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A Kinetic Investigation of Seeded Emulsion Polymerization of Styrene Using Reversible Addition−Fragmentation Chain Transfer (RAFT) Agents with a Low Transfer Constant

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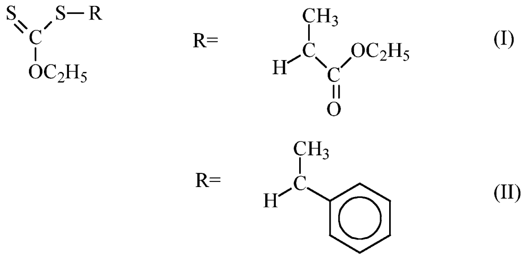
ABSTRACT: The mechanisms were investigated for the seeded emulsion polymerization of styrene mediated by xanthate-based reversible addition−fragmentation chain transfer (RAFT) agents with low transfer constants (ca. 0.7). γ-Radiolysis relaxation measurements were used to determine the exit rate coefficient directly; this increased with the amount of RAFT, consistent with the chain-transfer characteristics of RAFT and the standard transfer/diffusion mechanism for exit. Combining the exit data with measurements of the steady-state rate with chemical initiation showed that the entry rate coefficients decreased with the amount of RAFT, while with γ initiation the entry rate coefficients were unaffected, unless a very high RAFT concentration was used. This behavior is inconsistent with conventional assumptions about RAFT and the aqueous-phase propagation model for entry (which predicts the entry rate coefficient successfully for ordinary emulsion polymerization systems). It is postulated that the RAFT agents used in this work are surface active, which is not unexpected given the canonical forms of these RAFT agents. The dramatic decrease in entry rate coefficient for the chemically initiated system can be taken into account within the framework of the standard aqueous-phase model for entry if it is assumed that the surface activity gives an increased concentration of RAFT near the surface, which leads to increased transfer to radicals which desorb instead of entering, and whose subsequent reentry is "frustrated" by this event recurring, until they eventually undergo aqueous-phase termination.

Introduction

The recent advent of "living/controlled" radical polymerization has allowed the preparation of complex polymer architectures (e.g., block, hyperbranched, star) via free-radical polymerization.[1−3] One such technique is the reversible addition−fragmentation chain transfer (RAFT) polymerization,[3] in which dithioester or xanthate[4] compounds are used as the controlling agent. The present paper concentrates on the xanthates, Scheme 1 (sometimes referred to as MADIX chain transfer agents[4,5]).

While there is now extensive literature on the mechanism of these and other RAFT agents in solution or bulk polymerization,[6−9] the kinetics in emulsion polymerization are less well explored,[10−14] despite the well-known advantages of emulsions for the preparation of industrial polymers and polymer colloids. The origin of this problem is the presence of more than one phase in emulsion polymerizations and, hence, significantly different kinetic and thermodynamic effects.[12−15] As an example of the complications that can thus arise, the xanthates in particular are useful for preparing homocopolymers and block copolymers with a controlled molecular weight distribution (MWD) via emulsion polymerization using sodium dodecyl sulfate (SDS) as surfactant,[5,10] whereas the dithioesters[16] reduce the stability of the latex particles in the presence of SDS, forming a red layer at the start of polymerization.

Scheme 1. General Structure of the RAFT Agents Used and the Leaving Groups of *O*-Ethylxanthyl Ethyl Propionate (I) and *O*-Ethylxanthyl Ethyl Benzene (II)



However, xanthates have a low transfer constant, $C_{\mathrm{tr,RAFT}}$, and thus are not very effective as mediators for controlled radical polymerization. This low transfer constant results in the preparation of polymers with a polydispersity ∼ 2, and when applied to emulsion polymerizations, xanthates show a significant retardation effect,[10] ascribed to exit of the leaving group R after fragmentation of the xanthate, leading to termination with radicals either in the aqueous phase or with growing radicals in other particles. This effect was also suggested to be the cause of the retardation observed with the dithioesters in ab initio and seeded experiments,[16] although this inference was not conclusive, since colloidal destabilization was also a contributing factor.[16]

Understanding, and hence process optimization, requires improved mechanistic elucidation of the events specific to emulsion polymerization, such as the phase-transfer events of radical entry into, and exit (desorption) from, latex particles. The optimal way to obtain

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such information is by examining the rates in a seeded emulsion polymerization system, whereby the presence of a preformed latex enables one to obviate the complexities of particle formation.[15] The aim of this work is to study the effect of xanthates on the entry and exit rate coefficients for styrene using a poly(methyl methacrylate) (PMMA) seeded system. A PMMA seed was used since PMMA is transparent to UV at 254 nm, and hence by using appropriate detectors in size exclusion chromatography the MWD of the newly formed polystyrene can be readily obtained. Growing a polymer in a seed containing a different polymer has been denoted "heteroseeded emulsion polymerization",[17] in which one grows a seed of appropriate size and monodispersity using a convenient monomer such as MMA, where the second-stage monomer (in this case styrene) will swell the seed polymer (PMMA). Seeded studies are then carried out in the normal way.[15] Phase separation of the seed polymer and that of the new polymer are presumed negligible due to the small size of the seed and the presence of excess monomer, which is soluble in both polymers.

Knowledge of the entry and exit rate coefficients (including their dependence on controllable parameters such as particle size and initiator concentration) enables one to obtain mechanistic information. This in turn gives control of the rate of polymerization, particle nucleation and MWD. Recent work has shown that ab initio emulsion polymerizations of styrene in the presence of the xanthate are retarded in rate with an increased number of particles (or smaller average particle diameter), suggesting that exit plays a crucial role.[18]

Theory

Transfer Constants. The measured transfer constants to styrene for the RAFT agents used here are $C_{\mathrm{tr,RAFT}} = k_{\mathrm{tr,RAFT}}/k_{\mathrm{p}} \approx 0.7$ for styrene,[19] where $k_{\mathrm{tr,RAFT}}$ is the rate coefficient for the overall process $\mathrm{P}_n^{\bullet} + \mathrm{SC(OEt)SR} \rightarrow \mathrm{R}^{\bullet} + \mathrm{SC(OEt)SP}_n$ and k_{p} is the propagation rate coefficient. In comparison, the value of the transfer constant for the dithioesters is over 6×10^3.[6] For the present RAFT agents, this transfer constant was measured by the Mayo method, which can be used since the xanthate concentration, due to its low reactivity, remains relatively constant at very low conversions. The measured transfer constant incorporates both addition and fragmentation and kinetically does not distinguish between them; it is an overall kinetic parameter containing both the addition and fragmentation rate coefficients.

Obtaining Entry and Exit Rate Coefficients. Entry and exit rate coefficients are obtained as follows. For a system obeying "zero−one" kinetics (see below), one has the time evolution of the average number of radicals per particle, $\bar{n}$, for a first- and a second-order loss mechanism respectively given by[15]

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \rho(1 - 2\bar{n}) - k \tag{1a}$$

or

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \rho(1 - 2) - 2k\bar{n}^2 \tag{1b}$$

where ρ is the pseudo-first-order entry rate coefficient giving the number of entry events per particle per unit time (the sum of the components derived from chemical or radiolytic initiation, $\rho_{\mathrm{initiator}}$, and spontaneous or "thermal" initiation, ρ_{spont}), and k is the rate coefficient for exit of monomeric radicals per particle. The value of k is obtained from the conversion/time data of a γ relaxation experiment. Here, initiation is with γ radiolysis. Radiolytically initiated polymerization can be switched on and off by removing the reactor vessel from the radiation source; in a relaxation experiment the conversion as a function of time from the in-source steady state to the out-of-source steady state is measured, and these data yield k (and ρ_{spont}) directly, as described elsewhere[15] (the second and subsequent relaxations from the source should be free of inhibitor and equilibration artifacts). The ρ value is then obtained from the steady-state value of $\bar{n}$ determined in a chemically initiated experiment, $\bar{n}_{\mathrm{ss}}$, by using the value of k from the relaxation experiments together with the steady-state form of eq 1, viz., eq 2.

$$\rho_{\mathrm{initiator}} + \rho_{\mathrm{spont}} = \frac{k\bar{n}_{\mathrm{ss}}}{1 - 2\bar{n}_{\mathrm{ss}}}$$

or

$$= \frac{2k\bar{n}_{\mathrm{ss}}{}^2}{1 - 2\bar{n}_{\mathrm{ss}}} \tag{2b}$$

The RAFT Process. RAFT-mediated free-radical polymerization is accomplished by performing a conventional radical polymerization in the presence of a xanthate (Scheme 1), where the ethoxide group is the activating moiety and R the radical leaving group. A major advantage of the RAFT process is its success with a wide range of monomers and experimental conditions.[8] It is proposed that the RAFT mechanism involves a series of reversible addition−fragmentation steps. First, addition of a propagating radical to a xanthate gives an adduct radical, which can then further fragment to form a new radical, $\mathrm{R}^{\bullet}$. This new radical reinitiates polymerization, in which the polymeric radicals can undergo further addition−fragmentation steps. Once all xanthate is consumed, equilibrium is then established between propagating radicals ($\mathrm{P}_i^{\bullet}$) and dormant species, $\mathrm{S{=}C(OEt)S{-}P}_n$ in the case of xanthates. If the addition−fragmentation reaction is fast compared to propagation (i.e., $C_{\mathrm{tr,RAFT}} > 100$) the typical features of a "living" radical polymerization are obtained, that is, a linear increase in the number-average molecular weight $\bar{M}_{\mathrm{n}}$ with conversion and a low polydispersity (∼1.1). On the other hand, if $C_{\mathrm{tr,RAFT}} \approx 1$, $\bar{M}_{\mathrm{n}}$ and the polydispersity (approximately 2) reach limiting values at low conversions and remain at those values over the whole conversion range (see eqs 3 and 4).

Regardless of the RAFT agent used, the resulting polymers consist of a high percentage of dormant chains and a small percentage of dead chains. The amount of dead chains, formed through bimolecular termination, is proportional to the amount of initiator decomposed. The amount of dead polymer in emulsion polymerizations is also determined by entry and reentry of radicals to terminate growing chains in particles. Addition of a second monomer after full conversion results in further addition−fragmentation reactions with the dormant chains and formation of block copolymers.[10,12]

Müller et al.[20] derived equations to predict the molecular weights vs conversion for "group transfer polymerization”, which can be applied to the RAFT system assuming negligible termination:

$$\bar{M}_{\mathrm{n}} = \frac{\gamma_0 x}{1 - (1 - \alpha)(1 - x)^{\beta}} M_0 \tag{3}$$

$$\frac{\bar{M}_{\mathrm{w}}}{\bar{M}_{\mathrm{n}}} = \frac{1}{\gamma_0 x} + \frac{1}{x}\left[2 + \frac{\beta - 1}{\alpha - \beta}(2 - x)\right] - \frac{2\alpha(1 - \alpha)}{(\beta^2 - \alpha^2)x^2}\left[1 - (1 - x)^{1+\tilde{\beta}/\alpha}\right] \tag{4}$$

where M_0 = molecular weight of the monomer, $\gamma_0 = [\mathrm{M}]_0/[\mathrm{RAFT}]_0$, the subscript “0” refers to time = 0, x is fractional conversion, $\alpha = [\mathrm{P}_n^{\bullet}]/[\mathrm{RAFT}]_0$ and $\beta = C_{\mathrm{tr,RAFT}}$. Equations 3 and 4 are only valid if the initiator concentration is low compared to the amount of RAFT agent and if all the monomer, RAFT agent, and polymer formed are at the locus of polymerization throughout the process. The latter is not generally true for emulsion polymerizations, as in interval II (polymerization in the presence of monomer droplets) some of both monomer and RAFT agent are located in the monomer droplets (unless special techniques are used[12,13]). In the case where $C_{\mathrm{tr,RAFT}}$ is approximately 1, simulations (assuming that the rate of transportation equals the rate of consumption[21]) have found that these equations are valid throughout an emulsion systems: that is, both $\bar{M}_{\mathrm{n}}$ and $\bar{M}_{\mathrm{w}}$ are constant with conversion. For this reason any deviation of $C_{\mathrm{tr,RAFT}}$ from 1 excludes eqs 3 and 4 from being used in an emulsion system, but values of $C_{\mathrm{tr,RAFT}}$ close to 1 (between 0.7 and 1.5) are close to what is found by simulation. Therefore, these equations were used in this work, as the two RAFT agents (**I** and **II**) had $C_{\mathrm{tr,RAFT}}$ values for styrene close to 0.7.

Seeded Emulsion Polymerization. Seeded emulsion polymerizations are carried out in order to avoid the complex nucleation period (interval I). The polymerization, therefore, starts in interval II, where the number of particles and particle size are predetermined. If conditions are chosen such that entry of a radical into a particle that already contains a growing polymeric radical results in instantaneous termination, the system is considered to be under “zero−one” conditions. Thus, all particles will contain either zero or one radicals, and intraparticle termination is not rate determining. The following rate equation can be used for an interval II seeded emulsion polymerization assuming a constant monomer concentration in the particles and constant number of particles:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{k_{\mathrm{p}}[\mathrm{M}]_{\mathrm{p}} Nc\bar{n}}{n_{\mathrm{M}}{}^{0} N_{\mathrm{A}}} \tag{5}$$

where $[\mathrm{M}]_{\mathrm{p}}$ is the concentration of monomer in the particles, $n_{\mathrm{M}}{}^{0}$ is the initial number of moles of monomer, N_{c} is the number concentration of (seed) particles, and N_{A} is Avogadro’s constant. Because all quantities on the right-hand-side of eq 5 except $\bar{n}$ are fixed in a seeded emulsion polymerization during interval II, eq 5 shows that the time variation of $\bar{n}$ is the appropriate quantity to deduce kinetic information.

Model for Entry. The model proposed by Maxwell, Morrison, et al.[22] is now widely accepted as the mechanism for describing the events that lead to entry, at least for systems with ionic stabilizer, or smaller amounts of polymeric or electrosteric stabilizer.[23] A growing oligomeric radical, initiated with a charged radical I such as $\mathrm{SO}_4{}^{-\bullet}$ (the mechanism is also valid for cationic initiator[24]), will enter a particle only if it reaches a critical degree of polymerization, z. This z-mer, $\mathrm{IM}_z{}^{\bullet}$, is assumed to have no other fate except entry, and therefore the entry rate is equal to the rate of formation of these z-mers. However, for a radical to reach a z-mer it must survive termination with other aqueous-phase radicals. This leads to a simple expression for the entry rate coefficient ρ (number of radicals entering a particle per second) if it is assumed that the rate coefficients for water-phase propagation and termination ($k_{\mathrm{p,aq}}$ and $k_{\mathrm{t,aq}}$) are not chain-length dependent:

$$\rho_{\mathrm{initiator}} = \frac{2k_{\mathrm{d}}[\mathrm{I}]N_{\mathrm{A}}}{N_{\mathrm{c}}}\left\{\frac{\sqrt{2k_{\mathrm{d}}[\mathrm{I}]k_{\mathrm{t,aq}}}}{k_{\mathrm{p,aq}}[\mathrm{M}]_{\mathrm{aq}}} + 1\right\}^{1-z} \tag{6}$$

where $[\mathrm{M}]_{\mathrm{aq}}$ is the aqueous-phase concentration of monomer, [I] the initiator concentration, and k_{d} its dissociation rate coefficient.

In the presence of a RAFT agent in the aqueous phase, an additional reaction step must be taken into account:

addition−fragmentation:

$$\mathrm{IM}_i^{\bullet} + \mathrm{RAFT} \xrightarrow{k_{\mathrm{tr,RAFT}}} \mathrm{IM}_i - \mathrm{RAFT} + \mathrm{R}^{\bullet}$$

The leaving group $\mathrm{R}^{\bullet}$ may enter a particle. If this occurs at a significant rate for $i < z$, this will lead to an increased rate of entry, and therefore the equations usually used to calculate the entry coefficients become more complex than those for which eq 6 is valid. Proceeding in the same manner as used to obtain eq 6,[22] one obtains the following set of relations for aqueous-phase radical concentrations for this case:

$$[\mathrm{IM}_1^{\bullet}] = \frac{2k_{\mathrm{d}}[\mathrm{I}]}{k_{\mathrm{p,aq}}{}^{1}[\mathrm{M}]_{\mathrm{aq}} + k_{\mathrm{t,aq}}[\mathrm{T}^{\bullet}] + k_{\mathrm{tr,aq}}[\mathrm{RAFT}]_{\mathrm{aq}}}$$

$$[\mathrm{IM}_i^{\bullet}] = \frac{k_{\mathrm{p,aq}}{}^{i-1}[M_{\mathrm{aq}}][\mathrm{IM}_{i-1}^{\bullet}]}{k_{\mathrm{p,aq}}{}^{1}[\mathrm{M}]_{\mathrm{aq}} + k_{\mathrm{t,aq}}[\mathrm{T}^{\bullet}] + k_{\mathrm{tr,aq}}[\mathrm{RAFT}]_{\mathrm{aq}}} \tag{7}$$

where $k_{\mathrm{p,aq}}{}^{i}$ is the propagation rate coefficient of $\mathrm{IM}_i{}^{\bullet}$, $[\mathrm{RAFT}]_{\mathrm{aq}}$ is the concentration of the RAFT agent in the aqueous phase and $[\mathrm{T}^{\bullet}]$ is the total radical concentration in the aqueous phase. The components of the overall entry rate coefficient $\rho_{\mathrm{tot}} = \rho_{\mathrm{initiator}} + \rho_{\mathrm{RAFT}}$ arising from initiator-ended and RAFT-derived radicals are then respectively given by

$$\rho_{\mathrm{initiator}} = \frac{N_{\mathrm{A}}}{N_{\mathrm{c}}} k_{\mathrm{p,aq}}{}^{z-1}[\mathrm{M}]_{\mathrm{aq}}[\mathrm{Im}_{z-1}^{\bullet}]$$

$$\rho_{\mathrm{RAFT}} = \frac{N_{\mathrm{A}}}{N_{\mathrm{c}}}\sum_{i\text{-}1}^{z\text{-}1} k_{\mathrm{p,aq}}{}^{z-1}[\mathrm{RAFT}]_{\mathrm{aq}}[\mathrm{IM}_i^{\bullet}] \tag{8}$$

Equations 7 are solved numerically to find the entry efficiency $f = \rho_{\mathrm{tot}}/(2k_{\mathrm{d}}[\mathrm{I}]N_{\mathrm{A}}/N_{\mathrm{c}})$. It is assumed that $[\mathrm{RAFT}]_{\mathrm{aq}}$ can be calculated using[25]

$$f^{\mathrm{RAFT,droplet}} = \frac{[\mathrm{RAFT}]_{\mathrm{aq}}}{[\mathrm{RAFT}]_{\mathrm{aq,sat}}} \tag{9}$$

where $f^{\mathrm{RAFT,droplet}}$ is the molar ratio of RAFT agent to

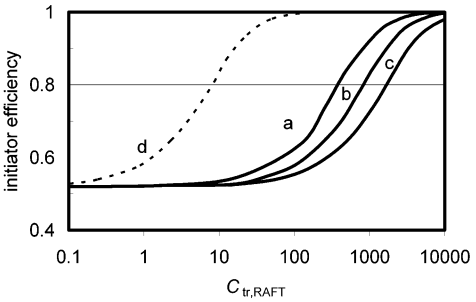

Figure 1. Calculated dependence of initiator efficiency $f = \rho_{\mathrm{tot}}/(2k_d[\mathrm{I}]N_A/N_c)$ on RAFT transfer constant, using eqs 7–9. Curves a–c are for a RAFT agent with a water solubility of 0.002 M and $f^{\mathrm{RAFT,\ droplet}} = 0.01$, 0.005 and 0.0025, respectively. Curve d is where the RAFT solubility is 0.1 M and $f^{\mathrm{RAFT,\ droplet}} = 0.01$.

monomer in the monomer droplet and $[\mathrm{RAFT}]_{\mathrm{aq,sat}}$ is the RAFT saturation concentration in water. This assumes that the polymer in the particles has no influence on the free energy of the low molecular weight components, i.e., the RAFT agent and monomer, because only combinatorial entropy of mixing is important. Maxwell et al.[26] showed that this assumption is valid for two low molecular weight species (two monomers being the usual case, but also applicable to monomer plus RAFT).

This model is evaluated for two RAFT agents: one with $[\mathrm{RAFT}]_{\mathrm{aq,sat}} = 0.002$ M (which is the solubility of **I**, Scheme 1), and a hypothetical RAFT agent with a high water solubility, 0.1 M. Figure 1 shows the calculated effect on entry as a function of RAFT transfer constant, for various amounts of RAFT agent. It is seen that a RAFT agent with the solubility of **I** will only have an effect on entry for $C_{\mathrm{tr,RAFT}} > 10$, which is much greater than that of **I** ($C_{\mathrm{tr,RAFT}} = 0.7$). This figure also suggests that RAFT agents with high water solubility will affect entry efficiency at much lower transfer constants. That is, with an effective RAFT agent in the water phase, aqueous-phase radicals will undergo transfer to RAFT, which will lead to a substantial effect on entry. However, this is not expected to be the case for the present system.

Note that this treatment assumes that the leaving group from a RAFT reaction in the water phase always enters a particle. If however the resulting radical were to be relatively water-soluble, then it would be more likely to undergo aqueous-phase termination prior to entry and thus lead to an *decrease* in entry efficiency.

Model for Exit. A monomeric radical inside a particle is formed by transfer to monomer or by an addition–fragmentation reaction with the RAFT agent. The rate coefficient for desorption, k_{dM}, of these radical species is given by[27]

$$k_{\mathrm{dM}} = \frac{3D_{\mathrm{aq}}[\mathrm{M}]_{\mathrm{aq}}}{[\mathrm{M}]_{\mathrm{p}}{r_{\mathrm{s}}}^2} \tag{10}$$

where D_{aq} is the diffusion coefficient of the desorbing radicals in water and r_{s} the swollen radius of the particle. Hence the probability that a monomeric radical will exit is $k_{\mathrm{dM}}/(k_{\mathrm{dM}} + k_{\mathrm{p}}^1[\mathrm{M}]_{\mathrm{p}})$. This suggests that by increasing the radius, the probability of exit decreases. In the presence of the RAFT agent, the leaving radical, $\mathrm{R}^\bullet$, will exit if it has a favorable partitioning into the aqueous phase and/or a low reactivity to the monomer. In any case, exit invariably leads to a reduction in and consequently a reduction in $\bar{n}$ and consequently a reduction in the rate of polymerization.

The design of the seed is crucial for understanding the events that control the molecular weight distribution. The size of the seed must be small to explore the effects of exit (see eq 10—however, note that if the particle is very small, desorption of monomeric radicals is so rapid that transfer to monomer becomes rate-determining for exit, and this size dependence is lost). The seed cannot be too small, for this reason and also because for extremely small particles, the concentration of monomer will change significantly during particle growth. Moreover, the seed needs to be relatively monodisperse in size, which again means that the size cannot be too small (the fundamentals of nucleation theory[15] show that an emulsion polymerization leading to large particles gives a latex which is more monodisperse in particle size than for an emulsion polymerization leading to smaller ones, all other things equal). The Morton equation[28,29] describes this semiquantitatively, and suggests that for particles with unswollen radius greater than 20 nm the monomer concentration inside the particle remains relatively constant during interval II. Therefore, the unswollen PMMA seed radius for our styrene polymerizations was chosen to be approximately 20 nm.

Experimental Section

Materials. Styrene (STY) and methyl methacrylate (MMA) from Aldrich were passed through an inhibitor-removal column (Aldrich Column 1344-28-1 for removal of *tert*-butylcatachol). Sodium dodecyl sulfate (SDS, Aldrich, ≥99%), sodium persulfate (SPS, Aldrich, ≥98%), potassium persulfate (KPS, Aldrich, ≥99%), $\mathrm{NaHCO_3}$ (Pronalys AR, ≥99.5%) and AMA 80 (Aerosol MA 80, disodium sulfosuccinate, Cytec, as a solution in ethanol and water) were used as received. All other materials were from Aldrich (unless otherwise stated) and used as received. Degassing was carried out with a water pump.

Synthesis of RAFT Agents. The following RAFT agents were synthesized according to the literature procedure.[4]

O-Ethylxanthyl ethyl propionate (**I**) was synthesized by adding potassium *O*-ethyldithiocarbonate (101.4 g, 0.633 mol, Merck, 99%) to a mixture of ethyl 2-bromopropionate (102 g, 0.563 mol, Merck, 99%) dissolved in ethanol (1 L) at 0 °C under a nitrogen atmosphere. The mixture was stirred for 4 h at 0 °C in the absence of light. Water (1 L) was added, and the product was extracted by a 1:2 mixture of diethyl ether and pentane. The solvent was removed and the remaining ethyl 2-bromopropionate distilled off under vacuum. **I** was obtained at >99% purity according to ^{1}H NMR.

O-Ethylxanthyl ethylbenzene (**II**) was synthesized by adding potassium *O*-ethyldithiocarbonate (104 g, 0.649 mol, Merck 99%) to a mixture of ethanol (1 L) and 1-bromoethylbenzene (80 mL, 0.586 mol, Aldrich, 97%) at 0 °C under a nitrogen atmosphere. The same procedure was carried out as for **I**, and the product was >98% purity according to ^{1}H NMR.

Synthesis and Characterization of PMMA Seed Latex. An important design parameter is that the number of particles must be high in order to avoid secondary nucleation. To meet this criterion, N_c was chosen for our experiments to be greater than $1 \times 10^{17}\ \mathrm{L^{-1}}$. In all cases the final latex was checked for secondary nucleation by capillary hydrodynamic fractionation[30] (CHDF, Matec Applied Sciences model 1100). New particles could not be observed in most cases and in the cases where it was observed the amount of new particles was always less than 5% based on particle number. Although CHDF may not reliably detect small particles among larger ones under some circumstances, the conclusion that secondary nucleation was negligible was confirmed by the observation that the final particle size was always close to the values expected from the conversion and that the polymerization rate was constant.

Both these observations indicate a constant particle number and thus no secondary nucleation.

The first PMMA seed latex (PMMA1) was prepared as follows: a 1.1 L stainless steel kettle was filled with water (927 g), SDS (3.0 g, 0.010 mol), NaHCO$_3$ (0.3 g, 4 mmol), and MMA (90.8 g, 0.904 mol), stirred at 350 rpm, and heated to 80 °C under an argon atmosphere. A mixture of KPS (0.3 g, 1 mmol) and water (15 g) was added, and the reaction was continued for 4 h. The resulting latex was dialyzed extensively. Solid contents after dialysis was 7.3%. The number-average diameter after measuring 284 particles by TEM (trasmission electron microscopy; Philips Biofilter, operating at 120 kHz) was 38.8 nm and the particle-size polydispersity ($\bar{D}_w/\bar{D}_n$) was 1.13. This seed was used in experiments to obtain the MWD of polystyrene as a function of conversion.

The second PMMA seed latex (PMMA2) was produced as follows: a 1.5 L glass kettle was filled with water (879.7 g), SDS (2.68 g, 9.29 mmol), NaHCO$_3$ (0.31 g, 3.7 mmol), and MMA (95.2 g, 0.954 mol), stirred at about 150 rpm, and heated to 80 °C under an argon atmosphere. A mixture of SPS (0.33 g, 1.4 mmol) in water (17.8 g) was added, and the reaction was continued for 2.5 h. The resulting latex was dialyzed extensively. Solid contents after dialysis was 7.1% from measuring 469 particles by TEM was 46.5 nm, and the polydispersity was 1.09. This seed was used in the dilatometry and γ-source experiments.

The 94 nm diameter polystyrene seed was made as follows: AMA 80 surfactant (11.35 g), NaHCO$_3$ (1 g, 1.2 mmol), and styrene (300 g, 2.88 mol) were added to water (560 mL). The reaction temperature was raised to 85 °C and stirred. Once the reaction temperature was reached, KPS (1 g, 4 mmol) in water (45 g) was added to the mixture and polymerization commenced. The resulting latex was dialyzed extensively. $\bar{D}_n$ was 94 nm, and the polydispersity was 1.02.

Styrene Seeded Emulsion Polymerizations. All ingredients except initiator solution were loaded in the 250 mL jacketed glass reactor and stirred at 400 rpm for 1 h at 50 °C under an argon atmosphere. After that, the initiator solution was added. A typical recipe contained water (155.1 g), SDS (0.339 g, 1.18 mmol), NaHCO$_3$ (0.046 g, 5.5 mmol), seed latex (PMMA1, 8.1 g), SPS (0.0476 g, 2.00 mmol), styrene (40.27 g, 9.60 mmol), and variable amounts of RAFT agents. Samples were taken using a syringe with a long needle through a rubber septum and conversion was determined by gravimetry. The same samples were used for subsequent GPC analysis.

For the long swelling experiments the mixture was stirred at 300 rpm for about 65 h at room temperature and at 400 rpm for 1 h at 50 °C, whereafter the initiator solution was added.

Rate from Dilatometry Dilatometry was performed in a jacketed dilatometer, using a temperature-controlled water bath. The ingredients except initiator solution were degassed under vacuum, mixed together and stirred for 1 h. A typical recipe contained water (43.37 g), SDS (0.102 g, 0.355 mmol), NaHCO$_3$ (0.014 g, 0.17 mmol), seed latex (PMMA, 24.25 g), SPS (0.0134 g, 0.563 mmol), styrene (11.90 g, 0.1143 mol), and variable amounts of RAFT agents. The dilatometer was heated at reaction temperature, and 1 mL of initiator solution was added. The capillary was installed and filled with dodecane. The volume contraction was followed by an automatic tracking device. The final conversion was measured by gravimetry after each experiment, and the conversion for each time was calculated using the final conversion and the contraction data assuming ideal mixing based on the final conversion.

γ-Radiolysis and Relaxation Experiments. A jacketed dilatometer was filled with all degassed ingredients at least 16 h before the start of the experiment. A typical recipe contained water (27.57 g), SDS (0.064 g, 0.22 mmol), NaHCO$_3$ (0.009 g, 0.11 mmol), seed latex (PMMA2, 2.703 g), styrene (3.57 g, 0.0343 mol), and variable amounts of RAFT agents. A typical recipe for the experiments was performed using a 94 nm polystyrene seed latex plus water (15.8 g), SDS (0.054 g, 0.19 mmol), NaHCO$_3$ (0.008 g, 0.1 mmol), seed latex (polystyrene, 21.47% solid contents, 94 nm diameter, 11.20 g), styrene (3.57 g, 0.0343 mol), and variable amounts of RAFT agents.

The dilatometer was heated to the reaction temperature and degassed again using a syringe and a rubber stopper. The capillary was installed and filled with dodecane. The volume contraction was followed with an automatic tracking device. After a constant temperature was reached the dilatometer was lowered into the γ-source (^{60}Co). When the reaction had reached a steady state, the dilatometer was removed from the source. After a new steady state was reached the dilatometer was lowered back into the source. This was repeated several times. The final conversion was measured by gravimetry after each experiment, and the conversion for each time was calculated using the final conversion and the contraction data. Confirmation that the relaxation kinetics were free of inhibitor artifacts was obtained by the observation that relaxations obtained by successive insertions into and removals from the source showed the same relaxation behavior (within experimental scatter).

Gel Permeation Chromatography. The dried polymer was dissolved in tetrahydrofuran (THF, Biosolve) to a concentration of 1 mg/mL. The solution was filtered through a 0.2 μm PTFE syringe-filter. GPC analyses were carried out using two 300 mm PLGel (5 μm Mixed-C) columns (Polymer Laboratories, linear range of molecular weight 2×10^2 to 2×10^6) at 40 °C. A Waters 486 UV-detector, operated at 254 nm, was used for detection. THF was used as eluent at a flow-rate of 1 mL/min. The injection volume was 100 μL. Narrow-distribution polystyrene standards (Polymer Laboratories) with molecular weights ranging from 580 to 7.1×10^6 were used for calibration.

ζ-Potential Measurements and Conductivity Measurements. ζ-Potentials were measured using a Malvern Zetasizer III, and conductivities were measured using a Radiometer Copenhagen CDM80 conductivity meter. The samples were prepared by stirring the PMMA1 seed latex ($\bar{D}_n$ = 38.8 nm), styrene, and RAFT agent for at least 24 h. The N_c was 1×10^{17} L^{-1}, [SDS] = 7.4 mM, [NaHCO$_3$] = 3.3 mM, $[M]_p = 5.0$ M, and the amount of RAFT agents was varied. All samples had a pH of approximately 7.

ζ-potentials for each sample were measured typically 10 times in the absence of electro-osmotic flow. To check for any aging of the latex, this was repeated 1 day later. No effect of aging was observed. The quoted ζ-potential values for each concentration of RAFT agent are average values of these measurements. The conductivity of each sample was measured and this was repeated 1 day later. The reported value is the average value of these two measurements.

Results and Discussion

The seeded experiments were carried out to determine the effects of the RAFT agents on the rates of polymerization, molecular weight distribution, and (using γ-relaxation) the entry and exit rate coefficients. The seed is designed (see Experimental Section) to be small enough to be considered under zero−one conditions in conventional styrene polymerizations, which allows the effects of entry and exit to dominate the kinetics. As stated, the formation of new polystyrene particles must be avoided, and in addition, the concentration of monomer inside the particles must be kept constant throughout the polymerization. Equation 5 can then be used to determine for all experiments.

Influence of RAFT on the Rate of Polymerization The conversion−time profiles of styrene in the presence of the two RAFT agents, **I** and **II**, over a range of RAFT:monomer ratios (0−2%) are given in Figure 2. Both the type and amount of RAFT agent influence the rate. As the amount of RAFT agent is increased in the recipes so too is the retardation, which is more pronounced for **II** as compared to **I**. From eq 5, $\bar{n}$ for all

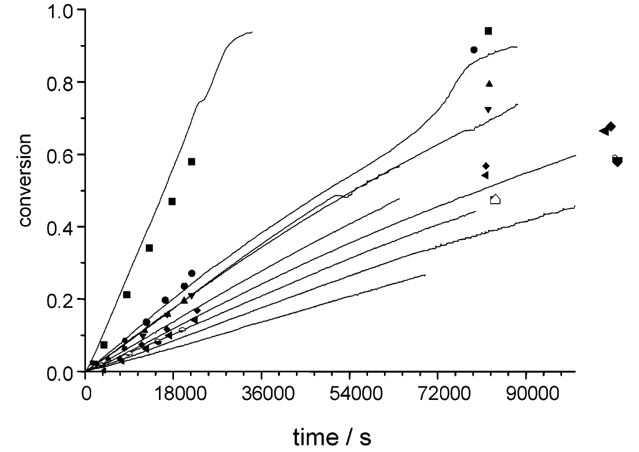

Figure 2. Fraction conversion−time plots of seeded emulsion polymerizations of styrene at 50 °C, determined by dilatometry (solid lines) and by gravimetry (symbols) for different RAFT agents and RAFT-agent concentrations.

Table 1. Values of Parameters Used for Calculations

	values (50 °C)	ref
k_d	1×10^{-6} s^{-1}	37
k_p	237 M^{-1} s^{-1}	38
$k_{p,aq}^1$	1000 M^{-1} s^{-1}	15
$k_{p,aq}^2$	500 M^{-1} s^{-1}	15
$k_t = k_{t,aq}$	1×10^9 M^{-1} s^{-1}	15
k_{tr} (to styrene)	0.009 M^{-1} s^{-1}	39
D_{aq}	1.5×10^{-5} cm^2 s^{-1}	40
$[M]_{aq,sat}$(monomer)	0.0043 M	41
z	3	15, 22
N_c	1×10^{17} L^{-1}	used in this work
r_s	50×10^{-9} m	used in this work
[SPS]	1.2 mM	used in this work
$[M]_p^{sat}$	6 M	this work (creaming expts)

Table 2. Average Number of Radicals per Particle for Seeded Emulsion Polymerizations of Styrene Determined by Dilatometry in the Steady State Region

	$\bar{n}_{ss}$	
[RAFT]/[STY]	**I**	**II**
no RAFT	0.326	
0.25%	0.109	0.098
0.5%	0.093	0.074
1%	0.065	0.056
2%	0.049	0.039

experiments can be determined (see Table 2). Without RAFT agent, $\bar{n}$ is 0.33. This compares favorably with the value (also 0.33, the same to two significant figures) calculated for these conditions from theory[15] using the full expression for the entry rate coefficient (including chain-length-dependent propagation rate coefficients) and the parameter values given in Table 1. This calculation (which is a numerical iteration rather than the simple analytical expression of eq 6) uses input parameters which have been shown elsewhere to reproduce $\bar{n}$ values for such experiments with good reliability. The addition of a small amount of RAFT (ratio to monomer 0.25%) results in reduction in $\bar{n}$ by a factor of 3, and increasing the ratio of RAFT further (2%) further reduced $\bar{n}$ by at least a factor of 6. The reduction in was greater for **II** than **I**. These results suggest that retardation is controlled by the type of leaving group R.

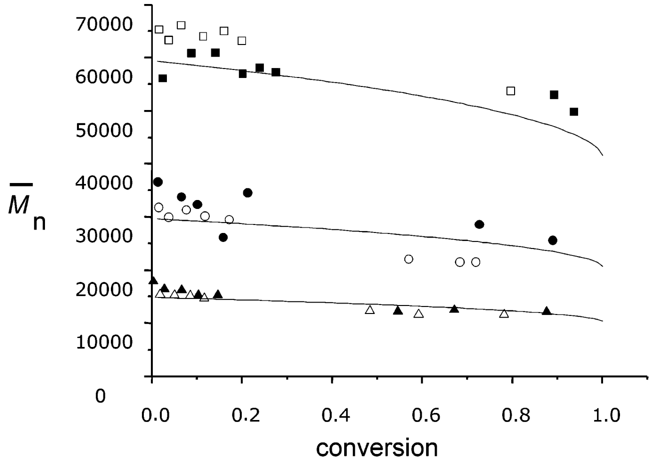

Figure 3. $\bar{M}_n$ as a function of fraction conversion of seeded emulsion polymerizations of styrene at 50 °C for different ratios of concentrations of RAFT agents (**I** and **II**—Scheme 1) to styrene. Solid lines are the calculated values from eq 3: (▲) [**I**]/[STY] = 1%; (△) [**II**]/[STY] = 1%; (●) [**I**]/[STY] = 0.5%; (○) [**II**]/[STY] = 0.5%; (■) [**I**]/[STY] = 0.25%; (□) [**II**]/[STY] = 0.25%.

Influence of RAFT on Molecular Weight Distribution Also shown in Figure 2 is the comparison between the dilatometric and gravimetric data. The agreement is good and suggests that we can use with confidence the polymer obtained from gravimetry to obtain the molecular weight distribution as a function of conversion. The polydispersities for all these experiments were close to 2, in accord with ideal RAFT behavior (eq 4), using a value for $C_{tr,RAFT}$ of 0.7 for both RAFT agents.

Figure 3 shows $\bar{M}_n$ as a function of conversion for a range of RAFT:monomer ratios (0.25−1%). The time allowed for the monomer and RAFT agents to swell into the latex was 1 h. As the ratio of both RAFT agents increased, $\bar{M}_n$ decreased, and the trends with conversion were the same for both **I** and **II**. The solid lines are theoretically determined from eq 3, using $C_{tr,RAFT} = 0.7$. At low conversions theory predicts a $\bar{M}_n$ slightly below the experimental values, but as the conversion increased the experimental points fit better with ideal RAFT behavior. This may be due to the slower rate of transportation of RAFT from the droplets into the particles on the propagation time scale in the initial stages of polymerization. However, simple calculations[15] based on the aqueous phase concentration and the diffusion rate of the RAFT agent suggest that the transportation rate of the RAFT agent is much faster than that of its consumption.

Further experiments using only **I** were carried out with longer swelling times for over 3 days. In these polymerizations (Figure 4, open symbols) the trends were similar for all ratios of **I**. The $\bar{M}_n$ values fit well with ideal RAFT behavior for the whole conversion range.

To avoid scatter due to inaccurate determination, $\bar{M}_n$ was calculated by dividing the weight-average molecular weight by 2.[31] The data above can be interpreted with the assumption that equilibrium of the RAFT agent between the droplets and the particles is established with a swelling time of just 1 h, which is in agreement with the above calculations.

γ-Relaxation Experiments. To determine values for the exit rate coefficient (k), γ-relaxation experiments were performed. Once k is known for a certain system, the entry rate coefficient ρ can be calculated from $\bar{n}_{ss}$-(chemical experiments) for the limit that is applicable to this system, as shown in eq 2. To differentiate between the various limits,[15] condition 1 is used to test

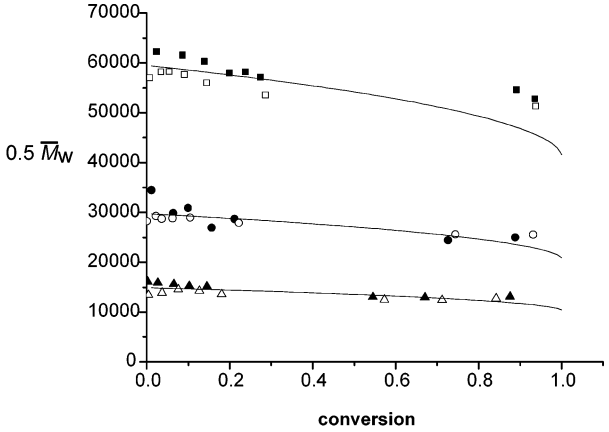

Figure 4. $\bar{M}_w/2$ as a function of conversion of seeded emulsion polymerizations of styrene at 50 °C with different concentrations of **I** and two different swelling times (1 h and 3 days). Lines are the calculated values from eq 3 with $\bar{M}_w/2 = \bar{M}_n$ (calculated): (▲) [**I**]/[STY] = 1%, 1 h swelling; (△) [**I**]/[STY] = 1%, 3 days swelling; (●) [**I**]/[STY] = 0.5%, 1 h swelling; (○) [**I**]/[STY] = 0.5%, 3 days swelling; (■) [[**I**]/[STY] = 0.25%, 1 h swelling; (□) [**I**]/[STY] = 0.25%, 3 days swelling.

whether exited radicals will terminate in the aqueous phase (Limit 1) or will reenter another particle (limit 2).

$$\text{reentry rate} = 4\pi N_c\, D_{aq}\, r_s \gg k_{t,aq}\,[T^\bullet] \qquad \text{(condition 1)}$$

If this condition applies it means that an exited radical reenters another particle and never undergoes termination in the aqueous phase. Condition 1 is met for both **I** and **II**, using the parameters in Table 1. This suggests that limit 2 is the dominant mechanism for these systems. However, to further differentiate whether the radicals after complete reentry will either remain in the particles to propagate (limit 2a) or reescape and reenter other particles to terminate (limit 2b), Condition 2 is tested.

$$k_{dM}\,\bar{n} \ll k_p{}^1[M]_p \qquad \text{(condition 2)}$$

To apply condition 2, the values for k_{dM} (eq 10) and $k_p{}^1$ must be determined. It is assumed that the R radicals from **I** and **II** have the same $[M]_{aq}{}^{sat}$ values as their nonradical equivalents, i.e., 0.2 and 4.3 × 10^{-3} M,[26] respectively (it is noted that this assumption may not be very accurate,[13] although it is adequate for the order-of-magnitude purposes required to check the validity of the above conditions). Using $[M]_p{}^{sat}$ = 6 mM for styrene, the k_{dM}'s found are 5.1 × 10^4 and 1.3 × 10^3 s^{-1} for **I** and **II**, respectively. The parameters used to determine the values of the left-hand side of condition 2 were $\bar{n}$ found from the RAFT experiments (Table 2), $k_p{}^1$ for a styryl radical of 1000 M^{-1} s^{-1},[15] and $k_p{}^1$ of addition of an ethyl acrylate radical to styrene[32] of 6 × 10^5 M^{-1} s^{-1}. It is found that condition 2 is satisfied, as 5.1 × 10^3 ($\bar{n}$ = 0.10) ≪ 3.6 × 10^6 (**I**) and 1.3 × 10^2 ($\bar{n}$ = 0.10) ≪ 6 × 10^3 (**II**), and therefore the system meets the criteria for limit 2a for both RAFT agents. In this case free-radical loss is second order with respect to $\bar{n}$. The kinetic expression is thus given by

$$\frac{d\bar{n}}{dt} = (\rho_{\text{initiator}} + \rho_{\text{spont}})(1 - 2\bar{n}) - 2k_{cr}\bar{n}^2 \qquad (11)$$

where

$$k_{cr} = \frac{k_{dM}^{RAFT} k_{tr,RAFT}[RAFT]_p + k_{dM}\, k_{tr}[M]_p}{k_p{}^1[M]_p} \qquad (12)$$

where $[RAFT]_p$ is the concentration of RAFT agent in the particles. In a typical γ-relaxation experiment, the reaction vessel is placed in the γ source until a steady-state polymerization rate is reached; it is then removed such that no new radicals are formed and the polymerization rate relaxes to a low steady-state value maintained by spontaneous initiation. This is repeated until a conversion of approximately 20% is reached (Figure 5). Using both the slope and intercept method[15] from the steady states in and out of the source and nonlinear least squares (NLLS) fitting with the integrated form of eq 11, values for k and $\rho_{thermal}$ were determined using limit 2a. Table 3 shows the comparison between the experimental exit rate coefficients and those calculated by eq 12. As expected, an increase in the ratio of RAFT shows an increase in the values of k_{cr}. No significant effect of different RAFT agents is observed for k_{cr}. Figure 6 shows that the observed dependence of the exit rate coefficient is linear in the molar ratio of RAFT:monomer, as predicted by eq 12. Further quantitative comparison between the predictions of this equation and the data cannot be made because the values of and the partition coefficient of the RAFT-derived radical between the particle and aqueous phase are both unknown. The similar exit rate coefficients for both RAFT agents, despite their different water solubilities, is ascribed to fortuitous similarities of the corresponding ratios in eq 12.

Influence of Particle Size on Radical-Loss Rate Coefficient. Equation 10 shows that the rate coefficient for radical loss by exit should be inversely proportional to the square of the radius. This was explored further by performing experiments with a larger seed, viz., 94 nm unswollen diameter, in which exit should be reduced. Now, calculations[15] indicate that this size is such that zero–one kinetics are no longer applicable, i.e., that intraparticle termination becomes a rate-determining event for radical loss. Two γ-relaxation experiments without and with **I** (ratio to monomer of 0.5%) were performed. Because both exit and termination can be rate-determining in this system, the data were simply fitted by a second-order loss equation of the same form as eq 1 but where the second-order loss rate coefficient k no longer has the physical interpretation applicable in zero–one conditions. Values for k = 0.016 s^{-1} (no RAFT) and 0.085 s^{-1} (RAFT) were obtained. The latter has a similar value to that found in the smaller seed under the same conditions (i.e., k_{cr} = 0.10 s^{-1}; ratio 0.5%, 46.5 nm seed). Because this system is somewhere between zero–one and pseudo-bulk kinetics, for which there is no simple means of fitting a phenomenological rate coefficient to theory,[15] no quantitative interpretation can be given. Qualitatively, one can see that the loss by exit should be smaller, which at first sight appears to be inconsistent with experiment. However, it must be realized that intraparticle termination will be rate-determining in this nonzero–one system. Because RAFT produces small species that diffuse rapidly, and because termination in these systems is diffusion-controlled,[33–35] it is apparent that the rate of radical loss by intraparticle termination will be increased. The observation that the rate of radical loss is similar in the small and large particles studied here can therefore

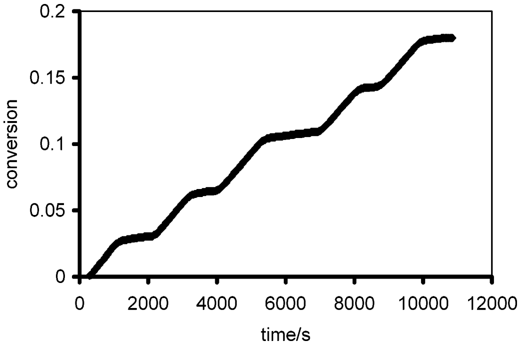

Figure 5. Conversion−time plot of a typical γ-relaxation experiment, with multiple insertions and removals, of a seeded emulsion polymerization of styrene at 50 °C in the presence of a RAFT agent.

readily be rationalized in terms of an approximate cancellation of these two effects.

Chemical and γ-Initiation: Determination of Entry Rate Coefficients. The entry rate coefficient for initiator-derived radicals, $\rho_{\text{initiator}}$, can be obtained from experiment using eq 2 from (chemical), with k and ρ_{spont} values obtained from the γ-relaxation experiments; results are given in Table 4 and Figure 7. Initially there is a drastic decrease of $\rho_{\text{initiator}}$ for increasing **I** and **II**, which then remains relatively constant.

The dependence on RAFT agent concentration of $\rho_{\text{initiator}}$ (chemical) is shown in Figure 7, and Figure 8 shows that for the entry rate coefficient from γ initiation. It is apparent that the RAFT agents used here also reduce the entry rate coefficient for γ-initiated systems, ρ_γ, provided that the RAFT concentration is sufficiently high. Now, while quantitative models for entry for chemical initiators are well established,[15,22,24,36] this is certainly not the case for γ initiation. This is because the initiation process for the latter involves several radical species, $H^\bullet$, $OH^\bullet$, and hydrated electrons, and these species arise in both the water and particle phases. Hence all that can be inferred from the data in Figure 8 is that the observed decrease in entry rate coefficient for γ initiation is apparently not consistent with the effect seen with chemical initiation.

The observed reduction in entry rate coefficients is surprising, given the well-established mechanism for entry in conventional systems: propagation to a z-mer, etc. In these styrene systems, $z \sim 2-3$. If this mechanism were operative in the present systems, entry should not be affected by the RAFT agents used here (see Figure 1): they are essentially insoluble in the water phase and have a low reactivity, and thus will not affect the rate of z-mer formation (any transfer would only occur at much higher degrees of polymerization). However, an effect is clearly seen.

One reasonable explanation for this unexpected effect is that the xanthate RAFT agents used here are surface active, that is, they reside near the surface of the particle. Surface activity of xanthates is not unexpected since their canonical structures included ionized forms.[8] Surface activity of **I** and **II** would mean that z-mers, whose radical locus passes through the particle surface, will have a very high probability of transfer to RAFT, resulting in exit instead of propagation into the interior of the particle. Hence reexit of the radical resulting from the transfer reaction between a z-mer and the RAFT agent will result in a decrease in the effective rate of entry.

ζ-Potential and Conductivity Measurements. The suggestion that surface activity of the RAFT agent can explain the unexpectedly large effect on entry and exit can be checked by directly measuring this surface activity. Should **I** and **II** act as surface-active species, they should displace surfactant from the surface of the particles, increasing the conductivity in the aqueous phase and altering the charge density on the particle surface. The measured conductivity and ζ-potential of styrene swollen latexes with different amounts of **I** and **II** are shown in Table 5. The pH was about 7 in all experiments.

These results show that as the amount of RAFT is increased, the conductivity is increased and ζ-potentials were decreased. While the differences are too small to conclude that there is a true effect, the data are consistent with the trend that the RAFT agent to a small extent displaces the surfactant from the particle surface. Although the explanation agrees with the trends in the entry rate coefficient, it does not seem to affect the MWD drastically. This is simply because the MWD is determined by the *average* concentration of RAFT inside the particle (since the growing chain randomly samples the whole particle interior), whereas the concentration of RAFT closer to the surface specifically affects entry because the z-mer enters through this surface.

Surface Activity as the Explanation for the Decrease in Entry Rate Coefficient. It seems that the results can be qualitatively explained with the postulate of surface activity. The dramatic decrease in $\rho_{\text{initiator}}$ and relatively unaffected ρ_γ for experiments carried out in the presence of RAFT agent support this postulate, since the initiating species are different for each system. In the chemical system the z-mers are themselves surface active and will have a higher probability of reacting with the surface active RAFT agents, whereas the initiating species from γ are uncharged and have a high propensity to be located within the bulk of the particle. The surface activity theory is also consistent with molecular weight and exit data. Although the RAFT agent is located at the surface it is still “seen” by growing radical in the interior of the particle, and thus molecular weight is as predicted and the exit rate increases linearly with RAFT concentration.

Next we turn to the large effect of these RAFT agents on entry. Assuming that all entering z-mers undergo transfer to a RAFT agent at the particle surface, the small radical formed from this reaction can either exit or enter the particle. Now, we have assumed that the RAFT system is in Limit 2a, as tested by conditions 1 and 2. However, as a result of surface activity it might also be possible that the system is in Limit 1, i.e. complete aqueous phase termination of exited radicals. This will occur if the RAFT at the surface is not only a barrier for z-mers but for all entering or reentering radicals, when there should be a linear increase in the exit rate coefficient with RAFT concentration. If Limit 1 were assumed, the exit rate coefficients would be determined using the equation for first-order loss, eq 1a. In this case, the slope and intercept method or NLLS fitting can be used again to obtain exit rate coefficients. The results are shown in Figure 9, which shows that when a first-order loss mechanism is assumed

$$\frac{d\bar{n}}{dt} = (\rho_{\text{initiator}} + \rho_{\text{spont}})(1 - 2\bar{n}) - k_{\text{ct}}\bar{n} \qquad (13)$$

Table 3. Experimental and Calculated Values for the Exit Rate Coefficient, Using Limit 2a

	I			II		
[RAFT]/[STY]	k_{cr}(calcd), s^{-1}	k_{cr}(expt), s^{-1} (slope−intercept)	k_{cr}(expt), s^{-1} (NLLS fitting)	k_{cr}(calcd), s^{-1}	k_{cr}(expt), s^{-1} (slope−intercept)	k_{cr}(expt), s^{-1} (NLLS fitting)
no RAFT	0.012	0.043	0.037	0.012	0.043	0.037
0.25%	0.063	0.082	0.069	0.81	0.079	0.103
0.5%	0.125	0.100	0.075	1.63	0.142	0.123
1%	0.250	0.199	0.166	3.25	0.186	0.158

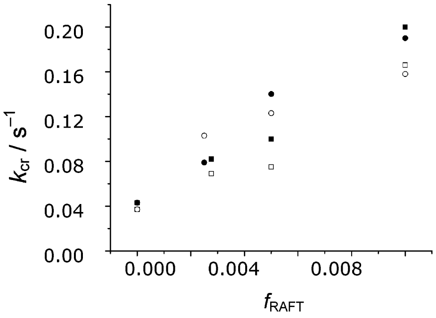

Figure 6. k_{cr} (Limit 2a exit rate coefficient) vs the RAFT to monomer ratio as determined by γ-relaxation experiments using the slope and intercept method[15] and using nonlinear least-squares fitting (integrated form of eq 11) of $\bar{n}$ vs time data, such as in Figure 5: (■) k_{cr} of **I** detemined by slope−intercept method; (□) k_{cr} of **I** determined by NLLS fitting; (●) k_{cr} of **II** detemined by slope−intercept method; (○) k_{cr} of **II** determined by NLLS fitting.

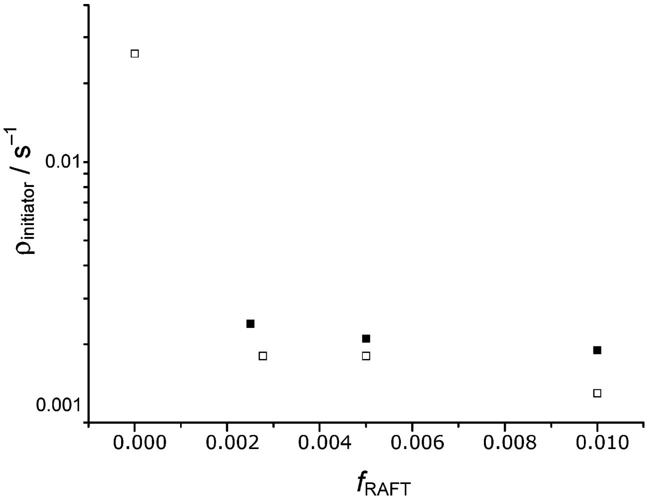

Figure 7. Entry rate coefficient $\rho_{initiator}$ vs the molar fraction of RAFT determined by eq 2b and the values from Tables 2 and 3 (slope−intercept k values): (■) **I**; (□) **II**.

Table 4. Values for $\rho_{initiator}$ Derived from $\bar{n}_{SS}$, k and ρ_{spont}

	$\bar{n}_{SS}$	k (lim **2a**), s^{-1}	ρ_{spont}, s^{-1}	$\rho_{initiator}$, s^{-1}
no RAFT	0.33	0.043	8.0×10^{-5}	2.6×10^{-3}
[**I**]/[STY] = 0.25%	0.11	0.082	5.8×10^{-5}	2.4×10^{-3}
[**I**]/[STY] = 0.5%	0.093	0.10	3.1×10^{-5}	2.1×10^{-3}
[**I**]/[STY] = 1%	0.065	0.20	1.1×10^{-5}	1.9×10^{-3}
[**II**]/[STY] = 0.25%	0.098	0.079	6.9×10^{-5}	1.8×10^{-3}
[**II**]/[STY] = 0.5%	0.074	0.14	3.6×10^{-5}	1.8×10^{-3}
[**II**]/[STY] = 1%	0.056	0.19	0.4×10^{-5}	1.3×10^{-3}

then the exit rate coefficients obtained, k_{ct}, are relatively independent of the RAFT concentration. On the basis of this consideration, first-order loss mechanisms can be rejected.

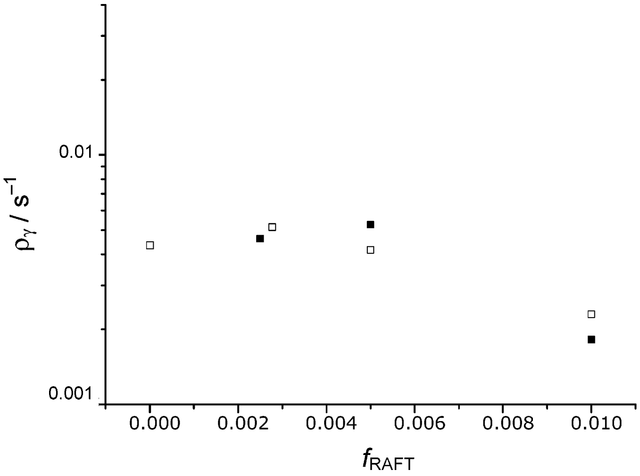

Figure 8. Entry rate coefficient $\rho_{initiator}$ vs the molar fraction of RAFT determined by eq 2b and $\bar{n}_{ss}$ in the γ-source (not shown) and the exit rate coefficients from Table 3 (slope−intercept k values): (■) **I**; (□) **II**.

Table 5. Conductivities and ζ-potentials of Monomer Swollen Latexes with Different Amounts of RAFT Agents I and II

	I		II	
[STY]/[RAFT]	conductivity, μS cm^{-1}	ζ potential, mV	conductivity, μS cm^{-1}	ζ potential, mV
no RAFT	652	−52.7	634	−52.6
400	656	−51.8	644	−50.3
100	655	−51.3	644	−51.6
50	663	−50.7	645	−50.8

An explanation for the unexpectedly large decrease in entry efficiency in the presence of these (probably surface-active) xanthate RAFT agents is that the oligomeric radical resulting from transfer to RAFT agent near the surface then desorbs, and that its reentry is almost always frustrated by the same effect until it eventually undergoes aqueous-phase termination: “frustrated entry”. This can lead to an arbitrarily low initiator efficiency, depending on the various rate parameters involved.

Further support of the surface-activity postulate is the preparation of core−shell block copolymer colloids under starved feed conditions.[18] Approximately 76.4% of the dormant PSTY chains (produced from an ab initio styrene polymerization with **II**) are formed into blocks of PSTY−PBA, which can only be the case if the RAFT moiety on the chain end has a high probability to reside at the surface of the particles.

Conclusions

The presence of xanthate RAFT agents with low transfer constants (~0.7) has a large effect on the kinetics of a seeded emulsion polymerization of styrene. Using γ-radiolysis relaxation measurements to determine the exit rate coefficient directly, this exit rate coefficient was found to increase with the amount of RAFT, with the linear dependence on the molar ratio of RAFT to monomer predicted by the transfer/diffusion theory for exit. Measurements of the steady-state rate

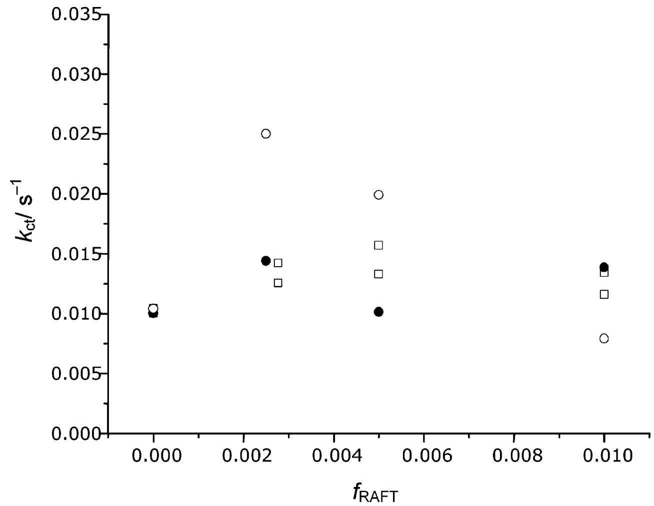

Figure 9. k_{ct} (Limit 1a exit rate coefficient, eq 13) vs the RAFT to monomer ratio as determined by γ-relaxation experiments using the slope and intercept method and using NLLS fitting of $\bar{n}$ vs time data: (■) RAFT agent **I**, detemined by slope−intercept method; (□) RAFT agent **I**, determined by NLLS fitting; (●) RAFT agent **II**, detemined by slope−intercept method; (○) RAFT agent **II**, determined by NLLS fitting.

with chemical initiator and also from γ-initiation showed that the entry rate coefficients decreased with the amount of RAFT. This is inconsistent with conventional emulsion polymerization assumptions using the aqueous-phase-propagation model for entry, which is however able to predict the entry rate coefficient successfully for ordinary emulsion polymerization systems. It is postulated based on these results that the RAFT agents used in this work are surface active, and thus are inhomogeneously distributed throughout the latex particle, unlike conventional emulsion polymerizations where concentrations are essentially homogeneous. Surface activity is not unexpected due to the canonical form of these RAFT agents. This modification of the aqueous-phase-propagation entry model with surface activity can, through the higher concentration of RAFT agent near the surface, account for the dramatic decrease in entry rate for the chemically initiated system in terms of transfer and desorption leading to “frustrated” entry and eventual aqueous-phase termination.

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