations. Casey *et al.*[3] derived kinetic equations based on some kinetic equations to be treated in a later section of this paper and on the following reaction scheme. Reactions in both the particle phase and the aqueous phase are considered as well as the phase exchange processes that kinetically important species can undergo. Initiator-derived radicals are distinguished from monomeric radicals, and they are assumed to enter a particle irreversibly after propagation to a critical degree of polymerization z in the aqueous phase, which effectively means that they can re-enter into and redesorb from a particle until they have propagated or undergone termination in the particle.

> *Aqueous phase*: Propagation and termination of initiator-derived radicals; propagation and termination of monomeric radicals
>
> *Polymer phase*: Propagation or termination of monomeric radicals; propagation of polymeric radicals; chain transfer of polymeric radicals to monomer
>
> *Phase exchange processes*: Entry of initiator-derived radicals into a particle (ϱ_{I}) that already contains a radical (giving instantaneous termination) or does not contain a radical; desorption of monomeric radicals from a particle (k_{dM}); re-entry of monomeric radicals (ϱ_{re}) or of thermally-derived radicals (ϱ_{th}) into a particle that already contains a radical (*giving instantaneous termination*) or does not contain a radical

The above considerations lead to the following basic rate equation:

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \varrho(1 - 2\bar{n}) - \varrho_{\mathrm{re}}\frac{k_{\mathrm{dM}}(1 - \bar{n})}{k_{\mathrm{dM}} + k_{\mathrm{p}}^{1}C_{\mathrm{p}}} - \frac{k_{\mathrm{tr}}C_{\mathrm{p}}k_{\mathrm{dM}}\bar{n}}{k_{\mathrm{dM}} + k_{\mathrm{p}}^{1}C_{\mathrm{p}}} \qquad (1)$$

where $\bar{n}$ is the average number of radicals per particle, ϱ is the entry rate coefficient of all types of radicals (hence $\varrho = \varrho_{\mathrm{I}} + \varrho_{\mathrm{re}} + \varrho_{\mathrm{th}}$), k_{p}^{1} is the propagation rate constant of a monomeric radical, which is generally assumed to be greater than the propagation rate constant of a polymeric radical (k_{p}),[4] C_{p} is the concentration of monomer in the particles, and k_{tr} is the rate constant of chain transfer to monomer. Depending on the fate of monomeric radicals in the aqueous phase and particle phase, two limits can be derived.

Limit 1: *No Re-entry of Desorbed Monomeric Radicals*

This limit is applicable when the rate of re-entry of monomeric radicals is much smaller than the rate of termination of the monomeric radicals in the aqueous phase. Equation 1 leads to

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \varrho_{\mathrm{A}}(1 - 2\bar{n}) - \frac{k_{\mathrm{tr}}C_{\mathrm{p}}k_{\mathrm{dM}}}{k_{\mathrm{dM}} + k_{\mathrm{p}}^{1}C_{\mathrm{p}}}\bar{n} \tag{2}$$

where $\varrho_{\mathrm{A}} = \varrho_{\mathrm{I}} + \varrho_{\mathrm{th}}$. Note that the rate of entry of initiator-derived radicals can be influenced by the monomeric radicals in this case. The loss rate is first order in $\bar{n}$.

Limit 2: *Complete Re-entry of Desorbed Monomeric Radicals*

This limit is applicable if the rate of re-entry is much higher than the rate of termination. The re-entry rate is equal to the exit rate, and eq 1 leads to

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \varrho_{\mathrm{A}}(1 - 2\bar{n}) - 2\frac{k_{\mathrm{tr}}C_{\mathrm{p}}k_{\mathrm{dM}}}{k_{\mathrm{dM}}\bar{n} + k_{\mathrm{p}}^{1}C_{\mathrm{p}}}\bar{n}^{2} \tag{3}$$

There are two possible sublimits with loss rates first and second order in $\bar{n}$:

Limit 2a: *Escape is More Probable Than Propagation*

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \varrho_{\mathrm{A}}(1 - 2\bar{n}) - 2k_{\mathrm{tr}}C_{\mathrm{p}}\bar{n} \tag{3a}$$

Limit 2b: *Escape Is Less Probable Than Propagation*

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \varrho_{\mathrm{A}}(1 - 2\bar{n}) - 2\frac{k_{\mathrm{tr}}k_{\mathrm{dM}}}{k_{\mathrm{p}}^{1}}\bar{n}^{2} \tag{3b}$$

The reader is referred to the paper by Casey *et al.*[3] for the complete derivation.

Zero–One Seeded Emulsion Copolymerization

As the aim of this paper is to study emulsion copolymerization, the corresponding rate equations will be derived for copolymerizations. The derivation of the equations for two monomers is based entirely upon the derivation for the homopolymerizations by making the same assumptions and considerations. In a further section the validity of the assumptions with respect to the more water-soluble monomer MA will be discussed. The propagation of copolymeric radicals in the particle phase is naturally different from a homopolymerization, but it can be described with an average rate coefficient, $\bar{k}_{\mathrm{p}}$, where any model can be used to describe the propagation process. For entry the Maxwell–Morrison theory is applied.[5] In this derivation it is assumed that it is not necessary to distinguish between different types of entering oligomers, although the value of the rate parameter ϱ_{I} will depend on the type and amount of either monomer used. The propagation of the initiator-derived radicals in the aqueous phase will be described with an average propagation rate coefficient, and termination with one rate constant $k_{\mathrm{t,aq}}$, neglecting any effect on these rates of chain length, microstructure, and colloidal properties of these oligomers. These effects are also not taken into account for the actual entry event, since this is assumed not to be rate-determining. It is stressed again that it is assumed that only radicals of critical degree of polymerization z will enter, or, equivalently, that the total entry rate of all oligomers possibly capable of entering, can be approximated by an average rate, which is equal to that of radicals of degree of polymerization z. No partitioning coefficients need to be known.

Since the source of thermal entry is unknown, it is also assumed that this entry rate can be described with a single rate parameter ϱ_{th}. In other words, for entry of initiator-derived radicals, thermal entry, and propagation of polymeric radicals, a pseudohomopolymerization approach is used. The main difference with the derivation for the homopolymerization case is that now a distinction has to be made between two types of monomeric radicals (either monomer type). This implies that for all reactions where monomeric radicals are involved (propagation and termination of monomeric radicals in the aqueous phase; propagation and termination of monomeric radicals and transfer to monomer in the polymer phase) and for phase exchange processes of monomeric radicals, this distinction has to be taken into account. With these considerations in mind, equations analogous to the homopolymerization case can be derived. The assumptions and the kinetic equations that describe the microscopic events and the resultant rate equation will be given.

A. Assumptions. The most important assumptions made by Casey *et al.*[3] are given below. Other assumptions are not as important with respect to the presence of two monomers rather than one.

(i) The latex particles are homogeneous (no phase separation) and are the dominant locus of polymerization.

(ii) No significant polymerization occurs when a particle contains two radicals; *i.e.*, upon entry of a radical into a particle that already contains a radical, termination between these radicals occurs before one escapes the particle or propagates significantly. This is instantaneous termination. It is now realized that instantaneous termination can only occur if one of the radicals is monomeric, as the monomeric radicals can rapidly diffuse through the particle. Oligomeric, persulfate-derived radicals are anchored to the surface due to their hydrophilic initiator group and are therefore not able to react quickly with a long polymeric radical. It is necessary that monomeric radicals capable of terminating instantaneously (see condition 1 below) are formed much more frequently than oligomers from the aqueous phase can enter the particle. This guarantees that the time during which two radicals can propagate in one particle is much shorter than the time scale of entry and that the entering oligomeric radical or the polymer radical is terminated by a monomeric radical long before the oligomer can become a polymeric radical. The conditions for instantaneous termination are as follows: (1) termination between a radical and a monomeric radical is much faster than escape or propagation of the monomeric radical and (2) transfer to monomer (resulting in a monomeric radical conforming to condition 1) is more frequent than entry.[3]

(iii) Monomeric radicals are the only radicals that can escape from a particle.

(iv) Monomeric radicals in the aqueous phase are more likely to re-enter or to terminate than to propagate.

(v) Thermally-derived radicals are assumed to enter into all latex particles at the same rate.

B. Kinetic Equations. The kinetic equations describing reactions that take place in the aqueous phase and the polymer phase will be given followed by the phase transfer processes. Where necessary, it is indicated that a distinction has to be made between different radical types i and j. Note that instantaneous termination is treated in the subsection Phase Exchange Processes.

(1) Aqueous-Phase Kinetics

initiator-derived radicals

initiator decomposition:

$$I_2 \xrightarrow{k_d} 2I^{\bullet} \tag{4}$$

where I_2 represents the initiator, $I^{\bullet}$ the initiator radical, and k_d the initiator decomposition rate constant.

initial propagation:

$$I^{\bullet} + M_{aq} \xrightarrow{\bar{k}_{pI}} IM_1^{\bullet} \tag{5}$$

where M_{aq} represents both monomers dissolved in the aqueous phase, $IM_1^{\bullet}$ is a radical with an initiator end group and one added monomer unit, and $\bar{k}_{pI}$ is the average rate coefficient of propagation of the initiator radical with both monomers. This is assumed to be very high and therefore not rate-determining.

subsequent propagation:

$$IM_n^{\bullet} + M_{aq} \xrightarrow{\bar{k}_{paq}} IM_{n+1}^{\bullet} \tag{6}$$

where $IM_n^{\bullet}$ is a radical with an initiator end group and n monomer units added and $\bar{k}_{paq}$ is the average, chain length independent rate coefficient for propagation in the aqueous phase, usually given the value of the organic-phase propagation rate constant $\bar{k}_p$.

termination:

$$IM_n^{\bullet} + T^{\bullet} \xrightarrow{k_{t,aq}} \text{oligomers} \tag{7}$$

where $T^{\bullet}$ represents all aqueous-phase radicals and $k_{t,aq}$ is the termination rate coefficient in the aqueous phase.

transfer-derived radicals

termination:

$$M_{iaq}^{\bullet} + T^{\bullet} \xrightarrow{k_{t,iaq}} \text{oligomers} \tag{8}$$

where $M_{iaq}^{\bullet}$ is an aqueous-phase monomeric radical of type i and $k_{t,iaq}$ is the rate coefficient of termination of monomeric radical of type i with any other aqueous-phase radical $T^{\bullet}$.

propagation:

$$M_{iaq}^{\bullet} + M_{aq} \xrightarrow{\bar{k}_{pi}^1} \text{dimeric radicals} \tag{9}$$

where M_{aq} represents both monomers dissolved in the aqueous phase and $\bar{k}_{pi}^1$ is the average propagation rate coefficient of monomeric radical of type i.

(2) Particle-Phase Kinetics

propagation in N_i^1:

$$N_i^1 \xrightarrow{\bar{k}_{pi}^1 C_p} N_p^1 \tag{10}$$

where N_i^1 is the fraction of latex particles that contain one monomeric radical of type i, N_p^1 is the fraction of latex particles which contain one polymeric radical, and C_p is the total monomer concentration in the particle phase.

propagation in N_p^1:

$$P^{\bullet} + M_p \xrightarrow{\bar{k}_p C_p} PM^{\bullet} \tag{11}$$

where $P^{\bullet}$ is a polymeric radical, M_p represents both monomers in the polymer phase, and $PM^{\bullet}$ is the result of propagation of $P^{\bullet}$.

transfer in N_p^1:

$$N_p^1 \xrightarrow{\bar{k}_{tr,i} C_{ip}} N_i^1 \tag{12}$$

where $\bar{k}_{tr,i}$ is the average rate coefficient for transfer to monomer i and C_{ip} is the concentration of monomer i in the particle phase.

(3) Phase Exchange Processes

transfer-derived radicals

desorption:

$$N_i^1 \xrightarrow{k_{di}} N^0 + M_{iaq}^{\bullet} \tag{13}$$

where N^0 is the fraction of latex particles that do not contain a radical and k_{di} is the rate coefficient for desorption of a monomeric radical of type i.

re-entry into N^0:

$$N^0 + M_{iaq}^{\bullet} \xrightarrow{k_{rei}} N_i^1 \tag{14}$$

where k_{rei} is the rate coefficient for re-entry of a monomeric radical of type i and the re-entry rate of monomeric radicals i is given by $k_{rei}N_c/N_A$, where N_c is the particle concentration and N_A is Avogadro's number.

re-entry into N^1:

$$N^1 + M_{iaq}^{\bullet} \xrightarrow{k_{rei}} N^0 + \text{polymer} \tag{15}$$

where N^1 is the fraction of particles that contain one radical. This results in instantaneous termination.

initiator-derived radicals

entry into N^0:

$$N^0 + IM_z^{\bullet} \xrightarrow{k_{ez}} N_p^1 \tag{16}$$

where $IM_z^{\bullet}$ is a surface-active initiator-derived radical which enters a particle irreversibly and k_{ez} is the pertaining rate coefficient for entry. The entry rate is given by $\varrho_I = k_{ez}[IM_z^{\bullet}]$. Since it is assumed that these radicals enter instantaneously, the entry rate ϱ_I is also given by the rate formation of these radicals.

entry into N^1:

$$N^1 + IM_z^{\bullet} \xrightarrow{k_{ez}} N^0 + \text{polymer} \tag{17}$$

This results in instantaneous termination.

thermally-derived radicals

entry into N^0:

$$N^0 \xrightarrow{\varrho_{th}} N_p^1 \tag{18}$$

entry into N^1:

$$\mathrm{N}^1 \xrightarrow{\varrho_{\mathrm{th}}} \mathrm{N}^0 + \text{polymer} \tag{19}$$

This results in instantaneous termination.

C. Rate Equations for Zero–One Seeded Emulsion Copolymerization. (1) Radical Balance Equations. Applying the steady-state assumption to the mass balance set up for all radical species (taking the above reactions and phase transfer processes into account) results in the rate equations to describe the emulsion polymerization process. An estimation can be given for the concentration of radicals in the aqueous phase ([T•]) via eq 20, which is obtained by equating the rate of termination of aqueous-phase radicals to the rate of initiator radical production. Maxwell *et al.*[5] stated that this equation is inaccurate by 10% at the most under a wide range of conditions. Equation 21 is then found for the total entry rate of initiator-derived radicals.[5]

$$[\mathrm{T}^\bullet] = \left[\frac{k_\mathrm{d} C_\mathrm{I}}{k_{\mathrm{t,aq}}}\right]^{1/2} \tag{20}$$

$$\varrho_\mathrm{I} = \left[2 k_\mathrm{d} C_\mathrm{I} \frac{N_\mathrm{A}}{N_\mathrm{c}}\right]\left[\frac{2(k_\mathrm{d} C_\mathrm{I} k_{\mathrm{t,aq}})^{1/2}}{\bar{k}_\mathrm{p} C_{\mathrm{aq}}} + 1\right]^{1-z} \tag{21}$$

where C_I is the concentration of initiator I_2, N_c is the particle concentration, and C_{aq} is the total monomer concentration in the aqueous phase. Alternatively, eqs 20 and 21 can be replaced by exact numerical solution of the steady-state equations.[5]

The resulting rate equation describing the radical balance in the particles is

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \varrho(1 - 2\bar{n}) - \sum_{\mathrm{k=i,j}}\left[\varrho_{\mathrm{rek}} \frac{k_{\mathrm{dk}}(1 - \bar{n})}{k_{\mathrm{dk}} + \bar{k}^1_{\mathrm{pk}} C_\mathrm{p}} + \frac{\bar{k}_{\mathrm{tr,k}} C_{\mathrm{kp}} k_{\mathrm{dk}} \bar{n}}{k_{\mathrm{dk}} + \bar{k}^1_{\mathrm{pk}} C_\mathrm{p}}\right] \tag{22}$$

where the average number of radicals per particle, $\bar{n}$, is given by $N^1_\mathrm{i} + N^1_\mathrm{j} + N^1_\mathrm{p}$, i and j represent the two monomers, and ϱ is the entry rate coefficient of all types of radicals (hence $\varrho = \varrho_\mathrm{I} + \varrho_{\mathrm{rei}} + \varrho_{\mathrm{rej}} + \varrho_{\mathrm{th}}$). Also in this case different limits can be derived depending on the fate of the monomeric radicals in the aqueous phase. Here only the limits that correspond to the ones given for homopolymerization are given:

Limit 1: No Re-entry of Either Type of Desorbed Monomeric Radical

This limit is applicable when the rate of re-entry of the monomeric radicals is much smaller than the rate of termination of the monomeric radicals in the aqueous phase. Equation 22 leads to eq 23 with a first-order loss rate:

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \varrho_\mathrm{A}(1 - 2\bar{n}) - \sum_{\mathrm{k=i,j}}\left[\frac{\bar{k}_{\mathrm{tr,k}} C_{\mathrm{kp}} k_{\mathrm{dk}} \bar{n}}{k_{\mathrm{dk}} + \bar{k}^1_{\mathrm{pk}} C_\mathrm{p}}\right] \tag{23}$$

Limit 2: Complete Re-entry of Either Type of Desorbed Monomeric Radical

This limit is applicable if the rate of re-entry is much larger than the rate of termination. The re-entry rate is equal to the exit rate, and eq 22 leads to

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \varrho_\mathrm{A}(1 - 2\bar{n}) - \sum_{\mathrm{k=i,j}}\left[\frac{\bar{k}_{\mathrm{tr,k}} C_{\mathrm{kp}} k_{\mathrm{dk}} \bar{n}^2}{k_{\mathrm{dk}} \bar{n} + \bar{k}^1_{\mathrm{pk}} C_\mathrm{p}}\right] \tag{24}$$

The rate equation that was derived by Nomura *et al.*[7] for an emulsion copolymer system is the same as derived here as Limit 2, in spite of a slightly different reaction scheme: Nomura *et al.* treat initiator radicals kinetically the same as monomeric radicals, although they then assume that these initiator radicals are so reactive that they propagate immediately as they enter a particle and that they are therefore not contributing to the exit rate.

(2) Propagation. Presently, a lot of research is being devoted to unraveling the mysteries surrounding the appropriate model for propagation in free radical copolymerizations.[12] As stated before, in the present kinetic model propagation will be treated with a pseudohomopolymerization approach so that it is not necessary to distinguish between different types of polymeric radicals. This is in contrast with the propagation of monomeric radicals or transfer to monomer. For propagation of monomeric radicals it is assumed that the value of the propagation rate constant of a monomeric radical is about 4 times higher than the corresponding long-chain value. This was found to be applicable in the evaluation of a large number of experimental data in styrene emulsion polymerizations.[4] There are also theoretical considerations that support this.[13] There are no further data available, so a simple approach is used based on the terminal model (since there is no penultimate unit) to obtain expressions for the propagation of monomeric radicals in copolymerizations:

$$\bar{k}^1_{\mathrm{pi}} = k^1_{\mathrm{pii}} f_\mathrm{i} + k^1_{\mathrm{pij}} f_\mathrm{j} = k^1_{\mathrm{pii}}\left[f_\mathrm{i} + \frac{f_\mathrm{j}}{r_\mathrm{i}}\right] \tag{25}$$

where k^1_{pii} is the propagation rate constant of monomeric radical i with monomer i, k^1_{pij} is the cross-propagation rate constant, f_i is the molar fraction of monomer i, and r_i is the reactivity ratio of monomer i according to the terminal model. It should be noted that the use of this model and the reactivity ratios of the terminal model for propagation in effect implies that the monomeric radicals have a structure that is very similar to that of the polymeric radicals.

(3) Chain Transfer to Monomer. For simplicity, a terminal model is applied for describing chain transfer to monomer:[14]

$$\bar{k}_{\mathrm{tr}} = \bar{k}_{\mathrm{tr,i}} f_\mathrm{i} + \bar{k}_{\mathrm{tr,j}} f_\mathrm{j} = \left(k_{\mathrm{tr,ii}} \frac{A_{\mathrm{ij}}}{1 + A_{\mathrm{ij}}} + k_{\mathrm{tr,ji}} \frac{1}{1 + A_{\mathrm{ij}}}\right) f_\mathrm{i} + \left(k_{\mathrm{tr,ij}} \frac{A_{\mathrm{ij}}}{1 + A_{\mathrm{ij}}} + k_{\mathrm{tr,jj}} \frac{1}{1 + A_{\mathrm{ij}}}\right) f_\mathrm{j} \tag{26}$$

where $\bar{k}_{\mathrm{tr}}$ is the average rate coefficient for transfer to monomer, $k_{\mathrm{tr,ii}}$ is the chain transfer constant of a radical with a terminal unit of type i to monomer i, $k_{\mathrm{tr,ij}}$ is the cross-transfer constant, and A_{ij} is the ratio of polymeric radicals with a terminal unit of type i and polymer radicals with a terminal unit of type j. As propagation is much faster than transfer (hence polymerization), this ratio A_{ij} is determined by the propagation reactions and given by eq 27:

$$A_{\mathrm{ij}} = \frac{\bar{k}_{\mathrm{pjj}} \bar{r}_\mathrm{i} f_\mathrm{i}}{\bar{k}_{\mathrm{pii}} \bar{r}_\mathrm{j} f_\mathrm{j}} \tag{27}$$

where $\bar{k}_{pii}$ is the homopropagation rate constant of monomer i and $\bar{r}_i$ is the reactivity ratio of monomer i if the terminal model is applied. If the penultimate model is applied, $\bar{k}_{pii}$ and $\bar{r}_i$ are as given in eq 28:

$$\bar{k}_{pii} = \frac{k_{piii}(f_i r_i + f_j)}{f_i r_i + f_j/s_i}; \qquad \bar{r}_i = \frac{r_i'(f_i r_i + f_j)}{f_i r_i' + f_j} \tag{28}$$

where r_i' and s_i are reactivity ratios in the penultimate model. As it is often assumed that $r_i' = r_i$, $\bar{r}_i$ is equal to r_i.

(4) Rate of Escape of Monomeric Radicals. The rate of escape from the particles is given by the following equation:[3]

$$k_{di} = \frac{3D_{iaq}C_{iaq}}{r_s^{\,2}C_{ip}} \tag{29}$$

In this equation the values of the various parameters for the monomeric radical are taken to be equal to those of the corresponding monomer. Hence D_{iaq} is the diffusion coefficient of monomer i in the aqueous phase, and C_{iaq} is the concentration of monomer i in the aqueous phase in equilibrium with the concentration C_{ip} in the polymer phase. r_s is the swollen radius of the particles. The derivation of this equation is based on the reversibility of diffusion toward and from the particle and the Smoluchowski expression for diffusion.

(5) Rate of Re-entry of Monomeric Radicals. The rate of re-entry of monomeric radicals is given by eq 30, based on the Smoluchowski expression:

$$k_{rei}\frac{N_c}{N_A} = 4\pi D_{iaq}N_c r_s \tag{30}$$

(6) Rate of Intraparticle Termination. The rate of termination is calculated with eq 31:

$$c_i^{1L} = \frac{k_{ti}^{1L}}{N_A V_s} = \frac{4\pi N_A D_{ip}\sigma_i}{N_A V_s} = \frac{3D_{ip}\sigma_i}{r_s^{\,3}} \tag{31}$$

where c_i^{1L} is the pseudo-first-order rate coefficient of termination of a monomeric radical of type i with a long polymeric radical,[15] estimated by applying the Smoluchowski expression. k_{ti}^{1L} is the second-order rate coefficient of the bimolecular termination reaction, V_s is the volume of the swollen particle, D_{ip} is the diffusion coefficient of the monomeric radical in the particle, and σ_i is the radius of interaction of the two radicals, which can be approximated with the Lennard-Jones diameter of the corresponding monomer.

Application of the Model to S–MA Emulsion Copolymerization

System Parameters. To be able to apply a model to a particular system, some characteristics and values of model parameters of the monomers have to be known as well as specific experimental parameters (Table 1).

It has been shown that in interval 2 the ratio of both monomers in the particles is exactly the same as that in the monomer droplets[17,24] ($f_{ip} = f_{id}$, the molar fractions of monomer i in the polymer and droplet phases). The total monomer concentration in the particles was shown to be dependent only on the monomer composition in the particles ($C_p = f_{ip}C_{ip,s,h} + f_{jp}C_{jp,s,h}$, where $C_{ip,s,h}$ is the saturation concentration of monomer i in the absence of the other monomer). The concentrations in the aqueous phase of both monomers were shown to be linearly dependent on the respective molar fractions in the particles/droplets ($C_{iaq} = f_{ip}C_{iaq,s,h}$). With these relations are calculated the monomer concentrations in the polymer and aqueous phase (Table 2) in the experiments performed. With these concentrations the swollen radii of the seeds were calculated: the lowest value of the swollen radius of the seed latices used is 28 nm and the highest 55 nm.

Table 1. Values of (Rate) Parameters of Styrene and Methyl Acrylate: Diffusion Coefficient in the Aqueous Phase (D_{iaq}) and in the Particle Phase (D_{ip}), Saturation Concentration in the Aqueous Phase ($C_{iaq,s,h}$), Propagation Rate Constant (k_p), Mutual Reactivity Ratios (r_i), Rate Constant for Transfer to Monomer (k_{tr}), Encounter Radius of Radicals (σ_i), and Termination Rate Coefficient in the Aqueous Phase ($k_{t,iaq}$)

parameter	S	MA
D_{iaq} (m^2/s)	1.5×10^{-9} (ref 16)	1.9×10^{-9} (ref 16)
D_{ip} (m^2/s)	1.13×10^{-9} (ref 3)	1.2×10^{-9} [a]
$C_{iaq,s,h}$ (mol/L)	4.3×10^{-3} (ref 3)	6×10^{-1} (ref 17)
k_p (L·mol^{-1}·s^{-1})	258 (ref 18)	10700 [b]
r_i	0.73 (ref 19)	0.19 (ref 19)
k_{tr} (L·mol·$^{-1}$·s^{-1})	9.3×10^{-3} (ref 20)	0.9 [c]
σ_i (Å)	6.0 (ref 21)	5.8 [a]
$k_{t,iaq}$ (L·mol^{-1}·s^{-1})	3.7×10^9 (ref 5)	3.7×10^0 [d]

[a] The value for D_{ip} of methyl methacrylate was taken as an approximation for D_{ip} of MA.[3] [b] This value was extrapolated from preliminary data of pulsed laser polymerization experiments at lower temperatures.[22] [c] Calculated from $C_m = k_{tr}/k_p = 0.8 \times 10^{-4}$ [23] and k_p = 10700 L·mol^{-1}·s^{-1}; see footnote *b*. [d] The termination reactions of small molecules like oligomeric radicals in the aqueous phase are in the diffusion limit.[5] Hence the same value as for S is adopted for MA.

Table 2. Total Monomer Concentration (C_p), Molar Fraction of Styrene (f_{Sp}), Partial Concentrations in the Polymer (C_{ip}) and Aqueous Phase (C_{iaq}), and Molar Fraction of Styrene (f_{Saq}) in the Aqueous Phase at Two Different S/MA Ratios

S/MA (mol/mol)	C_p (mol/L)	f_{SP}	C_{Sp} (mol/L)	C_{MAp} (mol/L)	C_{Saq} (mol/L)	C_{MAaq} (mol/L)	f_{Saq}
0.84/0.16	5.9 [a]	0.84	4.9 [a]	0.94 [a]	0.0036	0.096	0.036
0.57/0.43	5.9	0.57	3.37	2.52	0.0025	0.26	0.009

[a] These values apply to a poly(S-*co*-MA) seed. In poly(S) C_p is somewhat smaller (5.8 mol/L).

To obtain values for A_{SMA} and $\bar{k}_p$ use will be made of the penultimate model for the S–MA system. Propagation rate coefficients were experimentally determined with pulsed laser polymerization by Davis *et al.*[25] at 25 and 50 °C. They published an estimated lowest value for the homopropagation rate constant of MA of 3400 L·mol^{-1}·s^{-1} at 40 °C. Recently, a better estimate for the k_p of MA at 50 °C has become available.[22] This value and the value of k_p of S (Table 1) were used and combined with the copolymerization data of Davis *et al.* to recalculate the $\bar{k}_p$ at the compositions needed for the present work. Fitting the data with the penultimate model yields *s* values of $s_S = 0.59$ and $s_{MA} = 0.02$, when using the values for r_S and r_{MA} as given in Table 1. The last value seems physically unrealistic. Refitting the data with the restriction $s_S = s_{MA}$[26] gives *s* values of 0.41. This restriction is sometimes used if there is some scatter on the data and fitting with two parameters is not statistically correct. Both sets of *s* values were used in eq 27 to calculate the ratio A_{SMA} (in the case of the penultimate model A_{SMA} represents the ratio of (SS$^\bullet$ + MAS$^\bullet$) over (MAMA$^\bullet$ + SMA$^\bullet$)). The use of the first set of *s* values results in values for A_{SMA} that are lower by a factor of approximately 40 compared with the results

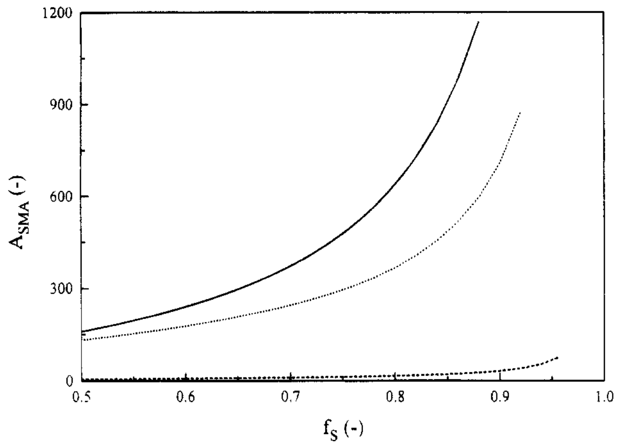

Figure 1. Ratio of concentrations of polymeric radicals with a S terminal unit and radicals with an MA terminal unit, calculated with $k_p(S) = 258$ L·mol^{-1}·s^{-1}, $k_p(MA) = 10700$ L·mol^{-1}·s^{-1}, $r_S = 0.73$, and $r_{MA} = 0.19$ according to (a) the terminal model (—), (b) the penultimate model with $s_S = 0.59$ and $s_{MA} = 0.02$ (- - -), and (c) the restricted penultimate model with $s_S = s_{MA} = 0.41$ (···).

with the terminal model, while the second set of *s* values give results that are comparable to those given by the terminal model (see Figure 1). Because in the case of S−MA the predictions of the ratio A_{ij} according to the terminal and penultimate models vary so much, this ratio could in principle be a third parameter (in addition to propagation rate coefficient and copolymer composition) that can be used to discriminate between different propagation models, if it can be measured, for example by electron paramagnetic resonance (EPR).

However, for the purpose of this work we are not concerned with a discussion on the penultimate model but merely wish to obtain reasonable parameter values for A_{SMA} and $\bar{k}_p$. The same exercise as above for S−MA with data for S−MMA[27] at 40 °C shows that in this case the penultimate model gives approximately the same results as the terminal model. Hence it is assumed that an estimated value for the ratio A_{SMA} can be obtained with eq 27 with $s_S = s_{MA} = 0.41$. The values for A_{SMA} are 455 for $f_S = 0.84$ and 162 for $f_S = 0.57$. For the calculation of the values of $\bar{k}_p$, $s_S = 0.59$ and $s_{MA} = 0.02$ were used. The calculated value of $\bar{k}_p$ at $f_S = 0.84$ is 276 L·mol^{-1}·s^{-1} and at $f_S = 0.57$ it is 303 L·mol^{-1}·s^{-1}.

Because A_{SMA} is so high (Figure 1), the contribution of radicals with an MA unit as terminal unit to transfer at these compositions can be neglected, unless the transfer rate from an MA terminal unit is extremely high in comparison. The literature gives values for $k_{tr,SS}$ and $k_{tr,MAMA}$ (Table 1). Although the latter is much higher than the former, it is not so much higher that it will contribute significantly. This means that in eq 26 the terms with the factor $1/(1 + A_{ij})$, where i stands for S and j for MA, can be neglected. Thus the rate of transfer should be linearly dependent on the monomer feed composition and it should be possible to calculate the value of $k_{tr,SMA}$ (see Experimental Results).

Discussion of Assumptions in the S−MA System

Casey *et al.*[3] gave a methodology for determining the applicability of the model and its assumptions. Their procedure will be followed here:

(i) Homogeneous Particle-Phase Propagation. The polymer in the seed latices used is either polystyrene or poly(styrene-*co*-methyl acrylate) with a molar fraction of S in the copolymer (F_S) = 0.80. Both these polymers dissolve well in the monomers. Since the kinetic runs are carried out in interval 2 (saturated polymer particles) and the kinetics can be evaluated at low conversions, it can therefore be assumed that there will be no phase separation in the particles and thus that the particle phase is homogeneous. However, it should be noted that at high conversions (and certainly in interval 3) there can be phase separation.[28] Another condition is that polymerization takes place in the particles only. It has been suggested that MA can give polymerization in the aqueous phase.[17,19,29] This may indeed occur, but hydrophobic Gibbs energy considerations[5] indicate that such a polymer would become insoluble/surface-active at a degree of polymerization of *ca.* 20 (see Experimental Results), which is negligible compared to the degree of polymerization obtained in the particles, and this polymerization is noticeable only when no seed latex is used.[19] This aqueous-phase polymerization is kinetically important when entry of particle nucleation is considered. After the particle nucleation stage, the composition of the polymer that is formed and the composition drift can be very well described by assuming propagation in the particle phase only.[17,19,29] A further condition is that the particles are not too large, and the maximal swollen radius of the seeds used is *ca.* 55 nm. Hence homogeneous particle-phase propagation is assumed.

Table 3. Rates of Termination (c_i^{IL}), Desorption (k_{di}), and Propagation ($\bar{k}_{pi}^1 C_p$) of Monomeric Radicals and Rates of Entry (ϱ_I) and Chain Transfer to Monomer ($\bar{k}_{tr,i}C_{ip}$) of S and MA at Two Different Fractions of S/MA (in Parentheses)

	S (0.84)	MA (0.16)	S (0.57)	MA (0.43)
c_i^{1L} (s^{-1})	(1−9) × 10^4	(1−9) × 10^4	1 × 10^4	1 × 10^4
k_{di} (s^{-1})	(1−5) × 10^3	(2−7) × 10^5	1 × 10^3	1 × 10^5
$\bar{k}_{pi}^1 C_p$ (s^{-1})	6 × 10^3	1 × 10^6	7 × 10^3	9 × 10^5
ϱ_I (s^{-1})		<5 × 10^{-2}		<4 × 10^{-2}
$\bar{k}_{tr,i}C_{ip}$ (s^{-1})	5 × 10^{-2}	2 × 10^{-2}	3 × 10^{-2}	6 × 10^{-2}

(ii) Instantaneous Termination. (a) The rates of termination (eq 31), monomeric radical desorption (eq 29), and monomeric radical propagation (eq 25) and (b) the rates of entry (eq 21) and chain transfer to monomer (eq 26) are to be compared (see Table 3).

(a) From Table 3 it becomes clear from these calculations that indeed S monomeric radicals should lead to zero−one kinetics, as the rate of termination is higher than either propagation or desorption. The situation with MA is quite different. Here the rate of propagation is the highest due to the very high propagation rate constant of MA. The rate of desorption is higher than the rate of termination, and it is quite likely that a homopolymerization of MA is a pseudobulk system. However, it is argued that in the present system the presence of two radicals, one of which is a monomeric MA radical, results in termination before significant polymerization has taken place: the most likely fate of such a monomeric radical would be propagation. If that happens it is most likely to propagate with S, as this monomer is more reactive. The dimer thus formed will not escape again. The propagation rate will drop significantly and termination would be the most likely fate if there were another radical present in the particle. However, even if it propagates with MA the desorption rate will drop significantly to about 1% of that of the monomeric radical, as can be calculated with eq 32. This equation was derived by Casey *et al.*[3] and is based on expressions for water solubilities[30] and diffusion coefficients[16,31] as a function of molecular weight. Equation

Table 4. Rates of Re-entry ($k_{\mathrm{rei}}N_c/N_A$), Termination ($k_{\mathrm{t,iaq}}[\mathrm{T}^\bullet]$), and Propagation ($\bar{k}^1_{\mathrm{pi}}C_{\mathrm{aq}}$) of Monomeric Radicals of S and MA

	S	MA
$k_{\mathrm{rei}}N_c/N_A$ (s^{-1})	$>5 \times 10^4$	$>7 \times 10^4$
$k_{\mathrm{t,iaq}}[\mathrm{T}^\bullet]$ (s^{-1})	<6	<6
$\bar{k}^1_{\mathrm{pi}}C_{\mathrm{aq}}$ (s^{-1})	$(0.4-1) \times 10^2$	$(0.5-1) \times 10^4$

32 gives an expression for an estimate of the ratio of the desorption rate coefficients of a dimeric radical D and a monomeric radical M:

$$\frac{k_{\mathrm{dD}}}{k_{\mathrm{dM}}} = 10^{-2.9\pm0.3}M_0S_{\mathrm{M}} \tag{32}$$

where M_0 is the molecular weight of the monomeric radical and S_{M} is the molar solubility of the monomeric radical ($=C_{\mathrm{iaq}}$) (mol/L). Also the propagation rate will drop quickly under a value of that of termination. Note that these arguments do not hold if there is no significant amount of S present, because then the propagation rate will never drop below that of termination, and chain length dependent termination has to be taken into account and kinetics are not zero–one. This would lead to an acceleration in $\bar{n}$ in interval 2,[32] which is not seen in the present system and so can be discarded.

(b) ϱ_{I} is calculated with eq 21 by assuming initiator efficiency is 100% and by using the highest initiator concentration and lowest particle concentration applied. This gives an overestimation (see Experimental Results). This means that usually the entry rate is much lower. It can be concluded that indeed the frequency of transfer to monomer is higher than the frequency of entry. From a comparison of the rates of formation of either type of monomeric radical, it is clear that in this system enough S monomeric radicals are formed to guarantee instantaneous termination, even if MA monomeric radicals do not lead to virtually instantaneous termination.

(iii) Only Monomeric Radicals Can Desorb. This has actually already been confirmed under (ii) with eq 32. It can be safely said that for all four possible dimeric radicals the desorption rate is kinetically unimportant in comparison to the desorption of the monomeric radicals, although it is interesting to note at this point that for instance the desorption rate of a dimeric radical $MA_2^\bullet$ is of the same magnitude as the desorption rate of a S monomeric radical.

(iv) Monomeric Radicals in the Aqueous Phase Are More Likely To Re-enter or Terminate Than To Propagate. Re-entry is given by eq 30 and termination in the aqueous phase by $k_{\mathrm{t,iaq}}[\mathrm{T}^\bullet]$, where it is sufficient to account for initiator-derived radicals only, as other radicals are present only in very low concentrations. Propagation is given by $\bar{k}^1_{\mathrm{pi}}C_{\mathrm{aq}}$. The estimated values of these rates are given in Table 4. For the calculation of re-entry the lowest values for r_s and N_c applied in the experiments are used and for termination the highest C_{I}. The propagation rates are calculated for S/MA = 0.84/0.16 and for 0.57/0.43. It is apparent that re-entry is the most likely fate of the monomeric radicals: they will neither propagate nor terminate in the aqueous phase. This is not true in systems with higher concentrations of MA. If only MA is present the rate of propagation in the aqueous phase is *ca.* 3×10^4 s^{-1}.

(v) Thermally-Derived Radicals Enter Particles at the Same Rate. In the experimental setup used here it is possible to determine the contribution of thermal entry to the total rate of entry. Although the source of this process is still unknown, there is no reason to assume that the rate of entry is expected to be the same in every particle in a monodisperse system.

Table 5. Recipes of the Seed Latices

seed latex	S (g)	MA (g)	H_2O (g)	AMA80 (g)	KPS (g)	SB (g)	*T* (°C)
S43	392		1558	19.25	2.6	2.6	85
SMA22	16.56	3.43	70	2.0	0.2	0.2	70
SMA31	16.56	3.43	70	1.0	0.2	0.2	70

A further conclusion from (iv) is that Limit 1 (complete aqueous-phase termination) is not applicable. Limit 2 seems the most likely limit for either monomer type. This means that the monomeric radicals of either type do not interfere with each other, because they do not react in the aqueous phase. Hence, the exit term in the rate equation is simply the sum of the exit rates of both types of monomeric radicals. If re-entry would not be complete, it would be possible that they interfere with each other, and this would become apparent in the rate equation, because re-entry would be a function of monomeric radical concentrations in the aqueous phase. From (ii) it can be concluded that both types of monomeric radical are formed at approximately the same rate. The rate of escape of MA monomer radicals is about 10^2 times higher than that of S monomer radicals, but this is counteracted by the fact that the rate of propagation is higher by the same factor. Hence it is not possible to neglect the contribution of S to the exit rate at this composition. At higher fractions of MA the rate of transfer to MA becomes relatively higher and exit may be predominantly by MA radicals. Nomura *et al.*[7] concluded in their S–MMA system that exit was predominantly by MMA. It should be noted, however, that chain transfer to S is still important with respect to the molecular weight distribution.

From Table 3 it can be concluded that propagation of the MA monomeric radical is more likely than desorption, so Limit 2b is the most likely sublimit. Therefore a dependence of the exit rate on r_s is expected.

Experimental Section

In this work seeded emulsion polymerizations were performed which enable one to study the kinetics of particle growth without the interference of the particle nucleation stage. The seed latices were prepared at relatively high temperatures and high initiator concentrations in a so-called bottle polymerizer. MA (Merck) and S (Ajax) were distilled before use and stored at 4 °C. Sodium dihexyl sulfosuccinate (AMA80, Cyanamid) was used as emulsifier, potassium persulfate (KPS, Merck) as initiator, and sodium bicarbonate (SB, Merck) as buffer. The recipes of the seeds used in the experiments are given in Table 5. One poly(S) seed with a radius of 43.3 nm (S43) and two poly(S-*co*-MA) seeds (S/MA = 0.80/0.20) with radii of 31.2 (SMA31) and 22.4 nm (SMA22) were used. The diameters were determined by analyzing at least 1000 particles on transmission electron micrographs. Transmission electron microscopy was also used to check for secondary nucleation.

Chemically-initiated runs, where KPS was used as initiator, and the so-called γ-relaxations, where initiation is by a γ-radiation source (^{60}Co), were performed in a two-piece dilatometer fitted with an automatic tracking device that measures contraction of the volume of the reacting system. In both initiation systems the seed latices were swollen overnight with the monomers. All kinetic runs were performed at 50 ± 0.5 °C. All seeds were used in both types of experiments, and in the chemically-initiated runs the initiator concentrations were varied over a wide range. In all cases conditions were such that reactions commenced in interval 2, *i.e.*, in the presence of monomer droplets. As it is expected that the kinetics are very dependent on the monomer composition in the latex particles and in the aqueous phase, most experiments were performed at a nearly azeotropic overall composition with $f_{S\mathrm{p}} = 0.84$. In the bulk system the azeotrope is at $f_S = 0.75$. In an emulsion system there is normally no real azeotrope, as in the course of the reaction the phase volumes change and therefore also the monomer ratios in each phase, except when the saturation concentrations of the monomers in the aqueous phase are exactly the same or very low. The kinetics were analyzed only at low conversions, so that hardly any composition drift occurred. It was therefore also possible to study the kinetics at a much lower $f_{S\mathrm{p}}$ (0.57).

Gel permeation chromatography (GPC) was done on a chromatographic system (Waters Division of Millipore) equipped with two Shodex linear columns (GPC KF80M, 30 cm) and a refractive index detector (Waters Model 410). THF was used as the eluent at a flow rate of 1 cm^3/min. Calibration is discussed later in the text.

Experimental Methodology. In experiments with γ-initiation the system is allowed to reach a steady state in the source. After this steady state has been reached, the reactor and tracking device are taken out of the γ-source, so that the entry rate drops virtually instantaneously from a relatively high value in the source to a low value, namely, that of thermal entry. The average number of radicals in the particles drops to a lower steady-state value. A change in polymerization rate is observed. This setup enables one to study the radical loss mechanism(s). Details have been described elsewhere.[4,33] The chemically-initiated runs should in principle give two pieces of information: the steady-state rate and the approach to steady state. It is possible to obtain mechanistic information from these runs. In γ-relaxations the radical loss mechanisms can be studied separately from radical creation mechanisms, whereas in chemically-initiated runs they cannot be separated. If γ-relaxation data are available, these can be used as an important and independent check for the interpretation of the data obtained in chemically-initiated runs. It should be noted that the approach to steady state in a chemically-initiated system can only be used in a meaningful way if there are no retardation effects. In S emulsion polymerizations oxygen acts as a true inhibitor (no retardation) and the steady states can be used to elucidate the kinetics.[33] For a new system it is therefore important to check for any inhibition effects. One of the main advantages of γ-relaxation runs is that it is possible to re-insert the reactor in the source in the same run. It is thus possible to compare approaches to steady state in subsequent insertions, which provides an excellent means for checking for inhibition artifacts. In the absence of any inhibition effect, the approaches to steady state should be the same.

Molecular weight distributions will be used to obtain information about chain transfer to monomer, which is needed to calculate exit rate coefficients. As stated before, a dependence of the exit rate on particle radius in the S–MA system is expected. Therefore relaxation runs were performed with seeds with varying particle sizes. The relaxation kinetics are interpreted as both first- and second-order loss processes. This results in two values for the exit rate coefficient, which are compared with theoretical predictions for the exit rate coefficient. The exit rate data will be used to elucidate the kinetics (entry) of the persulfate-initiated runs.

Experimental Results

γ-Relaxations and Chemically-Initiated Experiments. In Figure 2 are shown the conversion versus time plots for two of the experiments performed with γ-initiation (with seed latex S43). Figure 2a shows the results for four consecutive insertions into the γ-radiation source, and Figure 2b three consecutive relaxation runs. It appears that after the first insertion, the approach to the steady state in the source is slower than in the three consecutive runs. This was also found for the three other experiments performed with different seed latices and with the other monomer feed composition. The approach to steady state was always slower in the first insertions, whereas the approaches to steady state in the consecutive runs were always the same. As stated above, the approaches to steady state can be used to reveal any retardation effects. The results indicate that there is indeed a retardation effect in this system. It is quite possible there is a nonideal inhibitor. Once this has been consumed, there are no retardation effects any more, which explains why the approaches to steady state in consecutive runs are the same. This means, however, that the approach to steady state in the chemically-initiated runs cannot be used to obtain mechanistic information about the kinetics, as it is impossible to completely exclude inhibitor, presumably oxygen, from the system.

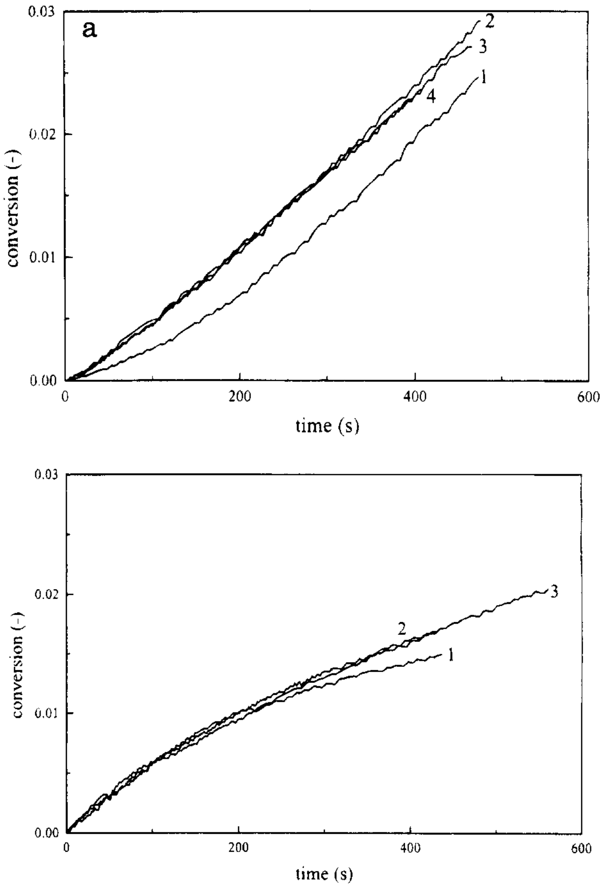

Figure 2. Conversion versus time of (a) four consecutive insertions into the γ-radiation source ($f_{S\mathrm{p}} = 0.57$, seed latex S43 (polystyrene, $r_S = 55$ nm)) and (b) three consecutive relaxation runs ($f_{S\mathrm{p}} = 0.84$, seed latex S43).

In Figure 3 a number of conversion versus time plots are shown for chemically-initiated runs, in this case with seed latex S43, where the initiator concentration was varied over a wide range. It can be seen that the system reaches a steady state after a few percent of conversion and that the rate in this steady state is constant, which is expected for a zero–one system. It can be seen that the higher the initiator concentration, the higher is the reaction rate, although at the highest initiator concentrations, the rate is only weakly dependent on initiator concentration. Note that the steady-state value of $\bar{n}$ in all runs was always smaller than 0.5, which is a necessary, but insufficient condition for zero–one kinetics.

Molecular Weight Distributions and Chain Transfer to Monomer. The copolymers which were obtained after stopping the chemically-initiated runs

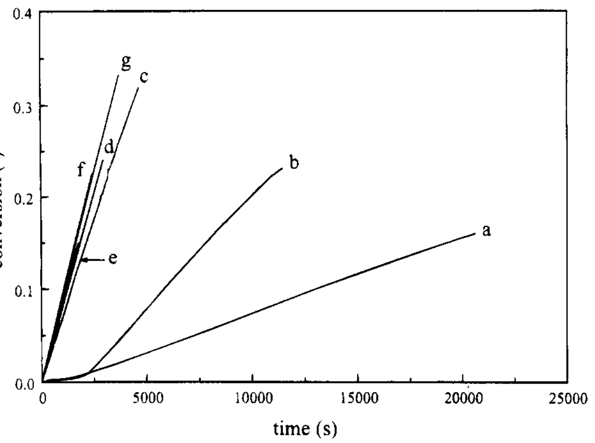

Figure 3. Conversion versus time for reactions initiated with varying concentrations of persulfate (seed latex S43 (polystyrene, r_S = 55 nm). Particle concentration $N_c = 2.1(\pm 0.1) \times 10^{17}$ L^{-1}, initiator concentration = (a) 9×10^{-6}, (b) 9×10^{-5}, (c) 9×10^{-4}, (d) 2.9×10^{-3}, (e) 5.1×10^{-3}, (f) 9.2×10^{-3}, and (g) 9.3×10^{-3} mol/L.

with hydroquinone were analyzed by GPC to obtain values for the average rate coefficient for transfer. In Figure 4 the differential log molecular weight distributions are shown for a series of copolymers polymerized onto the same seed latex with varying persulfate concentrations. The low molecular weight peak is the seed latex polymer (in this case polystyrene), and the peak on the high molecular weight side is the S–MA copolymer polymerized onto the seed latex. Since there is a relatively large difference between the molecular weight of the seed latex and the copolymer, it was not necessary to correct for interference of the seed polymer on the distribution of the copolymers. It is possible to calculate the average rate coefficient for chain transfer to monomer from the molecular weight distributions by using the linear part of the natural logarithm of the differential number fraction distribution (ln($P(M)$) versus M).[34–37] The differential number fraction distribution was calculated from the differential log molecular weight distribution (dW(log(M))/d log(M), which in turn is calculated by multiplying the GPC trace (dW(log(M))/dV_{el}) with dV_{el}/d log(M), the derivative of the calibration curve (eq 33).[38]

$$P(M) = \frac{dW(\log(M))}{dV_{el}} \frac{dV_{el}}{d(\log(M))} \frac{1}{M^2} \qquad (33)$$

where V_{el} is the elution volume. Universal calibration was applied to correct for the difference in hydrodyanmic volume of the polystyrene standards used in GPC and the S–MA copolymers. The molecular weight of a copolymer ($M_{copolymer}$) with a fraction of S equal to F_S was calculated according to eq 34.

$$M_{copolymer} = M_0^{copolymer}\left[\frac{F_S M_S}{M_0^S} + \frac{(1 - F_S)M_{MA}}{M_0^{MA}}\right] \qquad (34)$$

where M_0^i is the molar mass of monomer i, and $M_0^{copolymer}$ the average molar mass of the monomers in the copolymer. M_S is the molecular weight after calibration with monodisperse polystyrene standards, and M_{MA} is the molecular weight calculated from M_S with universal calibration. Values for the Mark–Houwink constants for polystyrene ($K = 16.2 \times 10^{-3}$ cm^3·g^{-1}, a = 0.71) and poly(methyl acrylate) ($K = 7.88 \times 10^{-3}$ cm^3·g^{-1}, a = 0.885) were taken from the literature.[25] An example of the resulting distribution is shown in Figure 5. The linear part was evaluated with the restriction of the highest reliable value of $M_{copolymer}$ corresponding to the highest GPC standard used. The slope of the linear part is equal to $M_0^{copolymer}$ times the ratio of the rate of chain termination and the rate of propagation (C_m). The values for C_m are plotted versus the ratio of initiator concentration (C_I) and particle number (N_c), which is a measure for the entry rate. By taking the minimum value, the ratio of the average transfer rate coefficient and the average propagation rate coefficient can be obtained, because in a zero–one system the chain-stopping mechanism is predominantly chain transfer, especially at low radical/initiator concentrations. This is shown in Figure 6 for four different series of experiments with varying particle sizes and monomer compositions. One can see that the ratio decreases slowly with decreasing initiator concentration, but at very low initiator concentrations the ratio increases significantly. This is a result of the fact that the molecular weights are so high that the linear part is at molecular weights higher than the highest standard used or even at molecular weights above the exclusion limit in GPC, so these data should not be taken into account. They are included in the plot to show that one must perform a number of experiments at varying initiator concentrations to be sure to be able to exclude artifacts.

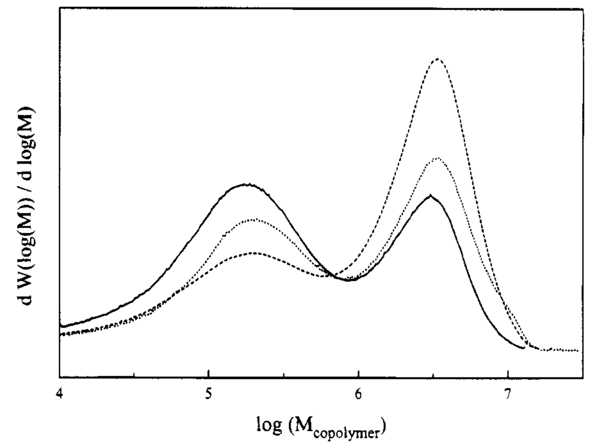

Figure 4. Differential log molecular weight distribution (dW(log(M))/d log(M)) of seed polymer (S43, polystyrene) and S–MA copolymer (F_s = 0.84) polymerized onto the seed latex with varying persulfate concentrations: 9×10^{-5} (—), 9.1×10^{-4} (- - -), and 5.1×10^{-3} mol/L (···). The high molecular weight peak is due only to the copolymer.

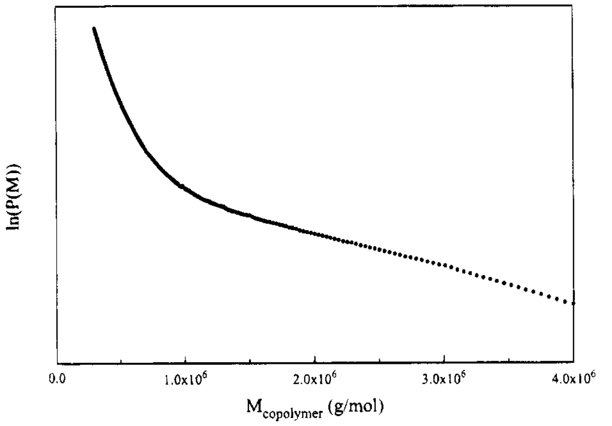

Figure 5. Example of a plot of the natural logarithm (ln(P(M))) of the differential number fraction distribution of seed polymer + copolymer versus $M_{copolymer}$.

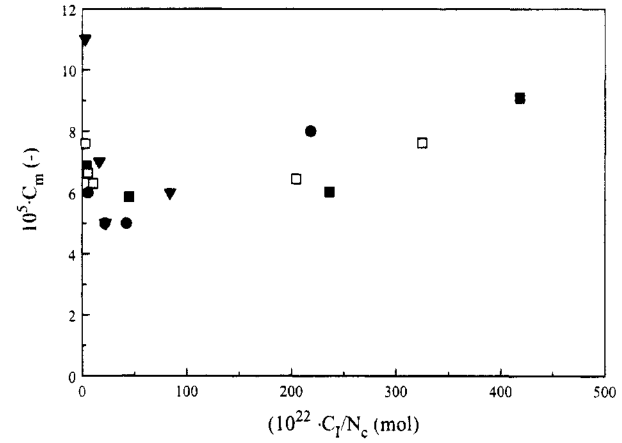

Figure 6. Ratio (C_m) of the average rate coefficient for chain transfer to monomer ($\bar{k}_{tr}$) and the average rate coefficient for propagation ($\bar{k}_p$) as determined from the ln(P(M)) plots versus the ratio of initiator concentration (C_I) and particle concentration (N_c). $f_{Sp} = 0.84$: (■) S43, (●) SMA31, (▼) SMA22; $f_{sp} = 0.57$: (□) S43.

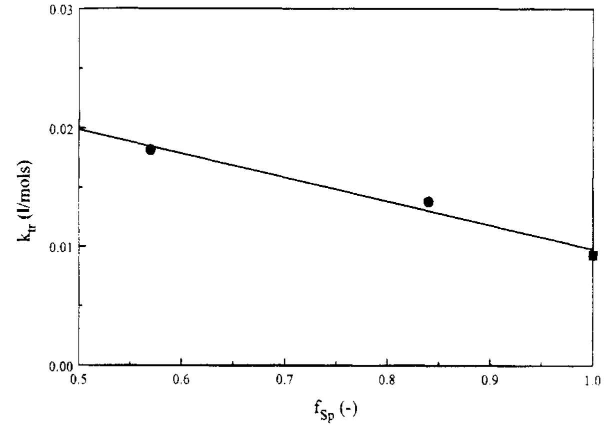

Figure 7. Average rate coefficient for chain transfer to monomer ($\bar{k}_{tr}$) versus mole fraction of S in the particles (f_{Sp}), fitted with eq 34: (●) data from the kinetic experiments; (■) literature value for $k_{tr,SS}$.

It was shown in an earlier section (Application of the Model to S−MA Emulsion Copolymerization) that the average rate coefficient for chain transfer can be expressed as follows for high fractions of S if A_{SMA} is very high:

$$\bar{k}_{tr} = k_{tr,SS}f_{Sp} + k_{tr,SMA}(1 - f_{Sp}) \qquad (35)$$

If the plot of the average rate coefficient of chain transfer to monomer versus f_{Sp} is linear, one can assume that A_{SMA} is indeed very high; *i.e.*, transfer is dominated by S-terminated radicals. It is then possible to extract a value for $k_{tr,SMA}$. In Figure 7 are plotted the average rate coefficients for chain transfer to monomer obtained from the experiments described above. It can be seen that in combination with the literature value for $k_{tr,SS}$ (Table 1) there is a linear dependence. Fitting eq 30 to these data results in a value for $k_{tr,SMA}$ of 3.0×10^{-2} $L \cdot mol^{-1} \cdot s^{-1}$. This value and the linearity of the plot are corroborated by results obtained from experiments carried out over the whole range of compositions.[39] It was shown that only at very high fractions of MA ($f_{MA} > 0.9$) the rate of transfer increases strongly. The value obtained for $k_{tr,SMA}$ was used in the discussion of the model assumptions in this system.

Exit Rate. The relaxation runs were analyzed by using the slope and intercept method and the following rate equations with both first- and second-order dependencies of the exit rate on $\bar{n}$.

$$\frac{d\bar{n}}{dt} = \varrho_{th1}(1 - 2\bar{n}) - k_1\bar{n} \qquad (36)$$

$$\frac{d\bar{n}}{dt} = \varrho_{th2}(1 - 2\bar{n}) - 2k_2\bar{n}^2 \qquad (37)$$

where ϱ_{th1} is the thermal entry rate calculated if the data are interpreted with a first-order dependence on $\bar{n}$ and k_1 is the corresponding exit rate coefficient, *etc.* These rate equations represent the two sublimits of eq 24 (Limit 2, complete re-entry): if the rate of escape from the particles is larger than the rate of propagation, a first-order dependence is found for the exit rate ($k_1\bar{n}$), and if the rate of propagation is larger than the rate of escape, a second-order dependence is found ($2k_2\bar{n}^2$). The results are shown in Table 6.

The results of fitting to a first-order dependence are included, although a second-order dependence was expected (see Discussion of Assumptions in the S−MA System). The average number of radicals per particle was always smaller than 0.5, a necessary, though not sufficient, condition for a zero−one system. In the same table the theoretical predictions for the exit rate coefficients based on the sublimits of eq 24 are given. If these simplifications are pursued in eq 24, the following expressions are found for the exit rate coefficients k_1 and k_2:

$$k_1 = 2\bar{k}_{tr,S}C_{Sp} + 2\bar{k}_{tr,MA}C_{MAp} = 2k_{tr,SS}C_{Sp} + 2k_{tr,SMA}C_{MAp} \qquad (38)$$

$$k_2 = \frac{k_{tr,SS}C_{Sp}k_{dS}}{\bar{k}^1_{pS}C_p} + \frac{k_{tr,SMA}C_{MAp}k_{dMA}}{\bar{k}^1_{pMA}C_p} \qquad (39)$$

Note that there are in principle also cases where the exit rate of one of the monomers shows a first-order dependence and the other a second-order dependence. However, for simplicity, these possibilities are not taken into account. Equations 38 and 39 were used to give predictions for the exit rate coefficients ($k_{1,pred}$, $k_{2,pred}$), by inserting values for the chain transfer constants, monomer concentrations, the rates of escape (depending on the swollen particle radius), and the propagation rates; see Table 3. It can be seen that the experimental values for k_1 are lower than the predicted values by at least a factor of 30. These are in effect rates of chain transfer to monomer, values which are obtained from independent experiments. Therefore there is no numerical agreement if the relaxation data are interpreted with a first-order dependence. However, if the experimental values for k_2 are compared with the predicted values, there seems to be reasonable accordance (within a factor of 2), except for the system with the lowest swollen particle radius (a factor of 6). This suggests that second-order dependencies for the exit rate like transfer−diffusion mechanisms are indeed correct but that other factors may play a role for small particle sizes. Exit with these particles is somehow slower than the model predicts. It has been suggested that this may be so, because these particles are hairy due to MA-rich oligomers at the surface. However, this would not explain why exit with the larger particles of SMA31 does not seem to be slowed down.

In Figure 8 the predicted exit rate coefficients of S and MA monomeric radicals are plotted versus the

Table 6. Results of γ-Relaxation Experiments with Varying Particle Radius and Composition: ϱ_{th1} and ϱ_{th2} Are the Thermal Entry Rates Calculated According to a First- or Second-Order Exit Rate, k_1 and k_2 Are the Corresponding Experimental Exit Rate Coefficients, and $k_{1,pred}$ and $k_{2,pred}$ Are the Predicted First- and Second-Order Exit Rate Coefficients

seed latex	ϱ_{th1} (s^{-1})	ϱ_{th2} (s^{-1})	k_1 (s^{-1})	$k_{1,pred}$ (s^{-1})	k_2 (s^{-1})	$k_{2,pred}$ (s^{-1})
S43 (0.84/0.16)	3.5×10^{-4}	1.8×10^{-4}	2.3×10^{-3}	1.5×10^{-1}	5.0×10^{-3}	1.4×10^{-2}
SMA31 (0.84/0.16)	3.3×10^{-4}	9.2×10^{-5}	5.2×10^{-3}	1.5×10^{-1}	1.3×10^{-2}	2.7×10^{-2}
SMA22 (0.84/0.16)	1.6×10^{-4}	7.6×10^{-5}	2.2×10^{-3}	1.5×10^{-1}	8.6×10^{-3}	5.3×10^{-2}
S43 (0.57/0.43)	1.9×10^{-3}	8.8×10^{-4}	6.9×10^{-3}	2.1×10^{-1}	9.4×10^{-3}	1.8×10^{-2}

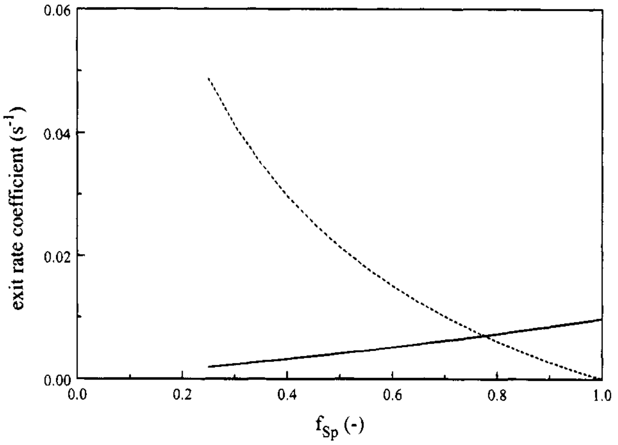

Figure 8. Predicted exit rate coefficients of S (—) and MA (- - -) monomeric radicals as a function of the molar fraction of S in the particles (f_{Sp}) at a constant swollen particle radius of 55 nm.

molar fraction of S in the particles at a constant particle size (r_s = 55 nm). It can be seen that MA monomeric radicals are dominant only at low fractions of S (f_{Sp} < 0.5), in contrast to what is found in the system S–methyl methacrylate (MMA).[7,8] In this system exit is completely dominated by MMA. This discrepancy can be explained easily if one realizes that, although MA is much more water soluble than S and has a higher rate of escape, the propagation rate of the MA monomeric radical is also much higher, and the ratio of rate of escape to rate of propagation is not much larger than that of S. The water solubility of MA is 4 times higher than that of MMA,[3] but the long-chain k_p (616 $L{\cdot}mol^{-1}{\cdot}s^{-1}$ [40]) is *ca.* 15 times higher at 50 °C.

Entry Rate. Now that it can be assumed that the model for radical exit from the latex particles is correct at least for the higher particle sizes, let us turn to the chemically-initiated runs. The other rate-determining mechanism in these systems is radical entry. As stated above, it is assumed that the rate-determining steps in the entry process are propagation and termination of oligomeric, initiator-derived radicals in the aqueous phase. It was shown that for monomers with a relatively high k_p and/or a high water solubility and/or a low z (*e.g.*, MMA) the initiator efficiencies are close to 100%, which means that almost all initiator radicals propagate in the aqueous phase reaching a critical degree of polymerization z, after which they enter a particle instantaneously. MA has both a very high k_p and a relatively high water solubility. It is therefore expected that systems with pure MA also show 100% entry efficiency. A value for z can be estimated from the expression given by Maxwell *et al.*,[5] for which the water solubility is needed (eq 40).

$$z = -1 + \mathrm{int}\left[\frac{-23}{RT\ln(C_{iaq,s,h})}\right] \quad (40)$$

with RT in kJ/mol and $C_{iaq,s,h}$ in mol/L. This gives z = 18 for MA. If the efficiency is then calculated with the second factor of the right-hand side of eq 21, it is found that the efficiency is always 100%.

In this way the entry rate was calculated for different initiator concentrations and particle concentrations. The slopes of the steady states in the conversion–time plots of the chemically-initiated runs were used to obtain steady-state values for $\bar{n}$. By inserting the values for the entry rate (calculated assuming 100% efficiency) and the values for $\bar{n}$ in eq 37, values for the exit rate coefficients (k_2) in the chemically-inititiated runs can be derived. The values for k_2 thus obtained vary greatly and do not accord with either the predicted values or the values found experimentally in the relaxation runs: the values from the chemically-initiated runs are always much higher. If the model for exit is correct, the discrepancy is so large as not to be consistent with the hypothesis that initiator efficiency is 100%.

Hence, the predicted and experimental values for the exit rate coefficients were taken, which are in accord with each other except at the lowest particle radius, and the entry rates in the chemically-initiated runs are calculated by inserting the values for k_2 and the experimental values for $\bar{n}$ in eq 37. The initiator efficiencies can then be calculated after subtraction of the experimental values for ϱ_{th2}. The resulting initiator efficiencies are plotted versus the initiator concentration in Figure 9. It can be seen that in spite of the scatter, especially at low initiator concentrations, there is clearly a dependence on the initiator concentration; *i.e.*, the initiator efficiency decreases with increasing initiator concentration. This means that the efficiency is not 100%. This can be understood as follows. Although MA is much more water soluble than S, there is still some appreciable amount of S in the aqueous phase, because the overall fraction of S in the recipes is much higher than that of MA. This can be seen in Table 2. The fraction of S in the aqueous phase (f_{Saq}) is very low; f_{Saq} = 0.036 when f_{Sp} = 0.84. If f_{Saq} were 0, then the k_p in the aqueous phase would be that of MA. But a small amount of S decreases the average propagation rate coefficient considerably: at f_{Saq} = 0.036, $\bar{k}_p$ = 740 $L{\cdot}mol^{-1}{\cdot}s^{-1}$. This is much lower than the value of 10700 $L{\cdot}mol^{-1}{\cdot}s^{-1}$ of pure MA. Also the total monomer concentration in the aqueous phase is much lower, because the concentration of MA in the aqueous phase is linearly dependent on f_{MAp}, which is 0.16. If it is assumed that the expression for the copolymer composition according to the terminal model, which is normally valid for long copolymer chains (eq 41), can be applied to the composition of the oligomeric radicals by using the reactivity ratios given in Table 1, it can be calculated that the fraction of S in the oligomers is nonnegligible and equal to *ca.* 0.15.

$$F_S = \frac{r_S f_S^2 + f_S(1 - f_S)}{r_S f_S^2 + 2f_S(1 - f_S) + r_{MA}(1 - f_S)^2} \quad (41)$$

The validity of the copolymer equation has been as-

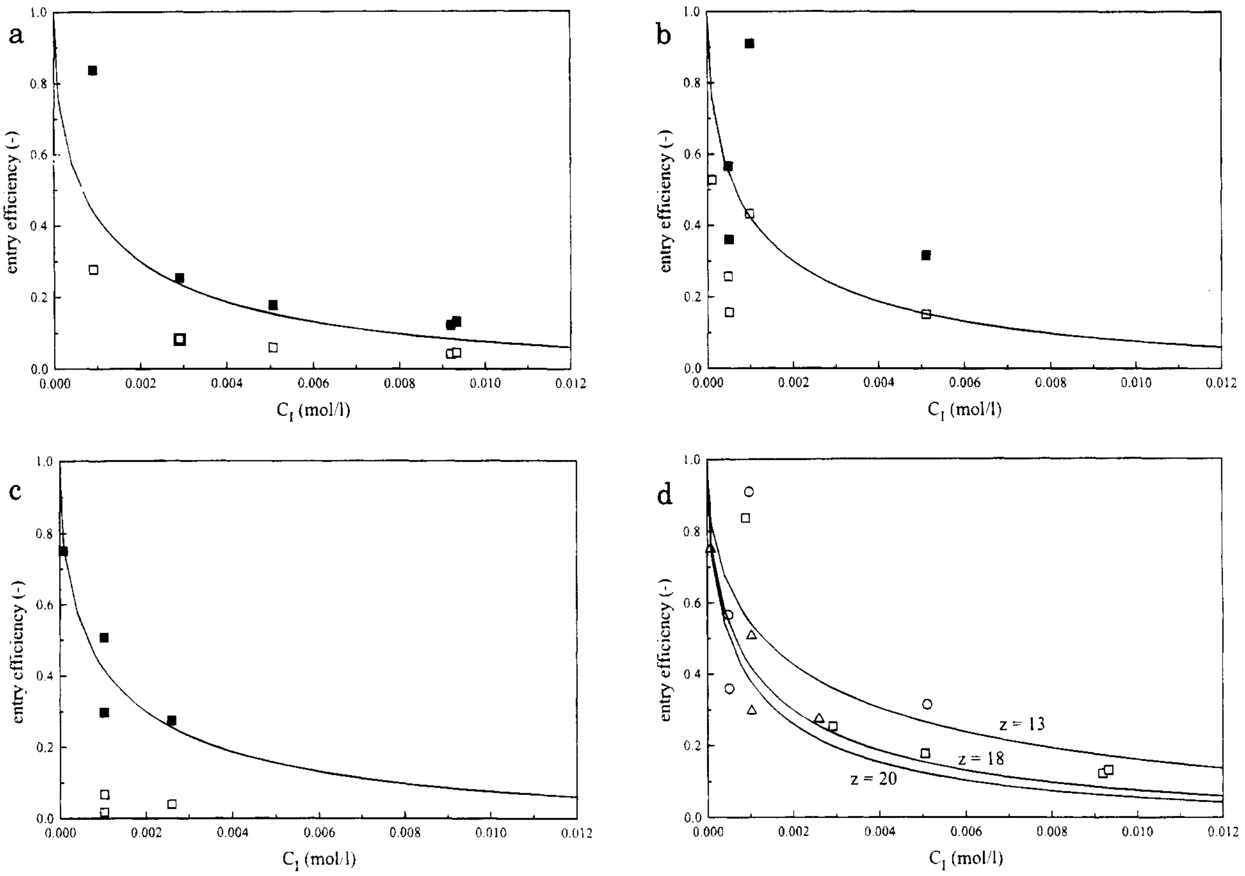

Figure 9. Entry efficiencies, calculated with experimentally determined (□), and predicted (■) second-order exit rate coefficients versus the initiator concentration (C_I) for seed latices with different swollen particle radii: (a) S43, r_s = 55 nm; (b) SMA31, 39 nm; (c) SMA22, 28 nm. The lines are predictions with eq 26: $\bar{k}_p$ = 740 L·mol^{-1}·s^{-1}, C_{aq} = 0.1 mol/L, $k_{t,aq}$ = 3.7 × 10^9 L·mol^{-1}·s^{-1}, and z = 18. In part d all data calculated with the *predicted* exit rate coefficients are combined. The lines are predictions with eq 26: values for z are indicated.

sumed before[28] and was claimed to be applicable to S–(meth)acrylic acid and S–MMA oligomers on the basis of FTIR spectroscopy and ^{13}C NMR.[41,42] Therefore the initiator efficiency is calculated with the low value for $\bar{k}_p$ of 740 L·mol^{-1}·s^{-1}, a total monomer concentration of 0.1 M (see Table 2), and z = 18. For the termination rate constant in the aqueous phase a value of 3.7 × 10^9 L·mol^{-1}·s^{-1} is taken. The result is shown in Figure 9. The scatter at low initiator concentrations is due to the fact that the thermal entry rate is considerable compared to the entry rate of initiator-derived radicals. The latter is calculated by subtracting two entry rates of comparable magnitude, so the error can be quite large. However, the trend of the efficiency as a function of initiator concentration with the highest particle size (Figure 9a) is in good agreement with the predicted line. The data with the intermediate particle size (Figure 9b) are not conclusive, as most reactions were performed at low initiator concentrations. With the lowest particle size (Figure 9c) the data with the experimental exit rate coefficient are very low, but the data calculated with the predicted exit rate coefficient are in accord with the predicted line. The conclusion from Figure 9 is that z = 18 fits the data reasonably well, which is in accord with eq 40.

It is realized that the use of eq 21 is a serious simplification. One could question both the use of a constant termination rate coefficient and one critical degree of polymerization. The first is in the diffusion limit, and one could therefore argue that it should be dependent on the size of the oligomer as the diffusion coefficient is size-dependent and inversely proportional to the degree of polymerization. This would then increase the predicted efficiency. However, the critical degree of polymerization is also dependent on the chemical composition of the oligomer, *i.e.*, on the number of S units: the more S units, the lower is z and the higher is the efficiency. However, virtually nothing is known of the effect of composition on the solubility for this kind of oligomer. As the experimental data show considerable scatter and the number of data at higher initiator concentrations is very limited (for the lower particle sizes), there is no point in trying to model the entry process with a size-dependent termination rate and a composition-dependent critical degree of polymerization. It is important to realize that the largest effect on the efficiency comes from the influence of a small amount of S on the average propagation rate: S slows the rate of propagation in the aqueous phase ($\bar{k}_pC_{aq}$) to such an extent that termination of the oligomers becomes rate-determining as well.

Finally, a very interesting observation is presented. The conversion–time curves in Figure 3 show that the rate of polymerization is not very dependent on initiator concentration if the initiator concentration is high. As $\bar{n}$ is smaller than 0.5, this must be a result of the entry rate becoming independent of the initiator concentration. If, for simplicity, it is assumed that the approach for describing the entry rate in this system is correct and the total entry rate is plotted as a function of initiator concentration (Figure 10), it can be seen that there appears to be a maximum or at least an upper limit for the entry rate. Apparently, z is so high that at high initiator concentrations termination in the

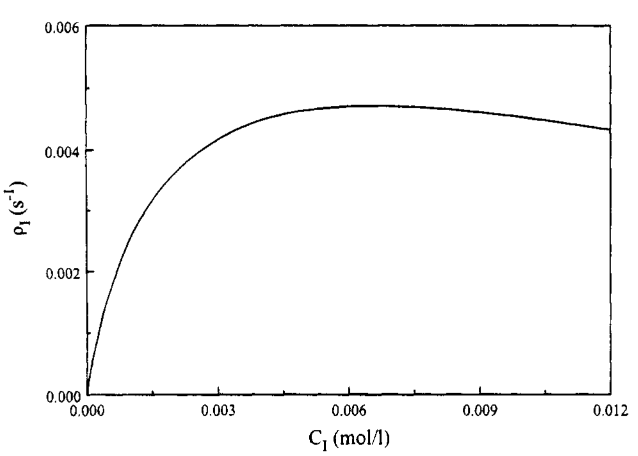

Figure 10. Total entry rate (ϱ_I) calculated with the predicted second-order exit rate coefficients versus the initiator concentration (C_I) calculated with eq 26: $\bar{k}_p = 740$ L·mol^{-1}·s^{-1}, $C_{aq} =$ 0.1 mol/L, $k_{t,aq} = 3.7 \times 10^9$ L·mol^{-1}·s^{-1}, $z = 18$, and $N_c = 2 \times 10^{17}$ L^{-1}.

aqueous phase becomes more and more dominant. This means that there is no point in increasing the initiator concentration to increase the rate of polymerization. This will only lead to the production of more water-soluble oligomers that can have an adverse effect on the properties of the resulting polymer, for instance low water resistance in coatings applications. This observation is in accord with unpublished results of emulsion copolymerizations with the water-miscible monomer 2-hydroxyethyl methacrylate and styrene, where an increase in the concentration of persulfate leads to a higher fraction of 2-hydroxyethyl methacrylate homopolymerizing in the aqueous phase, or a decrease in the contribution of polymerization in the polymer phase.[43]

Conclusions

This paper shows the results of a study on the kinetics of seeded particle growth of a styrene–methyl acrylate emulsion copolymerization. The seed was either a polystyrene or a poly(styrene-*co*-methyl acrylate) polymer latex; because the method used to obtain kinetic information only requires changes of a few percent in conversion, the use of a heteroseed (polymerization in a polymer swollen with another monomer (mixture)) will not lead to phase separation. The system was shown to obey "zero–one" kinetics ($\bar{n} < 0.5$, with entry of a free radical into a particle already containing a growing radical resulting in instantaneous termination), because enough S monomeric radicals are formed. Experiments were performed with persulfate as initiator or with γ-radiation as a source of radicals. The latter initiation system enables the relaxation kinetics to be observed, which are sensitive to radical annihilation events, such as radical exit followed by eventual termination. Propagation rate coefficients for data interpretation were obtained using data from pulsed laser polymerizations, and transfer rate coefficients were obtained from the high molecular weight part of the observed molecular weight distribution. Results of γ-relaxation experiments indicated that the styrene–methyl acrylate system is retarded in the initial stages (perhaps by oxygen), and it is likely that this retardation also holds for the persulfate-initiated system. Relaxation data show numerical agreement with the transfer–diffusion model for exit of radicals from latex particles, except possibly for small particle sizes. The exit rate is most likely to have a second-order dependence on the average number of radicals per particle. Exit is not dominated by the most water-soluble comonomer in this system at molar fractions of styrene higher than 0.5, in contrast to what is found in styrene–methyl methacrylate emulsion copolymerizations. By using the relaxation data to calculate entry efficiencies from runs initiated with persulfate, it could be shown that the initiator efficiencies in the styrene–methyl acrylate copolymer system, at the composition investigated, are not 100% but vary between ca. 5 and 50%, depending on the initiator concentration. The dependence on the initiator concentration is in accordance with the theory that states that the rate-determining step in entry is propagation of the initiator-derived oligomeric radicals in the aqueous phase, if the copolymer composition equation can be applied with these relatively short chains, which is not trivial. It was shown that the presence of a small amount of styrene in the aqueous phase slows the rate of propagation down considerably. It was also shown that the total entry rate can show a maximum as a function of the initiator concentration.

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Glossary

A_{ij}	ratio of concentrations of radicals with terminal unit i and radicals with terminal unit j
c_i^{1L}	pseudo-first-order rate coefficient of termination of a monomeric radical of type i with a polymeric radical (s^{-1})
C_{aq}	total monomer concentration in the aqueous phase (mol/L)
C_I	concentration of initiator in the aqueous phase (mol/L)
C_{iaq}	concentration of monomer i in the aqueous phase (mol/L)
$C_{iaq,s,h}$	saturation concentration of monomer i in the aqueous phase (mol/L)
C_p	total monomer concentration in the polymer phase (mol/L)
C_{ip}	concentration of monomer i in the polymer phase (mol/L)
$C_{ip,s,h}$	saturation concentration of monomer i in the polymer phase (mol/L)
C_m	ratio of the rate constants of chain transfer to monomer and the propagation rate constant
D_{iaq}	diffusion coefficient of monomeric radical i in the aqueous phase (m^2/s)
D_{ip}	diffusion coefficient of monomeric radical i in the polymer phase (m^2/s)
f_i	molar fraction of monomer i (based on monomers)

f_{iaq}	molar fraction of monomer i in the aqueous phase (based on monomers)
f_{id}	molar fraction of monomer i in the droplet phase
f_{ip}	molar fraction of monomer i in the polymer phase (based on monomers)
F_{i}	molar fraction of monomer i in the copolymer
I_2	initiator molecule, thermally decomposable in two similar radicals
$I^{\bullet}$	initiator radical
$\mathrm{IM}_z{}^{\bullet}$	initiator-derived oligomer with z monomer units added entering a particle instantaneously
$\mathrm{IM}_n{}^{\bullet}$	initiator-derived oligomer with n monomer units added
j_{crit}	critical degree of polymerization of an oligomer at which it can form a precursor particle
$k_{1/2}$	exit rate coefficient for first- or second-order dependence of exit rate on $\bar{n}$ (s^{-1})
$k_{1/2,\mathrm{pred}}$	predicted value of first- or second-order exit rate coefficient (s^{-1})
k_{d}	first-order initiator decomposition rate constant (s^{-1})
k_{di}	rate of escape from a latex particle of a monomeric radical of type i (s^{-1})
$k_{\mathrm{e}z}$	rate coefficient of entry of an oligomer with degree of polymerization z (L·mol^{-1}·s^{-1})
k_{p}	homopropagation rate constant (L·mol^{-1}·s^{-1})
$\bar{k}_{\mathrm{p}}$	average (long chain) propagation rate coefficient (L·mol^{-1}·s^{-1})
$\bar{k}_{\mathrm{pii}}$	composed rate coefficient of propagation in the penultimate model (L·mol^{-1}·s^{-1})
k_{piii}	homopropagation rate constant of monomer i in the penultimate model (L·mol^{-1}·s^{-1})
$\bar{k}_{\mathrm{paq}}$	average propagation rate coefficient in the aqueous phase (L·mol^{-1}·s^{-1})
k_{p}^{1}	propagation rate constant of a monomeric radical (L·mol^{-1}·s^{-1})
$\bar{k}_{\mathrm{pi}}^{1}$	average propagation rate coefficient of a monomeric radical of type i (L·mol^{-1}·s^{-1})
k_{pii}^{1}	propagation rate constant of a monomeric radical of type i with monomer i (L·mol^{-1}·s^{-1})
k_{pij}^{1}	cross-propagation rate constant of a monomeric radical of type i with monomer j (L·mol^{-1}·s^{-1})
$\bar{k}_{\mathrm{pI}}$	average propagation rate coefficient of an initiator radical (L·mol^{-1}·s^{-1})
k_{rei}	rate coefficient of re-entry of a monomeric radical of type i (L·mol^{-1}·s^{-1})
$k_{\mathrm{ti}}{}^{\mathrm{1L}}$	termination rate constant of a monomeric radical of type i with a polymeric radical (L·mol^{-1}·s^{-1})
$k_{\mathrm{t,aq}}$	termination rate constant of any radical in the aqueous phase (L·mol^{-1}·s^{-1})
$k_{\mathrm{t,iaq}}$	termination rate constant of monomeric radical of type i in the aqueous phase (L·mol^{-1}·s^{-1})
k_{tr}	rate constant of chain transfer (L·mol^{-1}·s^{-1})
$\bar{k}_{\mathrm{tr}}$	average rate coefficient of chain transfer (L·mol^{-1}·s^{-1})
$\bar{k}_{\mathrm{tr,i}}$	average rate coefficient of chain transfer to monomer i (L·mol^{-1}·s^{-1})
$k_{\mathrm{tr,ii}}$	rate constant of chain transfer of a radical with terminal unit i to monomer i (L·mol^{-1}·s^{-1})
$k_{\mathrm{tr,ij}}$	rate constant of cross-transfer of a radical with terminal unit i to monomer j (L·mol^{-1}·s^{-1})
M_0	molecular weight of a monomeric radical
M_0^{i}	molecular weight of monomer i
$M_0^{\mathrm{copolymer}}$	average molecular weight of the monomer units in the copolymer
M_{i}	molecular weight of a polymer obtained with universal calibration
M_{aq}	monomer dissolved in the aqueous phase
$\mathrm{M}_{\mathrm{iaq}}{}^{\bullet}$	monomeric radical of type i in the aqueous phase
M_{p}	monomer in the polymer phase
N_{A}	Avogadro's number (mol^{-1})
N_{c}	particle number concentration (per volume of aqueous phase (L^{-1}))
N^{0}	fraction of particles that contain no radical
N^{1}	fraction of particles that contain one radical
N_{p}^{1}	fraction of particles that contain one polymeric radical
N_{i}^{1}	fraction of particles that contain one monomeric radical of type i
$\bar{n}$	average number of radicals per particle
$P(M)$	differential number fraction distribution of dead polymer chains
$\mathrm{P}^{\bullet}$	polymeric radical
$\mathrm{PM}^{\bullet}$	polymeric radical with one monomer unit added
S_{M}	molar solubility of a monomeric radical (mol/L)
r_{s}	radius of a monomer-swollen particle (m)
r_{i}	reactivity ratio of monomer i in the terminal/penultimate model ($k_{\mathrm{piii}}/k_{\mathrm{piij}}$)
$\bar{r}_{\mathrm{i}}$	composed reactivity ratio of monomer i in the penultimate model
r_{i}'	reactivity ratio of monomer i in the penultimate model ($k_{\mathrm{pjii}}/k_{\mathrm{pjij}}$)
s_{i}	reactivity ratio of monomer i in the penultimate model ($k_{\mathrm{pjii}}/k_{\mathrm{piii}}$)
$\mathrm{T}^{\bullet}$	radical in the aqueous phase
V_{el}	elution volume
V_{s}	volume of a monomer-swollen particle (m^3)
z	critical degree of polymerization of an oligomer at which it enters a particle instantaneously
ϱ	total rate of entry (s^{-1})
ϱ_{A}	rate of entry of initiator-derived and thermally-derived radicals into a latex particle (s^{-1})
ϱ_{re}	rate of re-entry into a latex particle of monomeric radicals (s^{-1})
ϱ_{rei}	rate of re-entry into a latex particle of monomeric radicals of type i (s^{-1})
ϱ_{I}	rate of entry of initiator-derived radicals (s^{-1})
ϱ_{th}	rate of entry of thermally-derived radicals (s^{-1})
$\varrho_{\mathrm{th1/2}}$	rate of entry of thermally-derived radicals (s^{-1}), calculated with a first-order or second-order dependence of exit rate
σ_{i}	radius of interaction of a monomeric radical of type i with a polymeric radical (m)

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