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Ab Initio Emulsion Polymerization by RAFT-Controlled Self-Assembly[§]

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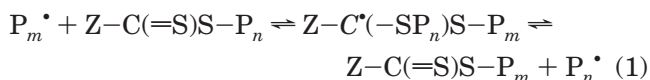
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ABSTRACT: A method is developed to enable emulsion polymerization to be performed under RAFT control to give living character without the problems that often affect such systems: formation of an oily layer, loss of colloidal stability, or loss of molecular weight control. Trithiocarbonate RAFT agents are used to form short stabilizing blocks from a water-soluble monomer, from which diblocks can be created by the subsequent polymerization of a hydrophobic monomer. These diblocks are designed to self-assemble to form micelles. Polymerization is initially performed under conditions that avoid the presence of monomer droplets during the particle formation stage and until the hydrophobic ends of the diblocks have become sufficiently long to prevent them from desorbing from the newly formed particles. Polymerization is then continued at any desired feed rate and composition of monomer. The polymer forming in the reaction remains under RAFT control throughout the polymerization; molecular weight polydispersities are generally low. The number of RAFT-ended chains within a particle is much larger than the aggregation number at which the original micelles would have self-assembled, implying that in the early stages of the polymerization, there is aggregation of the micelles and/or migration of the diblocks. The latexes resulting from this approach are stabilized by anchored blocks of the hydrophilic monomer, e.g., acrylic acid, with no labile surfactant present. Sequential polymerization of two hydrophobic monomers gives completely novel core-shell particles where most chains extend from the core of the particles through the shell layer to the surface.

Introduction

The successful application of RAFT (Reversible Addition-Fragmentation chain Transfer) techniques to both bulk and solution polymerizations is well documented.^{1–4} A RAFT agent has the generic formula $Z-C(=S)S-R$, where R is a leaving group that mediates the first transfer event and thereafter remains the non-active end group of the growing polymer chain and Z is an activating group. The essential steps in RAFT polymerization are



Propagation occurs with the polymeric radicals P_n^\bullet , whose “free” lifetime is very brief compared to the time that they spend as nonpropagating $S=C(Z)SP_n$ entities. The control that this method allows over molecular weight, polydispersity, and chain architecture has allowed many novel polymers to be produced.^{5–8}

While RAFT is well developed for use in homogeneous polymerizations, the same cannot be said for dispersed polymerization systems. Almost all published experiments for RAFT polymerization in conventional emulsion systems have reported one or more of the following

problems: poor colloidal stability, poor molecular weight control, or high polydispersity.^{3,9–14} There have been various mechanisms postulated to explain these problems,⁹ for example, problems with RAFT agent transport across the aqueous phase.¹⁵ This postulate has been supported by evidence from Prescott et al.¹⁶ who showed that these problems may be circumvented by ensuring that all of the RAFT agent is located in seed particles before polymerization is commenced. The procedure used by these authors is limited to cases where seed particles are used and thus does not allow ab initio (unseeded) emulsion polymerization under RAFT control (much of the final polymer comes from the seed and is thus not grown under controlled conditions). Another approach that has been used with success is miniemulsion polymerization.^{17–20} This method removes the need for the RAFT agent to migrate across the aqueous phase, as the particles form from the droplets initially present in the emulsion.

This paper expands on our earlier Communication²¹ describing an alternative method of applying RAFT techniques to ab initio emulsion polymerization (as distinct from miniemulsion).

Proposed Particle Formation Model

In a conventional ab initio emulsion polymerization, particle formation can occur by three mechanisms: micellar entry, homogeneous nucleation, and droplet nucleation.²² Whichever nucleation route is occurring in a conventional emulsion polymerization, in the presence of RAFT agents, this agent must still migrate into the newly formed particles (from monomer droplets, from monomer swollen micelles, or from the aqueous phase) for the reaction to proceed under RAFT control.

[§] Preliminary publication of some of this work appeared as a Communication: Ferguson, C. J.; Hughes, R. J.; Pham, B. T. T.; Hawkett, B. S.; Gilbert, R. G.; Serelis, A. K.; Such, C. H. *Macromolecules* 2002, 35, 9243–9245.

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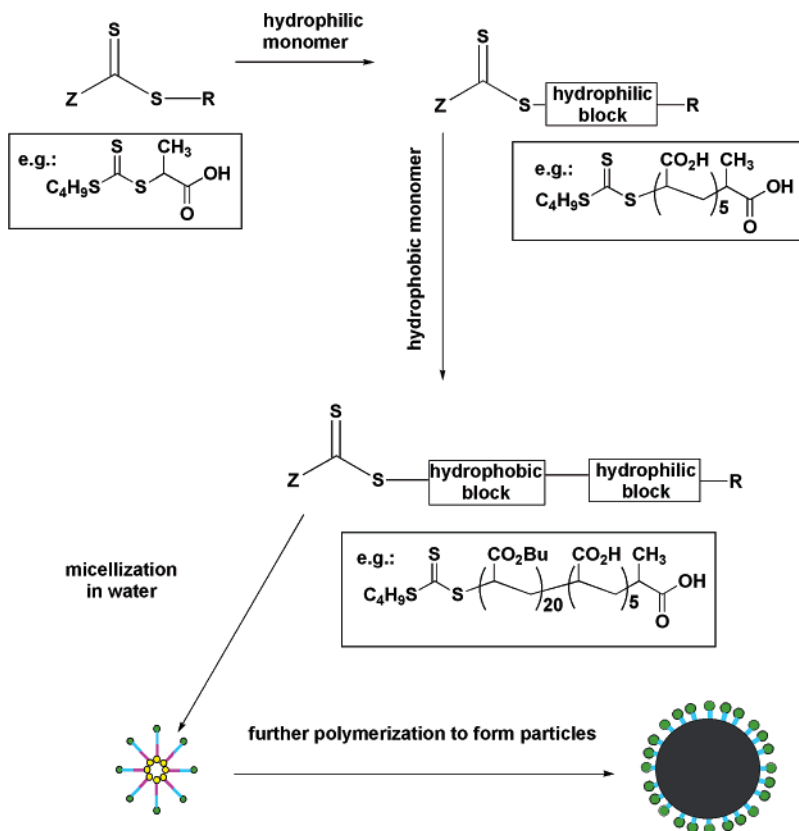


Figure 1. Process used to create particles.

If the diffusion of RAFT agent is slow on the time scale of particle formation and/or if there is significant RAFT agent in the monomer droplets while polymerization is occurring, then the previously reported problems will occur for the reasons suggested by Prescott et al.^{9,16}

The novel technique used in the present work ensures that the RAFT agent will be located exclusively in the particles as they form and, thus, that the entire polymerization will be under RAFT control. The fundamental idea is that the polymerization process is such that (a) all species formed from the RAFT agent are surface active and therefore able to self-assemble into micellar structures and (b) no other species capable of stabilizing particles are present. Propagation will occur to a point where chains are too hydrophobic to desorb from micelles, and particles will thus be created. As the chains in this newly formed particle grow and the size increases, other diblocks may absorb onto the newly created surface and in turn propagate to a point where they are also not able to desorb from the surface. The sequence of events then becomes similar to that which occurs when particles are nucleated from micelles in a conventional emulsion polymerization, with the obvious distinction that the surfactant molecules in this case are increasing in size and overall hydrophobicity. For this mechanism to operate, the growing RAFT agent must be able to self-assemble to form micelles in water, preferably with the active RAFT end located in the micelle interior to facilitate polymerization of hydrophobic monomer to yield particles. This model is more general than that put forward in our preliminary communication,²¹ where it was suggested that it was necessary to have the formation of rigid micelles from the diblocks.

One way to carry out the process described above is to use the RAFT agent to create amphipathic diblocks

that will self-assemble into micelles. This can be done by the sequential polymerization of first a hydrophilic and then a hydrophobic monomer in the presence of the RAFT agent. Thus, a hydrophilic monomer such as acrylic acid can be polymerized in the presence of a RAFT agent to yield a macro-RAFT agent containing a small number of hydrophilic groups (typically five in this work). Further polymerization with a hydrophobic monomer yields a diblock macro-RAFT agent that is capable of forming micelles. Subsequent polymerization will cause the diblock polymer to grow, and the micelles then evolve into latex particles, which will continue to grow under RAFT control. This process is illustrated in Figure 1.

When diblock structures are formed using RAFT-controlled polymerization, the original RAFT functionality is largely retained at the end of the chain. While any RAFT agent will suffice for the process of self-assembly by hydrophilic/hydrophobic growth, it is more useful to start with a RAFT agent that is amphipathic, specifically where one end is hydrophobic and the other is hydrophilic. This presents the opportunity of forming the amphipathic macro-RAFT agents by polymerizing appropriate monomers, either in separate synthetic steps or in situ. If they are surface active, these diblock polymers are able to self-assemble to form micelles in water. Creating the diblock polymer in situ provides a method that ensures the polymer is able to form micellar structures. The strategy of using an amphipathic RAFT agent ensures that each end of a diblock polymer chain will have character similar to that of the adjacent monomer unit. Having a hydrophilic R group reduces the likelihood of stabilizing chain ends associating strongly with other R groups or the latex particle surface to give rise to reduced stabilizer efficiency and high latex viscosity or colloidal instability through bridging flocc-

culution. A hydrophobic Z group will ensure that the RAFT process will occur in the particle interior rather than at the surface (although the latter might be desirable in some instances).

By this approach being employed, the problem of RAFT transport across the aqueous phase is avoided. The RAFT agent remains soluble in the aqueous phase until sufficient hydrophobic monomer has been added to make it nonlabile, at which point the RAFT agent will be located exclusively in the proto-particles. Gailard et al.²³ also used RAFT to synthesize AA/BA diblocks of varying sizes and then cleaved the RAFT end. They found that these diblocks behave as conventional surfactants in emulsion polymerization. This supports the basic ideas behind the protocols developed in the present paper.

It is important to avoid the presence of monomer droplets,^{9,16} at least up to the point where the RAFT agents have propagated with sufficient hydrophobic monomer to become locked into the particles since otherwise the macro-RAFT agents can migrate to the droplet surface and stabilize the monomer/droplet/water interface. In a conventional emulsion polymerization, labile surfactant can desorb from droplets as monomer is transported to the growing particles, thereby allowing the droplets to shrink. However, if one simply added the RAFT agent to a conventional emulsion polymerization with monomer droplets present, growth of the chain would then immobilize the macro-RAFT agent on the droplet surface and reduce monomer loss from the droplets, thereby giving rise to droplet nucleation.¹⁶ Having polymerization occurring in the droplets is undesirable, as the relative concentrations of RAFT agent and monomer will be different from what they are in the particles, thereby giving rise to a broader molecular weight distribution, as well as creating particles which are of a different size to those created from micelles and which are prone to coalescence.

This approach has many potential benefits. The most obvious is controlling polymer molecular weight and microstructure in a way not hitherto available in emulsion polymerization. This is a result of the particles all having RAFT agent present and attached to essentially all the chains from the time they were created. Another benefit is that the particles can be formed in the absence of free surfactant, as colloidal stability will be afforded by the hydrophilic chain ends located on the particle surface (either a species which can be charged, such as acrylic acid, or uncharged, such as acrylamide, or any combination of ionizable and nonionizable monomers), which cannot subsequently desorb from the particle. The absence of free surfactant is desirable in many technical applications. The method by which the particles are created also provides the opportunity to functionalize the particle surface (by beginning with a functionalized RAFT agent or adding functional monomer with the hydrophilic monomer) and control particle morphology (by changing the feed composition after the particles have formed).

Selection of Reaction Conditions

The basic procedure described could be carried out in a multitude of ways. In this work, it was considered important to have a system that was as simple as possible and also able to be easily characterized. As described above, it was desired to utilize a RAFT agent with a hydrophobic Z group and a hydrophilic R group.

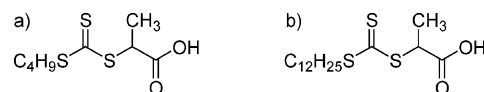


Figure 2. Structures of RAFT agents, 2-[(butylsulfanyl)carbonothioyl]sulfanylpropanoic acid, (a), and 2-[(dodecylsulfanyl)carbonothioyl]sulfanylpropanoic acid, (b).

The structures of the chosen RAFT agents, which are trithiocarbonates and where the R group is propanoic acid, are shown in Figure 2: 2-[(butylsulfanyl)carbonothioyl]sulfanylpropanoic acid (a) and 2-[(dodecylsulfanyl)carbonothioyl]sulfanylpropanoic acid (b). The carboxylic acid group was chosen to be similar to acrylic acid, which will be polymerized as the hydrophilic block. The R group yields a secondary radical on cleavage from the RAFT agent, which is sufficiently stable to allow both the cleavage process and monomer addition to occur under the reaction conditions chosen. This trithiocarbonate class of RAFT agents has a low susceptibility to hydrolysis in the pH range used here (although hydrolysis can occur under more alkaline conditions²⁴). This low susceptibility to hydrolysis, which we confirmed by UV-visible spectroscopic analysis of a water solution of the RAFT agent, contrasts to the higher susceptibility of the commoner dithioester RAFT agents.^{25–29}

Acrylic acid was chosen as a convenient monomer to make the hydrophilic block, as it polymerizes well under the control of the chosen RAFT agent, and short anchored blocks are able to stabilize latex particles when the acid groups are neutralized. Butyl acrylate was chosen as a convenient second-stage monomer due to its high propagation rate coefficient^{30,31} and favorable reaction kinetics with the RAFT agent and acrylic acid. This ensures that the polymerization will proceed at a reasonable rate.

The process could be sub-optimal during the aqueous polymerization step as a result of the monomer concentration being very low (due to the low water solubility of most monomers used in emulsion polymerization). This leads to a reduced rate of propagation in relation to termination, which will result in some terminated aqueous diblock species. While radicals would propagate mainly in micelles once they formed, aqueous-phase termination might still occur to some extent in the very early stages of the process, when there is some lability of chains (as inferred in a later section), leading to some transfer of radical activity between micelles. Any new chains that are initiated in the aqueous phase without a RAFT agent will still have a carboxylic group from the initiator, but this will be less effective in stabilizing the particles than the acrylic acid block, as well as producing chains that are free to desorb from the particles. Thus, it is important to optimize polymerization during this period to ensure that as many chains as possible have both the targeted acrylic acid block on the end and RAFT functionality.

To optimize the yield of the desired product and have an easily characterizable system, it was decided to preform the acrylic acid-containing macro-RAFT agent in concentrated aqueous solution. The initiator chosen for this purpose was 4,4'-azobis(4-cyanopentanoic acid) (V-501), as it is water-soluble and carries an acid functionality similar to the R group from the RAFT agent. An additional benefit is that this initiator does not contain a peroxide group, a class of compound that is thought to be responsible for oxidation of some RAFT agents.¹

The second stage involves the formation of diblock in water. Diblocks containing both hydrophobic and hydrophilic groups will form micelles as they become surface active. The strategy for formation of the hydrophobic part of the diblock is not straightforward, on account of the low water solubility of butyl acrylate. The proposed mechanism calls for all the chains to grow to a length where they are able to self-assemble as micelles, which will then swell with monomer, which in turn will give rise to an acceleration of the polymerization rate (the monomer concentration at the locus of polymerization increases dramatically at this stage).

There are many strategies for optimization of this second step. For example, the use of a more water-soluble monomer (e.g., methyl acrylate) would speed up this process. Counterbalancing this is the requirement that diblocks are able to come to a pseudo-equilibrium distribution (see eq 1) before further polymerization begins to lock them into particles. In another strategy, the number of aqueous propagation steps required could be reduced by beginning the diblock formation in an organic solvent. While this will have the desired effect of reducing the time taken to form micelles, the downside is that some organic solvent will still be present in the latex synthesis, which may be undesirable if not removed.

The other consideration for achieving RAFT-controlled emulsion polymerization by the present mechanism is to avoid the presence of monomer droplets, especially at early times in the reaction. To this end, the reactions were run under a controlled feed of monomer, with a feed profile chosen using conversion-time data from monomer-flooded experiments, i.e., experiments where excess monomer was always present. Monomer concentration needs to be kept as high as possible (while avoiding the presence of droplets) so as to maximize propagation in relation to chain-stopping events. Once all the particles have formed (and thus the RAFT agents are all locked into the particles), the presence of monomer droplets should not present a problem, and the monomer-saturated conditions in the particles will maintain the polymerization rate at a high value.

The acid groups on the initiator and macro-RAFT agent need to be at least partially neutralized in order for the RAFT agent and initiator to dissolve in water. This was accomplished by adding sufficient NaOH to bring the total added molar concentration (which includes that added during the macro-RAFT agent synthesis) to the same as that of the added acrylic acid. This ensures that there is some buffering action from the carboxylic acid species. This degree of neutralization leads to a measured pH of around 6 for latex preparation. Maintaining an acidic pH was considered important to minimize hydrolysis of the RAFT agent, as has been observed by a number of authors.^{28,29} The ionization of the acid groups ensures that the acid groups are able to provide electrostatic stabilization to the particles as they form.

Experimental Section

Reagents. Milli RO water was used in the synthesis of latexes and acrylic acid-containing RAFT agents. Acrylic acid (Sumika) and styrene (Synthetic Resins) were purified by distillation under reduced pressure. Butyl acrylate and methyl acrylate (Aldrich) had inhibitor removed by passing them through an inhibitor-removal column (Aldrich). Sodium hydroxide (NaOH) (Aldrich) and 4,4'-azobis(4-cyanopentanoic

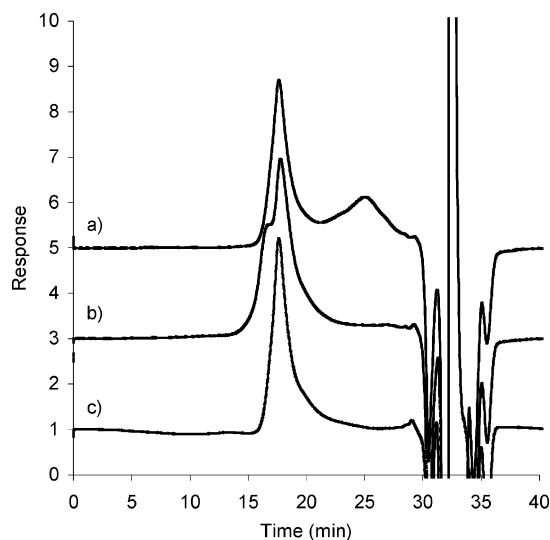


Figure 3. Raw GPC traces showing the effects of eluent and sample preparation: (a) latex sample dissolved directly and run in THF eluent, (b) dried latex sample dissolved in THF and run in THF/acetic acid, and (c) from procedure of dissolving latex directly and run in THF/acetic acid (the optimal procedure).

acid) (V-501) (Wako) were used as received. Dioxane (Aldrich) was distilled before use.

Electrospray Mass Spectrometer Analysis was carried out using a Finnigan Mat LCQ MS detector with Finnigan LCQ Data Processing and Instrument Control Software. Ten-microgram samples were dissolved in 10 mL of 50:50 methanol/H₂O and fed into the electrospray ionization unit at 0.2 mL min⁻¹. The electrospray voltage was 5 kV, the sheathing gas was nitrogen at 415 kPa, and the heated capillary was 200 °C.

GPC Analysis. Molecular weight distributions were determined using gel permeation chromatography (GPC). Analyses were carried out using a Shimadzu system fitted with a series of Waters columns (HR4, HR3, and HR2). Molecular weight was determined from refractive index data analyzed with Polymer Laboratories Cirrus software, with all molecular weights being relative to polystyrene standards and converted to poly(butyl acrylate) or poly(methyl acrylate) using "universal calibration"³² and the following Mark-Houwink parameters: ³³ styrene, $K = 11.4 \times 10^{-5} \text{ dL g}^{-1}$, $a = 0.716$; BA, $K = 12.2 \times 10^{-5} \text{ dL g}^{-1}$, $a = 0.70$; MA, $K = 26.1 \times 10^{-5} \text{ dL g}^{-1}$, $a = 0.659$.

Sample preparation for GPC analysis was an important aspect of this work. The presence of acrylic acid at the chain end was capable of producing artifacts in the chromatograms if precautions were not taken. It appears that acrylic acid on the chain ends can be responsible for two phenomena. (1) The first of these is that an irregular peak structure was often observed at longer elution times than that of the main polymer peak when the samples were analyzed using tetrahydrofuran (THF) as the eluent. Figure 3 shows the raw GPC traces with DRI detection for the same polymer sample run under different conditions. Trace (a) is typical of polymer samples that have been run with 100% THF as the eluent. An improved procedure was to mask carboxylic acid interactions³⁴ by adding 5% acetic acid to the eluent. (2) The other phenomenon is aggregation of polymer chains due to the low solubility of the acrylic acid chain ends in THF, which would also lead to a larger apparent molecular weight. This is assumed to be the reason it was very difficult to solubilize the polymer films in order to prepare GPC samples. This problem was overcome by adding a little water to the THF used to dissolve the dried polymer, or alternatively dissolving the latex directly into the eluent. If neither of these measures were taken, the GPC showed a peak at approximately 20 times the molecular weight of the main peak, as shown in trace (b) of Figure 3, which was assigned as an inverse-micelle structure forming in the THF.

Trace (c) illustrates the type of trace observed through the use of the adopted procedure of dissolving the latex directly in THF and using a 1:19 blend of acetic acid and THF as the eluent. It is noted that the use of this protocol was sometimes not completely effective in suppressing these artifacts.

Particle Size Analysis. Determination of particle size was carried out using CHDF (capillary hydrodynamic fractionation) with a Matec Applied Sciences CHDF 1100. It is noted that the calibration method for CHDF assumes that the latex has the same dependence of refractive index on size as do the standards used for calibration (polystyrene in this case). While this assumption is not always accurate, the particle size distributions will be semiquantitative (the refractive indices of bulk polystyrene, poly(butyl acrylate), and poly(methyl acrylate) being close in value³⁵), and the size polydispersities are likely to be quite reliable.

Preparation of RAFT Agents. Melting points were measured using a Perkin-Elmer Pyris 6 differential scanning calorimeter. Infrared spectra were determined using a Perkin-Elmer Spectrum One FTIR spectrometer. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Bruker DRX400 spectrometer as solutions in CDCl₃ using tetramethylsilane as an internal reference. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

2-[(Butylsulfanyl)carbonothioyl]sulfanylpropanoic acid (Figure 2a) was synthesized as follows. A 50% NaOH solution (32.00 g, containing 16.00 g, 400 mmol of NaOH) was added to a stirred mixture of butanethiol (36.00 g, 400 mmol) and water (60 mL). Acetone (20 mL) was then added, and the resulting clear, colorless solution was stirred for 0.5 h then cooled to near-room temperature and treated with carbon disulfide (27 mL, 34.2 g, 450 mmol) to give a clear orange solution. This was stirred for 0.5 h then cooled in an ice bath to an internal temperature of <10°. 2-Bromopropanoic acid (62.73 g, 410 mmol) was then added at such a rate that the temperature did not exceed 30° followed by 50% NaOH (32.80 g, 410 mmol), also added at such a rate that the temperature did not exceed 30°. When the exotherm had stopped, the ice bath was removed and water (60 mL) was added. The reaction was stirred at ambient temperature for 24 h then diluted with water (100 mL) and stirred and cooled in an ice bath while 10 M HCl (60 mL) was added at a rate which kept the temperature <10°. A yellow oil separated, and stirring of the mixture was continued at ice temperature until the oil solidified. The solid was collected by suction filtration, pressed and washed with cold water, and dried under reduced pressure to a state of semi-dryness. The lumps were crushed with a spatula; the now-granular solid was resuspended in fresh cold water and stirred for 15 min then refiltered. The residue was washed with cold water and air-dried to afford a powdery yellow solid, 84.98 g, which was recrystallized from hexane (180 mL) with gentle stirring to give bright yellow microcrystals (76.99 g, 81%), mp 53.5–54.5°. A small portion was recrystallized again from hexane to give mp 54.8–55.9°. IR (KBr): 2953, 2926, 2865, 2712, 2597, 1705, 1451, 1418, 1316, 1304, 1209, 1106, 1088, 1067, 1042, 910, 824, 648 cm⁻¹. ¹H NMR: δ (ppm) 10.6 (br, 1H, CO₂H), 4.87 (q, J = 7.4 Hz, 1H, SCH), 3.37 (t, J = 7.4 Hz, 2H, CH₂S), 1.69 (quint, J = 7.5 Hz, 2H, CH₂CH₂S), 1.63 (d, J = 7.4 Hz, 3H, SCHCH₃), 1.44 (sext, J = 7.5 Hz, 2H, CH₃CH₂CH₂), 0.94 (t, J = 7.4 Hz, 3H, CH₃CH₂). ¹³C NMR: δ (ppm) 221.8 (C=S), 177.3 (C=O), 47.5 (SCH), 37.2 (CH₂S), 30.0 (CH₂CH₂S), 22.1 (CH₃CH₂), 16.7 (SCHCH₃), 13.6 (CH₃CH₃). Anal. Calcd for C₈H₁₄O₂S₃: C, 40.31; H, 5.92; S, 40.35. Found: C, 40.60; H, 5.92; S, 40.18.

2-[(Dodecylsulfanyl)carbonothioyl]sulfanylpropanoic acid, Figure 2b, was synthesized by an analogous route. NaOH (0.50 g, 12.5 mmol) was dissolved with stirring and gentle heating in a mixture of dodecanethiol (3.0 mL, 2.5 g, 12.5 mmol), acetone (40 mL), water (5 mL), and tetrapropylammonium bromide (0.27 g, 0.10 mmol). The resulting solution was cooled in an ice bath and treated with carbon disulfide (0.75 mL, 0.95 g, 12.5 mmol). After 20 min, 2-bromopropanoic acid (1.13 mL, 1.91 g, 12.5 mmol) was added and the mixture was stirred at ambient temperature for 12 h. The solution was evaporated

to a quarter of the original volume and slowly acidified with 2 M hydrochloric acid (50 mL) then further diluted with water (150 mL). The precipitate was collected and recrystallized from ether/light petroleum to give the desired trithiocarbonate **2b** as fine yellow platelets (3.33 g, 76%), mp 77.5–78.4°. A second recrystallization (hexane) gave mp 77.8–78.8°. IR (KBr): 2955, 2919, 2851, 2711, 2596, 1706, 1464, 1450, 1420, 1318, 1298, 1209, 1097, 1069, 1042, 909, 824, 649 cm⁻¹. ¹H NMR: δ (ppm) 10.2 (br, 1H, CO₂H), 4.88 (q, J = 7.4 Hz, 1H, SCH), 3.36 (t, J = 7.4 Hz, 2H, CH₂S), 1.70 (quint, J = 7.5 Hz, 2H, CH₂CH₂S), 1.63 (d, J = 7.4 Hz, 3H, SCHCH₃), 1.40 (br quint, J = 7.5 Hz, 2H, CH₂CH₂CH₂S), 1.22–1.35 (br, 16H, CH₃(CH₂)₈), 0.88 (t, J = 7.4 Hz, 3H, CH₃CH₂). ¹³C NMR: δ (ppm) 221.8 (C=S), 177.2 (C=O), 47.5 (SCH), 37.5 (CH₂S), 32.0 (CH₃CH₂CH₂), 29.7 ($\times 2$), 29.6, 29.5, 29.4, 29.1, 28.9, 27.9 ((CH₂)₈CH₂S), 22.7 (CH₃CH₂), 16.7 (SCHCH₃), 14.1 (CH₃CH₂). Anal. Calcd for C₁₆H₃₀O₂S₃: C, 54.81; H, 8.62; S, 27.44. Found: C, 54.85; H, 8.76; S, 27.37.

Formation of Macro-RAFT Agent. The RAFT agents were reacted with acrylic acid in the presence of initiator to give a macro-RAFT agent expected to contain, on average, five acrylic acid units, as illustrated in Figure 1. A typical procedure to make a macro-RAFT agent from the RAFT agent having a butane thiol Z group (RAFT agent (a) in Figure 2) was as follows. 3.31 g (1.39 $\times 10^{-2}$ mol) of RAFT agent, 0.389 g (1.39 $\times 10^{-3}$ mol) of V-501, 5.0 g (6.94 $\times 10^{-2}$ mol) of acrylic acid, 0.555 g (1.39 $\times 10^{-2}$ mol) of NaOH, and 10.0 g of water were added to a round-bottom flask. This was capped with a rubber septum and swirled to dissolve the RAFT agent. The flask was deoxygenated by bubbling nitrogen through the solution. The flask was then immersed in an oil bath at 60 °C, and the polymerization allowed to proceed for 2 h. The resulting product was characterized by electrospray mass spectrometry. While electrospray MS does not give quantitative molecular weight distributions (as distinct from giving the precise molecular weight of each observed species), it is certainly semiquantitative, for example, in its indications of the relative abundances of tetramers, pentamers, and hexamers of the same species.

RAFT agent (b) with the dodecyl group was not soluble in water to the same degree as the butyl compound (a), even at the elevated pH used to dissolve the butyl RAFT agent. This necessitated that the creation of macro-RAFT agents from this species be carried out in an organic solvent to ensure solubility. The same molar quantities as given in the above recipe were used, but with dioxane used as the solvent instead of water.

The reaction proceeded in an acceptable fashion when the synthesis was attempted in water, as the RAFT agent became soluble as acrylic acid was polymerized. However, this method gave a slightly broader distribution of molecular weights, presumably because all chains do not begin polymerizing at the same time when some RAFT agent remains undissolved at the commencement of polymerization.

Emulsion Polymerization in the Presence of Macro-RAFT Agent A typical procedure is as follows on the basis of a butyl acrylate reaction (CF97.61 in Table 1). Macro-RAFT agent, V-501 initiator, NaOH, and water were added to a round-bottom flask which was then sealed with a rubber septum. The solution was swirled to disperse the macro-RAFT agent and then deoxygenated with a stream of bubbled nitrogen. The flask was immersed in an oil bath at 60 °C, and monomer addition was begun. An initial shot of 0.1 g was added, and then a feed of 1.0 g per hour was started. After 2 h, the monomer feed rate was increased to 6.0 g per hour for a further 3 h. The addition profile for this feed was formulated from experiments run with all the monomer added at the start of the reaction. The feed was tailored to keep the monomer concentration below that which would saturate the aqueous phase. A further hour was allowed after the completion of monomer feed for the reaction to reach high conversion. Samples were withdrawn via syringe at regular intervals to determine conversion gravimetrically and to provide polymer for subsequent GPC and particle-size measurements. Recipes used in this work are given in Table 1.

Table 1. Recipes for RAFT Emulsion Polymerizations^a

reaction	CF97.61	CF97.49	CF97.69	CF97.65	DN94.29	CF97.52
feature	basic recipe	methyl acrylate monomer	reduced RAFT agent concentration	further reduced RAFT agent concentration	polystyrene core	dodecyl RAFT agent
RAFT agent used to create hydrophilic block	a	a	a	a	a	b
moles of raft agent/10 ⁻⁴ monomer	5.06	4.95	2.49	1.28	5.85	4.15
	butyl acrylate	methyl acrylate	butyl acrylate	butyl acrylate	butyl acrylate/styrene	butyl acrylate
weight (g)	20.0	20.0	20.0	20.0	10.0/10.0	20.0
feed 1 weight (g)/duration (min)	2/120	2/60	2/120	2/120	ba 2/120	2/120
feed 2 weight (g)/duration (min)	18/180	15/120	18/180	18/180	ba 8/80 st 10/1	18/180
V-501 (g)	0.0730	0.0728	0.0736	0.0745	0.0806	0.0729
NaOH (g)	0.1033 ^b	0.1047 ^b	0.0544 ^b	0.0280 ^b	0.1171 ^b	0.1100
water (g)	80.3	80.7	80.1	80.3	80.2	80.5

^a Butyl RAFT agent was employed for all reactions except CF97.52. ^b Includes NaOH from macro-RAFT agent synthesis.

A round-bottom flask was used with a magnetic stirrer bar for agitation; the system did not need high shear because there was no need to emulsify monomer droplets that are normally present in conventional emulsion polymerizations. Mixing only needed to be sufficient to disperse the added monomer through the system, to keep the system homogeneous, and to maintain temperature control. Care needed to be taken to ensure that the stirring was sufficient to keep monomer from pooling on the top of the reaction, as the amount of surface-active species present in the reaction is very low once the particles have formed, thereby making monomer transport into the particles more difficult.

It is noted that the final particle size of the latex is sensitive to variations to the experimental procedures described above. This is an area of active investigation.

Results and Discussion

Preparation of Acrylic Acid Block. A trithiocarbonate RAFT agent with a butylsulfanyl Z group (Figure 2a) was used to prepare a macro-RAFT comprising, on average, five acrylic acid units in aqueous solution, as described earlier. The required ratio of RAFT agent to monomer was calculated using

$$\text{degree of polymerization} = \frac{\text{moles of monomer}}{n_{\text{RAFT}}} \quad (2)$$

where the degree of polymerization is the number of monomer units per macro-RAFT agent and n_{RAFT} is the number of moles of RAFT agent.

Electrospray mass spectroscopy was carried out on the product, with results shown in Figure 4. It can be seen that the resulting product was quite pure with a relatively narrow distribution of molecular weights. The main distribution corresponds to the expected RAFT agent molecular weight (238.12) with n acrylic acid units (of molecular weight 72.02). This provides good evidence that the vast majority of chains have ends that are derived from the original trithiocarbonate RAFT agent (Figure 2). This means that the chains are able to act as macro-RAFT agents and to be extended through further polymerization. The low level of products other than the intended ones should be noted. Such products would include chains with an initiator fragment on the end, as well as termination and hydrolysis products. The presence of these species would be undesirable in terms of the stated aim of this work.

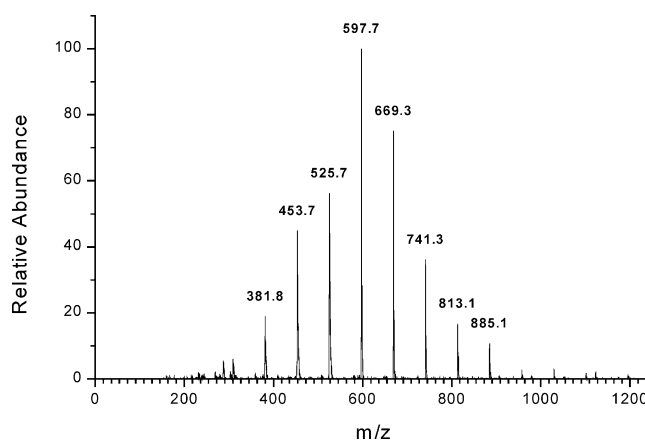


Figure 4. Electrospray mass spectrum of macro-RAFT agent designed to contain five acrylic acid groups.

A macro-RAFT agent was created in the same manner from the dodecyl trithiocarbonate RAFT agent (Figure 2b) with dioxane as solvent instead of water. Electrospray analysis of this macro-RAFT agent showed that the desired product had also formed, with a narrow molecular weight distribution. Having dioxane in the macro-RAFT agent solution is not ideal, as this material is not easy to remove, and the resulting dried macro-RAFT agent is not easy to disperse in water. If the macro-RAFT agent is used with the solvent still present in latex synthesis, then the dioxane will necessarily still be present at the completion of latex synthesis. While undesirable, the dioxane is only a minor component of the final latex.

Second-Stage Polymerization of Butyl Acrylate. The macro-RAFT agents could be used to synthesize a latex using the method discussed earlier. The primary criteria used to determine whether an emulsion polymerization under RAFT control was successful were colloidal stability and a narrow molecular weight distribution, which increased linearly with conversion and had a number-average molecular weight predicted from eq 2.

The amount of coagulum observed was normally very small and was always confined to the bottom of the magnetic stirrer bar used to stir the reaction. A colored layer was never observed in these reactions, and the reaction mixture remained homogeneous throughout the course of the reaction.

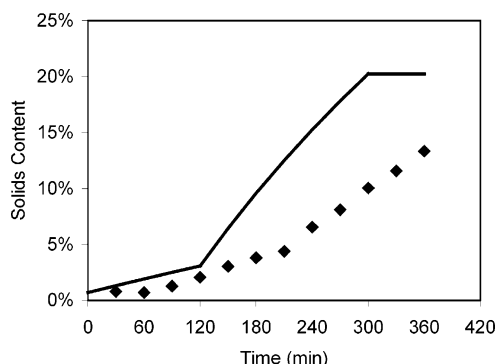


Figure 5. Conversion (measured gravimetrically) for CF97.61 as a function of time (points) with maximum possible conversion based on amount of monomer fed into the system (line).

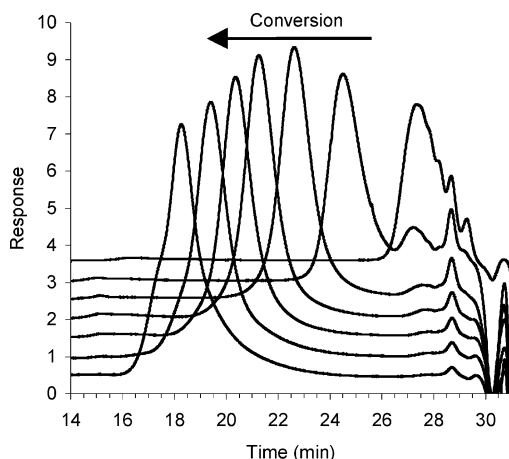


Figure 6. Unprocessed GPC chromatograms at different conversions, from CF97.61. The traces correspond to the starting macro-RAFT agent and samples taken at 90, 150, 210, 240, 300, and 360 min.

In a dispersed system such as those under consideration here, the RAFT agents may not be distributed evenly among the particles. Departure from this condition will increase the polydispersity of the molecular weight distribution. An increase in polydispersity was evident where the presence of droplets was noted at early stages in monomer-flooded reactions.

A typical conversion/time plot is shown in Figure 5 for a controlled-feed butyl acrylate polymerization in the presence of macro-RAFT agent. The solids content was determined gravimetrically. The maximum possible solids content is that which would result if all monomer added to that point had polymerized. The rate of polymerization after 2 h (when the feed rate was increased) is lower than might be expected for a BA polymerization. A possible explanation for this retardation is that put forward by Prescott et al.^{36–38} the dominant radical-loss event at these relatively low degrees of polymerization (which was 46 monomer units at 2 h) is termination between two relatively short radicals, which is faster than the short–long termination which predominates in conventional (non-RAFT) systems.

GPC analysis was carried out on the samples taken during the polymerization. The unprocessed chromatograms are shown in Figure 6 (it is felt to be important to include such raw data in discussing controlled radical polymerization, so that any baseline artifacts induced by subsequent data processing can be critically evaluated). It can be seen that the polymer is increasing in

molecular weight with time and that the distributions are all narrow.

The initial trace corresponds to the starting macro-RAFT agent. There appears to be a small amount of material in the second trace that has the same elution time (~ 27.5 min) as the starting macro-RAFT agent. This peak could correspond to macro-RAFT agent that has not undergone a significant number of propagation reactions or chains that have been terminated. The most likely explanation is deactivation of macro-RAFT agent by hydrolysis or other reactions in the aqueous phase. The high transfer constant of the RAFT agent in this system should ensure radical activity is shared among all chains, thereby preventing a population of chains that do not propagate.

There is some evidence for a high-molecular-weight shoulder on traces at later times in the polymerization. This is possibly due to grafting reactions and will be discussed further. Nevertheless, the GPC traces provide strong evidence that the great majority of polymer is formed under RAFT control and that all particles contain RAFT agent (i.e., no particles have formed via homogeneous nucleation).

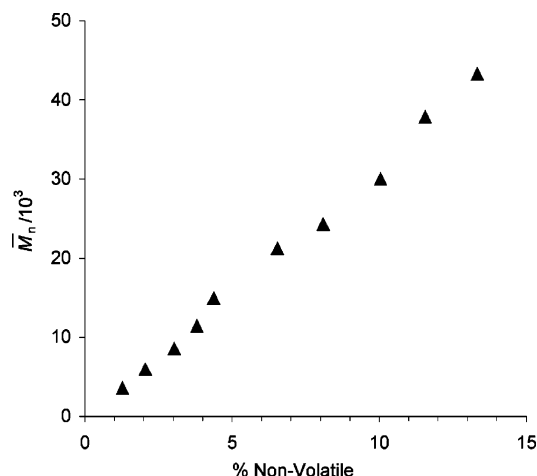
Table 2 gives the data from the GPC characterization of the same experiment, CF97.61. Here, the molar-mass polydispersity index ($PDI = \bar{M}_w/\bar{M}_n$) is not as low as might be expected in a similar bulk or solution experiment; however, the PDI has only risen to 1.5 at the end of the experiment (in this case, 67% monomer conversion). The relatively large PDI values could be explained by a combination of the following factors: that termination was playing a larger role than is desired, that grafting was occurring to a significant extent (the abstraction reaction leading to grafting has a fairly high rate coefficient for butyl acrylate), or that there was a variation between particles in the monomer to RAFT ratios. The initiator concentration could be reduced to lower the rate of termination in an attempt to obtain better RAFT control. Grafting reactions will increase the polydispersity of the formed polymer; this effect will be greatest at later times in the reaction where the grafting chains will be longer and the accumulated effects of grafting will be more apparent. There is some evidence for this hypothesis in the raw GPC chromatograms, which show high-molecular-weight shoulders for samples taken at later times in the reaction. The long feed of monomer will reduce the propagation rate over an extended period, with the effects of this being most pronounced at longer times. An additional factor is the reduction in monomer concentration as the reaction goes to completion at the end of the monomer feed, leading to an increased probability of termination and grafting reactions in relation to propagation.

The \bar{M}_n data obtained from GPC are about twice the expected values calculated using eq 2 and the measured conversion. However, such a comparison is not straightforward due to the experimental \bar{M}_n values not being absolute because of the use of universal calibration. The use of universal calibration with polystyrene/poly(BA) Mark–Houwink parameters is of questionable validity because of the presence of poly(acrylic acid) groups at the chain end. Moreover, the Mark–Houwink parameters of butyl acrylate vary with the amount of short- and long-chain branching, and therefore, strictly speaking, the Mark–Houwink parameters should be obtained using polymer prepared under the same conditions as the sample.³⁹ The acrylic acid groups may further

Table 2. Characterization of Samples from CF97.61 at Different Reaction Times; d_w and d_n Denote the Number- and Weight-Average Diameters^a

time (min)	% nonvolatile	calculated molecular weight	measured molecular weight		particle diameter	
		$\bar{M}_n/10^3$	$\bar{M}_n/10^3$	PDI = \bar{M}_w/\bar{M}_n	d_n (nm)	PDI = d_w/d_n
90	1.27	1.97	3.57	1.09		
120	2.05	2.98	5.92	1.09		
150	3.03	4.94	8.51	1.11	45.0	1.12
180	3.80	6.51	11.4	1.13	43.1	1.14
210	4.38	7.81	14.8	1.14	45.3	1.22
240	6.54	12.2	21.2	1.18	50.6	1.10
270	8.10	15.7	24.3	1.27	54.2	1.10
300	10.04	19.6	29.9	1.28	56.9	1.10
360	11.56	22.6	37.8	1.36	59.8	1.10
420	13.33	26.1	43.2	1.50	60.3	1.11

^a Molecular weights relative to polystyrene standards with universal calibration to convert to BA molecular weight. Sizes at 90 and 120 min were not able to be measured, as they fell outside the CHDF calibration range.

**Figure 7.** \bar{M}_n (relative to polystyrene standards with universal calibration to convert to BA molecular weight) as a function of the nonvolatile content for CF97.61.

complicate the issue through interactions with the column and themselves, although these interactions should largely be screened by the acetic acid in the eluent. Deactivation of RAFT agents at early times through deleterious side reactions in the aqueous phase would give rise to a higher molecular weight than expected while still yielding a linear increase in \bar{M}_n with monomer conversion at later times in the reaction.

At this stage, we have not been able to obtain absolute molecular weights for these polymers. The variation with nonvolatile content of the \bar{M}_n values inferred from universal calibration is shown in Figure 7. From eq 2, this plot is expected to be linear, as is indeed seen to an acceptable approximation. However, it is emphasized that the \bar{M}_n values are not absolute, and so no firm conclusion can be drawn from this linearity.

Particle-size analysis was carried out on samples taken through the course of this reaction, as shown in Table 2. It can be seen that the particle size is quite small. The size data are converted to N_p , the particle number concentration per unit volume of the water phase, using

$$N_p = \frac{\text{total mass polymer}}{\frac{4}{3}\pi(\bar{r}_w)^3 d_p} \quad (3)$$

where \bar{r}_w is the weight-average (unswollen) particle radius and d_p the density of polymer. The final particle

size corresponds to $N_p = 1.1 \times 10^{18} \text{ L}^{-1}$ (calculated using the density of poly(butyl acrylate) at 50 °C of 1.026 g cm⁻³). Dividing the RAFT agent concentration by the particle concentration gives ~2700 RAFT agents per particle. This is much larger than a typical surfactant aggregation number and shows the inapplicability of the original supposition²¹ that rigid micelles were formed and that all such micelles became particles. This number is in agreement with the hypothesis that diblocks are able to migrate to the surface of those micelles where polymerization is occurring from those micelles where polymerization has not yet taken place; it is also possible that some coagulation occurs at early times in the reaction. Coagulation at later times can be ruled out because the particle-size distribution is very narrow and because the increase in particle size throughout the reaction is also consistent with growth of the initial crop of particles rather than significant coagulation later in the reaction.

Chain Dimensions. It might be supposed at first that all the polymer chains in these systems are derived from the initial RAFT-controlled poly(AA)/poly(BA) block copolymers that formed the initial micelles. If this were the case, most of the polymer chains would be anchored to the surface of the particles by their poly-(AA) block (except possibly for the relatively small number of chains where the poly(AA) block only comprises one or two monomer units). This can be explored by considering what impact this would have on the chain conformation of the hydrophobic poly(BA) part of the chain.

The dimensions of a single chain in these systems is readily found from the well-known formulas (e.g., ref 40) for the radius of gyration or root-mean-square end-to-end distance, given the degree of polymerization and the characteristic ratio of the polymer. Although the characteristic ratio for butyl acrylate does not seem to be reported in the literature, values for similar acrylates in a range of solvents lie between 7 and 8.^{35,41,42}

Ignoring any effect of the hydrophilic component, the unperturbed dimension of the chains in runs such as CF97.61 is calculated to be ~9 nm at the highest conversion to which this run was taken (assuming an characteristic ratio of 7.5). This is much less than the particle size (diameter ~60 nm). If the chain were tethered to the interface, this would increase the unperturbed dimension because of the additional geometric constraint, but for chains of degree of polymerization typical of CF97.61, this increase is probably

~30%.⁴³ If all the chains were to occupy their unperturbed dimensions (say, 12 nm in size, this being ~30% more than the unperturbed dimensions of 9 nm) tethered to the surface of a particle of 60 nm diameter, they would not extend to the center of the particle. Obviously, there cannot be a hole in the middle of the particles to make up this apparent shortfall. There are various possibilities.

(a) Some chains are stretched from their average random-coil conformation. However, the stretching needed to make up the "gap" requires a high free energy and so would be possible only for a negligible fraction of the chains.

(b) A significant fraction of the chains might have both ends buried within the particle and could thus be located in the center of the particle while retaining their equilibrium conformation. Most chains would be expected to have around six carboxylic acid groups on one end (one from the RAFT agent R group and five from the polymerized acrylic acid). It would be expected that these acid groups would be preferentially located at the particle/water interface; however, some burial of surfactant is well accepted with electrostatically and polymerically stabilized latexes.^{44–46} There would be a fraction of chains with less than six carboxylic acid groups, and therefore these chains would have less affinity for the particle surface. The reduced number of acid groups might come from three sources, as follows.

(1) The electrospray data (although not quantitative for the relative number of chains) suggest that a small but significant fraction of the chains have fewer than five poly(AA) units attached; burial of chains with one or two poly(AA) units is physically reasonable.

(2) Transfer to monomer results in a new monomeric radical which will subsequently propagate. While the new chain so formed will be under RAFT control, the resulting chain will not have a terminal poly(AA) moiety and thus will not have any driving force to be tethered at the particle/water interface. Since the rate of transfer to monomer should be unaffected by the presence of a RAFT agent, the amount of transfer can be estimated from k_p/k_{tr} , the ratio of the propagation to transfer rate coefficients and the number of monomer units that have been polymerized within each particle. However, calculations for BA using the measured transfer constant⁴⁷ show that only about 1% of the polymer formed during the course of the reaction will be free polymer created as a result of transfer to monomer.

(3) Entry into the particles of initiator-derived radicals will create chains having only one carboxylic acid group. These chains will have an affinity for the surface of the particle that is relatively weak compared to that of a poly(AA) block and which would be relatively easily overcome as the growing chain became extended by the addition of hydrophobic monomer. Because of the high propagation rate coefficient of BA, it is reasonable to assume that entry efficiency is high in this system.⁴⁸ Calculations using the decomposition rate coefficient for V-501⁴⁹ show that ~13% of chains will have an end-group coming from the initiator. Since entry occurs over the life of the reaction, it is reasonable to expect entered chains, on average, to achieve about half the molecular weight of the bulk of the polymer in the particle. In the case in question, the entry events would therefore be expected to generate only 7% of the total polymer.

It is likely that a combination of these possibilities is responsible for determining the chain conformation. The

major conclusions are that the present methodology results in a significant, although small, fraction of chains which are not under RAFT control, and/or contain significantly less than the expected number of hydrophilic monomer units and hence have both ends buried within the particle.

Second-Stage Polymerization of Methyl Acrylate. The particle formation model outlined earlier is dependent on the growth of the acrylic acid-containing RAFT agent in the aqueous phase in order that the RAFT agent becomes surface active and forms micelles. This process will be hindered by a slow aqueous propagation rate, which will reduce the effectiveness of the RAFT process, resulting in more termination before the chains reach a length where they are surface active. This problem can be addressed through utilizing a hydrophobic monomer for which the product of the propagation rate coefficient and the water solubility is greater than for butyl acrylate; methyl acrylate was chosen here for this purpose. While choosing such a monomer, it must be borne in mind that the polymer formed must be insoluble in water or the required micelles will not form. Any reduction in the time needed to grow diblocks to a length to become insoluble in the aqueous phase will improve the living character of the latex.

Although no reliable measurements of the propagation rate coefficient of methyl acrylate are available, there are reliable values for butyl acrylate.^{30,31} Basic chemical dynamics theory,⁵⁰ as well as the observed similarity of Arrhenius parameters for propagation rate coefficients with methacrylates,⁵¹ suggests methyl acrylate has a similar k_p to that of butyl acrylate. The water solubility of methyl acrylate, 0.60 M at 20 °C,⁵² is considerably greater than that of butyl acrylate (0.013 M at 50 °C, determined in this laboratory by measuring the UV absorption at 260 nm with samples of increasing amounts of added monomer in water⁵³). This should allow creation of the micelles to proceed at a greater rate, despite the possibility that the chains would need to be longer before micelles would begin to form.

A methyl acrylate polymerization was carried out using the same macro-RAFT agent that had been employed for the butyl acrylate polymerization under similar conditions. The monomer feed profile was adjusted to take advantage of the greater water solubility of methyl acrylate. Specifically, the initial amount of methyl acrylate added was increased to 3.0 g, and a monomer feed over 3 h instead of 5 h as was employed for the CF97.61-type reaction. With the initiator concentration maintained at the same level as for CF97.61, the reduced reaction time will lead to fewer termination reactions. A latex was formed in the same manner as it had been for the previous example.

Results from GPC characterization of this latex are given in Table 3. It can be seen that the molar-mass polydispersity of the latex was higher through the course of the reaction than for CF97.61, with a final polydispersity of 2.61. The higher polydispersity may be related to the higher final conversion of this latex, with the effects of unwanted reactions such as grafting becoming more evident in the last part of the reaction. The ratios of measured to calculated molecular weights were also greater than the previous example. There are a number of feasible explanations for this observation. It is possible that the use of universal calibration is even more inappropriate for methyl acrylate than for butyl

Table 3. Characterization of CF97.49 (Methyl Acrylate as Hydrophobic Monomer)^a

time (min)	% nonvolatile	calculated $\bar{M}_n/10^3$	measured $\bar{M}_n/10^3$	PDI = \bar{M}_w/\bar{M}_n
30	0.97	1.30	28.09	1.04
60	4.92	7.89	32.46	1.27
90	8.03	13.6	47.29	1.36
120	12.14	21.7	57.55	1.50
150	15.31	28.5	69.86	1.67
180	18.57	36.0	72.78	1.79
210	19.88	38.5	71.78	1.84
240	20.08	38.9	80.48	2.61

^a Molecular weights relative to polystyrene standards with universal calibration to convert to BA molecular weight.

acrylate. The mass of second-stage monomer used in both experiments was the same, and thus the moles of methyl acrylate that needed to be added to achieve the same molecular weight is necessarily greater. All other things being equal, this will lead to a greater polydispersity. Comparison of the measured solids content with that which would be obtained if all monomer added to that point had polymerized reveals that the instantaneous conversion is higher through the course of this reaction than for CF97.61. However, despite these differences, the control of molecular weight is still evident.

The final number-average particle diameter for the methyl acrylate latex is larger than for the equivalent butyl acrylate latex, CF97.61: 68.1 nm compared to 60.3 nm. Calculating the particle number for the methyl acrylate from the size data (using eq 3 with the density of polymer calculated from group additivity,⁵⁴ 1.17 g cm⁻³) gave a value slightly less than for the corresponding butyl acrylate latex. This could be explained by the more water-soluble methyl acrylate increasing the time before the diblocks become water-insoluble. However, the difference is not large and is sensitive to uncertainties in the particle size. The similarity in particle numbers suggests that the particle-formation mechanism is similar in both cases, despite the large difference in water solubility between these two monomers.

Investigating Particle-Formation Mechanism. If the particle-formation mechanism operates in the manner described, then the final number concentration of particles that form should be related to the concentration of macro-RAFT agent for a given RAFT agent composition and (distribution of) acrylic acid block length. Particle number is determined from particle size using eq 3. For this purpose, it is necessary to have a large change in particle size so that the uncertainties can be reduced. With this in mind, it was decided to produce two latexes using half and one-quarter the concentration of macro-RAFT agent employed in CF97.61. The initiator concentration was retained at the same level as for the original experiment, and the concentration of added NaOH was chosen to be the same as the concentration of acrylic acid groups from the macro-RAFT agent. The latexes produced with reduced RAFT concentration were less stable to shear but presumably form in the same way as CF97.61.

Table 4 gives the effect that lowering the macro-RAFT agent concentration on particle number and particle diameter at the completion of the reactions, as measured by CHDF. As the RAFT agent concentration was reduced, the particle size increased and hence the particle number decreased.

Figure 8 shows the particle number as a function of conversion. The concentration of particles in each latex

Table 4. Size, Particle Concentration, and Number of RAFT Macromolecules Per Particle at the End of the Reaction

reaction	RAFT agent conc relative to CF97.61	final number- average particle diameter (nm)	particle conc (L ⁻¹)	final number of RAFT molecules per particle
CF97.61	1	60.3	1.13×10^{18}	2665
CF97.69	0.49	109	3.74×10^{17}	3990
CF97.65	0.25	187	4.83×10^{16}	15800

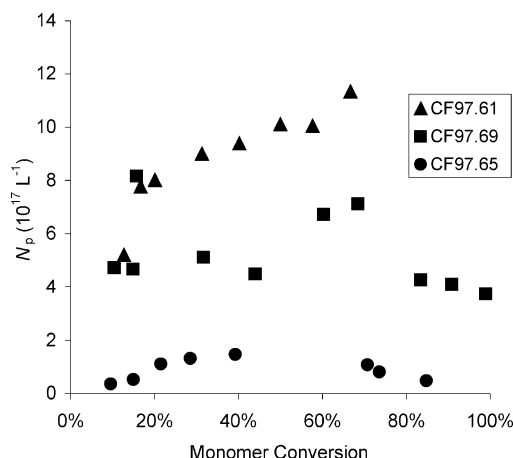


Figure 8. Particle concentration as a function of conversion for latexes made with reduced RAFT agent concentrations. Basic recipe CF97.61 (triangles), 0.5 times RAFT concentration CF97.69 (squares), and 0.25 times RAFT concentration CF97.65 (circles).

did not change significantly with conversion, within the uncertainty resulting from the particle-size measurement. This plot illustrates that particle formation was finished by the time the first measurements were made at around 10% monomer conversion. This monomer conversion corresponds to an average butyl acrylate chain degree of polymerization ~30 in the case of CF97.61 and ~120 in the case of CF97.65, at which point the chains would be expected to be insoluble in the aqueous phase. The slight decrease in particle number at higher conversion for the latexes with reduced RAFT concentration could be related to the tiny amount of coagulum observed in these reactions.

Table 4 shows that the decrease in RAFT concentration is also accompanied by an increase in the number of RAFT agents per particle. From this, the nominal area per stabilizing poly(AA) block was calculated under the assumption that all acrylic acid is located on the particle surface. Figure 9 shows the nominal area per RAFT agent as a function of conversion. The increase in nominal area per RAFT agent can be seen as a consequence of the particle size increasing after the RAFT agent becomes locked into the particles as the butyl acrylate chains extend to the point where they are no longer water-soluble. Now, as the calculations above imply, there are probably significant numbers of chains with both ends buried within the particle interior (at least for larger particles); hence, the calculated area per chain will be a lower bound to the actual value, at least at higher conversion. It can be seen that the nominal area per RAFT agent is similar in all cases at low conversion and the low-conversion limiting values are in the range for a typical ionic or polymeric surfactant, e.g., 0.43 nm² for sodium dodecyl sulfate⁵⁵ and up to 1.2 nm² for polyethylene oxide-based surfactants.⁵⁶ At low conversion, the radius of gyration of a chain is compa-

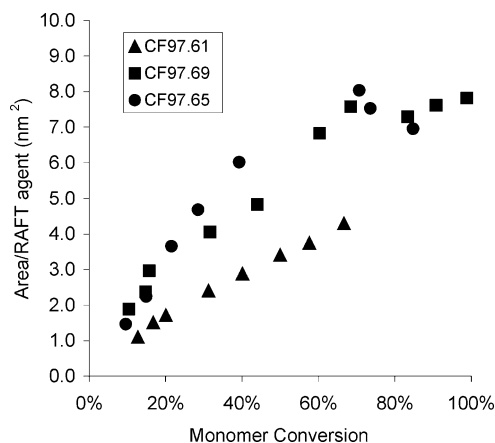


Figure 9. Nominal area per RAFT agent (calculated assuming all acrylic acid units are on the surface of the particle) as a function of conversion for latexes made with reduced RAFT agent concentrations. Basic recipe CF97.61 (triangles), 0.5 times RAFT concentration CF97.69 (open squares), and 0.25 times RAFT concentration (circles).

rable to particle size, and so it is likely that this low-conversion area is close to the actual area per RAFT chain. The foregoing is consistent with the supposed mechanism, although it does not preclude other possibilities.

Second-Stage Polymerization: Novel Core-Shell Particles. For the reasons outlined earlier, the polymerization of styrene in the aqueous phase was not thought to be optimal for the creation of diblocks. There are two straightforward options for creating a polystyrene latex using our RAFT method: to create a diblock macro-RAFT agent containing a styrene segment in organic solvent that would assemble into micelles when added to water or alternatively to begin with a more suitable hydrophobic monomer, such as butyl acrylate or methyl acrylate, to create the micelles. In the latter case, the monomer feed would then be switched to styrene and polymerization could continue in the particle interiors, which provide more favorable polymerization conditions (higher monomer concentration).

This type of feed profile also allows for the possibility of creating novel core-shell structures if the feed of initial monomer is continued for a longer period. Specifically, it should be possible to create core-shell latex particles where all chains are triblocks of the composition poly(hydrophilic monomer)-*b*-poly(hydrophobic monomer A)-*b*-poly(hydrophobic monomer B), where the hydrophilic component will provide the colloidal stabilization of the polymer colloid. One should therefore have a core-shell particle composed entirely of a *single type* of chain, as sketched in Figure 10. This is very different from conventional core-shell particles, also sketched in Figure 10, where the shell and core are composed of *different types* of chains.

This was investigated by employing a CF97.61-type reaction with the monomer feed changed from butyl acrylate to styrene part way through the reaction (quantities given in Table 1). Butyl acrylate (10 g) was added in a manner similar to the initial feed in CF97.61, and then 1 h was allowed for the reaction to go to high conversion (>99%). A 10 g shot of styrene was then added, and the temperature increased to 75 °C. The reaction was allowed to proceed for a further 90 min, at which point, the overall monomer conversion was 99%. The resulting latex was examined using transmis-

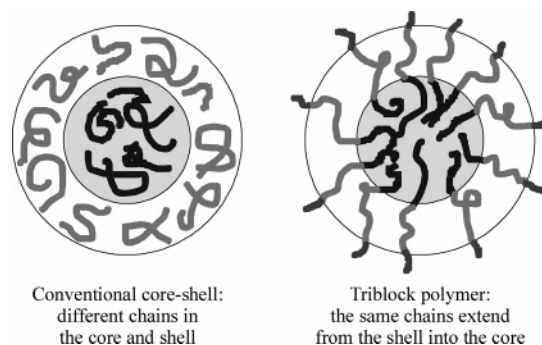


Figure 10. Schematic core-shell particles made with RAFT-based triblocks (present paper) and conventional core-shell particles.

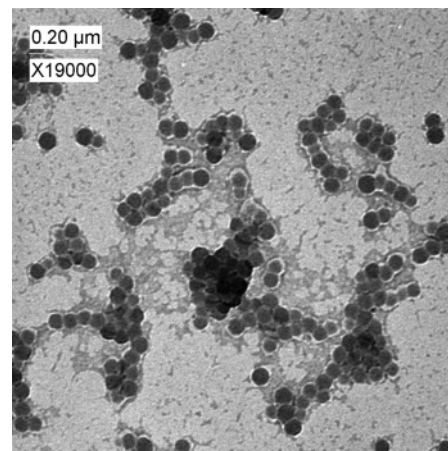


Figure 11. TEM of poly(acrylic acid)-*b*-poly(butyl acrylate)-*b*-polystyrene core-shell latex treated with ruthenium tetroxide to stain the polystyrene domains.

sion electron microscopy (TEM). The prepared grids were exposed to ruthenium tetroxide vapor to selectively stain the polystyrene domains to provide contrast with the poly(BA) domains.⁵⁷ A typical micrograph is shown in Figure 11. It can be seen that, as expected, the (darker) polystyrene is located in the particle interiors, with the softer poly(BA)/poly(AA) shells able to coalesce to some degree.

Confirmation that the system was indeed composed almost exclusively of triblocks was obtained from the raw GPC chromatograms, shown in Figure 12. The right trace is from the latex immediately prior to the styrene addition, while the left trace is from the latex at the completion of styrene polymerization. It can be seen that most of the original chains have been extended through the polymerization of styrene. This implies that the observed core-shell morphology is formed predominantly from chains that extend from the surface of the particles through the butyl acrylate shell and into the styrene core.

This observation also confirms the living character of the polymerization process.

The foregoing picture of chain conformation and morphology of these triblock systems must now be reconciled with the previous inference that, for larger particle sizes, not all the chains can have remained entirely under RAFT control with a pentameric AA block at the particle surface. It is seen from Figure 11 that a well-defined core-shell structure has formed. This structure is consistent with limited burial. Thus, the morphology suggested by Figure 10, with all poly-(acrylic acid) components at the particle water interface,

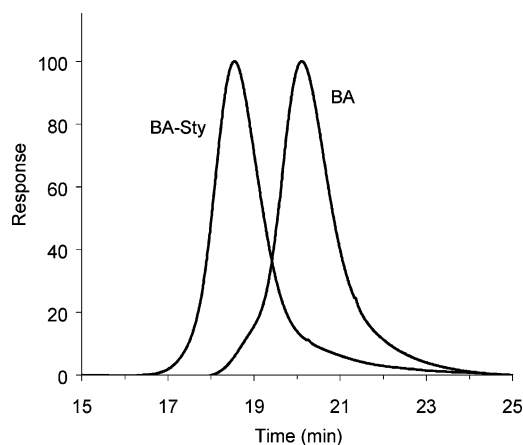


Figure 12. Raw GPC chromatograms of polymer from poly-(acrylic acid)-*b*-poly(butyl acrylate)-*b*-polystyrene core-shell latex before and after styrene feed. Right trace: latex immediately prior to styrene addition; left trace: latex at completion of styrene polymerization step.

is felt to be a good representation of the actual particle morphology.

Second-Stage Polymerization of Dodecyl RAFT Agent. It is possible that the amount of unwanted side reactions such as RAFT agent deactivation and termination at early times, while polymerization is occurring in the water phase, could be reduced by employing a macro-RAFT agent that has the ability to form micelles without any polymerization of hydrophobic monomer. This can be achieved through the use of diblock macro-RAFT agent, but another option is to employ a RAFT agent that has a large hydrophobic Z group. The dodecyl variant of the RAFT agent used in CF97.61 (Figure 2b) was employed to investigate this possibility. This RAFT agent is not soluble in water, so synthesis of the macro-RAFT agent containing acrylic acid was conducted in dioxane.

A latex was synthesized using this macro-RAFT agent in the same manner as before. The crucial difference is that the macro-RAFT agent, poly(acrylic acid)-C₁₂RAFT, is expected to be surface active, and likely to micellize without the need for further polymerization with a hydrophobic monomer.

Run CF97.52 gives the formulation for the emulsion polymerization with dodecyl macro-RAFT agent. GPC analysis was carried out to determine if the use of this RAFT agent had helped reduce the amount of termination or RAFT agent degradation at early times. It was apparent that termination and/or degradation had still occurred at early times, as a peak was still visible at the elution time of the starting material when the main peak had moved to smaller elution times. It would seem that the water solubility of the macro-RAFT agent is sufficiently high to allow aqueous-phase reactions to occur to a significant extent before particle formation occurs. The relationship between calculated and measured molecular weight was very similar to the butyl RAFT agent, CF97.61, as was the increase in polydispersity index toward the end of the reaction.

One important difference between this latex and CF97.61 is the final particle size. Measurement by CHDF gives a particle diameter of 49.9 nm and size polydispersity index of 1.09 for the final latex, which has 20% solid content but a very small amount of hydrophilic monomer. This is a very small and monodisperse latex, something that is often not easy to

achieve by conventional methods. It is significantly smaller than the final particle size for the analogous CF97.61 latex (which was 60.3 nm with 13% solid content). The smaller particle size corresponds to 830 RAFT agents per particle, considerably less than 2665 calculated for CF97.61. This reduction could be related to a reduced number of butyl acrylate units that need to be added to make the chains insoluble in water.

Conclusions

The work in this paper shows how polymerization under RAFT control can be implemented in an ab initio emulsion polymerization. The essence of the method is to use an amphipathic RAFT agent to produce an initial diblock with hydrophilic and hydrophobic components of degrees of polymerization chosen so that these can self-assemble into micelles. When polymerization is continued by feeding of the hydrophobic monomer, the chains cannot desorb from these micelles, and continued polymerization results in the formation of latex particles wherein all RAFT agent is contained within the particles and attached to the chains, assuming that at all times the monomer feed is such that droplets do not form. Polymerization can then be continued with any feed profile and monomer choice to maintain molecular weight control and good colloidal stability throughout the polymerization. In the early stages of the polymerization, there is aggregation of the micelles and/or migration of the diblocks, so that the number of RAFT-ended chains within a particle is much larger than the aggregation number at which the original micelles presumably self-assembled. At low conversion, the size of the particles is commensurate with the equilibrium dimensions of the component chains. At the latter stages of the polymerization, the size of the particles is greater than these equilibrium dimensions. At least at high conversion, this implies that a small but significant fraction of chains do not have the nominal pentameric acrylic acid units at the particle surface while the chain has grown under RAFT control throughout the whole course of the polymerization: for example, those chains with less than five AA units are buried within the particles.

The expected control over molecular weight and polydispersity is seen in all polymerizations without the reduction in colloidal stability or formation of an oily layer previously associated with ab initio emulsion polymerization in the presence of RAFT agents. This allows the traditional benefits of emulsion polymerization to be combined with those offered by RAFT-controlled polymerization.

While the foregoing requires that both the hydrophobic and hydrophilic monomers propagate quickly, variants can be used to polymerize virtually any conventional hydrophobic monomer. For example, a rapidly propagating hydrophobic monomer (e.g., butyl acrylate) can be used just for the particle formation step, which typically might result in a diblock containing (say) 5 acrylic acid and 20 butyl acrylate units. Once this stage is reached, effectively any monomer can be used that will polymerize in bulk or solution with the RAFT agent in question. Another method of working around any restriction concerning monomer selection at early times is to create a diblock in a suitable solvent then disperse the diblock in water. Care must be taken that the diblock is sufficiently soluble in water that an equilibrium distribution of micelles can form before the polymerization is begun.

There is also scope for varying the type of hydrophilic monomer and length of hydrophilic monomer blocks to influence the number of particles that form. This provides a method for tuning the system to obtain the desired combination of chain length and particle number. This methodology also provides a means of creating very small and monodisperse particles that can be used as seeds in further reactions. The ability to functionalize the particle surface further enhances the utility of this process.

The self-assembly micellization process explored in this paper enables one to synthesize polymer colloids wherein almost all colloidal stabilizer is anchored to the particle. While this can also be achieved using conventional electrosteric stabilizer methods (such as in an acrylic acid/styrene *ab initio* emulsion polymerization), the present methodology enables the stabilizing hairs to be of any desired length and essentially monodisperse in molecular weight. While polymerizable surfactants can also be used for the same general goal,⁵⁸ the RAFT process has certain advantages in synthesis and monomer choice. Moreover, once the particles have been formed, polymerization can be continued under RAFT control so that virtually any desired molecular architecture can be created. This wide adaptability is illustrated in the present paper through the synthesis of core-shell latex particles composed largely of poly-(acrylic acid)-*b*-poly(butyl acrylate)-*b*-polystyrene triblocks: a novel polymer colloid architecture wherein only a single type of polymer is present in the particle and each individual chain stretches from aqueous phase through the shell and to the core.

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References and Notes

- Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, G.; Moad, C. L.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559–5562.
- Rizzardo, E.; Chiefari, J.; Mayadunne, R. T. A.; Moad, G.; Thang, S. H. ACS Symposium Series 768; American Chemical Society: Washington, DC, 2000; pp 278–296.
- Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993–1001.
- Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, G.; Moad, C. L.; Thang, S. H. *Macromol. Symp.* **1999**, *143*, 291–307.
- Chong, Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071–2074.
- Barner-Kowollik, C.; Davis, T. P.; Heuts, J. P. A.; Stenzel, M. H.; Vana, P.; Whittaker, M. J. *Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 365–375.
- Moad, G.; Mayadunne, R. T. A.; Rizzardo, E.; Skidmore, M.; Thang, S. H. *Macromol. Symp.* **2003**, *192*, 1–12.
- Barner, L.; Barner-Kowollik, C.; Davis, T. P.; Stenzel, M. H. *Aust. J. Chem.* **2004**, *57*, 19–24.
- Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G. *Aust. J. Chem.* **2002**, *55*, 415–424.
- Monteiro, M. J.; de Barbeyrac, J. *Macromolecules* **2001**, *34*, 4146–4123.
- Uzulina, I.; Kanagasabapathy, S.; Claverie, J. *Macromol. Symp.* **2000**, *150*, 33–38.
- Monteiro, M. J.; Hodgson, M.; De Brouwer, H. J. *Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3864–3874.
- Monteiro, M. J.; Sjöberg, M.; Van der Vlist, J.; Gottgens, C. M. J. *Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4206–4217.
- Charmot, D.; Corpart, P.; Adam, H.; Zard, S. Z.; Biadatti, T.; Bouhadir, G. *Macromol. Symp.* **2000**, *150*, 23–32.
- Butté, A.; Storti, G.; Morbidelli, M. *Macromolecules* **2001**, *34*, 5855–5896.
- Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G. *Macromolecules* **2002**, *35*, 5417–5425.
- Butte, A.; Storti, G.; Morbidelli, M. *Macromolecules* **2000**, *33*, 3485–3487.
- Vosloo, J. J.; De Wet-Roos, D.; Tonge, M. P.; Sanderson, R. D. *Macromolecules* **2002**, *35*, 4894–4902.
- Lansalot, M.; Davis, T. P.; Heuts, J. P. A. *Macromolecules* **2002**, *35*, 7582–7591.
- Pham, B. T. T.; Nguyen, D.; Ferguson, C. J.; Hawket, B. S.; Serelis, A. K.; Such, C. H. *Macromolecules* **2003**, *36*, 8907–8909.
- Ferguson, C. J.; Hughes, R. J.; Pham, B. T. T.; Hawket, B. S.; Gilbert, R. G.; Serelis, A. K.; Such, C. H. *Macromolecules* **2002**, *35*, 9243–9245.
- Gilbert, R. G. *Emulsion Polymerization: A Mechanistic Approach*; Academic: London, 1995.
- Gaillard, N.; Guyot, A.; Claverie, J. J. *Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 684–698.
- Loiseau, J.; Doërr, N.; Suau, J. M.; Egraz, J. B.; Llauro, M. F.; Ladavière, C. *Macromolecules* **2003**, *36*, 3066–3077.
- Vasilieva, Y. A.; Thomas, D. B.; Scales, C. W.; McCormick, C. L. *Macromolecules* **2004**, *37*, 2728–2737.
- Bories-Azeau, X.; Armes, S. P.; Van den Haak, H. J. W. *Macromolecules* **2004**, *37*, 2348–2352.
- Thomas, D. B.; Convertine, A. J.; Hester, R. D.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2004**, *37*, 1735–1741.
- Baussard, J.-F.; Habib-Jiwan, J.-L.; Laschewsky, A.; Mertoglu, M.; Storsberg, J. *Polymer* **2004**, *45*, 3615–3626.
- McCormick, C. L.; Lowe, A. B. *Acc. Chem. Res.* **2004**, *37*, 312–325.
- Lyons, R. A.; Hutovic, J.; Piton, M. C.; Christie, D. I.; Clay, P. A.; Manders, B. G.; Kable, S. H.; Gilbert, R. G. *Macromolecules* **1996**, *29*, 1918–1927.
- Asua, J. M.; Beuermann, S.; Buback, M.; Charleux, B.; Gilbert, R. G.; Hutchinson, R. A.; Leiza, J. R.; N.Nikitin, A.; Vairon, J.-P.; Herk, A. M. v. *Macromol. Chem. Phys.* **2004**, *205*, 2151–2160.
- Mori, S.; Barth, H. G. *Size Exclusion Chromatography*; Springer: Berlin, 1999.
- Hutchinson, R. A.; Paquet, D. A.; McMinn, J. H.; Beuermann, S.; Fuller, R. E.; Jackson, C. *DEHEMA Monographs* **1995**, *131*, 467.
- Barner-Kowollik, C.; Heuts, J. P. A.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 656–664.
- Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; John Wiley and Sons: New York, 1999.
- Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G. *Macromolecules* **2005**, submitted for publication.
- Prescott, S. W.; Ballard, M. J.; Gilbert, R. G. *J. Polym. Sci. A Polym. Chem. Ed.* **2005**, in press.
- Prescott, S. W. *Macromolecules* **2003**, *36*, 9608–9621.
- Nikitin, A. N.; Castignolles, P.; Charleux, B.; Vairon, J.-P. *Macromol. Rapid Comm.* **2003**, *24*, 778–782.
- Bovey, F. A. *Chain structure and conformation of macromolecules*; Academic: New York, 1982.
- Mark, J. E.; Wessling, R. A.; Hughes, R. E. *J. Phys. Chem.* **1966**, *70*, 1895–1903.
- Zioga, A.; Ekizoglou, N.; Siakali-Kioulafa, E.; Hadjichristidis, N. *J. Polym. Sci. Part B: Polym. Phys.* **1997**, *35*, 1589–1592.
- Feigin, R. I.; Napper, D. H. *Colloid Polym. Sci.* **1980**, *258*, 1153–1158.

- (44) Wang, X.; Sudol, E. D.; El-Aasser, M. S. ACS Symposium Series 801; American Chemical Society: Washington, DC, 2002; pp 180–197.
- (45) Emelie, B.; Pichot, C.; Guillot, J. *Makromol. Chem., Suppl.* **1985**, 10–11, 43–57.
- (46) El-Aasser, M. S.; Ahmed, S. M.; Poehlein, G. W.; Vanderhoff, J. W.; Rovira, X.; Tabernero, J. I.; De la Morena, P. In *Polymer Colloids II*; Fitch, R. M., Ed.; Plenum: New York, 1980; pp 361–377.
- (47) Maeder, S.; Gilbert, R. G. *Macromolecules* **1998**, 31, 4410–4418.
- (48) Maxwell, I. A.; Morrison, B. R.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1991**, 24, 1629–1640.
- (49) Cheikhalard, T.; Tighzert, L.; Pascault, J. P. *Angew. Makromol. Chem.* **1998**, 256, 49–59.
- (50) Heuts, J. P. A.; Radom, L.; Gilbert, R. G. *Macromolecules* **1995**, 28, 8771–8781.
- (51) Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Kajiware, A.; Klumperman, B.; Russell, G. T. *Macromol. Chem. Phys.* **2000**, 201, 1355–1364.
- (52) Riddick, J. A.; Sakano, T.; Bunger, W. B. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1986.
- (53) Gordon, R. Honors Thesis, Sydney University, 1990.
- (54) van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier: Amsterdam, 1997.
- (55) Ahmed, S. M.; El-Aasser, M. S.; Micale, F. J.; Poehlein, G. W.; Vanderhoff, J. W. In *Polymer Colloids II*; Fitch, R. M., Ed.; Plenum: New York, 1980; p 265.
- (56) Saenger, W.; Müller-Fahrnow, A. *Angew. Chem.* **1988**, 100, 429–431.
- (57) Ferguson, C. J.; Russell, G. T.; Gilbert, R. G. *Polymer* **2002**, 43, 6371–6382.
- (58) Guyot, A.; Tauer, K.; Asua, J. M.; Van Es, S.; Gauthier, C.; Hellgren, A. C.; Sherrington, D. C.; Montoya-Goni, A.; Sjöberg, M.; Sindt, O.; Vidal, F.; Unzué, M.; Schoonbrood, H.; Shipper, E.; Lacroix-Desmazes, P. *Acta Polym.* **1999**, 50, 57–66.

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