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Molecular Watchmaking: *ab initio* Emulsion Polymerization by RAFT-controlled Self-assembly

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Summary: Controlled radical polymerization using RAFT has the potential to make polymers with virtually any desired molecular architecture. For this to be implemented on an industrial scale, it must be performed by polymerization in disperse media. However, simply adding a RAFT agent to a conventional emulsion polymerization recipe leads to a loss of molecular weight control and formation of coagulum, probably because of nucleation in droplets, which is normally an unlikely phenomenon in emulsion polymerizations. Recently, a method has been devised for implementing RAFT in *ab initio* emulsion polymerization that avoids droplets in the particle formation stage. The molecular weight distribution of the polymer thus formed shows that molecular weight control is maintained throughout the polymerization. A model is developed to predict the particle size formed in this new type of emulsion polymerization. The new methodology enables synthesis of novel dispersions where molecular architecture can be precisely controlled, such as structured core-shell particles.

Keywords: controlled radical polymerization; emulsion polymerization; particle size; surface coatings

Introduction

Free radical emulsion polymerization is used extensively in industry to synthesize a wide range of products such as paints, paper coatings, adhesives and specialty products such as rheology modifiers, cement additives and biomedical applications. The absence of organic solvents and the compartmentalization of the reaction give rise to the numerous advantages of the emulsion process. Water as continuous phase provides a good medium for the dissipation of the heat of reaction and guarantees a product (i.e. latex) that has a relatively low viscosity making it easy to handle. Free-radical emulsion polymerization systems are relatively economical and robust, with a low sensitivity to impurities.[1–3]

Emulsion polymerization is a heterogeneous polymerization process. A simple *ab initio* system comprises of water, initiator (usually water-soluble), a water-insoluble monomer and surfactant. The process involves the emulsification (by means of agitation) of monomer(s) in the continuous aqueous phase and the stabilization of the droplets by the surfactant. Free-radical polymerization is started by the initiator, with the locus of polymerization being within the monomer-swollen submicron particles that either form early during the process (an *ab initio* system) or are added at the start (a *seeded* system). The final product is a latex consisting of a colloidal dispersion of polymer particles in water with each of the polymer particles, stabilized by surfactant, (~100 nm diameter) containing many polymer chains.

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From a contemporary perspective, the interlinked scientific and technical history of emulsion polymerization can be divided into three periods, encompassing the first synthetic polymer latexes, the subsequent scientific and technical development which led to many of today's polymer products, and the dawn of fully designed polymer products based on recent scientific developments.

The first period, which might be termed the *Heroic Age*, started with the first attempts to imitate natural rubber latex. The earliest artificial latex products[4–6] were made based on the assumption that an oil-in-water emulsion was needed to effect such a polymerization and that polymerization occurred in the emulsion droplets. The term ''emulsion polymerization'' is in fact a misnomer, because it is now well understood that droplet polymerization generally is unimportant (exception for mini-emulsion polymerization). This incorrect supposition was the reason for poor quality of early products.

The *Age of Exploration* refers to the second period in emulsion polymerization. The first theories of the process appeared in the 40's, in particular the brilliant pioneering work of Harkins[7] and of Smith and Ewart.[8] This provided guidance for the development of a huge range of products, and indeed virtually all of the myriad products of emulsion polymerization we use today have evolved from the processes developed semi-empirically in the 40's and 50's. Moreover, inspection of the patent literature (e.g.[9]) shows that products such as SBR, PVA adhesives and neoprene are still made today by processes which are linearly descended from the original empirical ones.

As part of product improvement, ingredients are often added to a extant recipe, and historically these were sometimes chosen using mechanistically incorrect reasons. Alas, it is a cardinal rule in current emulsion polymerization technology that one should never take an ingredient out (even if no one knows why it was put in 30 years previously), just new ones are added; this can lead to obvious problems. At this stage no current latex product has been designed just from mechanistic knowledge and the question is asked: can we make new/improved latexes, processes and polymers starting from first principles?

The third period of emulsion polymerization might be termed the *Age of Enlightenment*, and is now under way. The scientific efforts of many teams over previous decades, aided by the advent of new physical techniques for investigating, have resulted in better understanding of the fundamentals of emulsion polymerization. One part of this is the availability of reliable techniques for measuring rate coefficients in free-radical polymerization. The best of these new methods is pulsed-laser polymerization (PLP), first put into practice by Olaj and others,[10,11] which has been developed as a reliable method with internal consistency tests by the combined efforts in an IUPAC Working Party.[12] There are also new techniques for measuring, e.g. transfer[13–15] and termination[16] rate coefficients, which have either verified or extended earlier techniques such as the Mayo method. These have enabled quantitative data to be obtained which can support or refute mechanistic hypotheses; as a result the fundamental mechanisms of emulsion polymerization are relatively well understood. We can now design latexes scientifically based on desired properties and structure relations, but this has not yet been done for commercial products.

One goal of technical importance is to use free-radical polymerization to grow a block copolymer, poly(A-block-B), e.g. for use as colloidal stabilizer or compatibilizer. One might think it would be possible to make this by commencing polymerization with monomer A, waiting until monomer A is consumed and then adding monomer B. However, taking styrene as an example, the growth lifetime of a styrene polymer chain at 50 °C (a transfer-dominated system, so the lifetime is $1/k_{tr}$[monomer]) is about 10 s; since it takes hours for polymerization to go to completion, this procedure will not enable a block copolymer to be grown: the chain lifetime is simply too short.

In order to have better control over the chain architecture of the polymer, the statistical destruction of the chain-propagating radicals through termination reactions must be minimized. The techniques developed for this purpose have been labeled controlled/living free radical polymerization processes.[17] The general feature of these techniques is that the chain-propagating radicals are converted into a ''dormant'' form which is in equilibrium with the ''active'' form.

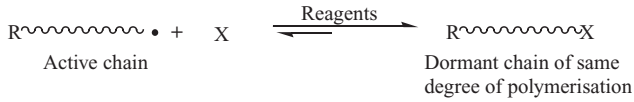
By keeping the concentration of the active propagating radicals very low, under the appropriate conditions, the rate at which they terminate by combination is also low. If exchange between active and dormant forms is rapid, the conditions are such that all living chains have an equal probability of growth per unit time. Because the dormant species always remain capable of adding monomer, i.e. do not have a short lifetime, then the goal of forming controlled architecture by letting one monomer be consumed and then continuing polymerization by addition of a second monomer can be achieved.

RAFT Polymerization

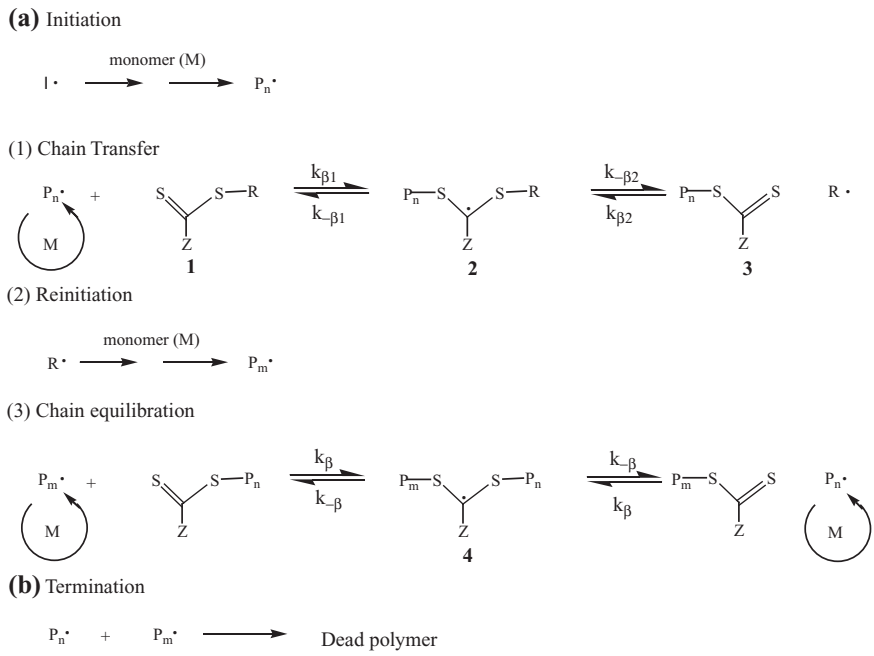
One of the most versatile ''living'' free-radical polymerization techniques involves a reversible addition-fragmentation chain transfer step, and is therefore named the RAFT process.[18] This has shown to be one of the more robust and versatile techniques by which to implement ''living'' radical polymerization. It is carried out by addition of a chosen quantity of a thiocarbonylthio compound to a conventional free radical polymerization mixture (same monomers, initiators, solvents and temperature). The thiocarbonylthio compound acts as an efficient reversible addition-fragmentation chain transfer agent (RAFT agent) and confers controlled characteristics to the polymerization.[18,19] Dithioesters,[18] dithiocarbamates,[20] xanthates[21] and trithiocarbonates[22,23] are examples of RAFT agents with different molecular structures that have been successfully used as chain transfer agents. A great advantage of the RAFT process is its compatibility with a wide range of monomers, including functional monomers. Scheme 2 shows the currently accepted RAFT mechanism.

The RAFT agent protects the growing chains from termination, since most of the chains are in the dormant form. While the overall rates of termination and transfer are the same as in an equivalent system without RAFT (since the actual propagation step involves a free macroradical which is the same as in a conventional system), the overwhelming majority of polymer is in the form of RAFT-capped dormant chains, which although not radicals, are capable of further propagation in the presence of radicals by the addition-fragmentation step. As with all the controlled-radical techniques, RAFT yields a final product where all the chains are of similar length, and because the chains are still able to propagate after all the monomer is consumed, this overcomes the chain-lifetime problem for growing block copolymers, etc. This therefore has the potential to be a major industrial process. Indeed, RAFT can be described as a molecular toolbox with which any desired polymer architecture can be created: in principle, one can place any monomer unit (and sequence of monomer units) anywhere on the chain, and even control branching structure.[24]

Significant commercialization of the RAFT process must be through emulsion polymerization, to capitalize on advantages such as low viscosity at high conversion,



Scheme 1.



Scheme 2.

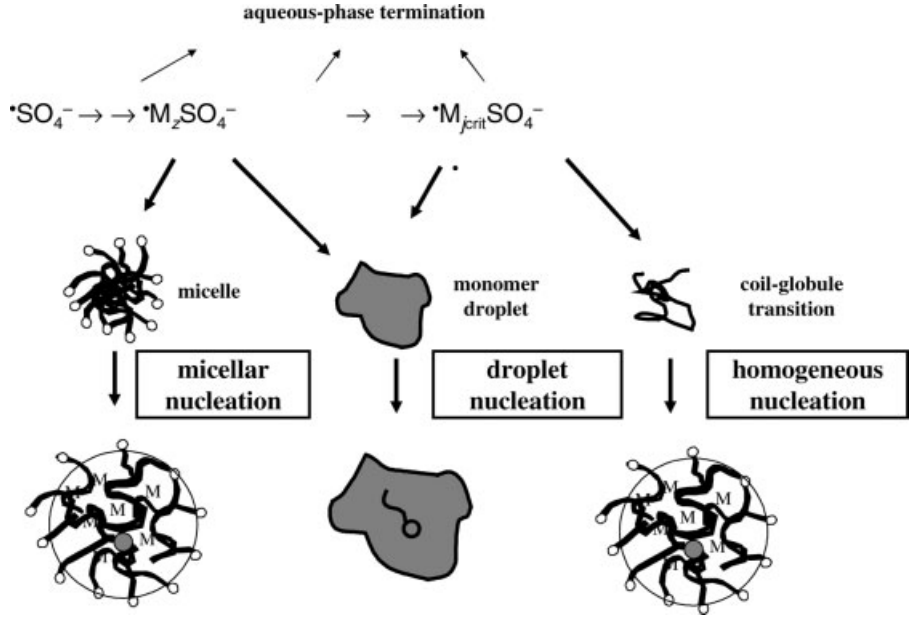
readily controlled addition of any ingredient, absence of solvents, and direct use of the latex in surface coatings.

RAFT in Emulsion

The use of RAFT polymerization techniques in solution and bulk polymerization systems is well developed,[18,25,26] but early attempts to use this technique in emulsion polymerization were quite unsuccessful. Initially published experiments exhibited one or more of the following problems: loss of colloidal stability,[27] loss of molecular weight control,[27] poor control of the molecular weight polydispersity,[26,28] formation of a red layer (phase separation of a RAFT-agent-rich phase, the color coming from the RAFT agent) during the polymerization reaction and very slow polymerization rates.[27] To understand what was going wrong, a closer look needed to be taken in regards to the mechanism of particle formation, the most important of which are shown in Scheme 3.

Transportation of the RAFT agent into the latex particles is one of the major obstacles in applying RAFT to emulsion polymerization.[29] Most RAFT agents are fairly water-insoluble, making the transportation process very slow and prone to variability, and the use of more water-soluble RAFT agents shows significant inhibition or retardation,[27] probably because this interferes with the process of radical entry into particles in an emulsion polymerization.[30]

The transportation problems were circumvented in small scale laboratory experiments by using a water-insoluble RAFT agent and using acetone to transport the RAFT agent from the monomer droplets to large preformed particles of a seed latex, and subsequently stripping the acetone prior to second-stage polymerization.[31] The result was a RAFT emulsion polymerization system that produced good control over the molecular architecture and retained the living characteristics of the polymer chains. The application of this technique is however limited to cases where



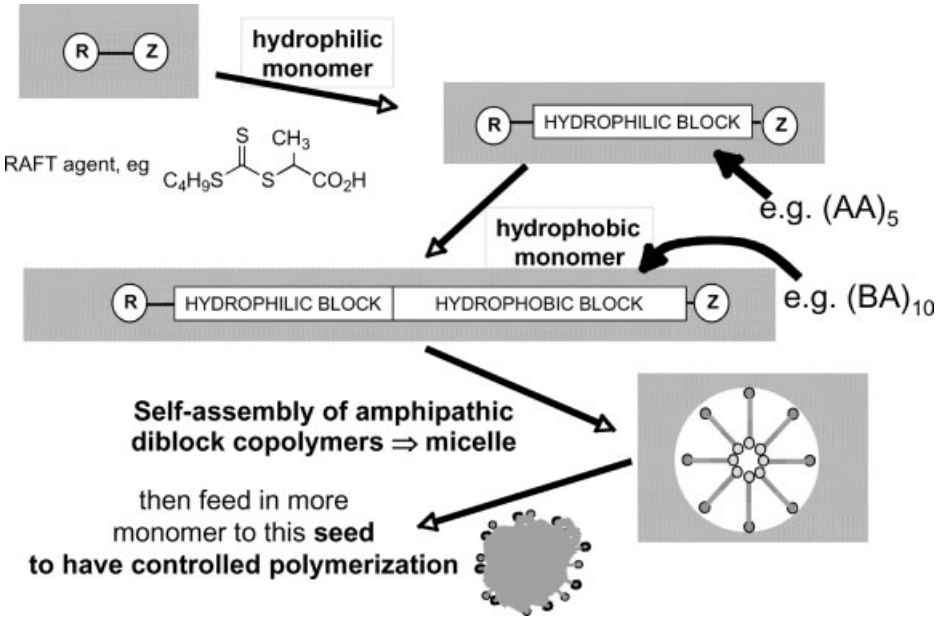
Scheme 3.

large seed particles are used, and thus does not allow *ab initio* (unseeded) emulsion polymerization under RAFT control. However, the experiment suggested that the problem with previous attempts to implement RAFT in emulsion lay in the presence of RAFT agents in monomer droplets, which was obviated by the acetone-transport method.

A process was then developed whereby *ab initio* emulsion polymerization could be performed under RAFT control to give living character[32,33] without the problems earlier mentioned such as formation of a red layer, loss of colloidal stability or loss of molecular weight control. With this new method, it is not necessary to use large preformed seed latex particles. The process used to create these particles is shown in Scheme 4; it avoids the presence of monomer droplets during the particle formation step. 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. Initial conditions for the polymerization reactions are chosen in such a manner as to avoid the presence of monomer droplets during the particle formation stage, or at least until all 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.

Particle Formation Mechanism

Calorimetric experiments permit the study of particle formation in these polymeric amphipathic RAFT systems, because this enable rates to be followed accurately, even while monomer is being fed.[34] Figure 1 shows the heat trace for a controlledfeed reaction of butyl acrylate (BA) and a macro-RAFT agent containing five acrylic acid units. The graph shown in Figure 1 has been divided into four sections. The first three sections involve a very slow starved feed of the monomer to avoid droplet formation followed by a faster rate of



Scheme 4.

addition in the fourth section after the formation of the seed particles.

The first section represents the aqueous phase polymerization of the macro-RAFT agent with a hydrophobic monomer (BA) to form amphipathic diblocks that are surface active and therefore able to self-assemble into micelles. Once micelles start to form, the system is in the second section, where propagation continues to a point where some chains are too hydrophobic to desorb from micelles, and particles are thus created. As the chains in the newly formed particle grow and the size of the particle increases, other diblocks adsorb onto the newly created surface, and in turn propagate to a point where they are also not able to desorb. Once all the labile macro-RAFT

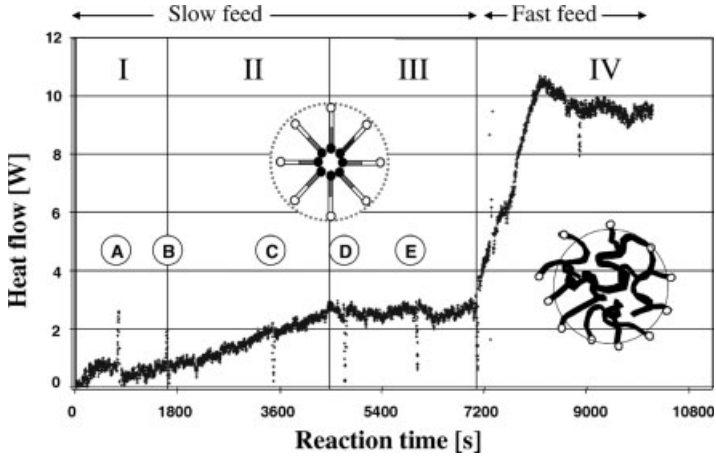


Figure 1.
Heat traces for a controlled feed reaction of butyl acrylate (BA) and a macro-RAFT agent containing five acrylic acid units.

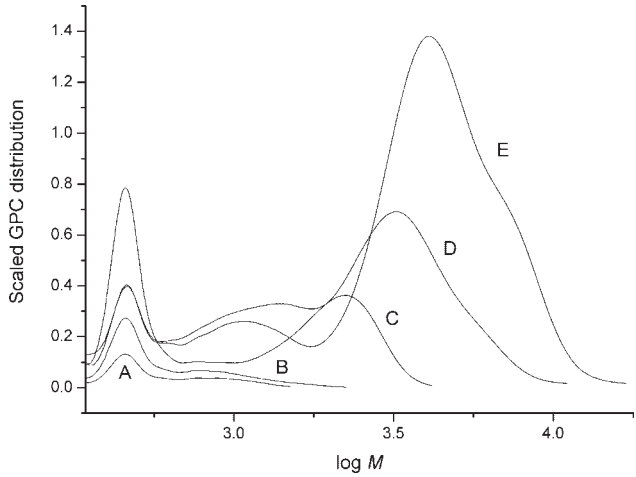


Figure 2.
GPC traces that show the evolution of molecular weight of a macro-RAFT agent. Letters A–E correspond to the same letters in Fig. 1, showing where the sample was taken. Distributions normalized to amount of polymer formed.

agent is fixed within the polymer particles, particle formation stops; this is characterized by the third section, which shows a constant polymerization rate. During the fourth section, there is an initial increase in the polymerization rate due to the increased feed rate of the monomer followed by a constant rate of polymerization for the remainder of this monomer feed section.

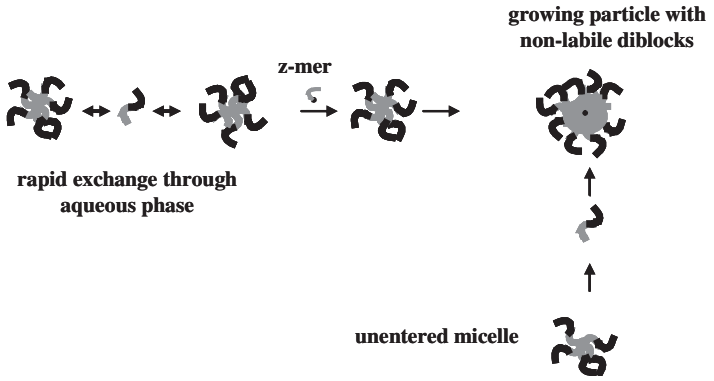
Figure 2 shows the evolution of the molecular weight of the labile macro-RAFT agent to the non-labile polymer chains that form the polymer particles. This indicates the living/controlled characteristics of the RAFT controlled emulsion polymerization reaction.

Initially it was thought that particle formation was due to the self-assembly of the diblocks into rigid micelles which keep on growing. Table 1 shows the average number of RAFT molecules per particle for various runs with different [RAFT]:[monomer]. The number of RAFT molecules per particle is much greater than the typical aggregation number expected and therefore the original micelles accumulate RAFT-ended polymer chains during particle formation and growth stage by migration, coalescence or coagulation.

Table 1.
The average number of RAFT molecules per particle for various runs with different [RAFT]:[monomer].

Final number-average particle diameter (nm)	Final number of RAFT molecules per particle
60	2700
109	4000
187	16000

The mechanism for this system can be explained (Scheme 5) if we look at a system where pre-formed diblocks are synthesized and then dispersed in water, where they may exist as micelles. At low conversion, the diblocks ('surfactant molecules') are still labile, and can migrate between micelles through the aqueous phase and/or by coalescence; these micelles thus have a transient existence. During the particle formation stage, some of these micelles are entered by radicals and grow under RAFT control (note that entry is slow on the timescale of particle formation). Migration of diblocks between micelles is unhindered until at least one diblock in a micelle is long enough to form a non-labile chain. The micelle containing this RAFT-capped entity is no longer transient, in the sense of being now unable to disappear through diblock migration or coalescence. It then



Scheme 5.

becomes a true particle. These growing particles then 'cannibalize' labile diblocks from transient micelles, which migrate from other micelles. These in turn grow until all particles contain only diblocks which are non-labile, when particle formation stops.

Some results are given in Figure 3, which shows the number of particles per litre for various runs using an acrylic acid–styrene amphipathic RAFT agent in small scale controlled feed experiments. For these runs the initiator concentration was kept constant and the ratio of monomer to amphipathic RAFT agent was varied. Some preliminary work has been carried out in developing a theoretical model describing particle formation by self assembly of amphipathic polymeric RAFT agents, which predicts particle number based on the precepts of Smith-Ewart theory.[8] It is assumed that the hydrophobic component of *each* chain needs to grow to a critical degree of polymerization X_{crit} after which particle formation stops, and exit and termination within the particles in the period of particle formation is ignored (i.e., assuming $\overline{n} = 1$). One obtains:

$$N_p = 2k_d[I] \times \left\{ \frac{\sqrt{2k_d[I]k_{t,w}}}{k_p[M]_w} + 1 \right\}^{1-z} \frac{X_{crit}^3 - \overline{X}_n^3}{B} N_A$$

$$B = \frac{k_p[M]_p a_{RAFT}^3}{12\pi} \left(\frac{M_0}{d_P N_A} \frac{d_M}{d_M - [M]_p M_0} \right)^{-2}$$

where N_p = particle number density, which is trivially related to particle size by conservation of mass:[1]

$$N_p = \frac{\text{mass polymer}}{\frac{1}{6}\pi \overline{d}_v^3 d_P}$$

where $\overline{d}_v^3$ = volume-average particle diameter, k_d = initiator dissociation rate coefficient, [I] = initiator concentration, $k_{t,w}$ = termination rate coefficient in water, k_p = propagation rate coefficient, $[M]_w$ = monomer concentration in water, z = critical degree of polymerization for entry of an oligomeric radical into a particle or micelle,[30] $\overline{X}_n$ = initial average degree of polymerization of diblocks, N_A = Avogadro's constant, $[M]_p$ = monomer concentration in particles, d_P = density of polymer,

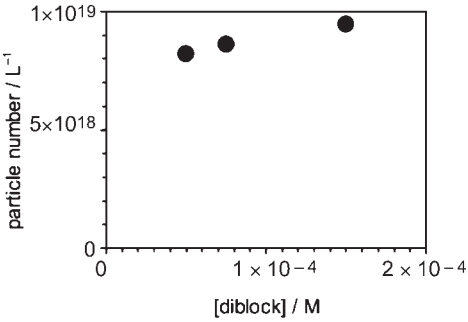


Figure 3.
Particle number using an acrylic acid styrene amphipathic RAFT agent as a function of final concentration of RAFT in the particles (constant [I]).

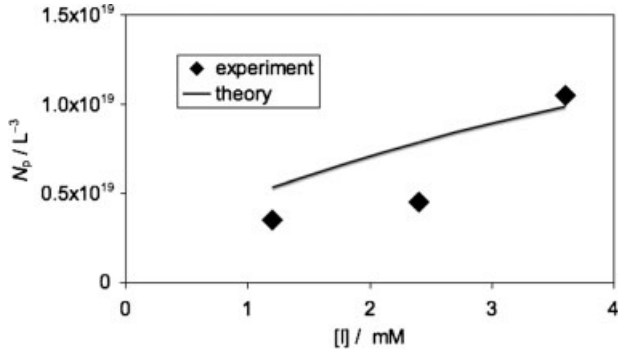


Figure 4.
Particle number with acrylic acid styrene amphipathic RAFT agent, showing particle number against initiator concentration (constant [monomer]:[RAFT]).

and d_M = density of monomer, M_0 = monomer molecular weight and a_{RAFT} = ''head-group'' area of a RAFT-ended chain.

Figure 4 shows results for a series of runs where the ratio of monomer to amphipathic RAFT agent was kept constant and the initiator concentration varied. The predicted particle numbers are in the same order of magnitude as experimental results for small scale experiments with controlled feed of styrene. Fitting to the data of Fig. 3 gave values of $X_{crit} = 20$ and $a_{RAFT} = 0.4$ nm^2.

The detail of the theory developed will be described in more detail in a forthcoming paper that will focus purely on the particle formation mechanism of this particular system. More experiments are currently being conducted to make the theoretical model applicable to more monomer systems.

Conclusions

The application of the self-assembly RAFT emulsion polymerization process to surface coatings is leading to some major advances in this area and will result in the first latex products designed entirely from first principles.

Novel core-shell particles are given as an example of what can be achieved. In ordinary paint systems, core-shell nanoparticles are synthesized by starting with a monomer which forms a hard (glassy) polymer core followed by the addition of a second monomer which forms a soft (rubbery) shell. The core and shell are made up of different polymer chains. With the new method, the sequential addition of hydrophobic monomers leads to chains having two distinct hydrophobic blocks. The polymerization of butyl acrylate followed by styrene gives a core-shell structure with the core and the shell of the same chain, in other words the same chain is going from the core to the shell.[32]

RAFT as a living radical polymerization process has given access to a wide variety of polymer architectures. The successful development of RAFT emulsion polymerization has made it possible to make structured nanoparticles with a wide range of monomer compositions to be used on an industrial scale. One can look at the RAFT process as a ''molecular watchmaker'' whereby any monomer group can be placed in any location in a nanoparticle.

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