Macromolecules

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Effect of Stabilizer Functionality on the Kinetics of Emulsion Polymerization in Hairy Particles

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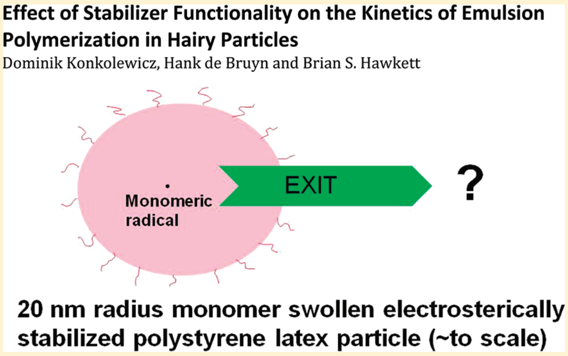
Supporting Information

ABSTRACT: Two model polystyrene seed-latexes were studied by γ-irradiation dilatometry, with one latex stabilized by short chain poly(acrylic acid) the other stabilized by short chain poly(methacrylic acid), anchored to the surface. The distinction between the two latexes studied is that the poly(acrylic acid) stabilized latex has abstractable hydrogens in the backbone which could form midchain radicals while the poly(methacrylic acid) stabilized latex does not have abstractable hydrogens. Despite this difference in functionality of the hairs, these two latexes displayed essentially the same kinetics. The overall polymerization rates, average number of radicals per particle and the rate coefficients for radical entry and exit were comparable for the two different latexes, and both latexes showed significantly better agreement with first order than second order radical loss. These data are consistent with the idea that exit of a radical from a latex particle leads to complete loss of that radical, rather than re-entry and reinitiation. In the past, the apparent first order radical loss observed in small particle size poly(acrylic acid) stabilized latexes was attributed to termination of the exiting radical with mid chain radicals on the poly(acrylic acid) hairs. However, the poly(methacrylic acid) stabilized latex cannot form these mid chain radicals and the similarity between the polymerization kinetics of both the poly(acrylic acid) and poly(methacrylic acid) stabilized latexes suggests that the apparent first order loss cannot be due to termination with mid chain radicals. We demonstrate that the lower than expected exit rate coefficients observed in these small particle size systems can be explained by a competition between particle growth and radical exit.



INTRODUCTION

The emulsion polymerization of styrene is one of the simplest and most intensively studied of the emulsion polymerization systems. Hydrophobic polymers such as polystyrene and its copolymers have been produced by emulsion polymerization for seven decades and the process of emulsion polymerization is extensively used in industry.[1,2] In the simplest case the emulsion polymerization of styrene is stabilized by ionic surfactants,[1] although electrosterically stabilized emulsions are becoming increasingly popular,[3−5] since they can have increased colloidal stability imparted by both steric and electrostatic interactions, and have significantly reduced problems due to surfactant migration. However, as with all polymerization systems, it is important to understand the reaction kinetics and mechanisms in order to optimize the process for desired final properties.

Until 1980, the kinetics of the styrene emulsion polymerization system was thought to largely obey the Smith−Ewart case 2 initially and subsequently case 3 kinetics,[6−8] and exit of radicals from latex particles was regarded as negligible. However, in that year Hawkett et al.[9] demonstrated that radical exit was not only significant but was fundamental in understanding the kinetics of the electrostatically stabilized emulsion polymerization of that monomer. In the earliest work, the loss was assumed to be first order, and this assumption was sufficient to explain the experimental data. Since that time there have been various experimental and theoretical studies of the kinetics of emulsion polymerization.[10−14] First order loss is a significant theoretical question because if the radicals that undergo first order loss from particles take no further part in the kinetics of the system their loss from the disperse phase as a whole is also first order. Under these circumstances the rate of change of the average number of radicals per latex particle, $\bar{n}$, is described by eq 1:[14]

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

where ρ is the rate coefficient for entry of radicals into latex particles and k the radical exit rate coefficient.

Alternatively, if these radicals reenter particles and terminate if the particle already contains a radical or initiate further polymerization if it does not, the overall loss of radicals from the disperse phase of the system as a whole is actually second order, and the rate of change of the average number of radicals per

Received: August 14, 2011
Revised: October 10, 2011
Published: October 28, 2011

particle is given by eq 2:[14]

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

Indeed, if exit of radical activity from latex particles is due to transfer of radical activity from a growing polymer chain to a monomeric styrene molecule which then exits from the particle it is very difficult to conceive of a mechanism that would not have that radical returning to the disperse phase to take a further significant part in the kinetic events of the polymerizing system. The monomeric styryl radical would be expected to have similar solubility to styrene monomer and partition toward the disperse phase while the probability of it undergoing termination in the aqueous phase would be expected to be low due to the low concentration of radicals in that phase. First order loss would appear to require a mechanism that produced an exiting radical that had a significant barrier to reentry into particles, thus encouraging termination in the aqueous phase; no plausible mechanism has been proposed. Although it has been proposed that transfer in styrene is not the simple transfer of a radical from a growing polymer chain to a monomer molecule but involves the Diels–Alder adduct (also thought to be at the origin of background thermal polymerization[14]), it is difficult to envisage this mechanism generating an exiting radical with the required properties.

Thus, it would seem to be obvious that the loss of radicals from the system as a whole must be second order. Although, after the publication of the 1980 paper,[9] several papers considered both first and second order loss,[15,16] the assumption of second order loss of radicals from the system as a whole was taken[16] from then on. For the reasons outlined above, second order loss has been the typical assumption for the description of styrene emulsion polymerization.[14] It is nevertheless the case that while much kinetic data are not able to unambiguously distinguish between first and second order loss many results are more suggestive of first order loss than second order loss and kinetic results on very small seed latex particles is probably the most significant of these.

One interesting case of emulsion polymerization is the use of polymeric surfactants as electrosteric stabilizers.[3,17,18] In the past, it has been difficult to synthesize well controlled block copolymers that can act as stabilizers for the emulsion polymerization of styrene. However, the development of living radical polymerization (LRP) has opened up the possibilities of polymer synthesis and allowed amphiphilic block copolymers to be used as electrosteric stabilizers. In particular, nitroxide mediated polymerization,[19,20] atom transfer radical polymerization (ATRP),[21−23] and reversible addition–fragmentation chain-transfer (RAFT) polymerization[24−27] are LRP techniques that have been widely used to synthesize block copolymers from a wide range of monomers. RAFT has been adapted to the widest range of monomers to date under relatively mild conditions,[25,28] making it particularly well suited to the synthesis of block copolymers, which can be used as electrosteric stabilizers. The use of amphiphilic block copolymers as macro-RAFT agents has been extensively employed by our group and others to produce well controlled latex particles in emulsion polymerization.[3,4,29−35] The advantages of using an amphiphilic macro-RAFT agent over a conventional surfactant is that these reactions give improved stability and access to well controlled latex particles with diameters around 20 nm. In addition, this approach of using RAFT in emulsion was used by Ganeva et al.[36] to study the particle formation mechanisms, and Thickett et al.[11,37−42] to prepare monodisperse polystyrene seed latexes that were used as model systems to study the kinetics of emulsion polymerization, with these RAFT synthesized systems offering significant improvements in the definition of the electrosterically stabilized latexes over those synthesized by other methods.[17,18,43,44] This improved definition and characterization of the latex improves the quality of the kinetic parameters obtained.

One of the most powerful techniques for studying the kinetics of emulsion polymerization is γ-relaxation dilatometry.[14−16,40,45] This is because the reaction can be initiated by lowering the sample into the γ-source, or effectively ceased by removing the sample from the γ-source. During the insertion phase the radical entry and exit can be studied. When the reaction mixture is removed from the γ-source the system is dominated by exit and excellent estimates of the exit rate coefficients and background thermal entry rates can be obtained from the data.[14] This method has been used to determine rate coefficients and reaction mechanisms for both electrostatically,[15,16,45] and more recently electrosterically stabilized latexes.[40]

In their extensive studies of the kinetics of emulsion polymerization of styrene in electrosterically stabilized latexes, Thickett et al.[11,39−42] found that the kinetic behavior of their system was consistent with the first order loss of radicals from the disperse phase of the system as a whole. A difficulty arises with the RAFT mediated approach to forming small monodisperse particles in that the particles formed are typically electrosterically stabilized by short chain poly(acrylic acid) chains and are therefore different from the electrostatically stabilized seed particles generally used in styrene emulsion polymerization kinetics studies in the past. Thickett et al. used this difference to rationalize the observed first order behavior as second order behavior modified by the influence of long-lived midchain radicals formed by hydrogen abstraction from the stabilizing poly acrylic acid chains.[39,46] These long-lived radicals were argued to influence the values of the entry and exit parameters by terminating with other radicals in the system.

While poly(acrylic acid) chains have labile tertiary hydrogens that are readily abstracted to leave relatively unreactive radicals on the stabilizing chains, this is not true of poly(methacrylic acid) chains. Although conducting similar γ-relaxation experiments using seed latex particles stabilized by poly(methacrylic acid) chains would seem an obvious experiment to do, well characterized short block copolymers of styrene and methacrylic acid have proved very difficult to prepare.[47] In this work we describe the preparation of well characterized block copolymers of styrene and methacrylic acid, their use to form well characterized, small particle size seed latexes and the use of these seed latexes in γ-relaxation kinetic studies. The results obtained are compared to those derived from latexes stabilized by similarly prepared block copolymers of styrene and acrylic acid.

EXPERIMENTAL SECTION

Materials. *Tert*-butyl methacrylate (tBMA), *tert*-butyl acrylate (tBA), styrene (Sty), 2,2′-Azobis(isobutyronitrile) (AIBN), 4,4′-Azobis-(4-cyanovaleric acid) (ACVA), 1,4-dioxane were purchased from Aldrich. Toluene, benzoyl peroxide (BPO) hydrochloric acid (32% in water), tetrahydrofuran (THF) were purchased from Ajax chemicals. (Propanoic acid)yl butyl trithiocarbonate, PABTC was received from Dulux Australia. Cyanoisopropyl dithiobenzoate (CPDB) was synthesized following methods outlined in the literature.[48] All reagents were used as received, unless otherwise specified. AIBN was recrystallized from ethanol. Styrene was passed over a column of basic alumina to remove the inhibitor prior to use. tBMA and tBA were passed over inhibitor removal columns prior to use.

Nuclear Magnetic Resonance (NMR). All NMR analysis was performed on a Bruker AVANCE200 NMR Spectrometer, with an Oxford narrow bore magnet and 5 mm dual(CH) probes with z-gradients. NMR analysis was performed on the XWINNMR3.5 and iNMR 0.7 software.

Size Exclusion Chromatography (SEC). Molecular weights were determined by size exclusion chromatography (SEC) at 40 °C on a system equipped with a Polymer Laboratories 10 μm guard column, and Polymer Laboratories Mixed B column with both the differential refractive index detector (Shimadzu, RID-10A) and UV detector-(Shimadzu, SPD-10A). Tetrahydrofuran was used as the eluent at a flow rate of 1 mL min^{-1}, and toluene was used as a flow rate marker. Polystyrene standards with a molecular weight range of 483 000−580 g/mol, were used for calibrations.

Hydrodynamic Chromatography (HDC). Particle sizes were characterized by HDC using a Polymer Laboratories Particle Size Distribution Analysis system. The system was calibrated with standards of diameters between 20 and 350 nm.

Synthesis of Dithiobenzoate-Capped *tert*-Butyl Methacrylate Homopolymer. CPDB (0.2015 g, 0.912 mmol) was placed in a vial and combined with AIBN (15.0 mg, 0.0914 mmol). To this mixture tBMA (1.5508, 10.92 mmol) and toluene (1.6619 g, 18.06 mmol) were added. This mixture was homogenized by vigorous shaking and transferred to a round-bottom flask containing a magnetic stirrer. The flask was capped with a rubber septum and deoxygenated by bubbling nitrogen for 10 min. The reaction mixture was heated at 60 °C for 14 h and 50 min. The product was characterized by NMR and SEC. It was found to have reached a conversion of 70%, and included a significant amount of unreacted CPDB RAFT agent. This unreacted RAFT agent was removed by precipitating the polymer 5 times into 15% water in methanol at −78 °C. The resulting pink polymer was collected, dried in vacuo overnight and analyzed by SEC to give a number-average molecular weight of 1900 g/mol and weight-average molecular weight of 2400 g/mol (PDI = 1.26).

Synthesis of *tert*-Butyl Methacrylate−Styrene Block Copolymer. ACVA (0.0115 g, 0.0411 mmol) was added to *tert*-butyl methacrylate homopolymer (0.8450 g, 0.44 mmol). Sty (3.4248 g, 32.93 mmol) and dioxane (0.6473 g, 7.346 mmol) were added to this mixture. This mixture was homogenized by vigorous shaking, transferred to a round-bottom flask equipped with a magnetic stirrer and capped with a rubber septum. The reaction mixture was deoxygenated by bubbling with nitrogen for 10 min, and placed in an oil bath set at 70 °C for 49 h. The product was characterized by NMR to determine conversion, which was found to be 44%. The polymer was precipitated 3 times into 5% water in methanol at −78 °C. The resulting red polymer was collected, dried in vacuo overnight and analyzed by SEC to give a number-average molecular weight of 4600 g/mol and weight-average molecular weight of 5800 g/mol (PDI = 1.25).

Removal of Dithiobenzoate End Group from the *tert*-Butyl Methacrylate−Styrene Block Copolymer. *tert*-Butyl methacrylate−styrene block copolymer (1.8748 g, 0.41 mmol), BPO (0.7569 g, 3.124 mmol) and AIBN (1.344 g, 8.195 mmol) were dissolved in a mixture of toluene (3.81 g, 41.4 mmol) and dioxane (6.86 g, 77.6 mmol). The solution was transferred to a flask equipped with a magnetic stirrer, and deoxygenated by bubbling nitrogen for 10 min. The reaction mixture was placed in an oil bath set at 80 °C, and allowed to react for 4 h. After the allotted reaction time, the mixture was cooled to room temperature and precipitated three times into 5% water in methanol. The resulting colorless polymer was collected and analyzed by SEC and NMR. The SEC number-average molecular weight was 5500 g/mol and weight-average molecular weight was 7000 g/mol (PDI = 1.27). The small increase in molecular weight is due to the small amount of bimolecular polymer coupling that occurs during the radical catalyzed removal of the RAFT group.

Hydrolysis of the *tert*-Butyl Methacrylate−Styrene Block Copolymer. The *tert*-butyl methacrylate-styrene block copolymer (1.85 g, 0.34 mmol) was dissolved in dioxane (9.19 g, 104 mmol). A solution of 1.91 M HCl was prepared by diluting 32% HCl (0.5088 g, 4.47 mmol) into water (1.8968 g, 105.3 mmol). The solution of dilute HCl (1.42 g, 2.71 mmol) was added to the solution of polymer in dioxane. The reaction mixture was refluxed for 24 h, after which the solvents were removed under reduced pressure. The removal of the *tert*-butyl esters was confirmed by NMR analysis in deuterated acetone. The polymer was redispersed in THF, the small fraction of insoluble material was removed by centrifugation, and the THF removed under reduced pressure. This afforded the block copolymer of methacrylic acid and styrene.

Synthesis of *tert*-Butyl Acrylate Homopolymer. PABTC (0.2498 g, 1.05 mmol) was placed in a vial and combined with AIBN (8.6 mg, 0.052 mmol). To this mixture tBA (1.8201, 14.22 mmol) and toluene (1.9253 g, 20.91 mmol) were added. This mixture was homogenized by vigorous shaking and transferred to a round-bottom flask containing a magnetic stirrer. The flask was capped with a rubber septum and deoxygenated by bubbling nitrogen for 10 min. The reaction mixture was heated at 60 °C for 16 h and 40 min. The product was characterized by NMR and SEC and found to have reached a conversion of 99%. The residual solvent and traces of monomer were removed under reduced pressure. The resulting yellow polymer was collected, dried in vacuo overnight and analyzed by SEC to give a number-average molecular weight of 1700 g/mol and weight-average molecular weight of 1900 g/mol (PDI = 1.14).

Synthesis of *tert*-Butyl Acrylate−Styrene Block Copolymer. ACVA (0.0316 g, 0.113 mmol) was added to *tert*-butyl acrylate homopolymer (2.08 g, 1.05 mmol). Styrene (5.6905 g, 54.71 mmol) and dioxane (6.0580 g, 68.75 mmol) were added to this mixture. This mixture was homogenized by vigorous shaking, transferred to a round-bottom flask equipped with a magnetic stirrer and capped with a rubber septum. The reaction mixture was deoxygenated by bubbling with nitrogen for 10 min, and placed in an oil bath set at 70 °C for 24 h. After this reaction time the mixture was cooled to room temperature and an additional amount of ACVA (0.0250 g, 0.0893 mmol) and styrene (2.0985 g, 20.18 mmol) were added to the reaction mixture. This reaction mixture was deoxygenated by bubbling nitrogen for 10 min. The reaction mixture was placed in an oil bath set at 70 °C for 8 h, after which time it was cooled to room temperature. The product was characterized by NMR to determine conversion, which was found to be 68%. The polymer was precipitated 3 times into 7.5% water in methanol at −78 °C. The resulting yellow polymer was collected, dried in vacuo overnight and analyzed by SEC to give a number-average molecular weight of 5600 g/mol and weight-average molecular weight of 6900 g/mol (PDI = 1.25).

Removal of Trithiocarbonate End Group from the *tert*-Butyl Acrylate−Styrene Block Copolymer. *tert*-Butyl acrylate−styrene block copolymer (5.24 g, 0.95 mmol), BPO (1.6844 g, 6.954 mmol), and AIBN (3.4485 g, 21.02 mmol) were dissolved in a mixture of toluene (6.39 g, 69.4 mmol) and dioxane (18.79 g, 213.2 mmol). The solution was transferred to a flask equipped with a magnetic stirrer, and deoxygenated by bubbling nitrogen for 10 min. The reaction mixture was placed in an oil bath set at 80 °C, and allowed to react for 4 h. After the allotted reaction time, the mixture was cooled to room temperature and precipitated once into 15% water in methanol and four times into 5% water in methanol. The resulting colorless polymer was collected and analyzed by SEC and NMR. The SEC number-average molecular weight was 6700 g/mol and weight-average molecular weight was 8700 g/mol (PDI = 1.30). The small increase in molecular weight is due to the small amount of bimolecular polymer coupling that occurs during the radical catalyzed removal of the RAFT group.

Hydrolysis of the *tert*-Butyl Acrylate−Styrene Block Copolymer. The *tert*-butyl acrylate−styrene block copolymer (4.4696 g, 0.67 mmol) was dissolved in dioxane (19.60 g, 222 mmol). A solution of 1.91 M HCl was prepared by diluting 32% HCl (1.0322 g, 9.06 mmol) into water (3.8576 g, 214.1 mmol). The solution of dilute HCl (2.77 g, 5.29 mmol) was added to the solution of polymer in dioxane. The reaction mixture was refluxed for 24 h, at which point an additional amount of dioxane (6.27 g, 71.2 mmol) was added, and refluxed for an additional 22 h, affording a clear solution at the end of the 46 h total reaction time. After the reaction the solvents were removed under reduced pressure. The removal of the *tert*-butyl esters was confirmed by NMR analysis in a mixture of deuterated acetone and chloroform. The polymer was redispersed in THF, the small fraction of insoluble material was removed by centrifugation and the THF removed under reduced pressure. This afforded the block copolymer of acrylic acid and styrene.

Preparation of Micelles Based on Block Copolymers of Methacrylic Acid and Styrene. Poly(methacrylic acid-*b*-styrene) (0.417 g, 0.091 mmol) was dissolved in THF (9.425 g, 130.7 mmol) and stirred vigorously. To this solution a 0.03004 M sodium hydroxide solution was added (46.8 mL, 1.41 mmol) over 2 h with vigorous stirring. The THF was removed under reduced pressure, and the polymer micelle solution stirred for an additional 2 h at room temperature.

Synthesis of Seed Latex Based on Block Copolymers of Methacrylic Acid and Styrene. The poly(methacrylic acid-*b*-styrene) micelle solution was placed in a flask equipped with a magnetic stirrer. A solution of ACVA (0.0976 g, 0.349 mmol), sodium hydroxide (0.0271 g, 0.678 mmol) and sodium dodecyl sulfate (0.0141 g, 0.0489 mmol) in water (2.0266 mL) was added to the micelle solution, capped with a rubber septum and vigorously stirred. The aqueous solution was bubbled with nitrogen for 15 min to remove oxygen. In a separate vial styrene was bubbled with nitrogen for 15 min to remove oxygen. Initially, deoxygenated styrene (0.81 g, 7.8 mmol) was added to the micelle solution via syringe, and stirred for 30 min at room temperature. The reaction mixture was subsequently placed in an oil bath at 80 °C, and concurrently styrene (1.14 g, 11.0 mmol) was added at a rate of 1.32 mL/h. After allowing the reaction mixture to polymerize at 80 °C for 2 h, the temperature was reduced to 70 °C, and polymerized for an additional 14 h. The resulting latex was subsequently cooled to room temperature and conversion measured by gravimetry, showing full conversion. The latex was passed over glass wool to remove any coagulum, and placed in a small pore dialysis membrane (2000 g/mol cut off) and dialyzed for 2 days, with twice daily water changes. After dialysis the MAA-Sty seed latex was passed over glass wool, and characterized by gravimetry and HDC. The average hydrodynamic diameter was found to be 25 ± 3 nm, as measured by HDC, and the particle number concentration was found to be 7.4×10^{18} particles per liter.

Preparation of Micelles Based on Block Copolymers of Acrylic Acid and Styrene. The poly(acrylic acid-*b*-styrene) polymer (0.490 g, 0.089 mmol) was dissolved in THF (9.369 g, 129.9 mmol) and stirred vigorously. To this solution a 0.03004 M sodium hydroxide solution was added (46.8 mL, 1.41 mmol) was added over 2 h with vigorous stirring. The THF was removed under reduced pressure, and the polymer micelle solution stirred for an additional 2 h.

Synthesis of Seed Latex Based on Block Copolymers of Acrylic Acid and Styrene. The poly(acrylic acid-*b*-styrene) micelle solution was placed in a flask equipped with a magnetic stirrer. A solution of ACVA (0.0982 g, 0.351 mmol) and sodium hydroxide (0.0280 g, 0.700 mmol) in water (2.0123 mL) was added to the micelle solution, capped with a rubber septum and vigorously stirred. The aqueous solution was bubbled with nitrogen for 15 min to remove oxygen. In a separate vial styrene was bubbled with nitrogen for 15 min to remove oxygen. Initially, deoxygenated styrene (0.81 g, 7.8 mmol) was added to the micelle solution via syringe, and stirred for 30 min at room temperature. The reaction mixture was subsequently placed in an oil bath at 80 °C, and concurrently styrene (0.17 g, 1.6 mmol) was added at a rate of 1.32 mL/h. After allowing the reaction mixture to polymerize at 80 °C for 2 h, the temperature was reduced to 70 °C, and polymerized for an additional 18 h and 30 min. The resulting latex was subsequently cooled to room temperature and conversion measured by gravimetry, showing full conversion. The latex was passed over glass wool to remove any coagulum, and placed in a small pore dialysis membrane (2000 g/mol cut off) and dialyzed for 2 days, with twice daily water changes. After dialysis the AA-Sty seed latex was passed over glass wool, and characterized by gravimetry, hydrodynamic chromatography and transmission electron microscopy. The average hydrodynamic diameter, measured by HDC was found to be 24 ± 3 nm. The particle number concentration was found to be 4.6×10^{18} particles per liter.

Preparation of Samples for γ-Irradiation Dilatometry Studies. In a typical sample prepared for γ-irradiation dilatometry, a dry dilatometer equipped with a magnetic stirrer bar was charged with seed latex (14 g) and deionized water (13 g). Sodium dodecyl sulfate (56 mg) was added at 0.9 of the critical micelle concentration in neat water in order to stabilize monomer droplets. The latex was deoxygenated by bubbling nitrogen for 15 min. A sample of styrene was prepared by passing the monomer twice over an inhibitor removal column, and deoxygenated by bubbling nitrogen for 15 min. The deoxygenated styrene (5 g) was added to the latex solution in the dilatometer and the resulting mixture bubbled with nitrogen for an additional 10 min. Each sample was sealed with a glass stopper and stirred overnight to ensure effective swelling of the seed latex.

γ-Irradiation Experiments. In a typical γ-relaxation experiment a water-jacketed dilatometer prepared as described above was sealed with a SUBA seal and placed in the irradiation chamber which was in the "raised" position i.e. out of the gamma source. The emulsion was brought to 50 °C under vigorous stirring and a partial vacuum. The partial vacuum was achieved by evacuating part of the dilatometer headspace with a syringe. This was done in order to prevent the formation of bubbles due to outgassing of the emulsion during the experiment. A capillary tube was then fitted to the dilatometer, the headspace and the capillary were charged with degassed water, and the tube was capped with hexadecane. The meniscus height was monitored by an automated tracking device at 20 s intervals. When the temperature of the swollen latex had stabilized (constant meniscus height) the chamber was lowered into the ^{60}Co source (49.25Gy/h) where, after an inhibition period, polymerization commenced. When the reaction had reached a steady-state the dilatometer was removed from the source and the meniscus height monitored until a new (thermal) steady-state was reached. This procedure was repeated several times per run.

■ RESULTS AND DISCUSSION

Block Copolymer Syntheses. RAFT polymerization offers an excellent route to synthesizing oligomers of a variety of monomers.[49] In the case of the poly(*tert*-butyl methacrylate) oligomer, there was a significant amount of uninitiated RAFT agent, evidenced by a signal in the UV trace at very long retention time. The amount of unreacted RAFT agent was estimated as approximately one-third of the total RAFT concentration. These results are qualitatively similar to those of Gilbert et al.[47] who also found a significant amount of low molecular weight tailing when synthesizing oligomers of methacrylic monomer, although Gilbert et al. used significantly higher initiator concentrations than reported in this work. Once this unreacted RAFT agent is

Table 1. Average Size, Breadth Data, and Aggregation Data for the Micelles Based on AA_{14}-Sty_{37} and MAA_{13}-Sty_{26}

sample	average core + shell diameter (nm)	standard deviation (nm)	PDI (d_w/d_n)	average core diameter (nm)	aggregation number
AA_{14}-Sty_{37}	17	1	1.02	10	100
MAA_{13}-Sty_{26}	15	1	1.03	9	90

accounted for the number-averaged molecular weight of 1900 g/mol (PDI = 1.26) determined by SEC, agrees well with the theoretical molecular weight of 1800 g/mol. This residual RAFT agent was removed by multiple precipitations, affording pure RAFT capped poly(*tert*-butyl methacrylate) homopolymer. Upon chain extension with styrene a block copolymer with a number-averaged molecular weight of 4600 g/mol (PDI = 1.25), determined by SEC, was obtained. This agrees reasonably well with the theoretical molecular weight of 5300 g/mol, with differences attributable to the use of polystyrene standards to characterize the block copolymer, and the fact that the RAFT polymerization generates new chains continuously by initiator dissociation, which can lower the molecular weight. The block lengths determined by NMR are 12 units for the tBMA and 23 units of styrene (Figures S1 and S2, Supporting Information). The dithiobenzoate end group was removed using the radical transfer-termination method outlined originally by Takolpuckdee et al.,[25] and modified by Rizzardo et al.[50] This allows the complete cleavage of the RAFT group from the polymer, and by subsequent precipitation the complete separation of the RAFT agent from the polymer. As outlined by Rizzardo et al.,[50] this method can induce a small amount of bimolecular termination, which is seen by the small increase in the average molecular weight after the removal of the RAFT group, however a small amount of coupled polymer should not affect the surface properties of the final block copolymer, since the coupled polymer is equivalent to two of the initial polymers. The final step was the conversion of the *tert*-butyl methacrylate groups to methacrylic acid groups. This was achieved by acid catalyzed hydrolysis methods, as outlined in the literature,[51,52] and the NMR spectrum indicating removal of the *tert*-butyl groups is shown in Figure S3, Supporting Information. This yielded a block copolymer with 13 units of methacrylic acid and 26 units of styrene, henceforth referred to as MAA_{13}-Sty_{26}. The SEC molecular weight distributions of the tBMA, tBMA-Sty polymers with and without the RAFT group are shown in Figure S4, Supporting Information.

The synthesis of the poly(*tert*-butyl acrylate) homopolymer closely followed that of the methacrylic analogue. The poly(*tert*-butyl acrylate) homopolymer was synthesized under typical RAFT conditions, giving a polymer with number-averaged molecular weight of 1700 g/mol (PDI = 1.14), which was in excellent agreement with the theoretical molecular weight of 1700 g/mol. Upon chain extension with styrene a polymer with number-averaged molecular weight of 5500 g/mol (PDI = 1.25) was obtained. This is in reasonable agreement with the theoretical molecular weight of 6700 g/mol, and differences are most likely due to the use of polystyrene standards to characterize the block copolymer, and the fact that the polymerization used a relatively large amount of initiator (20% in the styrene chain extension with respect to RAFT), which creates new chains, thus lowering the molecular weight. The block lengths determined by NMR are 15 for the tBA block and 39 for the Sty block (Figures S5 and S6, Supporting Information), in agreement with the SEC data. The trithiocarbonate end-group was removed by the same radical catalyzed process as the poly(*tert*-butyl methacrylate-styrene) block copolymer, giving similar results to the methacrylic case. Similarly, the *tert*-butyl groups were converted to carboxylic acid groups by an acid catalyzed hydrolysis (Figure S7, Supporting Information). This yielded a block copolymer of 14 acrylic acid units and 37 styrene units, and henceforth referred to as AA_{14}-Sty_{37}. The SEC molecular weight distributions of the tBA, tBA-*b*-Sty polymers before and after cleavage of the RAFT group are shown in Figure S8.

Micelle and Seed Particle Syntheses. The seed particles were synthesized by a variation of the RAFT in emulsion approach originally outlined by Ferguson et al.[3,4,29] One significant difference between the current work, and the original RAFT in emulsion technique is the fact that in the current approach the RAFT end-group is removed before the self-assembly into micelles, and subsequent growth into seed particles. This approach offers the advantage of ensuring that the RAFT group is completely removed before the formation of particles, rather than requiring the modification of the RAFT group after the formation of a seed particle.[40]

In each case, micelles were first created by dissolving the block copolymer in THF, and slowly adding the sodium hydroxide solution. This allows the system to reach an equilibrium structure as the solvent is changed from one that is a good solvent for both blocks to one that is only good for the hydrophilic block. At the end of this process the micelles are no longer labile and become locked in. The diameters of these locked in micelles, as measured by HDC, are given in Table 1. The core plus shell sizes were determined directly from the HDC, while the hydrophobic core size was determined by assuming that the hydrophilic polymeric stabilizers formed a corona that extended out from the particle surface a distance equal to a fully extended average hydrophilic chain length. This assumption is consistent with the SANS results obtained by Ganeva et al.[36] for similar particles. In all cases the monomer length was assumed to be 0.24 nm.

The micelles formed from the two diblock copolymers are substantially the same. The MAA_{13}-Sty_{26} micelles are slightly smaller than the AA_{14}-Sty_{37} micelles, which is likely to be due to the slightly shorter hydrophobic block on the MAA_{13}-Sty_{26} polymer compared to the AA_{14}-Sty_{37} polymer. The aggregation number was determined from the ratio of the number of molecules of diblock added, to the number of particles in the latex. Interestingly both the methacrylic and acrylic based systems have aggregation numbers in the range of 90−100, which is consistent with earlier studies on related systems which also showed aggregation numbers of approximately 90.[36]

Seed latexes were synthesized from these micelles, by the addition of styrene and polymerization at elevated temperatures, and in the case of MAA stabilized latexes a small amount of SDS was added to reduce the polydispersity and minimize the formation of coagulum. The SDS was needed for the MMA latexes, probably because the AA based latexes are more efficient steric stabilizers than the MAA based latexes, due to the lower hydrophilicity of the MAA system. In all cases studied the polymerization reached essentially full conversion. After the

Table 2. Average Size, Breadth Data, and Particle Number Data for the Seed Latexes Based on AA_{14}-Sty_{37} and MAA_{13}-Sty_{26}

sample	average core + shell diameter (nm)	standard deviation (nm)	PDI (d_w/d_n)	average core diameter (nm)	initial swollen particle diameter (nm)	particle number (L^{-1})
Seed-AA_{14}-Sty_{37}	24	2	1.02	17	31	4.6×10^{18}
Seed- MAA_{13}-Sty_{26}	25	3	1.05	19	34	7.6×10^{18}

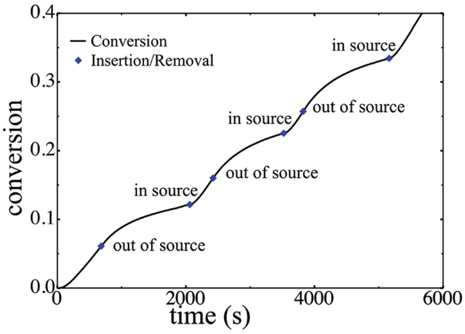


Figure 1. Typical evolution of conversion with time in a γ-initiated experiment with multiple relaxation−insertion events, marked by the blue points. Experiment for a poly(acrylic acid) stabilized latex. Conversion here refers to fractional conversion.

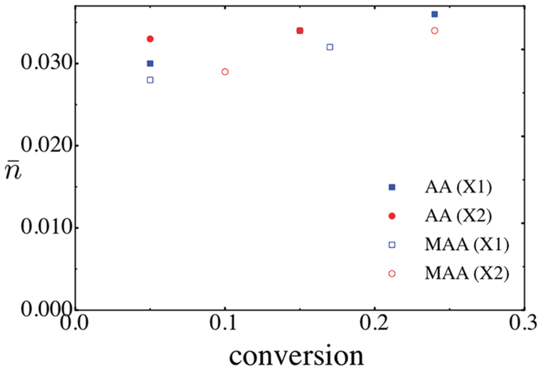


Figure 2. In source steady state values of $\bar{n}$, for the two repetitions of the AA and MAA stabilized latexes for the first (X1) and second repetition (X2).

synthesis of each seed, the latex was extensively dialyzed. This allowed the synthesis of well-controlled, small seed particles. The properties of the seed latexes are given in Table 2. The hydrophobic core sizes were calculated using the same method as for the micelles, and the particle number was determined from gravimetry, in conjunction with the core particle size. The initial swollen particle size was calculated on the basis of a monomer concentration in the particles of 5.5 M, which is typical of polystyrene latexes. The monomer concentration in the particle decreases with decreasing particle size, however, the block copolymer is expected to be a very efficient stabilizer, somewhat canceling the effect of small particle size. Therefore, the monomer concentration in the particle is taken to be 5.5 M. All sizes refer to diameters.

The two seed latexes were very similar in terms of both their size and their particle numbers. Interestingly, the latex particles are narrowly distributed, and the PDIs were similar in magnitude, albeit slightly lower, to those obtained by Thickett and Gilbert in their study.[40] This could be due to the slightly larger particle sizes used in these experiments.

γ-Initiated Kinetic Studies. The advantage of using γ-relaxation dilatometry to study the kinetics is that the entry and exit rate coefficients can be separately probed in a single experiment, by lowering the sample into the source and then removing it from the source. Each latex was analyzed twice by γ-relaxation dilatometry, in order to provide an estimate of the error associated with the rate coefficients. A typical conversion versus time profile is shown in Figure 1 and the steady state values of the average number of radicals per particle, $\bar{n}$, are given in Figure 2. The average $\bar{n}$ in Figure 1differ by a factor of 5−6 between the in source and out of source values (see Tables S3−S6, Supporting Information), and the results are similar for the other AA and MAA stabilized latexes, with the difference often approaching 1 order of magnitude between in source and out of source values. This difference leads to a difference of a factor of approx 5−6 in the polymerization rate between the in source and out of source values.

In a typical emulsion polymerization the conversion is related to $\bar{n}$ by the following expression[14]

$$\frac{d(\text{conversion})}{dt} = \frac{k_p C_p N_p}{n_M{}^0 N_A} \tag{3}$$

where k_p is the propagation rate coefficient of the monomer (237 $M^{-1}\,s^{-1}$ at 50 °C),[53] C_p is the concentration of monomer in the particle (taken to be 5.5 M), N_p is the number of particles per liter, $n_M{}^0$ is the initial concentration of monomer, and N_A is Avogadro's number.

For each relaxation and insertion (except the first insertion, due to oxygen inhibition) the kinetic coefficients ρ and k were estimated under the assumption of first order loss (Limit 1), as well as second order loss (Limit 2a). In the case of Limit 1, the radical that exits is assumed to fully terminate in the aqueous phase, therefore the average number of radicals per particle, $\bar{n}$, is governed by eq 1. While in the case of Limit 2a, the exited radical is assumed to re-enter once and terminate if the entered particle already contains a radical, or otherwise reinitiate a new chain, therefore the average number of radicals per particle is governed by eq 2.

Each data set was analyzed by the "slope−intercept" method[14] as well as by directly fitting eqs 1 and 2 to the conversion data. The details of all kinetic parameters determined from these experiments, as well as the equations used to describe them are given in the Supporting Information, while a summary of the kinetic parameters obtained for the first relaxation and first reinsertion are given in the Tables below. The subsequent relaxations and reinsertions are similar to the first ones and therefore not included in the main text, but instead left exclusively to Supporting Information.

Table 3 shows the average parameters for γ-relaxation studies, determined by the slope−intercept method, while Table 4 gives the equivalent parameters, when they are determined by directly fitting the conversion data. The Supporting Information gives the corresponding γ-reinsertion studies (Table S1 and S2,

Table 3. First and Second Order Entry and Exit Rate Coefficients Obtained by Applying the Slope−Intercept Method to the First Relaxation of Two Poly(acrylic acid) and Two Poly(methacrylic acid) Stabilized Latexes, As Studied by γ-Relaxation Dilatometry[a]

experiment	$\rho_{(thermal)}$ (s^{-1}) [1st order]	k (s^{-1}) [1st order]	$\rho_{(thermal)}$ (s^{-1}) [2nd order]	k (s^{-1}) [2nd order]
AA-relaxation	$(1.7 \pm 0.7) \times 10^{-5}$	$(3.5 \pm 0.1) \times 10^{-3}$	$(4 \pm 3) \times 10^{-6}$	$(9 \pm 1) \times 10^{-2}$
MAA-relaxation	$(9 \pm 2) \times 10^{-6}$	$(3.3 \pm 0.1) \times 10^{-3}$	$(1.7 \pm 0.5) \times 10^{-6}$	$(1.0 \pm 0.1) \times 10^{-1}$

[a] The result is the average of the repeat experiments.

Table 4. First and Second Order Entry and Exit Rate Coefficients Obtained by Directly Fitting the Conversion Data of the First Relaxation for Two Poly(acrylic acid) and Two Poly(methacrylic acid) Stabilized Latexes, As Studied by γ-Relaxation Dilatometry[a]

experiment	$\rho_{(thermal)}$ (s^{-1}) [1st order]	k (s^{-1}) [1st order]	$\rho_{(thermal)}$ (s^{-1}) [2nd order][b]	k (s^{-1}) [2nd order]
AA-relaxation	$(8 \pm 2) \times 10^{-6}$	$(2.8 \pm 0.2) \times 10^{-3}$	$(1 \pm 1) \times 10^{-7}$	$(6 \pm 1) \times 10^{-2}$
MAA-relaxation	$(1.5 \pm 0.1) \times 10^{-6}$	$(2.5 \pm 0.2) \times 10^{-3}$	$(1 \pm 1) \times 10^{-7}$	$(6.9 \pm 0.2) \times 10^{-2}$

[a] The result is the average of the repeat experiments. [b] These values were set to 10^{-7} because the fitting program wanted to take them negative when fitting to the second order theory.

Table 5. Expected First and Second Order Exit Rate Coefficients for the First Relaxation for Two Poly(acrylic acid) and Two Poly(methacrylic acid) Stabilized Latexes

experiment	k_{ct} (s^{-1}) [1st order] empirical (Hawkett et al.)	k_{ct} (s^{-1}) [1st order] theoretical	k_{cr} (s^{-1}) [2nd order] theoretical
AA-relaxation	1.44×10^{-2}	2.97×10^{-2}	7.08×10^{-2}
MAA-relaxation	1.53×10^{-2}	3.04×10^{-2}	7.52×10^{-2}

Supporting Information) using both the slope intercept and direct fitting approaches. One interesting observation is that in general the background thermal entry rate coefficients determined by a first order fit to kinetic data are supportive of the notion that water saturated with styrene tends to generate radicals at a rate of approximately 10^{13} L^{-1} s^{-1} at 50 °C, whereas second order fitting to kinetic data tends to produce values that have little rational consistency.

Table 5 shows the exit rate coefficients expected for a system that reached the same conversion as those given in Tables 3 and 4, that is for the first relaxation in acrylic acid and methacrylic acid stabilized latexes.

The value predicted by Hawkett et al.[9] assumes first order loss, and is given by the empirical relationship $k = (5.6/r^2)$, where r is taken to be the particle swollen radius, plus the length of the hairy layer in nm. The hairy layer was included in this calculation since the radical is not free of the particle until it leaves both the core and hairy layer. The theoretical estimates are given by the expressions:[14]

$$k_{ct} = k_{tr} C_p \frac{k_{dM}}{k_{dM} + k_p{}^1 C_p} \tag{4}$$

$$k_{cr} = \frac{k_{tr} k_{dM}}{k_p{}^1} \tag{5}$$

where $k_{dM} = ((3\ D_w C_w)/(r^2 C_p))$, k_{tr} is the transfer rate coefficient, C_p is the saturated concentration of the monomer in the particle, $k_p{}^1$ is the propagation rate coefficient of the transferred (monomeric) radical, D_w is the diffusion coefficient of the radical in water and C_w is the saturated concentration of the monomer in the aqueous phase. In this case k_{ct} corresponds to the complete termination (first order loss) and k_{cr} corresponds to complete re-entry (second order loss). Equations were fitted to the experimental data using $k_p{}^1 = 4k_p$ in accordance with Thickett et al.[40]

In general, the experimental second order loss exit rate coefficients (Tables 3 and 4) show better agreement with the theoretically predicted values (Tables 5). This is true of both the values obtained by studying relaxation or reinsertion data, regardless of the fitting method. As will be demonstrated later this agreement appears to be fortuitous. In contrast, the first order loss exit rate coefficients are appreciably lower than theoretical prediction. Typically these exit rate coefficients, measured in relaxations, are about an order of magnitude smaller than those predicted by the theoretical model, and these values are about a factor of 4 smaller than those predicted by the empirical relationship of Hawkett et al.[9] Because of the long relaxation period, and short time in source, the exit rate coefficients determined from relaxations should be more accurate than those determined from insertions.

One of the advantages of γ-initiated polymerizations is that the thermal (background) production of radicals can be probed at the same time as the in source and exit rate coefficients are measured. This is because the ρ determined out of source, or during a relaxation, corresponds to the thermal production rate, while the in source ρ contains a majority contribution from the γ-source, as well as a small component due to the thermal production. In addition, γ-initiated experiments allow the determination of accurate exit rate coefficients, due to the ability to increase or decrease radical production. Furthermore, by fitting different models to relaxation data it is possible to discriminate between different loss mechanisms, since the relaxation period is dominated by radical loss. Figure 3 shows relaxation data for both acrylic acid (top) and methacrylic acid (bottom) stabilized latexes, under the assumption of first order and second order loss. The data presented was for the first relaxation for an acrylic or methacrylic stabilized latex, however, subsequent relaxations

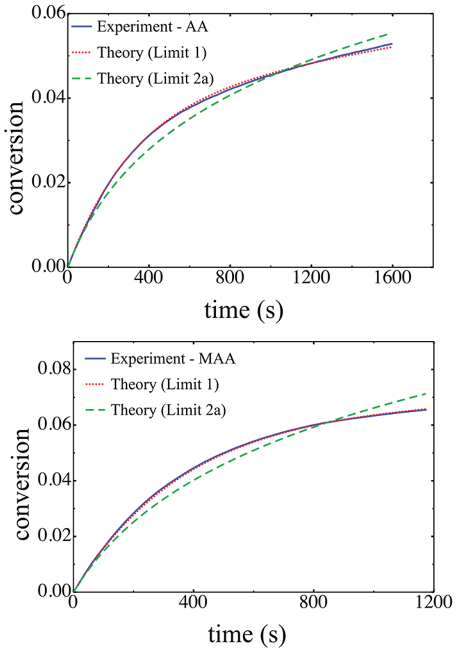


Figure 3. Fit of first order (limit 1) and second order (limit 2a) loss models to γ-relaxation data for acrylic acid (top) and methacrylic acid (bottom) stabilized latexes. The conversion and time was set to zero at the point of removal from the γ-source.

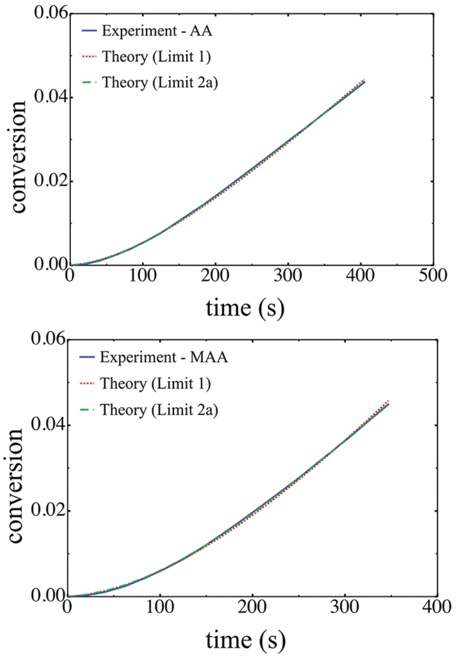


Figure 4. Fit of first order (limit 1) and second order (limit 2a) loss models to γ-insertion data for acrylic acid (top) and methacrylic acid (bottom) stabilized latexes. The conversion and time was set to zero at the point of insertion into the γ-source.

and a repeat experiment show essentially the same behavior. Both the acrylic acid and methacrylic acid stabilized latexes show significantly better agreement with the first order loss mechanism (limit 1) than the second order loss mechanism (limit 2a). This suggests that once the radical is lost to the aqueous phase, it is unlikely to re-enter and reinitiate polymerization. Figure 4 shows the first and second order fits to the γ-reinsertion experiments for both acrylic acid (top) and methacrylic acid (bottom) stabilized latexes. Unlike the relaxation experiments, the reinsertion experiments are unable to distinguish between the loss mechanisms.

One of the interesting outcomes from these γ-relaxation experiments is that, in general, the methacrylic and acrylic systems have essentially the same rate coefficients, regardless of whether relaxations or insertions are being studied. These results suggest that the abstractable proton on the acrylic backbone has minimal influence on the emulsion polymerization kinetics, at least in the latexes studied here. This is in contrast to the midchain radical hypothesis, which would predict significant differences between the kinetics of acrylic and methacrylic acid stabilized latexes. This is true of both the rate coefficients, and the similar agreement between the experimental data and the fitted models. In particular, the relaxation data of both the acrylic and methacrylic acid stabilized latexes show significantly better agreement with the first order loss mechanism, than the second order loss mechanism.

Because of the superior fit of the first order loss model (limit 1), compared to the second order loss model (limit 2a), to every relaxation curve it is argued that these electrosterically stabilized latexes follow a first order loss mechanism in both acrylic acid and methacrylic acid stabilized latexes. This is consistent with the studies of Thickett et al, who also found better agreement with the first order loss model, as compared to the second order loss model.[39] However, the exit rate coefficients observed in these systems, under the assumption of first order loss, are much smaller than predicted on the basis of both theory and empirical relationships. One possible explanation for the low exit rate coefficients is a restricted diffusion model,[40] which can correctly predict the trend in exit rate with increasing thickness of the hairy layer.[54] This model predicts that as the length of the hairy layer increases there is a commensurate decrease in the exit rate coefficient due to the additional distance of the hairy layer needing to be traversed before the radical exits. However, this model is unlikely to explain the observation that the first order exit rate coefficients are approx 0.5−1 orders of magnitude below their expected values. Indeed, the hairy layer is only about 3.4 nm thick and is > than 95% water; although such a layer needs to be traversed by the radical before it can escape the particle, diffusion in that layer is unlikely to be restricted relative to that in the core of the particle for small, noninteracting molecules.

It would appear that our expectation that we could calculate the exit rate for very small particles on the basis of the initial average swollen particle radius, in the same way as for much larger particles, was a naïve expectation. For a large particle the change in particle radius that the particle undergoes between a single entry event and exit is quite small, whereas a small amount of polymer growth in a very small particle causes a relatively large change in particle size. Thus, the goal posts for a monomeric radical trying to exit a very small particle are constantly changing as the particle grows.

If we consider a particle in the present system with a swollen particle radius of 20 nm we would predict an exit rate coefficient of about 1.4×10^{-2} s^{-1} on the basis of the empirical relationship of Hawkett et al. However, if a radical enters such a particle and initiates the growth of a polymer chain that chain will grow on average to the chain transfer molecular weight limit (a DP of about 18,000, based on the average value for k_{tr}/k_p in the Polymer Handbook[55]) before the radical becomes a candidate for exit Once this extra polymer is saturated by monomer, we

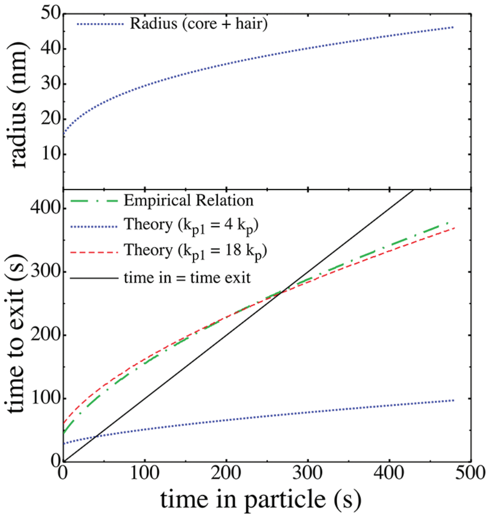


Figure 5. Radius of the particle (top) the time to exit (bottom) versus time in particle for a typical latex particle. The empirical relation was obtained by Hawkett et al.[9] and the theory is outlined by Gilbert.[14]

have a 22 nm particle, for which the predicted exit rate coefficient would be 1.2 × 10^{-2} s^{-1}. On the basis of the same empirical relationship, such a particle would be expected to grow for an average of about 86 s before exit, during which time another 1.2 × 10^5 monomer units would be turned into polymer. After swelling the new polymer with monomer, we would have a particle of 29 nm radius and would predict an exit rate coefficient of 7 × 10^{-3} s^{-1}. To a first approximation, we might consider that exit will on average occur when the particle has been growing for a time that is equal to the time that it would take to exit from a particle of the size achieved. Time to exit is plotted against the time the radical has been growing in the particle in Figure 5. On the basis of the empirical relationship of Hawkett et al., these calculations lead to an exit rate coefficient of 3.6 × 10^{-3} s^{-1}, which is in acceptable agreement with our present experimental results (Tables 3 and 4). If we take the same approach using both the theory for first order and second order loss using the generally used value of $k_{p1} = 4k_p$ we obtain a much higher value for the predicted exit rate coefficient in both cases. However, if we use an arguably much more realistic value for k_{p1}[56−59] of $18k_p$, we obtain an exit rate coefficient that agrees with both the experimental results and those predicted by the empirical relationship of Hawkett et al. It would thus appear that there is an upper limit to exit rate coefficients in emulsion polymerization based on the competition between exit and particle growth when considering very small particles.

These systems all have $\bar{n}$ values of the order of 0.03, or equivalently only one particle in 30 contains a radical. This implies that a particle that contains a radical will grow very much larger than those that contain no radical.

Another strong indicator of first order behavior in these systems is the values obtained for the background thermal entry rate coefficients by curve fitting to the relaxation data. When using a second order fit, it was necessary to set these coefficients to a very small number; 10^{-7} s^{-1} was chosen in this work (Table 4), to prevent their values going negative. However, the first order fit yielded values on the order of 10^{-6}–10^{-5} s^{-1}. Indeed, when one takes the average value for the first relaxation for the poly(acrylic acid) stabilized latexes of 1 × 10^{-5} s^{-1}, taken as the average of the value obtained by direct fitting and the slope intercept method, and multiply it by the number of particles in the poly(acrylic acid) stabilized latexes, N_p = 2.3 × 10^{18} L^{-1}, the total thermal radical production is found to be approx 2.3 × 10^{13} radicals L^{-1} s^{-1}. Similarly, multiplying the average thermal entry rate coefficient for the poly(methacrylic acid) stabilized latexes of 5 × 10^{-6}, by the number of particles in the poly(methacrylic acid) stabilized latexes, N_p = 3.2 × 10^{18}, the total thermal production of radicals is found to be 1.6 × 10^{13} radicals L^{-1} s^{-1}. This average thermal productions of radicals of 2.0 ± 0.4 × 10^{13} radicals L^{-1} s^{-1}, agrees very well with other studies in the literature which typically find the thermal production of radicals in the order of 10^{13} radicals L^{-1} s^{-1}.[9,16] Moreover, these calculations provide further evidence that the background thermal radicals are a property of pure styrene in pure water and not a property of a particular latex.[9]

Overall, this kinetic study of electrosterically stabilized latexes is in good agreement with the studies of Thickett et al.[39,40] on poly(acrylic acid) stabilized latexes. However, this study has used both poly(acrylic acid) and poly(methacrylic acid) stabilized latexes and shown that there is minimal effect of the nature of the stabilizing chain on the kinetics of the emulsion polymerization. Since the methacrylic acid groups have no abstractable protons on the backbone, this suggests that the midchain radicals that could be formed on an acrylic acid backbone are not kinetically significant. These data do not refute the existence of midchain radicals; however, the fact that the poly(methacrylic acid) based system is essentially the same as the poly(acrylic acid) shows that the midchain radical hypothesis cannot explain the kinetics of poly(acrylic acid) systems.

These results are important since they imply that chemically initiated emulsion polymerization experiments, or in fact any other initiation system, should follow a similar mechanism for both poly(acrylic acid) and poly(methacrylic acid) stabilized latexes. Therefore, the conclusions of the extensive studies performed by Thickett et al. should apply to a wide variety of emulsion polymerizations. Interestingly, both the poly(acrylic acid) and poly(methacrylic acid) based systems are consistent with first order loss. This can be seen by the significantly better agreement with the relaxation profiles for first order loss, compared to second order loss, which is generally believed to occur in styrene emulsion polymerization. Despite the excellent agreement of the first order loss with the experimental data for both systems, the question still remains as to why the loss follows a first order mechanism. This remains a question to be explained in future work.

■ CONCLUSIONS

The kinetics of the electrosterically stabilized emulsion polymerization of styrene were studied by developing two model systems. These two model systems were stabilized by short chains of either poly(methacrylic acid) or poly(acrylic acid). These two model systems differ in that the poly(acrylic acid) has abstractable protons in the backbone while poly(methacrylic acid) does not. The results of γ-insertion and relaxation dilatometry experiments show essentially the same average number of radicals per particle and the same entry and exit rate coefficients for similar poly(methacrylic acid) and poly(acrylic acid) stabilized latexes. Furthermore, both the poly(methacrylic acid) and poly(acrylic acid) stabilized systems showed significantly better agreement with first order radical loss, compared to the second order loss, which is surprising for styrene emulsion polymerization where conventional wisdom would have the radical reenter after radical desorption. In the poly(acrylic acid) system the first order loss was previously attributed to termination of the exiting radical with mid chain radicals on the poly(acrylic acid) backbone, however, for poly(methacrylic acid) this is not possible due to the absence of abstractable protons on the backbone. The similarity between the kinetics of the poly(methacrylic acid) and poly(acrylic acid) stabilized latexes suggests that the midchain radicals do not play a significant role in defining the entry and exit rate coefficients for electrosterically stabilized latexes. However, the mystery remains as to why a process that is so logically a second order process should exhibit such markedly first order kinetic behavior. Moreover, we have shown that what were previously regarded as very low exit rates in these systems can be readily explained by taking into account the relatively rapid rate of growth of the very small seed particles used.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Characterization of block copolymers, equations for obtaining estimates of the kinetic parameters from conversion data, tables of estimated kinetic parameters for γ-reinsertion dilatometry, and tables of all kinetic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We are very grateful to AINSE, Lucas Heights, NSW, Australia, for maintaining and making available the unique ^{60}Co γ-facility fitted with the automated meniscus tracking device without which this, and many previous papers, would not have been possible. We thank Prof. Sébastien Perrier and especially Dr. Stuart Thickett for fruitful discussions.

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