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RAFT Polymerisation in Water-Borne Organic Dispersions

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SUMMARY: Two different approaches to achieving controlled reversible addition-fragmentation chain transfer polymerisation in water-borne dispersions have been attempted, both giving reasonable control over molar mass evolution. Molar mass increased linearly with conversion, and the colloidal instability that has sometimes been observed in similar systems (*e.g.* [de Brouwer, H.; Monteiro, M. J.; Tsavalas, J. G.; Schork, F. J. *Macromolecules* **2000**, *33*, 9239]) was avoided. The similarity of results for the two quite different approaches can largely be reconciled utilising the theory of Luo *et al.*[Luo, Y.; Tsavalas, J.; Schork, F. J. *Macromolecules* **2001**, *34*, 5501]

The average number of radicals per particle, in terms of both propagating and RAFT intermediate radicals were compared, using two current models in the literature for the ratio of propagating to intermediate species.[Barner-Kowollik, C.; Quinn, J. F.; Morsley, D. R.; Davis, T. P. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 1353; Monteiro, M. J.; de Brouwer, H. *Macromolecules* **2001**, *34*, 349; Kwak, Y.; Goto, A.; Tsujii, Y.; Murata, Y.; Komatsu, K.; Fukuda, T. *Macromolecules* **2002**, *35*, 3026] Possible implications for water-borne dispersions under such conditions are that the *maximum* value of the average number of *propagating* radicals per particle may be significantly lower than 0.5, depending on the dominant mechanism for radical loss.

Introduction

Controlled radical polymerisation (CRP) allows the synthesis of previously unavailable polymers that have a controlled molar mass and novel chain architecture.[1-11]

Achieving CRP in water-borne dispersed systems is an important goal for the widespread commercialisation of CRP techniques. Reasonable progress has been achieved to date[12-17] in the area of reversible addition fragmentation transfer (RAFT) free radical controlled polymerisation.[5,7]

The RAFT process provides very good control of molar mass, with narrow polydispersities for a wide variety of systems. It is a particularly suitable method for

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achieving controlled radical polymerisation in emulsion systems for several reasons:

- It is robust.
- It differs from standard free radical polymerisation reactions only in the addition of an extra component: the RAFT agent.
- It is applicable to a wide range of monomers and reaction conditions.
- No particularly water-sensitive components are required.
- The resulting RAFT-endcapped polymer may be further modified/used for subsequent reactions, for example, to yield complex chain architectures.

However, despite the robustness of the RAFT process in bulk or solution systems, reaction in water-borne dispersion systems has met with only limited success.

Compartmentalisation of propagating radicals into separate particles in dispersions prevents radicals in one particle from encountering radicals in another particle, in the absence of transport between particles via the continuous phase. This often reduces the probability of termination, and thus increases the rate of reaction, since termination requires the encounter of two radicals. This phenomenon of compartmentalisation is described in detail by Gilbert.[18] Initiation events are also sensitive to this compartmentalisation; the major initiation event in emulsion polymerisation is entry of short, surface-active radicals from the aqueous phase, into the latex particles.[19]

A further effect of compartmentalisation is the physical separation of various reactants, and possibly partitioning of reactants between phases, which may lead to complications in the case of poor interphase transport. This is particularly germane to RAFT and other types of controlled radical polymerisation reactions, where the controlling agent must be either located in the locus of polymerisation, and/or capable of easy transport between phases, to maintain access to reaction sites. Thus, the following inter-phase events are important for RAFT polymerisation in water-borne organic dispersions: entry and exit of radicals from particles, and transport of reactants between particles and phases.

For a particular system, the important factors pertaining to compartmentalisation may vary, depending on reaction type, reactant solubilities, and kinetics.

A major problem associated with RAFT in water-borne dispersions is colloidal destabilisation of either monomer droplets or latex particles early in the reaction, to form a phase-separated red layer.[14] Until recently, good control and colloidal stability was achieved only under limited conditions or by using special techniques.[14,17]

Luo *et al.*[20] modeled the particle swelling and colloidal stability of living free radical miniemulsion systems under various initial conditions, by considering the thermodynamics of mixing, and comparing chemical potentials of the monomer droplets and latex particles. The model (successfully) predicts that, under the conditions under which several previous RAFT systems in water-borne dispersions have been studied, monomer droplets would undergo "superswelling", leading to colloidal destabilisation of the latex, as observed in the corresponding studies. The results of the RAFT polymerisations in this paper will be discussed in terms of the predictions of this model. The mechanism of the RAFT process is extremely important for water-borne dispersions, and thus will be discussed in detail.

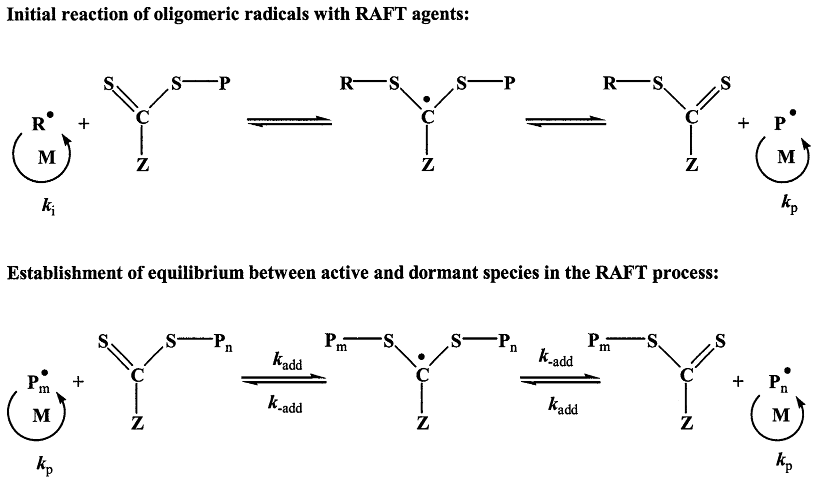
The accepted mechanism. The main reactions of the RAFT process as proposed by Rizzardo *et al.*[7] are shown in scheme 1. In this process, initiator-derived primary radicals ($I^\bullet$) react with monomer units (M) to form oligomeric radicals ($R^\bullet$), which undergo addition to the carbon-sulfur double bond of the dithioester chain transfer agents. The resulting species then loses the group ($P^\bullet$), a good homolytic leaving group, as a radical capable of initiating a polymerisation reaction or propagating. Equilibrium is then established between active (propagating) and dormant polymer chains, via the addition (rate coefficient k_{add}) and fragmentation (rate coefficient $k_{-\mathrm{add}}$) steps.

$$K_{\mathrm{eq}} = \left(\frac{k_{\mathrm{add}}}{k_{-\mathrm{add}}}\right) = \left(\frac{[\mathrm{Y}^\bullet]}{[\mathrm{P}^\bullet][\mathrm{PX}]}\right) \tag{1}$$

Here $[P^\bullet]$ and $[Y^\bullet]$ refer to the propagating and intermediate radical concentrations, respectively, and [PX] is the concentration of dormant RAFT-capped chains (taken as equal to the initial concentration of the RAFT agent).

For the current system, the RAFT equilibrium favours the intermediate rather than the propagating radical form, and the concentration of the intermediate species is usually significantly higher than that of the propagating species. The fates of both types of radicals are important for understanding the limitations of the RAFT process.

The two models for the RAFT mechanism. There are two types of models for the RAFT process: those that do not allow reactions of the intermediate radicals (the originally proposed mechanism[7]), and those that allow reactions of the intermediate radicals.[15,21] Since in the current RAFT system there are usually more intermediate than propagating radicals, the differences between these two classes of mechanisms may be significant. This may be particularly important for (mini)emulsion polymerisations, in which many systems with small latex particles obey "zero-one" kinetics, where the fates of radical species entering latex particles already containing a radical will differ, depending on the possibility of reaction of intermediate radical species. In a "zero-one" emulsion polymerisation in the absence of a RAFT agent, the number of radicals (all propagating) per latex particle, $\bar{n}$, is dependent on the relative rates of inter-phase events, and has a maximum possible value under such conditions of 0.5. In this case, the average number of propagating radicals ($\bar{n}_{\text{prop}}$) per particle is the same as the average *total* number of radicals per particle ($\bar{n}_{\text{total}}$). This gives two main limits, i.e., "classical" RAFT involving no intermediate radical reactions (model 1), and RAFT where reactions of the intermediate radical may occur (model 2).



Initial reaction of oligomeric radicals with RAFT agents:

Establishment of equilibrium between active and dormant species in the RAFT process:

Scheme 1: The elementary reactions of the central equilibrium of the RAFT process.

Model 1: Assuming the classical mechanism in which intermediate radicals are unreactive, a radical entering a latex particle in a zero-one system is expected to rapidly terminate with only propagating radicals in that particle, and will ignore radicals found in the intermediate form. Since any intermediate radicals in the system may undergo multiple addition/fragmentation steps during the lifetime of an entering radical, the probability of termination may be represented statistically for each other radical in the particle by a factor dependent on the relative times (amounts) that the radicals spend in the propagating and intermediate forms. For the current choice of RAFT agent (cumyl dithiobenzoate), the radicals spend most of their time in the intermediate form, and thus for a particle containing a small number of radicals, rapid termination of an entering species might only occur when there is already a *propagating* radical in the particle. Thus, the average number of propagating radicals per latex particle, $\bar{n}_{\text{prop}}$, might be expected to be approximately the same as for a comparable system in the absence of a RAFT agent. The total number of radicals per latex particle, $\bar{n}_{\text{total}}$, will be higher by a factor of the ratio of the number of intermediate to propagating radicals in the system. Thus, the limiting values of the average numbers of radicals per latex particle for a zero-one system will be $\bar{n}_{\text{prop}} = 0.5$, and $\bar{n}_{\text{total}} = 0.5 \times \{([Y^\bullet]+[P^\bullet])/[P^\bullet]\}$.

Model 2: If intermediate radicals also undergo reaction, their most likely fate is termination of intermediate radicals with propagating radicals, as suggested by Kwak *et al.*[21] and Monteiro *et al.*[15] Other possibilities also exist, such as reversible deactivation of intermediate radicals ("pseudo-termination") by either intermediate-intermediate or intermediate-propagating radical reactions. These possibilities will be ignored here, although some preliminary evidence suggesting that such reactions do occur has been discovered in this research group, and will be the subject of a future publication. So, assuming that termination of intermediate with propagating radical species occurs with the same (or nearly the same) probability ($p_{\text{X-term}}$) as for propagating radicals,[21] a radical entering a latex particle in a zero-one system would be expected to rapidly terminate with any other radicals in that particle, regardless of whether those radicals are in the propagating or intermediate forms. In such a case, where $p_{\text{X-term}} = 1$ (Kwak *et al.*[21] suggest that $p_{\text{X-term}} = 0.8$), in a zero-one system, the maximum average *total* number of radicals per particle will be 0.5. The number of propagating radicals per particle will then be lower by a factor of $\{([Y^\bullet]+[P^\bullet])/[P^\bullet]\}$, and the maximum value of the average number of propagating radicals per particle will be $\bar{n}_{\text{prop}} = 0.5 \times \{[P^\bullet]/([Y^\bullet]+[P^\bullet])\}$. If this limit holds, it will obviously limit the maximum rate of reaction, by reducing the maximum possible concentration of propagating radicals in the system.

Clearly, if $[Y^\bullet]/[P^\bullet]$ is greater than zero, the two models will give different behaviours, with the difference increasing with the value of $[Y^\bullet]/[P^\bullet]$. In reality, the situation is probably more complex than either limit, and additional processes, such as the reversible deactivation reactions, are also possible. In some cases, these may be modeled using model 2, with modifications made for a low value of $p_{\text{X-term}}$ (< 1). A reasonable approximation is that the situation lies somewhere between the limits of models 1 and 2, that the maximum rate of reaction is somewhat limited by the presence of the RAFT agent, that the maximum value of $\bar{n}_{\text{prop}}$ is somewhat less than 0.5, and that the maximum rate of reaction is correspondingly somewhat limited by the presence of the RAFT agent.

The kinetic data that is presented later will be used to test whether the RAFT agent/monomer combination used give systems that obey either of these models.

As can be seen for either model, the relative concentrations of intermediate and propagating radicals are important for understanding the kinetics and possibilities of RAFT polymerisation in water-borne dispersions. The value of $[\text{Y}^\bullet]/[\text{P}^\bullet]$ can in principle be calculated from the equilibrium rate coefficients k_{add} and $k_{\text{-add}}$ in eq 1. The two main models existing at the moment for the cumyl dithiobenzoate (CDB) system are those of Barner-Kowollik *et al.*[24] (corresponding to model 1) and Kwak *et al.*[21] (corresponding to model 2, and consistent with that of Monteiro *et al.*[15]) These models give very different values for the equilibrium rate coefficients, and the corresponding ratio $[\text{Y}^\bullet]/[\text{P}^\bullet]$.

The rate coefficients for the CDB/styrene system, as derived by Barner-Kowollik *et al.*[24], give a ratio $k_{\text{add}}/k_{\text{-add}} = 1.7\times10^{7}$ dm^{3} mol^{-1}. The same rate coefficients, as derived by Kwak *et al.*,[21] which include termination of intermediate radicals, give a very different ratio $k_{\text{add}}/k_{\text{-add}} = 10 - 100$ dm^{3} mol^{-1}. For both cases, these values strongly favour the intermediate over the propagating radical form.

The kinetic results of the RAFT polymerisations studied here, the implications for the values of $\bar{n}_{\text{prop}}$ and $\bar{n}_{\text{total}}$, and possible implications for water-borne dispersions under similar conditions will be discussed in terms of these models in the results section.

Current approaches to RAFT in water-borne dispersed systems. In this study, two different approaches to using RAFT polymerisation in miniemulsion/water-borne dispersed systems are used. The two approaches, both of which use miniemulsion-like systems, have been used to avoid the red layer formation and associated instability. The common major factor is the attempted elimination of transport and particle formation by nucleating previously-formed particles that contain all necessary reactants. These systems act as useful model systems for some aspects of RAFT in emulsion polymerisation, and for understanding of the effects of water on the RAFT process.

There are two main advantages of using miniemulsion/water-borne dispersed model systems: they avoid the complications of the particle formation process, and they (attempt to) may avoid transport-related issues for water-insoluble components, such as the RAFT agent. Both approaches used attempted to avoid colloidal instability and transport problems by initially encapsulating all water-insoluble components in the locus of polymerisation prior to reaction.

- Approach A:[25] form RAFT-endcapped oligomers in bulk, disperse into water under shear with surfactant and hydrophobe, and recommence polymerisation.
- Approach B:[26] find conditions under which a miniemulsion is stable while containing a RAFT agent, then optimise performance.

These are now described in more detail.

Approach A was as follows: a RAFT bulk reaction of styrene was performed with *in situ* production of the CDB RAFT agent by reaction of bis(thiobenzoyl) disulfide with AIBN, to produce oligomeric RAFT agents, and the reaction stopped at low conversion. The reaction mixture was immediately mixed with surfactant (sodium dodecyl sulfate, SDS) and a hydrophobe, and dispersed in water by the application of shear. The resulting dispersion was then heated and stirred throughout the reaction. Typical particle sizes were approximately 600 – 700 nm diameter, with high polydispersity.

Approach B was as follows: conditions were found under which miniemulsions containing RAFT agents were stable, by varying surfactant and hydrophobe concentrations, and preparation conditions. These were then optimised for better RAFT performance. Particles were typically of 50 – 60 nm diameter.

Both of these systems are described in detail in Vosloo *et al.*[25] and McLeary *et al.*[26]

Results and Discussion

Effectiveness of the two approaches. The results of the RAFT polymerisation reactions using the two approaches will now be discussed.

Approach A. This approach gave reasonable control under some conditions, but success was dependent on both the lengths of the preformed oligomers, and the type of hydrophobe (cosurfactant) used to stabilise the dispersion. The molar mass control was better when *n*-HD was used as hydrophobe, rather than when 1-hexadecanol (1-HD) was used. It was found that oligomers prepared after 60 minutes reaction time (the shorter oligomers) gave better control than those reacted for 80 minutes. The molar mass distributions as a function of conversion for the system using *n*-HD and oligomers prepared by 60 minute reaction time are shown in Fig. 1, and for the system using 1-HD and oligomers prepared by 80 minute reaction time are shown in Fig. 2. The molar mass control was better for the system shown in Fig. 1. This is consistent with the observation that fatty alcohols have been reported not to stabilize droplets in miniemulsions as efficiently against Ostwald-ripening as do the corresponding alkanes.[27]

The second distribution of approximately constant molar mass that increases with conversion for the 1-HD system is indicative of a significant amount of propagation in the absence of RAFT agent. The remaining component of the original fraction continues to grow in a controlled manner. Both of these observations suggest that nucleation sites outside of the preformed droplets are being formed.

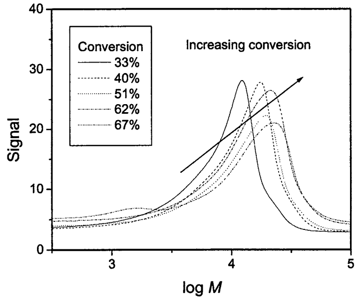


Fig. 1: Molar mass distributions for the polymer produced by the reaction at 80 °C of oligomers synthesised by the *in situ* RAFT bulk reaction of AIBN (0.162 g), bis(dithiobenzoyl) disulfide (0.201 g) and styrene (26.25 g) at 80 °C for 60 minutes, and emulsified in water (150 g) employing a SDS (0.433 g)/*n*-HD (1.359 g) system emulsifier combination (approach A).

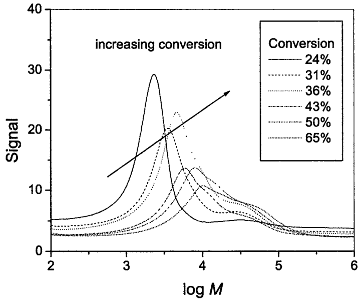


Fig. 2: Molar mass distributions for the polymer produced by the reaction at 80 °C of oligomers synthesised by the *in situ* RAFT bulk reaction of AIBN (0.162 g), bis(dithiobenzoyl) disulfide (0.201 g) and styrene (26.25 g) at 80 °C for 80 minutes, and emulsified in water (150 g) employing a SDS (0.433 g)/1-HD (1.455 g) system emulsifier combination (approach A).

The conversion-time data (Fig. 3) were used to calculate the rate of reaction, and to thus estimate the average number of propagating radicals per particle ($\bar{n}_{\text{prop}}$). Note that the rate of reaction was approximately the same for each system, as might be expected for a "pseudo-bulk" system, as is predicted to be the case here. This will be discussed later.

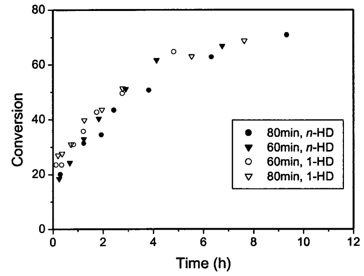


Fig. 3: Conversion versus time at 80 °C for the polymerisation of two different oligomers synthesised by the *in situ* RAFT bulk reaction of AIBN (0.162 g), bis(dithiobenzoyl) disulfide (0.201 g) and styrene (26.25 g) at 80 °C for 60 and 80 minutes, and emulsified in water (150 g) employing a SDS (0.433 g)/*n*-HD (1.359 g) and a SDS (0.433 g)/1-HD (1.455 g) emulsifier combination (approach A). Note that the conversion is with respect to the initial amount of monomer in the bulk step, and a typical starting conversion in the second stage (water-borne dispersion) stage is 20 %.

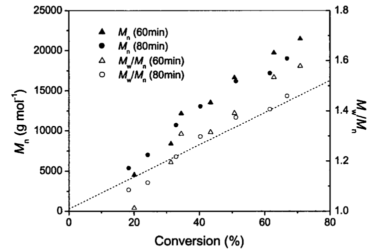


Fig. 4: Number average molar mass and polydispersity versus conversion at 80 °C for the polymerisation of two different oligomers synthesised by the *in situ* RAFT bulk reaction of AIBN (0.162 g), bis(dithiobenzoyl) disulfide (0.201 g) and styrene (26.25 g) at 80 °C for 60 and 80 minutes, and emulsified in water (150 g) employing a SDS (0.433 g)/*n*-HD (1.359 g) emulsifier combination (approach A). The dotted line indicates predicted molar masses.

The dependence of the number average molar mass on conversion for each of the oligomers in the *n*-HD system is shown in Fig. 4. In both cases, the molar mass increased linearly with conversion, and was slightly greater than that predicted.

Note that for both oligomer lengths, the molar mass polydispersity increases with conversion. This increasing polydispersity may be due to a number of factors, including loss of RAFT agent throughout the reaction and to termination processes, and the nature of chains formed through the *in situ* process for the generation of the RAFT agent. A number of possible side reactions may occur as a result of this *in situ* generation of the RAFT agent, which can result in higher molar masses than predicted, and increasing polydispersities with conversion. The possible implications of these side reactions are described in more detail in Vosloo *et al.*[25]

Overall, this approach using the *n*-HD system offers a simple means of preparing controlled polymers by RAFT polymerisation in water-borne organic dispersions.

Approach B. The results using this approach were very good. It was found that stable RAFT miniemulsions were obtained when high concentrations of the *n*-HD hydrophobe and surfactant were used. Under these conditions, neither colloidal destabilisation nor red layer formation were observed.

For the anionic (SDS) and cationic (CTAB) surfactants used, the miniemulsions that gave suitable stability had the following characteristics:

- High surfactant concentrations (10 % by mass with respect to monomer); less than 5 % led to colloidal destabilisation, and red layer formation.
- High hydrophobe (*n*-HD) concentrations (> 4 % with respect to monomer).

Miniemulsion RAFT polymerisation in these systems gave excellent results in terms of molar mass control and colloidal stability.

The kinetics of a typical reaction is shown in Fig. 5. Reactions usually showed an initial retardation period, a rapid acceleration, followed by slowly decreasing rate.

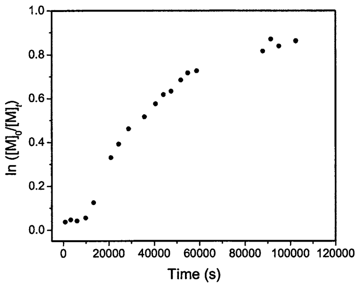


Fig. 5: Typical plot of $\ln\{[M]_0/[M]_t\}$ versus time for RAFT miniemulsion polymerisation of styrene using approach B. RAFT agent: 4-cyano-4-((thiobenzoyl)sulfanyl) pentanoic acid, T = 70 °C.

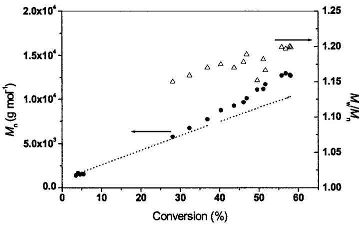


Fig. 6: Molar mass (circles) and polydispersity (triangles) for RAFT miniemulsion polymerisation of styrene using approach B. Miniemulsion conditions: 20% solids, using styrene (20.00 g), *n*-HD (0.88 g), AIBN (0.01 g), CTAB (2.02 g), RAFT agent: PMMA-based (M_n = 913 g mol^{-1}, M_w/M_n =1.41, 1.05 g) RAFT macroinitiator from 4-cyano-4-((thiobenzoyl)sulfanyl) pentanoic acid; T = 70 °C. Dotted line: predicted molar mass using equation 2.

For all of the systems, including those using RAFT-based macroinitiators, molar mass control was in good accord with predictions, with low polydispersity (< 1.3). Molar mass as a function of conversion for a typical reaction is shown in Fig. 6. Molar mass increased linearly, and was in good accord with predictions. The number average molar masses were predicted using the formula of de Brouwer *et al.*[14]

$$\bar{M}_n = M_{RAFT} + \frac{x[M]_0 M_M}{[RAFT]_0 + 2f[I]_0(1-e^{-k_d t})} \qquad (2)$$

Here $\bar{M}_n$ is the predicted molar mass, M_M is the monomer molar mass, M_{RAFT} is the molar mass of the RAFT agent. $[\mathrm{M}]_0$, $[\mathrm{RAFT}]_0$, and $[\mathrm{I}]_0$ are the initial concentrations of the monomer, RAFT agent, and initiator respectively, k_d the initiator dissociation constant; f is the initiator efficiency, and x is the fractional conversion at time t.

Block polymers starting with polymers formed by this process could also be formed with high reinitiation efficiency, to form a second, controlled block. This indicated good living characteristics, and allows the possibility of further polymerisation or modification of the RAFT end-groups.

This approach worked very well for both styrene and methyl methacrylate polymerisations, using both anionic and cationic surfactants. No phase separation of a red layer was observed, and the amount of coagulum was minimal.

Rationalisation of the two approaches. Good to excellent control of the molar mass has been obtained by the two different approaches to RAFT polymerisation in water-borne dispersions. The results for both of these systems at first appear to contradict previous results, where particle stability was unattainable in SDS-stabilised RAFT miniemulsion polymerisations. What are the differences here?

Approach A attempted to avoid destabilisation early in the reaction by preventing the stage at which a large number of oligomers were present. Particle sizes were large and polydisperse. Approach B attempted to avoid destabilisation by finding conditions under which the system was stable in the presence of a RAFT agent. Particle sizes were small and relatively monodisperse. Both successful systems used the same hydrophobic co-stabiliser (*n*-HD) at higher concentrations than typically used in miniemulsion reactions. Both approaches attempt to prevent or reduce inter-particle transport phenomena.

These approaches will now be discussed in terms of the theory of Luo *et al.*[20]

For approach A, no superswelling-based destabilisation is predicted for larger droplets and for high hydrophobe concentrations, such as is the case here. Both of these conditions are significantly different from those of previously studied systems.

For approach B, Luo *et al.*[20] predict instability of many miniemulsions containing RAFT agents, due to "superswelling" of particles with monomer that attempts to solubilise the RAFT agent. Under "typical" miniemulsion conditions, this superswelling destabilises the initially formed droplets/particles. It is thus predicted that for most ionically-stabilised miniemulsions run under "typical" miniemulsion conditions, control and stability are not possible; this is the probable reason for the previous failures in the literature. The main difference between approach B and those previously studied is that the current system uses very high hydrophobe concentrations. Under such conditions, superswelling is not predicted; this is the probable reason for the better stability.

Thus, the relative stability of both systems seems to be consistent with the predictions of Luo *et al.*[20] Colloidal instability is not predicted for systems containing large amounts of hydrophobes (as in both cases here), or for large particles (as in approach A). Approach A may also avoid some of the destabilisation induced by large amounts of very short oligomers early in the reaction.

Thus, despite the differences, both systems were predicted to be relatively colloidally stable under the reaction conditions. This fits the observation that both give good control under appropriate conditions.

Kinetic analysis of results. The value of $\bar{n}_{\text{prop}}$ was calculated for each system from the slope of $\ln\{[M]_0/[M]_t\}$ versus time, the particle size, and the fractional volume of the organic (particle) phase for each latex, since $\bar{n}_{\text{prop}} = const\ [P^\bullet]$ for a particular system. The results were compared with the predictions of the two classes of models for the RAFT process (Models 1 and 2), where appropriate. It will be shown that the predicted rate coefficients of Barner-Kowollik *et al.*[24] are not reasonable for the current system, and will not be used in subsequent calculations. The questions of whether these systems obey zero-one kinetics, and the effect of the intermediate radicals on the reactions, will now be addressed.

For the systems using approach A, the estimated value of $\bar{n}_{\text{prop}}$ early in the reaction was very high (approximately 40). This system is predicted to obey pseudo-bulk kinetics, due to the large particle size. This system could therefore not be used for addressing the above questions.

In approach B, observed $\bar{n}_{\text{prop}}$ values were much lower (typically 0.02 - 0.04, a value of 0.03 is used for subsequent calculations). These systems are candidates for obeying zero-one kinetics, due to the small particle sizes with polystyrene latices.[28] The systems in approach B will be used to address the above questions.

The number of intermediate radicals per particle ($[Y^\bullet]_{\text{per particle}}$) can be estimated using the models 1 and 2, from the estimated values of $\bar{n}_{\text{prop}}$ and the relationship between $\bar{n}_{\text{prop}}$ and $[P^\bullet]$ (the same scaling factor will also apply to $\bar{n}_{\text{total}}$ or the average number of intermediate radicals per particle), obtained by rearrangement of eq 1, to give eq 3:

$$[\mathrm{Y}^{\bullet}]_{\text{per particle}} = \bar{n}_{\text{prop}}\,[\mathrm{PX}]\left(\frac{k_{\text{add}}}{k_{\text{-add}}}\right) \tag{3}$$

For this system, eq 3 gives very different results for the two models:

- Model 1, using the model of Barner-Kowollik *et al.*[24]: $[\mathrm{Y}^{\bullet}]_{\text{per particle}} = 5 \times 10^4$.
- Model 2: $[\mathrm{Y}^{\bullet}]_{\text{per particle}} = (0.03 - 0.3)$.

The predictions of model 1, using the rate coefficients of Barner-Kowollik *et al.*,[24] are contradicted by ESR observations of the intermediate radical concentration.[21,23] However, using the ratio $[\mathrm{Y}^{\bullet}]/[\mathrm{P}^{\bullet}]$ (= 1 – 10), as suggested by the data of Kwak *et al.*[21] and Calitz *et al.*,[23] and assuming model 1, the predicted range of $[\mathrm{Y}^{\bullet}]_{\text{per particle}}$ values is less than 0.5, thus it is possible that intermediate radicals are not reactive. Model 2 is consistent with the possibility of zero-one kinetics with respect to either propagating or total radical concentrations, since the values of both $\bar{n}_{\text{prop}}$ and $\bar{n}_{\text{total}}$ are below 0.5. Overall, it was not possible to discriminate between models with the available data.

What do the two models imply for RAFT polymerisation in zero-one water-borne organic dispersions? In both cases the maximum average number of radicals per particle is 0.5, but the limitation applies to different species for each case.

In the case of model 1, this maximum applies only to *propagating* radicals, since the intermediate radicals do not react with the propagating radicals. Thus, the maximum reaction rate corresponds to 0.5 propagating radicals per particle, as for a standard emulsion polymerisation. Additionally, there may be many intermediate radicals per particle, depending on the ratio $[\mathrm{Y}^{\bullet}]/[\mathrm{P}^{\bullet}]$. In such a case, generation of pairs of radicals by initiator decomposition inside latex particles might not result in rapid termination, since intermediate radical formation is rapid. Thus, entry of radicals from the aqueous phase may be unnecessary in such a system, and latices of unusual morphologies and functionalities might be prepared. This is illustrated in Fig. 7, where the effects on survival of an entering radical to a significant degree of polymerisation, when CDB is added, to what would normally be a zero-one system are compared with the same system without the RAFT agent. The model used here is a modified version of that of Maeder *et al.*,[28] and accounts for the probability of the encounter of two *propagating* radicals. The probability of encounter when using the RAFT agent is greatly reduced, and the survival probability is significantly enhanced.

In Model 2, since the intermediate radicals may undergo termination, the total (propagating *and* intermediate) maximum number of radicals per particle is 0.5, thus the maximum number of propagating radicals per particle is then $0.5\times\{[P^\bullet]/([Y^\bullet] + [P^\bullet])\}$, and the maximum rate is thus greatly limited if $[Y^\bullet]/[P^\bullet]$ is large. The reduction will be smaller if $p_{X\text{-term}} < 1$. The primary source of initiation events in these cases is likely to remain unchanged, *i.e.* entry of radicals from the aqueous phase.

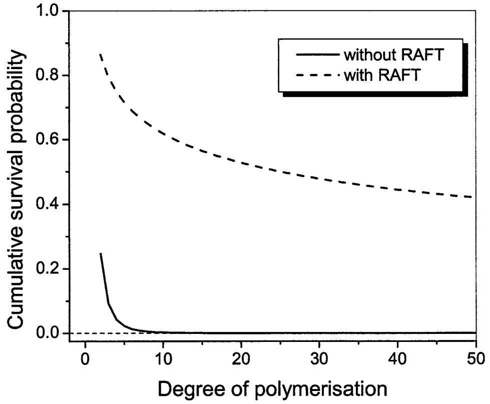


Fig. 7: Simulated cumulative probability of survival under "zero-one" conditions, of a radical species entering a latex particle containing another radical, to reach each degree of polymerisation up to 50, assuming termination of intermediate radical species is not possible. Solid line: no RAFT agent present ("normal"); dashed line: RAFT agent present. Conditions: $T = 50$ °C, styrene monomer, $w_p = 0.1$, $r = 50$ nm, $[Y^\bullet]/[P^\bullet] = 0.1$.

Conclusions

Two different approaches to obtaining controlled RAFT polymerisation in water-borne dispersions were attempted. Both approaches gave good control of molar mass, and colloidally stable latices, for systems similar to those that showed earlier failures in the literature, *e.g.* RAFT in miniemulsion with ionic surfactants. This shows that well-controlled polymers can be synthesised by RAFT in water-borne dispersions.

The observed colloidal stability in these systems is consistent with the predictions of the model of Luo *et al.*,[20] and appears to be related primarily to the use of large amounts of added hydrophobe (cosurfactant) in the preparation phase for both approaches, and to the large particle size in approach A. These results suggest that understanding of some of the potential pitfalls for new systems may be possible based on this model.

Kinetic analysis of the two approaches used here did not yield conclusive results regarding the fate of entering radicals for zero-one systems containing RAFT agents. It was found that the system used in approach A was not a zero-one system, whereas the system in approach B may be. Investigations into this problem are currently in progress, and it is expected that the solution may correspond, in part, to both models. The results of this problem are dependent on an understanding of the basics of the mechanism of the RAFT process, and are essential for understanding RAFT in water-borne dispersion.

A number of outstanding problems and dilemmas were identified:

- The concept of phase transfer events in RAFT in water-borne dispersions is currently poorly understood, and needs to be addressed.
- The zero-one concept for RAFT systems is complex: the meaning of $\bar{n}$ is poorly understood, and the extent of intermediate radical termination is unknown.
- Some RAFT reactions in water-borne dispersions appear to reach a limiting conversion, and suddenly cease polymerisation. This needs further investigation.
- The basic mechanism of the RAFT process is poorly understood. This is currently under intensive investigation.

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